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Tetramethylcyclopropanone. I. Isolation and Characterization

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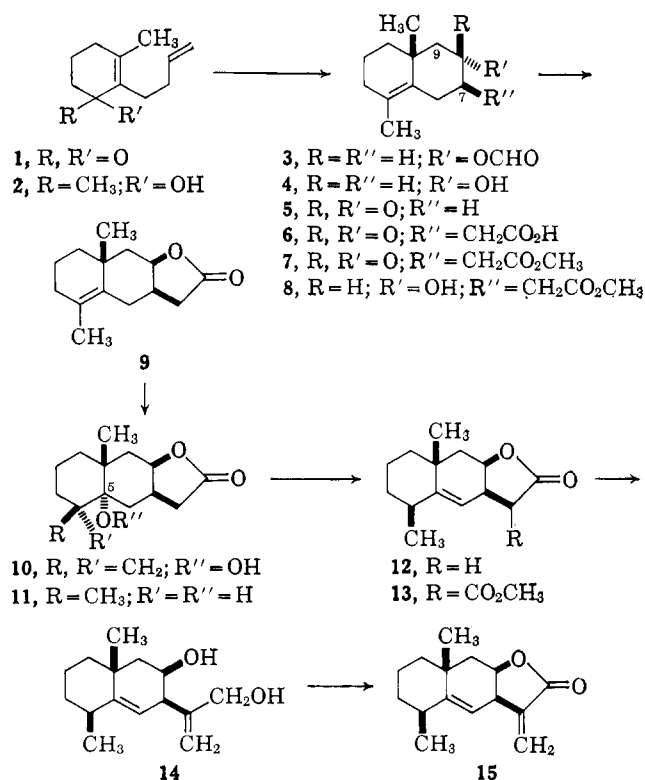


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firmed by its n.m.r. spectrum [$\delta_{\text{TMS}}^{\text{CCl}_4}$ 1.69 (vinyl CH₃), 1.00 p.p.m. (angular CH₃); essential absence of absorption in the range 5–7 p.p.m. (vinyl H)].

Alkylation of octalone 5 with ethyl bromoacetate via the Stork enamine procedure⁸ and saponification of the crude product afforded keto acid 6 (m.p. 128–130°) in 53% over-all yield (70% crude yield). The n.m.r. spectrum of the pyrrolidine enamine [$\delta_{\text{TMS}}^{\text{CCl}_4}$ 4.05 p.p.m. (vinyl H; half-height line width = 10 c.p.s.)] derived from octalone 5 provided assurance that the Δ^7 -isomer was the predominant species. Had the Δ^8 -isomer been the predominant enamine a relatively sharp⁹ (half-height line width < 4 c.p.s.) vinyl hydrogen signal would be expected. The high yield of C-alkylation product 6 constitutes additional evidence for this conclusion since steric effects should render alkylation difficult at C-9 and thus cause the Δ^8 -enamine isomer to alkylate principally on the nitrogen atom.⁸

Keto acid 6 was esterified (diazomethane) and the keto ester 7 was reduced with methanolic potassium borohydride giving lactone 9 ($\lambda_{\text{max}}^{\text{film}}$ 5.63 μ) directly in 75% yield. The remainder of the material consisted of hydroxy ester 8 which was readily separated from lactone 9 by chromatography and oxidized to keto ester 7 in high yield, thus increasing the over-all yield of lactone 9.

Photooxygenation of unsaturated lactone 9 according to the procedure of Nickon and Bagli¹⁰ afforded hydroperoxide 10 [m.p. 117.5–118.5°; $\lambda_{\text{max}}^{\text{CHCl}_3}$ (μ) 2.86, 3.00 (OOH), 5.67 (lactone CO), and 6.08, 11.0 (C=CH₂); $\delta_{\text{TMS}}^{\text{CHCl}_3}$ 5.19, 4.88 p.p.m. (C=CH₂)]. The

(8) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963); J. Szmuszkovicz, *Advan. Org. Chem.*, **4**, 1 (1963).

(9) Allylic 1,3-coupling often causes peak broadening. Cf. T. A. Wittstruck, S. K. Malhotra, and H. J. Ringold, *J. Am. Chem. Soc.*, **85**, 1699 (1963).

(10) A. Nickon and J. F. Bagli, *ibid.*, **83**, 1498 (1961).

stereochemistry of the newly formed asymmetric center at C-5 in 10 is assigned by analogy with the stereochemical preference for α -attack by oxygen on steroidal olefins under comparable conditions. The marked tendency toward abstraction of a primary (vs. secondary) allylic hydrogen cannot be explained at present. Whether this preference results from steric or electronic factors is currently under investigation.

Since recrystallization caused its partial decomposition, hydroperoxide 10 was reduced directly to alcohol 11 [m.p. 183.5–184.5°; $\lambda_{\text{max}}^{\text{CHCl}_3}$ (μ) 2.79, 2.86 (OH), and 5.68 (lactone CO)] by hydrogenation over platinum in acetic acid.

Alcohol 11 upon treatment with thionyl chloride in pyridine¹¹ gave unsaturated lactone 12 [m.p. 90–91°; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 5.23 (H-6; doublet, J = 3 c.p.s.), 4.82 (CH-O-), 1.29 (angular CH₃), and 1.19 p.p.m. (C-4 CH₃ doublet, J = 7 c.p.s.)]¹² in 75% yield. Carbomethoxylation of lactone 12 using sodium hydride in dimethyl carbonate followed by reduction of the resulting enolate of lactone ester 13 (not isolated) with lithium aluminum hydride in 1,2-dimethoxyethane after removal of the excess dimethyl carbonate yielded diol 14 [m.p. 150.5–151°; $\lambda_{\text{max}}^{\text{CHCl}_3}$ (μ) 3.0, 6.08, and 10.87; $\delta_{\text{TMS}}^{\text{CHCl}_3}$ 5.46, 5.13 (C=CH₂), and 5.34 p.p.m. (H-6, doublet, J = 5 c.p.s.)]. Oxidation of diol 14 with manganese dioxide¹³ in benzene afforded racemic alantolactone, m.p. 58–59°, whose identity with (+)-alantolactone¹⁴ was established by superimposition of their richly detailed infrared spectra. Additional confirmation of identity was provided by t.l.c. mobility and gas chromatographic retention times (peak enhancement).

Acknowledgment. We thank the Public Health Service for support of this work through a Research Grant (AI-04965, National Institute of Allergy and Infectious Diseases) and a Fellowship (5-FI-Gm-19,839).

(11) Cf. V. Benešová, V. Herout, and F. Šorm, *Collection Czech. Chem. Commun.*, **26**, 1350 (1961).

(12) Compare with the published spectrum of alantolactone (ref. 2).

(13) O. Mancera, G. Rosenkranz, and F. Sondheimer, *J. Chem. Soc.*, 2189 (1953).

(14) Obtained from Chemical Procurement Inc. and purified by crystallization and chromatography to give material of m.p. 76–77°. Cf. ref. 2.

(15) Fellow of the National Institute of General Medical Sciences, Public Health Service, 1963–1965.

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Tetramethylcyclopropanone. I. Isolation and Characterization

Sir:

A number of attempts to prepare cyclopropanones have been reported in the chemical literature.^{1,2} In general, derivatives of cyclopropanones but not the cyclopropanones themselves were isolated. However, a number of unsubstantiated reports of stable cyclo-

(1) Recently successful syntheses of hetero analogs of cyclopropanones have been reported: (a) F. D. Greene and J. C. Stowell, *J. Am. Chem. Soc.*, **86**, 3569 (1964); (b) H. E. Baumgarten, *ibid.*, **84**, 4975 (1962); (c) *ibid.*, **85**, 3303 (1965); (d) J. C. Sheehan and I. Lengyel, *ibid.*, **86**, 746, 1356 (1964).

(2) (a) P. Lipp and R. Koster, *Ber.*, **64**, 2823 (1931); (b) P. Lipp, J. Buchkremer, and H. Seeles, *Ann.*, **499**, 1 (1932); (c) A. Kende, Ph.D. Dissertation, Harvard University, Cambridge, Mass., 1957; (d) W. L. Mock, Ph.D. Dissertation, Harvard University, Cambridge, Mass., 1965.

propanones still persist,³ but in light of present knowledge of these species these reports are undoubtedly erroneous. Recently, the photolysis⁴⁻⁷ of tetramethyl-1,3-cyclobutanedione (**1**) has been proposed as a method for the preparation of tetramethylcyclopropanone (**2**).

Thus, the formation of a number of derivatives⁴⁻⁶ suggestive of the intermediacy of **2** from photolyses of **1** and the detection^{7,8} of a C=O stretching vibration at 1840 cm.⁻¹ in rapidly scanned photolyzed solutions of **1** provide strong circumstantial evidence for the presence of **2**. However, the chemistry of **2** has been inferred from the results of a photochemical reaction, so that it is conceivable that the products result from the reactions of excited states and not of **2**. Furthermore, the presence of an infrared band at the "expected" C=O stretching frequency is suggestive but not conclusive evidence for the existence of **2** since other carbonyl compounds such as anhydrides⁹ and lactones¹⁰ also absorb in this spectral region.

We wish to report that the band assigned to the C=O stretching vibration of **2** disappears when furan, oxygen, or methanol is added to purified pentane solutions of **2** after photolysis of **1**. This spectroscopic observation coupled with the chemical data given below compel the conclusion that tetramethylcyclopropanone is a fairly stable, distillable compound which can be handled in pentane solution and which thermally undergoes the reactions⁴⁻⁶ reported to occur when **1** is photolyzed. Photolyses of saturated pentane solutions of **1** were conducted in a Pyrex Hanovia 450-w. immersion apparatus at 36° for 1-2 hr. As reported earlier,^{4,7} tetramethylethylene (**3**) and dimethylketene (**4**) are formed in addition to **2**. Prolonged photolysis resulted in the appearance of the lactone **5** in low yields.¹¹

(3) (a) J. D. Cogdell, *Dissertation Abstr.*, **19**, 2751 (1959); (b) F. La Forge and F. Acree, *J. Org. Chem.*, **6**, 2081 (1941); (c) M. Jacobson, M. Beroza, and R. T. Yamamoto, *Science*, **139**, 48 (1963).

(4) (a) N. J. Turro, G. W. Byers, and P. A. Leermakers, *J. Am. Chem. Soc.*, **86**, 955 (1964); (b) P. A. Leermakers, G. F. Vesley, N. J. Turro, and D. C. Neckers, *ibid.*, **86**, 4213 (1964); (c) N. J. Turro, P. A. Leermakers, H. R. Wilson, D. C. Neckers, G. W. Byers, and G. F. Vesley, *ibid.*, **87**, 2613 (1965).

(5) R. C. Cookson, M. J. Nye, and G. Subrahmanyam, *Proc. Chem. Soc.*, 144 (1964).

(6) H. G. Richey, Jr., J. M. Richey, and D. C. Claggett, *J. Am. Chem. Soc.*, **86**, 3906 (1964).

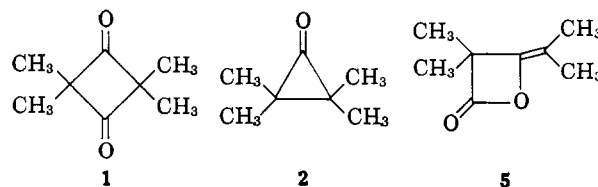
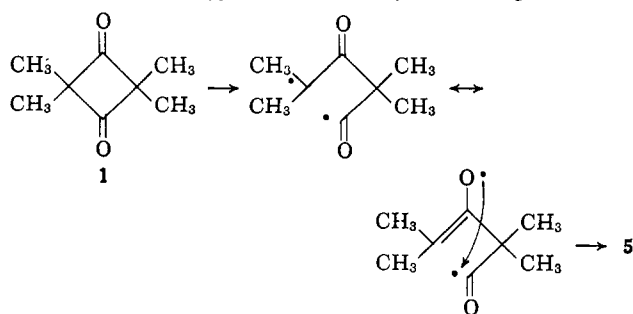
(7) I. Haller and R. Srinivasan, *ibid.*, **87**, 1144 (1965).

(8) Cyclopropanone is reported to absorb at 1825 cm.⁻¹ at 20°K. [W. D. DeMore, H. O. Prichard, and N. Davidson, *ibid.*, **81**, 5874 (1959)] while at 25° it is reported to absorb at 1800 cm.⁻¹ [A. Kende, Ph.D. Dissertation, Harvard University, Cambridge, Mass., 1957].

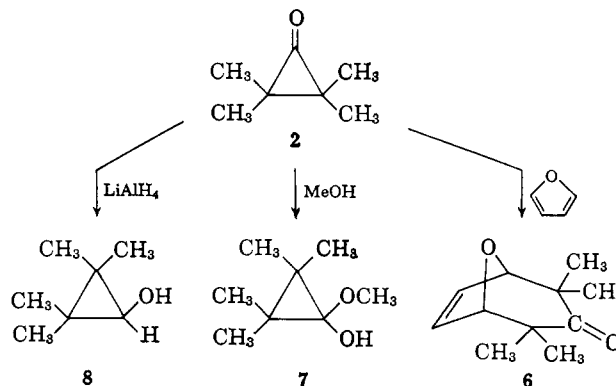
(9) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 127.

(10) The lactone **5** shows three bands in the 2000-1600 cm.⁻¹ region at 1860, 1835, and 1750 cm.⁻¹.

(11) The formation of the lactone **5** conceivably may result from photochemical dimerization of dimethylketene (thermal dimerization yields **1** exclusively). We have irradiated **4** under our reaction conditions and find that **5** is not produced in significant amount. An internal rearrangement of the type shown below may be occurring.

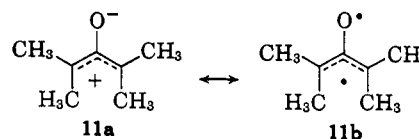


The concentration of **2** reaches a maximum value after about 1 hr. of irradiation and then falls off.^{4b,c,12} As a result, irradiation beyond the formation of this maximum concentration is not advantageous. The photolyzed solution of **1** was stripped of **3** and pentane until an approximately 10% solution of **2** (estimated by infrared spectroscopy) was obtained. This pentane solution was in turn purified¹³ by bulb to bulb distillation at 1 mm. and 20°. Treatment of such solutions with furan,^{5,6} methanol,^{4,6} and ethereal lithium aluminum hydride¹⁴ results in formation of **6**, **7**, and **8**, respectively. Treatment of a pentane solution of **2** with oxygen^{4,15} leads to formation of acetone (**9**)



and carbon monoxide as the major products, and **2** is cracked during vapor chromatographic analysis^{4b,c} to isopropenyl isopropyl ketone (**10**).

The combination of physical and chemical properties described above clearly demonstrates that **2** is a fairly stable but exceedingly reactive compound. The reactions of **2** are consistent with an intact three-membered ring structure which may be in equilibrium with or may achieve transition states similar to the dipolar ion **11a** or biradical **11b**.



Since cyclopropanones and dipolar ions are proposed to be intermediates in Favorskii reactions¹⁶

For example, see R. C. Cookson, A. G. Edwards, J. Hudec, and M. Kingsland, *Chem. Commun. (London)*, 98 (1965). The formula labeled II in this paper is apparently a misprint and should be replaced by **5** since these authors have probably observed the same rearrangement we report here.

(12) Insertion of a uranium glass filter between the lamp and solution did not noticeably increase the net yield of **2**. This filter has a narrow pass and maximum transmission near 3700 Å.

(13) At this point the only contaminant detectable by infrared or v.p.c. analysis was **1** (about 3%), plus tetramethylethylene, both of which remained unchanged during treatment with all reagents except LiAlH₄.

(14) N. J. Turro, W. B. Hammond, P. A. Leermakers, and H. Thomas, *Chem. Ind. (London)*, in press.

(15) In our hands the absorption at 1840 cm.⁻¹ disappears extremely rapidly when the solution is exposed to oxygen at 25°. In ref. 7 it is claimed that this band disappears slowly. We do not know the reason for this discrepancy.

(16) (a) For a review see A. S. Kende, *Org. Reactions*, **11**, 261 (1960);

a direct investigation of this hypothesis is now possible. The results of such studies will be reported shortly.

Acknowledgments. We wish to thank the National Science Foundation (Grant No. GP-4280) and the Petroleum Research Fund (216-G) for their generous support of this research.

(b) A. W. Fort, *J. Am. Chem. Soc.*, **84**, 2620 (1962); (c) *ibid.*, **84**, 2625, 4979 (1962); (d) R. C. Cookson and M. J. Nye, *J. Chem. Soc.*, 2009 (1965); (e) R. Loftfield, *J. Am. Chem. Soc.*, **72**, 632 (1950); (f) *ibid.*, **73**, 470 (1951); J. G. Burr, Jr., and M. J. S. Dewar, *J. Chem. Soc.*, 1201 (1954).

(17) National Science Foundation Predoctoral Fellow 1964–1965.

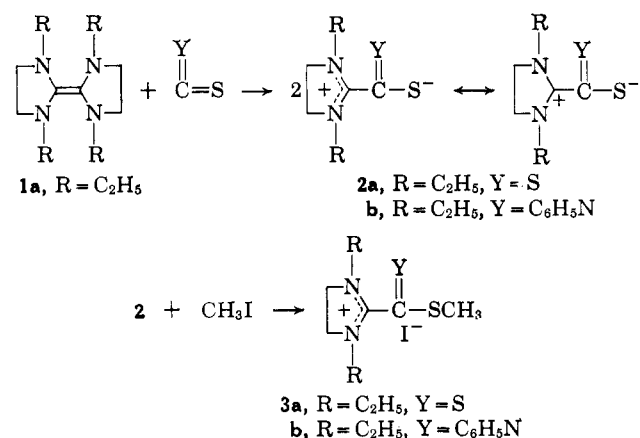
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Chemistry of Peraminoethylenes

Sir:

Aliphatic peraminoethylenes, particularly the $\Delta^{2,2'}$ -bis(imidazolidines) (**1**), are extremely reactive, powerful π -bases.¹ They are readily converted by carbon disulfide to orange- to red-colored stable dithioquaternary salts (**2**, Y = S) or by aryl isothiocyanates to stable yellow-colored mercapto-N-arylformimidoyl-imidazolinium inner salts (**2**, Y = ArN) in high yield.² The inner salts **2** undergo rapid alkylation by methyl iodide forming the water-soluble iodides (**3**). For



example, 1,1',3,3'-tetraethyl- $\Delta^{2,2'}$ -bis(imidazolidine) (**1a**) reacts exothermally with carbon disulfide, precipitating **2a** (dark red, m.p. 178–179°, 98% yield), which is converted quantitatively by methyl iodide to **3a** (dark red, m.p. 164–166°).³ The exothermic reaction of **1a** in tetrahydrofuran with phenyl isothiocyanate gives **2b** (light yellow, m.p. 145–147°, 91% yield). Methyl iodide quantitatively converts **2b** to **3b** (colorless, m.p. 184–186°). S-Methylation rather than N-methylation occurs as indicated by spectral

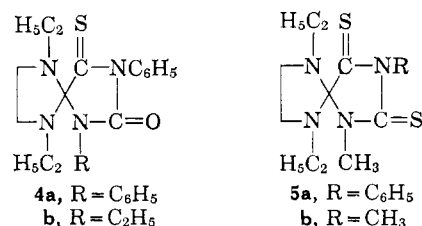
(1) H. E. Winberg, J. E. Carnahan, D. D. Coffman, and M. Brown, *J. Am. Chem. Soc.*, **87**, 2055 (1965).

(2) The inner salts are formally analogous to the adducts of tertiary phosphines with carbon disulfide and phenyl isocyanate; see (a) L. Horner and H. Hoffmann in "Newer Methods of Preparative Organic Chemistry," Vol. II, Academic Press Inc., New York, N. Y., 1963, p. 164; (b) T. N. Margulis and D. H. Templeton, *J. Am. Chem. Soc.*, **83**, 995 (1961).

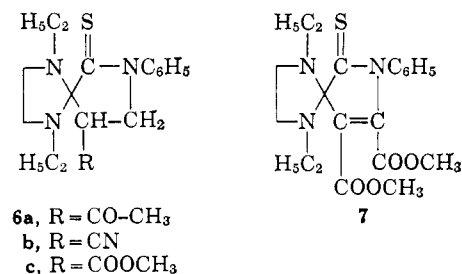
(3) Satisfactory elemental and spectral analyses were obtained for all compounds. All reactions involving the peraminoethylenes were carried out under nitrogen.

analysis of the iodides and isolation of aniline after acid hydrolysis of **3b**.

The inner salts **2** (Y = ArN) derived from aryl isothiocyanates represent a new 1,3-dipolar system⁴ which undergoes cycloaddition with suitable dipolarophiles, including aliphatic and aromatic isocyanates, aliphatic isothiocyanates, and multiple carbon-carbon bonds. Thus, reaction of **2b** with isocyanates under mild conditions forms the spiroheterocyclics **4**. For example, addition of phenyl isocyanate to **2b** suspended in tetrahydrofuran causes a mild exothermic reaction with the formation of **4a** as a bright yellow solid, m.p. 142–144°. Hydrolysis of **4a** gives 1,3-diphenylurea, confirming the assigned structure. Ethyl isocyanate and **2b** give **4b** (bright yellow, m.p. 104–106°, 75% yield). In a similar manner cycloaddition of methyl isothiocyanate to **2b** gives the dithiohydantoin derivative **5a** (bright yellow, m.p. 129.5–131°, high yield).



Unsaturated compounds such as methyl vinyl ketone, methyl acrylate, and acrylonitrile readily cycloadd to **2b** forming compounds **6**. The reaction, carried out in refluxing tetrahydrofuran, gives the following light yellow-colored adducts: **6a**, m.p. 123.5–124.5°, 76%; **6b**, m.p. 115–117°, 79%; and **6c**, m.p. 123–124° dec., 73%. Under the same conditions, dimethyl acetylenedicarboxylate forms 79% of the unsaturated spiroheterocyclic **7**, m.p. 137–138.5°.



Although under mild conditions the reaction of aliphatic peraminoethylenes with aromatic isothiocyanates proceeds only to the inner salts **2b**, the more reactive aliphatic isothiocyanates give dithiospiroheterocyclics directly, presumably by 1,3-addition of the aliphatic isothiocyanate to unisolated inner salts **2** (Y = RN). Reaction of **1a** with methyl isothiocyanate in refluxing ether gives 74% of bright yellow **5b**, m.p. 86–88°.⁵

The aliphatic bicyclic peraminoethylenes react readily with azides to give diazoiminoimidazolidines (**8**) along with the corresponding iminoimidazolidines con-

(4) See R. Huisgen [*Proc. Chem. Soc.*, 357 (1961); *Angew. Chem.*, **75**, 604 (1963); *Angew. Chem. Intern. Ed. Engl.*, **2**, 565 (1963)] for a discussion of 1,3-dipolar cycloadditions. J. E. Baldwin, G. V. Kaiser, and J. A. Romersberger [*J. Am. Chem. Soc.*, **86**, 4509 (1964)] suggest that 1,3-dipolar cycloadditions may be less mechanistically homogeneous than has been previously supposed.

(5) H. W. Wanzlick and his co-workers have extensively studied the chemistry of aryl-substituted bis(imidazolidines) (**1**, R = aryl); see H. W. Wanzlick and H. Ahrens, *Chem. Ber.*, **97**, 2447 (1964); H. W. Wanzlick and F. Esser, *Angew. Chem.*, **76**, 614 (1964), and earlier