

Photochemical Synthesis at Low Temperatures. Part III.† Ready Synthesis of Bicyclo[4,2,0]octan-2-ones from Cyclohexenones and Ethylene

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The photochemical [2 + 2] cycloadditions of ethylene to cyclohex-2-en-1-one and 3,5,5-trimethylcyclohex-2-en-1-one at -70° in dichloromethane produce the corresponding bicyclo[4,2,0]octan-2-one derivatives in 90 and 85% yields, respectively, in one step and in preparatively useful amounts. Under the same conditions, or in acetone as solvent at -70° , acetylene does not undergo a [2 + 2] cycloaddition with either ketone.

PHOTOCHEMICAL cycloaddition reactions of enones have been studied extensively in recent years.¹ Of considerable interest is the photochemical [2 + 2] cycloaddition of enones to olefins and acetylenes.¹⁻³ The majority of the work hitherto reported in this area has dealt with the synthesis of cyclobutanes from enones and substituted olefins.^{1,2} We report that under suitable conditions ethylene can undergo [2 + 2] cycloadditions to simple enones.

Only one addition of ethylene to a simple enone has

† Part II, D. C. Owsley and J. J. Bloomfield, *J. Org. Chem.*, in the press.

‡ The filter used in these photolyses is called Corex 9700 by Hanovia and is constructed of borosilicate glass. However, Corex glass is an aluminosilicate glass which does not have the transmission characteristics of the Corning 9700 glass. The 9700 glass is in general use by photochemists and is commonly called Corex. This error must have been perpetrated by the misnomer in the Hanovia catalogue.

¹ For reviews see (a) P. E. Eaton, *Accounts Chem. Research*, 1968, **1**, 50; (b) P. G. Bauslaugh, *Synthesis*, 1970, 287; (c) P. de Mayo, *Accounts Chem. Research*, 1971, **4**, 41.

² (a) E. J. Corey, J. D. Bass, R. Lemathieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, 1964, **86**, 5570; (b) P. de Mayo, H. Takeshita, and A. B. M. A. Sattar, *Proc. Chem. Soc.*, 1962, 119; (c) P. E. Eaton, *J. Amer. Chem. Soc.*, 1962, **84**, 2454; (d) O. L. Chapman, T. H. Koch, F. Klein, P. J. Nelson, and E. L. Brown, *ibid.*, 1968, **90**, 1657; (e) P. J. Nelson, D. Ostrem, J. D. Lassila, and O. L. Chapman, *J. Org. Chem.*, 1969, **34**, 811; (f) E. J. Corey and S. Nozoe, *J. Amer. Chem. Soc.*, 1964, **86**, 1652; (g) H. Hinko and P. de Mayo, *ibid.*, p. 3582; (h) P. E. Eaton, *Tetrahedron Letters*, 1964, 3695; (i) L. Duc, R. A. Mateer, L. Brassier, and G. W. Griffin, *ibid.*, 1968, 6173; (j) R. L. Cargill, J. R. Damewood, and M. M. Cooper, *J. Amer. Chem. Soc.*, 1966, **88**, 1330.

been reported. Nakanishi and his co-workers^{3a} added ethylene to 3-methylcyclohex-2-en-1-one in 40% yield at room temperature. We have found that by lowering the temperature of the photolysis mixture it is possible to carry out the photoaddition of ethylene to a variety of photoactivated double bonds.⁴ We have now prepared two bicyclo[4,2,0]octan-2-ones which are unsubstituted in the cyclobutane ring in a simple, high-yield, one-step procedure from ethylene and readily available starting materials. Previous syntheses of such materials either have consisted of many steps⁵ or have not given the desired product in high yield and in preparatively useful amounts.⁶

Irradiation of a solution of cyclohex-2-en-1-one (1) (0.3 mol) in ethylene-saturated dichloromethane (2.8 l) at -70° through a Corning 9700 glass filter ‡ in the

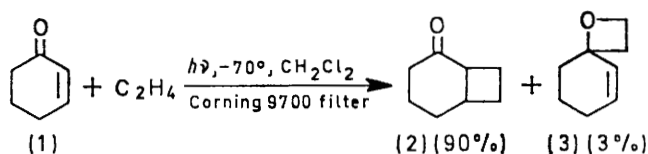
³ For photoadditions of enones to ethylene cf. (a) Y. Yamada, H. Uda, and K. Nakanishi, *Chem. Comm.*, 1966, 423; (b) P. E. Eaton, Abstracts of Papers, 156th National Meeting of the American Chemical Society, San Francisco, April 1968; (c) P. H. Nelson, J. W. Murphy, J. A. Edwards, and J. H. Fried, *J. Amer. Chem. Soc.*, 1968, **90**, 1307; (d) W. C. Agosta and W. W. Lowrance, *Tetrahedron Letters*, 1969, 3053; *J. Org. Chem.*, 1970, **35**, 3851.

⁴ (a) D. C. Owsley and J. J. Bloomfield, *Org. Prep. Proc. Internat.*, 1971, **3**, 61; (b) D. C. Owsley and J. J. Bloomfield, *J. Amer. Chem. Soc.*, 1971, **93**, 781.

⁵ (a) H. O. House and T. H. Cronin, *J. Org. Chem.*, 1965, **30**, 1061; (b) A. C. Cope and R. W. Gleason, *J. Amer. Chem. Soc.*, 1962, **84**, 1928; (c) G. Büchi and E. M. Burgess, *ibid.*, p. 3104.

⁶ J. Y. Vanderhoek, *J. Org. Chem.*, 1969, **34**, 4184.

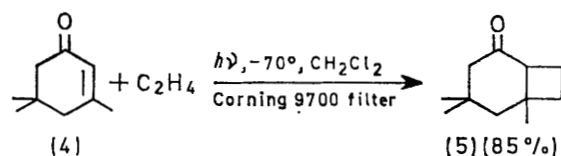
variable temperature photolysis apparatus previously described^{4a} for 20 h gave a 90% yield of *cis*-bicyclo[4,2,0]octan-2-one^{5a} (2) and a 3% yield of the oxetan (3). The photolysis was monitored by g.l.c. A third product, isomeric with compound (2) and which made



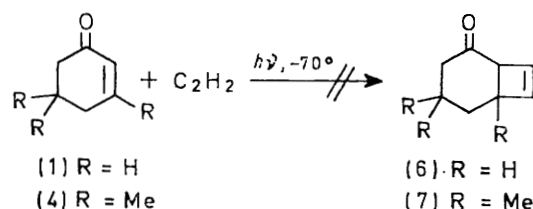
up ca. 30% of the area of the product peaks, disappeared when the solvent was removed from the photolysis mixture. The high yield of compound (2) suggests that the isomeric product was *trans*-bicyclo[4,2,0]octan-2-one, which underwent isomerisation^{2a,5} upon work-up.

The use of the Corning 9700 filter is very important in these transformations. When the irradiation was carried out through quartz, the yield of the photoproduct (2) was 53% after 36 h and only 33% after 52 h. These results suggest that photodecomposition of compound (2) is occurring at the shorter wavelengths (see later).

Similar irradiation of 3,5,5-trimethylcyclohex-2-en-1-one (4) and ethylene gave 4,4,6-trimethylbicyclo[4,2,0]octan-2-one (5) in 85% yield. No evidence was obtained for either a *trans*-isomer or an oxetan.



It was surprising to find that neither of the cyclohexenones (1) and (4) would react with acetylene under the foregoing conditions or in acetone solution at -70° . Viscous oils, which may be the result of dimerisation or polymerisation of the enones, were produced. No intermediates were detected by g.l.c. but it is not unlikely that initially formed bicyclo[4,2,0]oct-7-en-2-ones would be very reactive photochemically, and would rapidly be converted into less useful products.



EXPERIMENTAL

N.m.r. spectra were obtained with a Varian T-60 spectrometer. I.r. spectra were obtained with a Beckman IR-8 and mass spectra with a Varian-MAT CH-7 instrument. G.l.c. analyses were carried out on a column (2 m \times 3.2 mm) of 15% Carbowax 20M on Chrom. G by use of a Varian-Aerograph model 1200 instrument with flame

ionisation detector. Microanalyses were carried out by the Physical Sciences Center, Monsanto Co.

Cyclohex-2-en-1-one (Mobil) was used without further purification. 3,5,5-Trimethylcyclohex-2-en-1-one (Eastman) was distilled from calcium hydride before use. Dichloromethane (Mallinkrodt), acetone (J. T. Baker), ethylene (Matheson; C. P. grade), and acetylene (welding grade) were used without further purification.

General Photolysis Procedure.—Solutions of the substrate in 2.8 l of dichloromethane or acetone were prepared in the variable temperature photolysis apparatus.^{4a} The solutions were degassed by bubbling nitrogen as the apparatus was cooled to -70° . Then ethylene or acetylene was bubbled through the solution at 6 l min⁻¹ for 15 min and at 1 l min⁻¹ for 30 min. A flow rate of 100 ml min⁻¹ was maintained throughout each photolysis. All irradiations were carried out with a Hanovia 450 W medium-pressure mercury arc.

Bicyclo[4,2,0]octan-2-one (2).—(a) *Irradiation through Corning 9700 glass.* Cyclohex-2-en-1-one (28.6 g, 0.3 mol) in dichloromethane (2.8 l) saturated with ethylene was irradiated through a Corning 9700 glass filter for 20 h at -70° . G.l.c. analysis on the Carbowax column programmed from 70 to 180° at 10° min⁻¹ showed the presence of the oxetan (3), R_t 5.4 min, *cis*-bicyclo[4,2,0]octan-2-one, R_t 10.3 min, and a compound thought to be the *trans*-isomer, R_t 10.5 min. The solution was concentrated *in vacuo* to give a pale yellow oil which was distilled through a Teflon spinning band column (1 m) to yield two fractions. Fraction (I) (2.1 g) had b.p. 48–65° at 5 mmHg. Fraction (II) (33.3 g, 0.27 mol, 90%) consisted of pure *cis*-bicyclo[4,2,0]octan-2-one, b.p. 65–66° at 5 mmHg (lit.,^{5b} 89–91° at 18 mmHg), the i.r. and n.m.r. spectra of which were identical with those reported.^{5a} The mass spectrum showed peaks at m/e 124 (M^+) and 96 ($M - \text{CO}$).

Fraction (I) contained a mixture of compounds (3), (1), and (2) in the approximate ratio of 5 : 3 : 2. A g.l.c.-mass spectrum of this mixture showed that the mass spectrum of compound (3) differed greatly from that of compound (2), but that the former had a molecular weight of 124 and did not yield a large peak at m/e 96. Thus compound (3) was not a ketone. The n.m.r. spectrum of fraction (I) showed vinyl resonances different from those of cyclohex-2-en-1-one; thus compound (3) was identified as 1-oxaspiro[3,5]non-5-ene.

(b) *Irradiations through quartz.* Cyclohex-2-en-1-one (0.3 mol) was irradiated for 36 h in ethylene-saturated dichloromethane (2.8 l) with unfiltered light from the 450 W medium-pressure mercury arc. Work-up as in (a) gave compound (2) (19.7 g, 0.16 mol, 53%) and a residue (20 g). A similar irradiation for 52 h gave compound (2) (12.7 g, 0.1 mol, 33%) and a non-volatile residue (29.5 g).

4,4,6-Trimethylbicyclo[4,2,0]octan-2-one (5).—3,5,5-Trimethylcyclohex-2-en-1-one (41.4 g, 0.3 mol) was irradiated through a Corning 9700 glass filter in ethylene-saturated dichloromethane (2.8 l) for 20 h at -70° . The yellow oil which was obtained after the solution was concentrated *in vacuo* was distilled through a short Vigreux column at 44° and 0.8 mmHg to yield the bicyclo-octanone (5) (42.3 g, 0.26 mol, 85%), δ 0.92 (3H, s), 1.05 (3H, s), 1.27 (3H, s), and 2.73–1.40 p.p.m. (9H, complex m), ν_{max} 1700 cm⁻¹ (Found: C, 79.45; H, 11.05. $\text{C}_{11}\text{H}_{18}\text{O}$ requires C, 79.45; H, 10.9%).

Attempted Photoaddition of Acetylene to Cyclohex-2-en-1-one (1).—Cyclohex-2-en-1-one (10.0 g, 0.104 mol) and

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3447

acetylene were irradiated in acetone (2.8 l) through quartz for 63 h at -70° . G.l.c. analysis indicated that all of the starting material had been consumed in this time. No product peak was observed at long retention time. Concentration of the solution *in vacuo* gave a viscous yellow oil (10.0 g) which showed no vinylic proton signal in the n.m.r. spectrum.

Similar results were obtained with cyclohex-2-en-1-one (1) and acetylene in dichloromethane at -70° and with the trimethyl derivative (4) and acetylene in either acetone or dichloromethane. No differences were observed when the Corning 9700 filter was used.

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