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Photochemistry of 2,3-homotropone

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Photolysis of V in Methanol. A solution of 2.50 g of 2-(2-methyl-1-phenylpropenyl)benzophenone (V) in 200 ml of methanol was irradiated in the Rayonet reactor for 24 hr. The solution was concentrated *in vacuo* and chilled to give 2.0 g (72%) of 4,4-dimethyl-1,3-diphenyl-1-methoxyisochroman (X), mp 125–130°. After one recrystallization from methanol the melting point was 128–145°. Although a sharp melting product could not be obtained, the nmr was consistent with the presence of a single isomer with singlets at τ 4.91 (one tertiary H), 6.88 (one OCH₃), 8.72 (one CH₃), and 8.77 (one CH₃).

Anal. Calcd for C₂₄H₂₄O₂: C, 83.69; H, 7.02; mol wt, 344. Found: C, 83.62; H, 7.00; *m/e* 344.

4,4-Dimethyl-1,3-diphenyl-1-hydroxyisochroman (XI). A solution of 100 mg of X in 5 ml of acetic acid and 5 ml of 6 *N* sulfuric acid was warmed on the steam bath for 1 hr. The solution was poured into ice water to give XI as a colorless solid, mp 60–80°. Attempted recrystallization of this material was unsuccessful, presumably due to equilibration between the two possible stereoisomers.

Anal. Calcd for C₂₃H₂₂O₂: C, 83.60; H, 6.71. Found: C, 83.73; H, 6.74.

Infrared spectra of the product in a mull or solution showed no carbonyl absorption. The nmr spectrum in CCl₄ showed an aromatic multiplet centered at τ 2.73 (14 H) and singlets at τ 4.75 (one tertiary H), 7.25 (one OH, exchanged with D₂O), 8.71 (one CH₃), and 8.79 (one CH₃).

Oxidation of 4,4-Dimethyl-1,3-diphenyl-1-methoxyisochroman. A warm solution of 172 mg of X in 10 ml of acetic acid was diluted to the cloud point with 6 *N* sulfuric acid and then treated with 300 mg of solid sodium dichromate dihydrate. The resulting solution was heated on the steam bath for 2 hr, cooled, and diluted with a large volume of water. The colorless product, which crystallized on standing, was filtered off and washed with water to give 160

mg (97%) of 2-(*o*-benzoylphenyl)isobutyrophenone (XII), mp 113–114.5°. Recrystallization from ethanol–water raised the melting point to 115–116° which was identical with the melting point previously reported for this compound.¹³ The infrared spectrum displayed aryl and diaryl ketone absorption at $\lambda_{\text{max}}^{\text{mull}}$ 5.97 and 6.02 μ .

Anal. Calcd for C₂₃H₂₀O₂: C, 84.12; H, 6.14. Found: C, 83.75; H, 6.18.

4,4-Dimethyl-1,3-diphenylisochroman (XIII). A cold stirred slurry of 40 mg (0.001 mole) of lithium aluminum hydride in 5 ml of ether was treated dropwise with a solution of 530 mg (0.004 mole) of anhydrous aluminum chloride in 20 ml of ether.²³ A solution of 340 mg (0.001 mole) of X in 10 ml of ether was then added, and the reaction mixture was stirred at room temperature for 2 hr and then at reflux for 0.5 hr. After cooling the mixture in an ice bath and decomposing the unreacted lithium aluminum hydride by cautious dropwise addition of water, about 10 ml of 6 *N* sulfuric acid was added, and the ether layer was separated, dried, and evaporated. The colorless solid residue was recrystallized from methanol to give 220 mg (70%) of XIII as colorless crystals, mp 117–118°. The nmr spectrum displayed singlets at τ 4.06 (one H), 5.23 (one H), and 8.70 (six H) together with a 14 H aromatic multiplet.

Anal. Calcd for C₂₃H₂₂O: C, 87.86; H, 7.05. Found: C, 88.08; H, 7.10.

Acknowledgment. The authors wish to thank Dr. J. E. Lancaster and Mrs. M. Neglia for the nmr spectra, Mr. T. E. Mead and associates for the mass spectra, and Mr. R. Francel and associates for the microanalyses. Mr. N. B. Colthup aided in the interpretation of some of the infrared spectra.

(23) Cf. procedure of E. L. Eliel, V. G. Badding, and M. N. Rerick, *J. Am. Chem. Soc.*, **84**, 2371 (1962).

The Photochemistry of 2,3-Homotropone¹

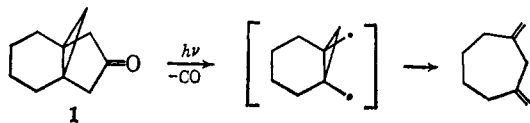
Leo A. Paquette² and Osvaldo Cox

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. Received April 20, 1967

Abstract: Irradiation of 2,3-homotropone under a variety of conditions gives rise principally to a lone tricyclic photoisomer (two are possible) and lesser quantities of tropilidene, bicyclo[4.2.0]octa-4,7-dien-2-one, and 1,3,5-cyclooctatrien-7-one. The configuration of the tricyclic ketone has been established by an unequivocal synthesis of its dihydro derivative starting with norbornene. The possible mechanistic pathways to the four photoproducts are discussed.

An organic molecule which possesses a cyclopropane ring in close proximity to a carbonyl group may be expected to be photolabile because of the unsaturated character of the three-membered ring.^{3,4}

Thus, the effect of a cyclopropyl group positioned β, γ to a ketone carbonyl function frequently is to facilitate photodecarbonylation because of the stabilization available to the resulting (di)radical.⁴ In the case of



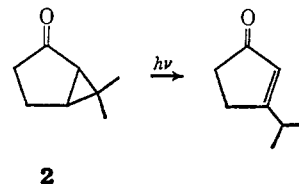
(1) Support of this research by means of a grant from The Graduate School of The Ohio State University is gratefully acknowledged.

(2) Alfred P. Sloan Foundation Research Fellow.

(3) For a recent compilation of many examples, see R. O. Kan, "Organic Photochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1966.

(4) J. E. Starr and R. H. Eastman, *J. Org. Chem.*, **31**, 1393 (1966).

"conjugated" ketones such as 2,⁵ the primary photochemical process often involves ring opening.³



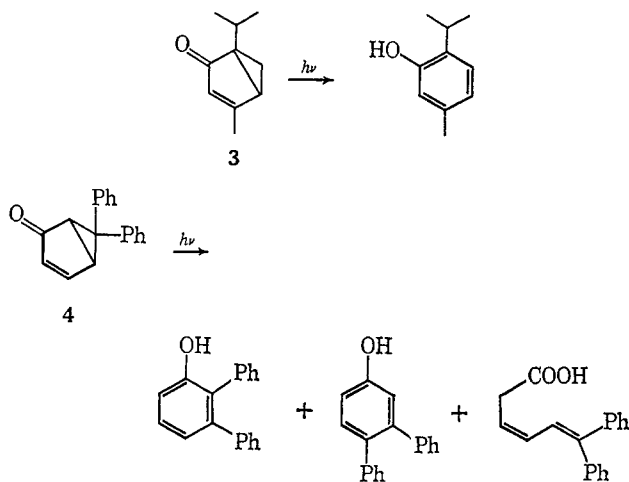
The presence of added unsaturation of the type displayed by the bicyclo[3.1.0]hexenones 3⁶ and 4⁷ may or may not foster more deep-seated rearrangements.⁸

(5) O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton, and P. Fitton, *Tetrahedron Letters*, 2049 (1963).

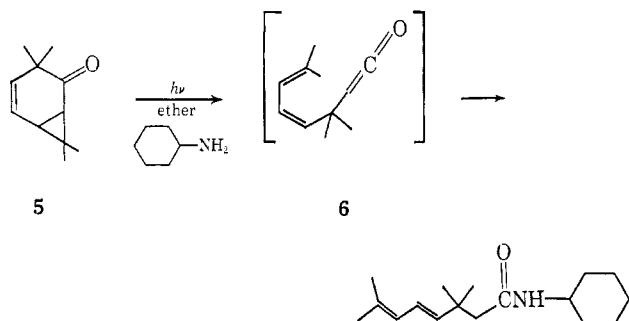
(6) J. W. Wheeler, Jr., and R. H. Eastman, *J. Am. Chem. Soc.*, **81**, 236 (1959).

(7) H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *ibid.*, **88**, 4895 (1966).

(8) For additional recent examples, refer to A. M. Small, *Chem. Commun.*, 243 (1965); H. Dürr, *Tetrahedron Letters*, 5829 (1966);

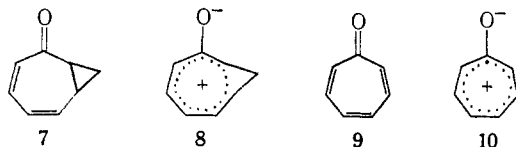


In any event, the nature of the principal photoreaction appears to be dependent upon the size of the cyclic system. For example, 3-methyl-4-carene-2-one (**5**) is transformed principally to ketene **6** when exposed to



light.⁹ In larger rings of similar construction, bond reorganization of this type would be precluded and alternative modes of rearrangement can be expected; such studies remain to be performed.

In the present instance, the photochemical behavior of 2,3-homotropone (**7**) was examined.¹⁰ Because of its structural features, this cyclic ketone was expected to undergo several competitive reactions from its photoexcited state; **7** not only has a cyclopropyl group α,β



to the carbonyl function, but also has a conjugated diene chromophore. Among other properties of **7** worth mentioning, the most significant is perhaps the fact that it is potentially a homoaromatic analog of tropone (**9**). Many of the unusual properties of tropone (*e.g.*, dipole moment, basic strength, site of reaction with electrophilic entities, etc.) have been attributed to strong carbonyl polarization and resonance of six π electrons among seven π orbitals, *viz.*, **10**.¹¹ For the same strong polarization to be operative in **7** (see structure **8**), the cationic portion of the molecule

B. Miller and H. Margulies, *J. Am. Chem. Soc.*, **89**, 1678 (1967); B. Miller, *ibid.*, **89**, 1690 (1967); H. Hart and D. W. Swatton, *ibid.*, **89**, 1874 (1967).

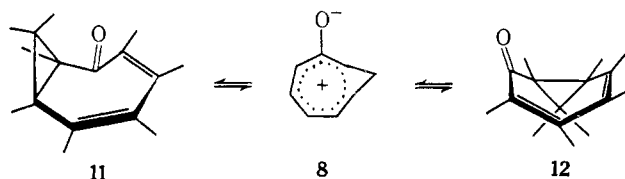
(9) A. J. Bellamy and G. H. Whitham, *J. Chem. Soc.*, 4035 (1964).

(10) A preliminary report of this work has appeared: L. A. Paquette and O. Cox, *J. Am. Chem. Soc.*, **89**, 1969 (1967).

(11) (a) H. J. Dauben, Jr., and H. J. Ringold, *ibid.*, **73**, 876 (1951); (b) W. von E. Doering and F. L. Detert, *ibid.*, **73**, 876 (1951).

must be stabilized by a "pseudoaromatic" sextet of electrons, two of which in the classical structure **7** form part of the cyclopropane ring. Such orbital overlap which is intermediate between that of the customary σ and π types is presently believed to occur in the homotropylum cation^{12,13} and its molybdenum tricarbonyl complex.^{13a} The tropone-like description of 2,3-homotropone (**8**), with a relatively even distribution around the C_1 - C_7 carbon atom framework, is supported by its basic strength ($pK_{BH^+} = -2.8$) which is several pK units higher than that of model compounds, its carbonyl stretching frequency (1650 cm^{-1}), and by the fact that the ketone forms a hexachloroantimonate salt with $HSbCl_6$ (**7** apparently does not, however, form salts with hydrogen halides).¹⁴ In contrast, the nmr spectrum of **7** indicates the absence of a ring current.¹² Thus, it may be concluded that the effects of the cyclopropyl group in **7** are not insignificant, but that such conjugation does not allow a ring current.

Examination of Dreiding models of **7** revealed the possibility of a *cis* and a *trans* conformer.¹⁵ In an attempt to ascertain the conformational preference(s) of the 2,3-homotropone molecule, the nmr spectrum of **7** was examined and was found to be unaltered down to -100° .¹⁶ This was surprising in view of the rate of ring inversion of 1,3,5-cyclooctatrien-7-one which is easily measurable at -80° ; in this system, a planar transition state appears to be involved.¹⁷ The ease of ring inversion in **7** may result from a lowering of the barrier between **11** and **12** (at least with respect to 1,3,5-cyclooctatrien-7-one) by contributions from dipolar form **8**. Although less likely, the possibility also exists that the two possible conformers so differ in stabilization energy that only one is actually observed over the temperature range studied.



Results

2,3-Homotropone was synthesized by modification (see Experimental Section) of the procedure of Holmes and Pettit.^{14,18} Exposure of dilute solutions of **7** in a variety of solvents to a Hanovia 200-w mercury arc lamp for short periods of time, using internally cooled quartz or Pyrex vessels, resulted in the complete disappearance of **7** and clean conversion to a variety of products. The data are summarized in Table I. Preparative vapor phase chromatography of photolysis mixtures obtained from runs in ether solution permitted

(12) C. E. Keller and R. Pettit, *ibid.*, **88**, 606 (1966).

(13) (a) S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *ibid.*, **87**, 3267 (1965); (b) S. Winstein, C. G. Kreiter, and J. I. Brauman, *ibid.*, **88**, 2047 (1966).

(14) J. D. Holmes and R. Pettit, *ibid.*, **85**, 2531 (1963).

(15) For definition of the conformational nomenclature in such systems, see W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

(16) The authors wish to thank Professor Joseph B. Lambert, Northwestern University, for the low-temperature nmr measurements.

(17) C. Ganter, S. M. Pokras, and J. D. Roberts, *J. Am. Chem. Soc.*, **88**, 4235 (1966).

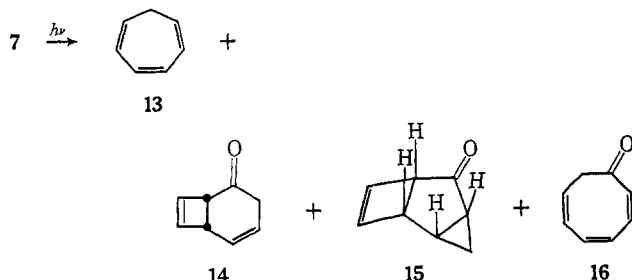
(18) The authors wish to thank Professor R. Pettit for making available to them the experimental details of their synthetic procedure prior to publication.

Table I. Photochemical Transformations of 2,3-Homotropone (7)

Solvent	Time, hr	Yield, % ^a					Un-known	7
		13	14	15	16			
Ether ^b	0.5	7	7	54	17	<1		15
	1.5	10	17	68	5	<1		0
Methanol ^b	0.5	1	0	89	11 ^c	0		0
	0.5	4	<1	23	9	~5		59
Pentane ^b	1.5	9	9	46	17	<1		18
	2.5	12	10	27	5	<1		0
	0.5	4	2	32	15	2		40
Piperylene ^b	1.5	10	8	64	13	<1		0
	2.5	10	17	58	9	<1		0
	0.5	1	<1	17	8	1		73
Ether ^{c,d}	0.5	1	1	25	11	<1		46
	1.5	9	7	47	11	<1		0
Ether ^{b,d}	2.5	9	12	41	5	<1		0
	0.5	1	<1	15	7	1		68
Piperylene ^c	1.5	4	4	38	12	2		24

^a Percentage composition was calculated as described in the Experimental Section. ^b Using quartz optics. ^c Using Pyrex optics. ^d Naphthalene was added in these runs. ^e Actually, this material was methyl *trans*-1,3,5-octatrienoate formed from the further rapid photoinduced transformation of 1,3,5-cyclooctatrien-7-one in methanol solution.¹⁹

the purification and isolation of four components. An additional photoproduct whose average yield was approximately 1% was not present in quantities sufficient for characterization. The products were identified in their order of elution from the gas chromatographic column as cycloheptatriene (13), bicyclo[4.2.0]octa-4,7-dien-2-one (14), 1 α ,2 α ,4 α ,6 α -tricyclo[4.2.0.0^{2,4}]oct-7-en-5-one (15), and 1,3,5-cyclooctatrien-7-one (16). Spectral comparisons with authentic samples served to confirm the structures of 13, 14,¹⁹ and 16.¹⁷



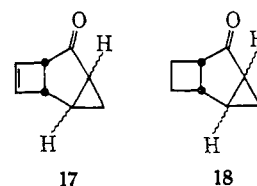
The elemental analysis of the major product indicated that this substance was isomeric with 7. The colorless liquid exhibited pertinent infrared absorption (in CCl₄) at 3030 and 1720 cm⁻¹, a near-infrared band at 1.6339 μ (molar absorptivity = 0.385),²⁰ and the following ultraviolet spectrum: $\lambda_{\max}^{\text{isooctane}}$ 271 (76), 278 (86), 296 (114), 306 (118), 318 (107), and 334 m μ (ϵ 56). These spectral characteristics were strongly indicative of a nonplanar β,γ -unsaturated five-membered ring ketone, as indicated by the high intensity $n \rightarrow \pi^*$ transition,²¹ in which the cyclopropyl group had been retained and a strained double bond had been introduced. These conclusions were reinforced by the nmr spectrum which suggested, *inter alia*, the presence of only two vinyl protons. Furthermore, catalytic

(19) The authors are indebted to Professor George Büchi, Massachusetts Institute of Technology, for making available to them the infrared spectrum of 14: G. Büchi and E. M. Burgess, *J. Am. Chem. Soc.*, **84**, 3104 (1962).

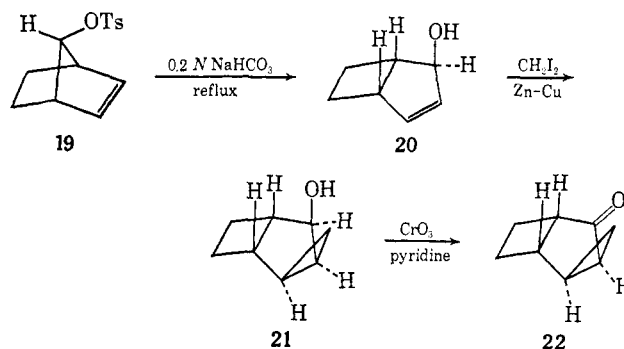
(20) P. G. Gassman and F. V. Zalar, *J. Org. Chem.*, **31**, 166 (1966).

(21) A. Moscovitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 1945 (1962).

hydrogenation of this ketone led to the uptake of 1 molar equiv of hydrogen; the resulting dihydro derivative afforded a semicarbazone, mp 196.5–197°. The structure of this photoproduct could now be defined as 17 and its dihydro derivative as 18, and it remained to elucidate the stereochemical configuration of the cyclopropyl group.



To this end, the two possible isomers of 18 were synthesized. Hydrolysis of *syn*-7-norbornenyl *p*-toluenesulfonate (19) with aqueous 0.2 *N* sodium bicarbonate solution at 100° led to the formation of *exo*-bicyclo[3.2.0]hept-2-en-4-ol (20).²² Treatment of allylic alcohol 20 with the Simmons-Smith reagent²³ gave 1 α ,2 β ,4 β ,6 α -tricyclo[4.2.0.0^{2,4}]octan-5 α -ol (21²⁴), which on oxidation with the Sarett reagent²⁵ afforded the cyclopropyl ketone 22. The assignment of a *cis* relationship to the hydroxyl and cyclopropyl groups in 21 is consistent with the well-recognized stereospecificity consistently observed in the addition of iodomethylzinc iodide to allylic alcohols.²⁶ Ketone 22 was, however,

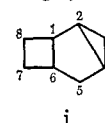


found *not* to be identical with the dihydro derivative of 15; not only were its vpc retention times and infrared and nmr spectra at variance with those of dihydro 15,

(22) This rearrangement was first recognized by S. Winstein and E. T. Stafford, *ibid.*, **79**, 505 (1957); *cf.* also S. Winstein, F. Gadiant, E. T. Stafford, and P. E. Klinedinst, Jr., *ibid.*, **80**, 5895 (1958).

(23) H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959); E. P. Blanchard and H. E. Simmons, *ibid.*, **86**, 1337 (1964); H. E. Simmons, E. P. Blanchard, and R. D. Smith, *ibid.*, **86**, 1347 (1964).

(24) In view of the lack of official rules for expressing the stereochemical configuration of compounds of the tricyclo[4.2.0.0^{2,4}]octane type, we have adopted the α and β convention as used in the steroid field. Since the orientation of the parent ring system is designated by formula i,



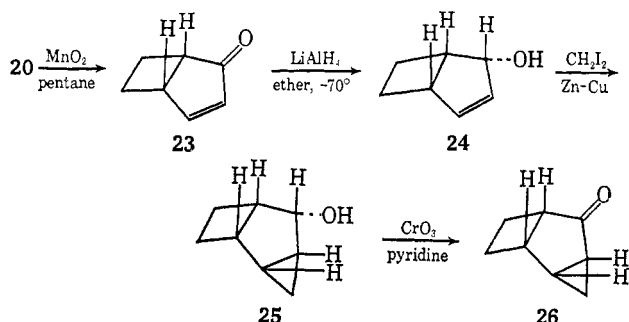
it should be noted that the structures utilized in the body of the manuscript need to be rotated by 180° along the horizontal axis prior to naming. The assistance of Dr. Cecil Langham of the Chemical Abstracts Service in suggesting the feasibility of this method of nomenclature is acknowledged.

(25) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 422 (1953).

(26) S. Winstein and J. Sonneberg, *ibid.*, **83**, 3235 (1961); W. G. Dauben and G. H. Berezin, *ibid.*, **85**, 968 (1963); W. G. Dauben and A. C. Ashcraft, *ibid.*, **85**, 3673 (1963); R. Wiechert, O. Engelfried, U. Kerb, H. Laurent, H. Miller, and G. Schiltz, *Chem. Ber.*, **99**, 1118 (1966).

but **22** also afforded a nonidentical semicarbazone (mp 148.5–149°).

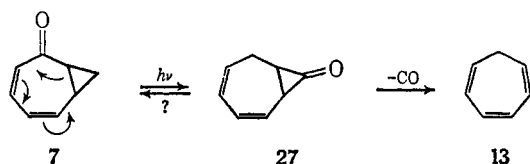
Alternatively, manganese dioxide oxidation²⁷ of **20** gave the α,β -unsaturated ketone **23**. Lithium aluminum hydride reduction of **23** in ether at -70° led preferentially to *endo* alcohol **24**,²⁸ which when subjected to the Simmons–Smith cyclopropanation reaction and subsequent mild oxidation yielded 1 $\alpha,2\alpha,4\alpha,6\alpha$ -tricyclo-[4.2.0.0^{2,4}]octan-5-one (**26**), identical in all respects



with dihydro **15** (see Experimental Section). Thus, structure **15** for the tricyclic photoproduct was demonstrated.

Discussion

Several mechanisms may be advanced to explain the formation of cycloheptatriene (**13**). The data of Table I suggests that the formation of this hydrocarbon is not subject to quenching or sensitization. Such behavior is, in general, typical of photoinduced valence-bond isomerization reactions which appear not to proceed *via* triplet states.³⁰ The possibility that **13** results from a valence-bond rearrangement to the cyclopropanone derivative **27** and subsequent loss of



carbon monoxide therefore appears attractive.³¹ In the hope that **27** might have a finite existence and therefore be susceptible to capture as the methyl hemiketal derivative,³² the irradiation of **7** was performed in methanol (Table I). Although hemiketal formation was not detected under these conditions, the quantity of **13** was observed to diminish substantially.

(27) J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1094 (1952).

(28) Temperatures in the order of -70° appear to be necessary to maximize stereoselectivity and to minimize concomitant saturation of the conjugated double bond [cf. P. R. Story and S. R. Fahrenholz, *J. Am. Chem. Soc.*, **87**, 1623 (1965), for a similar example of overreduction]. In a paper published since the completion of this work, Tanida and co-workers²⁹ have observed that lithium aluminum hydride reduction of **23** in the absence of such precautions leads to a mixture of **24** and **20** in a ratio of 75:25.

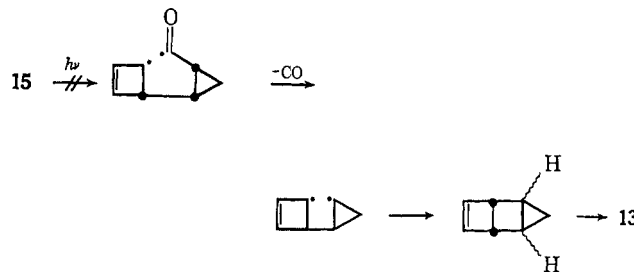
(29) H. Tanida, T. Tsuyi, and T. Irie, *J. Org. Chem.*, **31**, 3941 (1966).

(30) For a summary of the literature and a discussion of the two exceptions to this general rule, refer to R. S. H. Liu, *J. Am. Chem. Soc.*, **89**, 112 (1967).

(31) A similar mechanistic pathway has been invoked for the low yield conversion of tropone into benzene: O. L. Chapman, *Advan. Photochem.*, **1**, 323 (1963). A referee has suggested that **13** could also arise, at least in part, from decarbonylation of the vibrationally excited cyclopropanone derived from zwitterion **28a**.

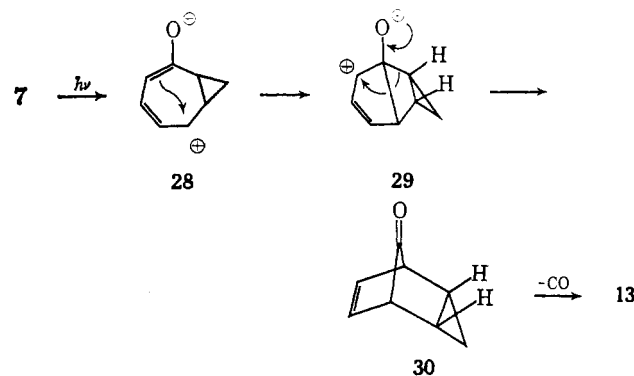
(32) See, for example, N. J. Turro and W. B. Hammond, *J. Am. Chem. Soc.*, **88**, 3672 (1966), and earlier work of these and other workers.

It was also considered likely that **13** could have arisen from the more rapidly generated tricyclic ketone **15** in the manner described below. However, this



path is inconsistent with the observation that irradiation of **15** under conditions identical with those employed earlier produced no **13**, **14**, or **16**; rather, **15** was observed to give rise slowly to a polymeric solid.

By analogy to the secondary process noted in the photolysis of eucarvone,³³ dipolar intermediates such as **28** and **29** could conceivably be involved in tropilidene formation. Especially pertinent in this instance is the fact that the bridged ketone **30** has recently been pre-



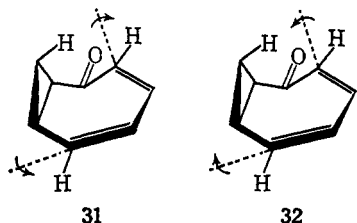
pared in unequivocal fashion and shown to decarbonylate readily to **13** with a half-life of 10 min at 30° .³⁴ However, this mechanistic route is presently viewed as unlikely because the production of **13** is not enhanced in solvents of increasing polarity (as expected from charged intermediates) and because the cyclopropylcarbinyl cation system of **28** may be expected to undergo rapid cleavage of the three-membered ring (see below) rather than rebonding as in **29**.

The formation of a lone tricyclic valence-bond isomer (**15**) is likewise theoretically interesting. This particular photochemically induced electrocyclic reaction very likely follows a concerted, disrotatory pathway.³⁵ However, as depicted in **31** and **32**, two disrotatory modes of cyclization are possible; yet, the process illustrated by structure **31** is followed exclusively. We attribute this high degree of stereospecificity to secondary steric forces operative during the bond reorganization. Thus, as bond rotation in **32** commences, the two vinyl protons at the terminus of the diene system and the *endo*-cyclopropyl hydrogen atom

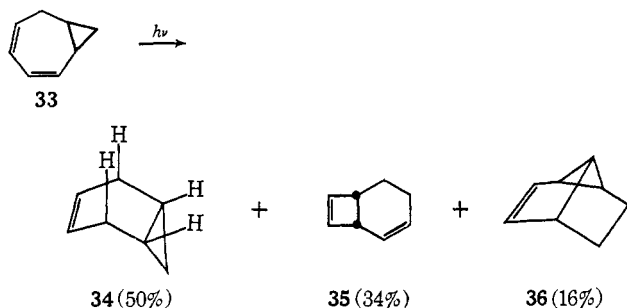
(33) O. L. Chapman, *Advan. Photochem.*, **1**, 355 (1963); J. J. Hurst and G. H. Whitham, *J. Chem. Soc.*, 710 (1963).

(34) S. C. Clarke and B. L. Johnson, *Tetrahedron Letters*, 617 (1967). It is to be noted that on the basis of orbital symmetry considerations the *exo* isomer of **30** would not be expected to decarbonylate as readily when heated; cf. M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *J. Am. Chem. Soc.*, **89**, 1954 (1967).

(35) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965); R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965).



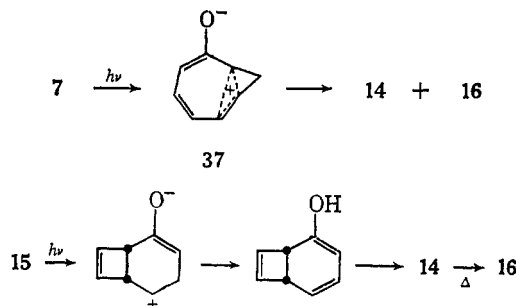
are effectively brought into close proximity.³⁶ Such repulsive forces, which are absent when the same process is effected with **31**, are apparently sufficient to raise the energy of activation which would lead to the *exo*-cyclopropyl counterpart of **15** to an extent which permits exclusive formation of **15** *via* **31**. Significantly, the lone tricyclo[4.2.0.0^{2,4}]oct-7-ene (**34**) obtained in the photoisomerization of homotropilidene **33**³⁷ bears



a direct stereochemical relationship to **15**, and thus the same forces appear to be operative when the carbonyl group of **7** with its sp^2 hybridization is replaced by a tetrahedral carbon atom.

Table I reveals a dramatic enhancement in the rate of formation of **15** in passing from pentane to ether to the more polar methanol as solvent. This increased yield of the tricyclic photoisomer is explainable on the basis of a solvent polarity effect which causes a bathochromic shift in the $\pi \rightarrow \pi^*$ electronic transition believed to be responsible for this conversion.³⁸

The direct conversion of 2,3-homotropone to **14** and **16** can be conveniently depicted in terms of the polar state concept,^{31,39} the key feature of which in the present instance lies in the possible intervention of the mesoionic bicyclobutonium ion **37**.⁴⁰ Initially,



(36) For the sake of simplicity of illustration, **31** and **32** are depicted only in the *cis* conformation. The identical interpretation applies to the *trans* conformer (see 12).

(37) W. R. Roth and B. Peltzer, *Ann.*, **685**, 56 (1965).

(38) The various ultraviolet spectra of 2,3-homotropone are in agreement with this conclusion; for example, $\lambda_{\text{max}}^{\text{isooctane}}$ 285 μ (ϵ 7000) and 345 μ (ϵ 515); $\lambda_{\text{max}}^{\text{EtOH}}$ 293 μ (ϵ 4500) and 340 μ (ϵ 1400).

(39) H. E. Zimmerman, D. Döpp, and P. S. Huyffer, *J. Am. Chem. Soc.*, **88**, 5352 (1966), and references cited therein.

(40) The possibility that **15** could be a precursor of **14** and **16** was eliminated earlier; thus, the following mechanism is apparently not operative.

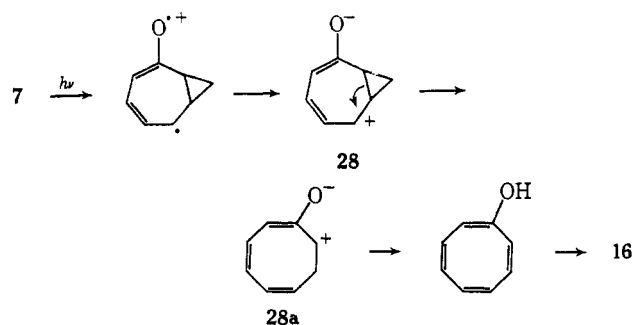
this proposal appeared especially attractive in view of the suggestion of Büchi and Burgess¹⁹ that the rate of photorearrangement of 1,3,5-cyclooctatrien-7-one (**16**) to bicyclo[4.2.0]octa-4,7-dien-2-one (**14**) is very slow and would not be expected to assume importance during the short reaction times employed in this study. However, in several runs (see Table I) an increase in the amount of **14** at the expense of **16** was encountered and we therefore undertook an investigation of the rate of photorearrangement of 1,3,5-cyclooctatrien-7-one. The results which are summarized in Table II demonstrate unequivocally that the rate of formation of **14** from **16** is sufficiently rapid under our conditions to account for its genesis in the photoisomerization of 2,3-homotropone. Therefore, it appears that **14** is not a primary photoproduct of **7**, but results preponderantly, if not exclusively, from photorearrangement of 1,3,5-cyclooctatrien-7-one.

Table II. Photorearrangement of 1,3,5-Cyclooctatrien-7-one (**16**)

Solvent	Time, hr	Yield, % ^a	
		14	16
Ether ^b	0.5	9	83
	1.0	18	78
	16.0	37 ^c	0
Pentane ^b	0.67	16	84

^a Percentage composition was calculated as described in the Experimental Section. ^b Quartz optics employed. ^c Isolated yield (by distillation) in this case; remainder of material was polymeric.

Although these results remove **37** from consideration, the following closely related mechanism is compatible with the available data. The details of this proposed pathway may be considered analogous to the documented photochemical behavior of 2,4-cycloheptadienones.^{3,31} As indicated in Table I, the formation



of **16** (and, of necessity, also **14**) is not overly affected by added piperylene or naphthalene. Although the absence of quenching by piperylene is frequently taken to indicate that triplet states are not involved, this argument is not without certain inherent assumptions.⁴¹ The experiments using added naphthalene are more difficult to interpret because of the complication that the ultraviolet regions of 2,3-homotropone and naphthalene overlap considerably. Therefore, a definitive answer regarding the nature of the excited state which gives rise to **16** is not yet possible.

We also wish to call attention to the wide difference in the photochemical behavior of 2,3-homotropone (**7**) and tropone (**9**). The latter molecule has been

(41) H. E. Zimmerman and J. S. Swenton, *J. Am. Chem. Soc.*, **89**, 906 (1967), and references cited therein.

reported to yield a small amount of benzene plus a complex mixture of products under unspecified conditions.³¹ More recently, however, irradiation of **9** in 2 *N* H₂SO₄⁴² or acetonitrile⁴³ has afforded at least four dimers of unusual structure.

Experimental Section⁴⁴

Bicyclo[5.1.0]octa-2,4-dien-6-oliron Tricarbonyl (39). To a stirred mixture of 7.6 g of sodium hydroxide in 650 ml of water, 1500 ml of ether, and 1500 ml of acetone cooled to -50° by means of an acetone-Dry Ice bath, was added 55 g (0.165 mole) of bicyclo[5.1.0]octa-2,4-dienyliron tricarbonyl fluoroborate⁴⁵ in small portions over a 30-min period. The mixture was allowed to warm to -10° over a period of 1.5–2 hr. The water layer was separated and extracted with three 200-ml portions of ether. The combined ether layers were washed with water (three 500-ml portions) and dried. Evaporation left 42 g (96%) of a yellow solid, mp $84-87^{\circ}$ dec (lit.¹⁴ mp $90-91.5^{\circ}$). This material was employed without further purification.

Bicyclo[5.1.0]octa-2,4-dien-6-oneiron Tricarbonyl (40). Chromium trioxide (25 g, 0.25 mole) was added in small portions to 300 ml of pyridine with stirring at 0° . The mixture turned yellow and was stirred for an additional 30 min; then 12 g (0.046 mole) of **39** in 50 ml of pyridine was added in one portion. The mixture was kept cold for 4 hr and allowed to stir at room temperature for 12 hr. The precipitate was removed by filtration and washed with pyridine. The combined filtrate and washings were evaporated at 65° (30 mm). The residue was triturated with ether and filtered. Evaporation of the ether gave 2.0 g (17%) of yellow crystals, mp $132.5-133.5^{\circ}$ (from benzene-hexane) (lit.¹⁴ mp $131-132.5^{\circ}$).

2,3-Homotropone (7). To a stirred mixture of 83.0 g (0.151 mole) of ceric ammonium nitrate and 166.2 g (1.17 moles) of anhydrous disodium hydrogen phosphate in 660 ml of acetone cooled to 0° was added a solution of 12.0 g (0.046 mole) of **40** in 250 ml of acetone over a 45-min period. The stirred mixture was maintained at 0° throughout the addition and for an additional 3 hr. Then it was poured into 1500 ml of a 1:1 ether-benzene mixture and 1000 ml of a 5% sodium carbonate solution. The precipitate which formed was removed by filtration through diatomaceous earth and was thoroughly washed with additional 1:1 ether-benzene mixture. The aqueous layer was extracted with three 200-ml portions of the same solvent system, and the combined organic layers were washed several times with 200-ml portions of 5% sodium carbonate solution (until the aqueous layer remained colorless) followed by two 200-ml portions of saturated sodium chloride solution. The organic phase was dried over anhydrous magnesium sulfate, filtered, and evaporated. The remaining oil was distilled to yield 3.84 g (68.7%) of a pale yellow liquid, bp $55-56^{\circ}$ (0.15 mm), n_D^{20} 1.5689 [lit.¹⁴ bp $61-62^{\circ}$ (0.2 mm), n_D^{20} 1.5697].

The semicarbazone of **7** was obtained as pale yellow prisms from 80% ethanol, mp $146-147^{\circ}$ (lit.¹⁴ mp $146-147^{\circ}$).

Irradiation of 7 on a Preparative Scale. A solution of 1.00 g (8.30 mmoles) of pure **7** in 200 ml of anhydrous ether was irradiated with a Hanovia 200-w mercury arc for 2.5 hr in a nitrogen atmosphere. The solvent was carefully removed under reduced pressure at room temperature to leave 0.950 g of a pale yellow oil. This material was found to be a four-component mixture in the ratio of 1.0:2.5:11.5:1.9 by vpc.⁴⁶ No starting material remained. The mixture was purified by preparative scale vpc.⁴⁶

The first component was identified as cycloheptatriene (**13**); $\nu_{\text{max}}^{\text{CCl}_4}$ 3.35 (s), 6.98 (m), 7.19 (m), and 7.72 μ (m); $\delta_{\text{TMS}}^{\text{CCl}_4}$ 2.21 (multiplet

2 H), 5.28 (multiplet, 2 H), 6.13 (multiplet, 2 H), and 6.58 (multiplet, 2 H).

The second component proved to be bicyclo[4.2.0]octa-4,7-dien-2-one (**14**); $\nu_{\text{max}}^{\text{CCl}_4}$ 5.85, 7.63, 7.88, 8.10, and 10.70 μ ; the nmr spectrum ($\delta_{\text{TMS}}^{\text{CCl}_4}$) displayed multiplets at 2.90 (2 H), 3.52 (1 H), 3.71 (1 H), 5.73 (2 H), and 6.20 (2 H).¹⁹

The third fraction proved to be a colorless liquid which was subsequently shown to be **15**; $\nu_{\text{max}}^{\text{CCl}_4}$ 5.82, 7.63, 7.82, 7.91, 8.07, 8.45, 8.57, 9.43, 9.58, 9.99, 10.35, 11.02, and 12.02 μ ; the nmr spectrum ($\delta_{\text{TMS}}^{\text{CCl}_4}$) displayed complex patterns at 0.75–1.43 (2 H) and 1.66–2.18 (2 H), and multiplets centered at 3.15 (1 H), 3.63 (1 H), and 6.13 (2 H).

Anal. Calcd for C₈H₈O: C, 79.97; H, 6.71. Found: C, 79.95; H, 6.78.

The semicarbazone of **15** was obtained as colorless crystals from aqueous ethanol, mp $189.5-191^{\circ}$.

Anal. Calcd for C₉H₁₁N₃O: C, 61.00; H, 6.26; N, 23.72. Found: C, 60.30; H, 6.41; N, 23.87.

The fourth component was identified as 1,3,5-cyclooctatrien-7-one (**16**); $\nu_{\text{max}}^{\text{CCl}_4}$ 5.93, 6.07, 8.81, and 12.02 μ ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 2.95 (doublet, *J* = 8 cps, 2 H), 5.77 (multiplet, 1 H), and 6.00–6.60 (complex multiplet, 4 H).¹⁷

Photolysis Runs. The results of the irradiation of **7** under a variety of conditions are tabulated in Table I. All of the photolyses were performed in quartz test tubes held in a vertical position 1 cm away from a water-cooled quartz insert of an immersion type Hanovia 200-w mercury arc lamp. In a typical experiment 104 mg (0.87 mmole) of **7** and 98 mg of cyclooctane (internal standard) were weighed in a 5-ml volumetric flask and diluted to volume with anhydrous ether. This solution was placed in a quartz test tube (21 × 1.2 cm), flushed with nitrogen, and tightly stoppered with a serum cap which permitted the withdrawal of aliquot samples with a microsyringe. An aliquot was removed at time zero and analyzed by vpc.⁴⁷ The course of the photolysis was examined in similar fashion at appropriate intervals.

For purposes of instrument calibration, the internal standard method was employed. The calibration curves were obtained by preparing accurate standard mixtures of cyclooctane with each of the photoproducts (**13**–**16**). A plot of the ratios (weight of compound)/(weight of cyclooctane) vs. (area of compound)/(area of cyclooctane) gave straight lines for the four compounds over the range of concentrations employed. From these plots a correction factor was obtained for each photoproduct, and the percentages of each component in the photolysis runs were obtained by use of the equation⁴⁸

% photoproduct =

$$\frac{(\text{area of photoproduct})(\text{cor factor})(\text{wt of cyclooctane})}{(\text{area of cyclooctane})(\text{wt of 2,3-homotropone})} 100$$

By this procedure, the absolute percentages of each component in the reaction mixture was determined. The fact that in some cases the percentages add up to less than 100% can be accounted for in terms of polymer formation, a discrete amount of carbon monoxide evolution, and experimental error. The areas of the various gas chromatographic peaks were measured with a Keuffel and Esser compensating polar planimeter.

Pyrolysis of 15. A small ampoule containing 50 mg of pure **15** was flushed with nitrogen, sealed, and immersed in a bath at 300° . After heating the sample for 1 min, the ampoule was cooled and opened and its contents analyzed by vpc.⁴⁶ The pyrolysate consisted chiefly of 2,3-homotropone and unreacted **15**, although small quantities of several unidentified products were also observed.

Tricyclic ketone **15** also reverted partially to 2,3-homotropone when injected into a gas chromatograph heated at 200° or above.

No appreciable amount of **14** or **16** was observed in these experiments.

Prolonged Irradiation of 15. A solution of 123 mg (1.03 mmoles) of **15** in 2.5 ml of anhydrous ether contained in a 1.0-cm quartz cell was blanketed with nitrogen and irradiated externally with a Hanovia 200-w mercury arc lamp. Aliquot portions were withdrawn after 0, 1, 4, and 16 hr, and analyzed by vpc.⁴⁶ After 4 hr,

(47) A 0.125 in. × 5.5 ft stainless steel column packed with 20% SF-96 on 60–80 mesh Chromosorb W at 115° was employed in conjunction with an Aerograph Hi-Fi Model 600D gas chromatograph equipped with a flame ionization detector.

(48) W. T. Casazza and R. J. Steltenkamp, *J. Gas Chromatog.*, **3**, 253 (1965); Instrumental Analysis Subcommittee, Scientific Section Essential Oil Association of the USA, *ibid.*, **3**, 103 (1965).

(42) T. Mukai, T. Tezuka, and Y. Akasaki, *J. Am. Chem. Soc.*, **88**, 5025 (1966).

(43) A. S. Kende, *ibid.*, **88**, 5026 (1966).

(44) Melting points were determined with a Thomas-Hoover melting point apparatus and are corrected. Infrared spectra were recorded with a Perkin-Elmer Infracord Model 137 spectrometer fitted with sodium chloride prisms. Ultraviolet spectra were determined with a Cary 14 recording spectrometer. Nuclear magnetic resonance spectra were obtained with a Varian A-60 spectrometer purchased with funds made available through the National Science Foundation. The microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

(45) G. N. Schrauzer, *ibid.*, **83**, 2966 (1961); A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4822 (1962).

(46) A 0.25 in. × 5.5 ft aluminum column packed with 20% SF-96 on 60–80 mesh Chromosorb W at 90° was employed in conjunction with an Aerograph A90-P3 thermal conductivity gas chromatograph.

the concentration of **15** was found to have been halved while after 16 hr no **15** remained. During this time none of the products observed in the photochemical rearrangement of 2,3-homotropone was detected. Work-up of the reaction afforded a polymeric substance.

cis,exo-Bicyclo[3.2.0]hept-2-en-4-ol (20). Alcohol **20** was prepared from norbornene by initial conversion to *exo*-2-chloro-*syn*-7-acetoxynorbornane and *syn*-7-norbornenol according to the procedure of Baird.⁴⁹ This alcohol was converted to *syn*-7-norbornenyl *p*-toluenesulfonate (**19**) in the customary manner. When **19** was refluxed in 0.2 *N* sodium bicarbonate solution for 9 days,²² **20** was obtained in 95–98% yield in a high state of purity.

1 α ,2 β ,4 β ,6 α -Tricyclo[4.2.0.0^{2,4}]octan-5 α -ol (21). To a stirred mixture of 3.40 g of zinc–copper couple prepared by the Shank–Shechter method,⁵⁰ 0.02 g of iodine, and 25 ml of anhydrous ether was added 10.4 g (39.0 mmoles) of methylene iodide. The flask was heated in the absence of atmospheric moisture until a spontaneous reaction began as evidenced by continued refluxing of the ether when the heat source was removed. Upon completion of the exothermic reaction, the mixture was refluxed for 30 min. The heat was removed and to this mixture there was added a solution of 2.0 g (0.018 mole) of **20** in 10 ml of anhydrous ether at a rate sufficient to maintain constant reflux. When the addition was completed, reflux was maintained for an additional 2 hr. The flask was cooled and 20 ml of a saturated ammonium chloride solution was carefully added. The precipitated salts were filtered through diatomaceous earth, and the filter cake was washed thoroughly with ether. The aqueous layer was separated and twice extracted with 50-ml portions of ether. The combined organic phases were washed successively with saturated sodium carbonate (two 50-ml portions) and sodium chloride (two 50-ml portions) solutions. The ether layer was dried, filtered, and carefully evaporated to give 2.0 g of pale yellow oil. Vpc analysis (102°)⁴⁶ showed the material to consist of methylene iodide (13%), starting material (45%), and a new substance (42%). The crude product was purified directly by preparative scale vpc at 100°.⁴⁹ A total of 300 mg of pure **21** was collected; $\nu_{\text{max}}^{\text{CCl}_4}$ 3.01, 3.45, 7.54, 9.50, and 9.70 μ ; $\delta_{\text{TMS}}^{\text{neat}}$ 0.40 (multiplet, 2 H), 1.24 (multiplet, 1 H), 1.51–2.34 (complex absorption, 6 H), 2.68 (unresolved multiplet, 1 H), 4.32 (broad peak, 1 H), and 4.51 (twin peaks, 1 H).

The 3,5-dinitrobenzoate of **21** was obtained as colorless crystals from hexane, mp 82.5–83°.

Anal. Calcd for C₁₅H₁₄N₂O₆: C, 56.60; H, 4.43; N, 8.80. Found: C, 56.80; H, 4.55; N, 8.84.

1 α ,2 β ,4 α ,6 β -Tricyclo[4.2.0.0^{2,4}]octan-7-one (22). The chromic trioxide–pyridine complex was prepared as previously described²⁵ from 11.1 g (0.11 mole) of chromium trioxide and 100 ml of pyridine cooled to 0°. With stirring at 0°, 2.80 g of a mixture consisting of 37% **20** and 63% **21** dissolved in 5 ml of pyridine was added in one portion. The mixture was stirred at 0° for 4 hr and at room temperature for 20 hr. The precipitated solids were filtered, and the filter pad was washed thoroughly with ether. The combined filtrates were poured into 300 ml of water, and the aqueous layer was separated and extracted with ether (five 50-ml portions). The combined organic phases were in turn washed with cold 0.1 *N* hydrochloric acid, sodium bicarbonate, and sodium chloride solutions. The ether solution was dried and carefully evaporated to give 1.50 g of an oil which consisted of 70% **22** and 30% of a component later identified as ketone **23**. Pure **22** was obtained by preparative scale vpc at 90°;⁴⁶ $\nu_{\text{max}}^{\text{CCl}_4}$ 3.40, 5.80, 6.93, 7.64, 7.71, 8.40, 9.10, 10.20, 10.65, 11.05, and 11.12 μ ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 0.54 (four-line pattern, 1 H), 1.20 (multiplet, 1 H), 1.61–2.53 (complex absorption, 7 H), and 2.92 (multiplet, 1 H).

The semicarbazone of **22** was obtained as colorless crystals from ethyl acetate–hexane, mp 148.5–149°.

Anal. Calcd for C₉H₁₃N₃O: C, 60.31; H, 7.31. Found: C, 60.30; H, 7.69.

(49) W. C. Baird, Jr., *J. Org. Chem.*, **31**, 2411 (1966). The authors are indebted to Dr. Baird for his laboratory directions prior to publication.

(50) R. S. Shank and H. Shechter, *ibid.*, **24**, 1825 (1959).

cis-Bicyclo[3.2.0]hept-2-en-4-one (23). A mixture of 4.50 g (40.9 mmoles) of **20** and 12.0 g (0.14 mmole) of activated manganese dioxide²⁷ in 200 ml of pentane was stirred at room temperature for 24 hr. The reaction mixture was filtered through diatomaceous earth, and the filter cake was washed with pentane. The solvent was removed under reduced pressure, and the crude product was distilled to give 3.75 g (85.0%) of a colorless liquid, bp 54–56° (2.7 mm), n_D^{25} 1.5045; $\nu_{\text{max}}^{\text{CCl}_4}$ 5.83, 6.31, 7.44, 7.71, 8.50, 8.72, and 12.30 μ ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 1.40–3.10 (complex absorption, 5 H), 3.40 (broad peak, 1 H), 6.21 (doublet with additional long-range coupling, *J* = 6 cps, 1 H), and 7.68 (doublet of doublets, *J* = 6 and 3 cps, 1 H).

The 2,4-dinitrophenylhydrazone of **23** was obtained as deep orange needles from 95% ethanol, mp 200.5–201.5°.

Anal. Calcd for C₁₃H₁₂N₄O₄: C, 54.16; H, 4.20; N, 19.44. Found: C, 53.92; H, 4.28; N, 19.11.

cis,endo-Bicyclo[3.2.0]hept-2-en-4-ol (24). To a stirred slurry of 1.20 g (34.0 mmoles) of lithium aluminum hydride in 150 ml of anhydrous ether cooled to –70°, there was added a solution of 2.90 g (26.8 mmoles) of **23** (containing 5% **20**) in 25 ml of ether at such that the temperature remained near –70°. After the addition was completed (*ca.* 5 min), the mixture was stirred for an additional 10 min at –70°; an excess of ethyl acetate (20 ml) was added slowly, and the temperature was allowed to reach 0°. The mixture was poured into 300 ml of a saturated solution of disodium tartrate and extracted with ether (five 50-ml portions). The combined ether layers were washed with cold 0.1 *N* sulfuric acid, 0.2 *N* sodium bicarbonate, and finally saturated sodium chloride solution. After drying, the ether solution was carefully evaporated to afford 2.80 g (91%) of an oil which by vpc analysis at 140°⁴⁶ was found to be composed of three components in the ratio of 2.3:1.0:7.1. Distillation *in vacuo* (3 mm) led to the isolation of 1.0 g of **24** (97% pure), bp 66–67°; $\nu_{\text{max}}^{\text{neat}}$ 2.98, 3.39, 3.47, 7.42, 9.12, 9.35, 9.52, 9.71, and 13.46 μ ; $\delta_{\text{max}}^{\text{CCl}_4}$ 1.05–2.33 (complex absorption, 5 H), 3.00 (unresolved multiplet, 1 H), 3.77 and 4.98 (broad peaks, 1 H each), and 5.73 (multiplet, 2 H).

The phenylurethan of **24** was obtained as white needles from petroleum ether, mp 106.8–107.3°.

Anal. Calcd for C₁₄H₁₅NO₂: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.24; H, 6.82; N, 5.98.

1 α ,2 α ,4 α ,6 α -Tricyclo[4.2.0.0^{2,4}]octan-5-one (26). **A. Oxidation of 25.** A 1.00-g (9.1 mmoles) sample of **24** was treated with 1.57 g of zinc–copper couple in the manner described above. The crude oil obtained after a similar work-up was found to consist of methylene iodide (33%), **24** (31%), and the tricyclic alcohol **25** (35%). The mixture was oxidized directly with the chromium trioxide–pyridine complex prepared from 4.0 g (4.0 mmoles) of chromium trioxide and 30 ml of pyridine. When the oxidation mixture was worked up as described earlier, there resulted 400 mg of a yellow oil which was subjected directly to preparative scale vpc at 112°.⁴⁶ Tricyclic ketone **26** was obtained as a colorless liquid; $\nu_{\text{max}}^{\text{CCl}_4}$ 3.40, 5.80, 7.74, 8.48, 9.68, 10.10, and 11.21 μ ; the nmr spectrum of **26** (neat sample) consisted of a complex pattern between δ 1.0 and 3.0.

The semicarbazone of **26** was obtained as white crystals from 50% ethanol, mp 196–197°, identical in all respects with the sample prepared in part B.

B. Hydrogenation of 15. A solution of 333 mg (2.79 mmoles) of **15** in 30 ml of anhydrous ether was hydrogenated over 10% palladium on charcoal. One equivalent of hydrogen was absorbed at which point the catalyst was removed by filtration. The solvent was evaporated and the residual oil was molecularly distilled to give 200 mg (59%) of pure **26** as a colorless liquid displaying infrared and nmr spectra identical with those of the above sample.

The semicarbazone of **26** was found to melt at 196–197°; a mixture melting point determination showed no depression.

Anal. Calcd for C₉H₁₃N₃O: C, 60.31; H, 7.31; N, 23.45. Found: C, 59.98; H, 7.48; N, 23.28.

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