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THE CHEMISTRY OF 7-SUBSTITUTED NORBORNENES

7-KETONORBORNENE.

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Although the norbornane system has been widely investigated, relatively little is known about the chemistry of 7-substituted norbornenes due to the lack of a simple synthetic route to these bicyclic molecules.[2] Especially conspicuous is the absence of information about 7-ketonorbornene (I) and 7-ketonorbornane (II).[3] We wish to report a convenient synthesis of 7-ketonorbornene and its derivatives, thus making these compounds readily available for investigations which will fill the void in this area of norbornene chemistry.

The reaction of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (III) with ethylene in an inert atmosphere at 180° gave a 75 percent yield of the expected Diels-Alder product,

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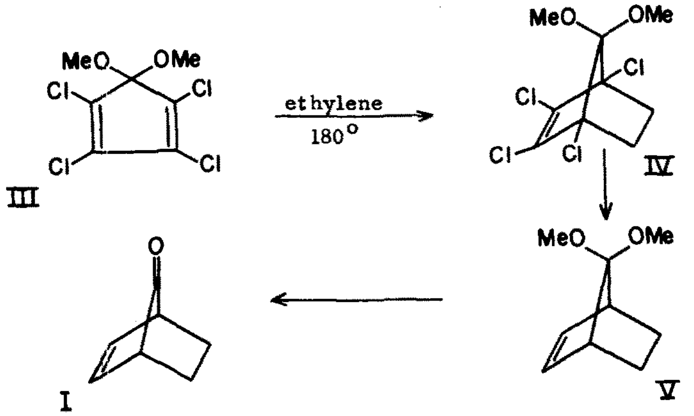
[1] National Science Foundation Summer Fellow, 1962.

[2] For leading references see C. H. DePuy and P. R. Story, J. Amer. Chem. Soc. 82, 627 (1960), and P. Wilder and A. Winston, J. Amer. Chem. Soc. 78, 868 (1956).

[3] The preparation of these compounds by a tedious method has been described by C. Norton, Thesis, Harvard University, 1955; also see H. M. Walborsky and D. F. Loncrini, J. Org. Chem. 22, 1117 (1957).

IV.[4] Dechlorination with lithium - tertiary butanol - tetrahydrofuran[5] gave a mixture of V and VI in the ratio of 63 to



37 in 65 percent yield.[6,7] The unsaturated ketal was readily separated from the saturated ketal by extraction of a pentane solution of the mixture with aqueous silver nitrate solution.[8] Substitution of sodium for lithium in the dechlorination step

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[4] P. E. Hoch, J. Org. Chem. 26, 2066 (1961).

[5] P. Bruck, D. Thompson and S. Winstein, Chem. and Ind. 405 (1960).

[6] E. T. McBee, W. L. Dilling and H. P. Braendlin, J. Org. Chem. 27, 2704 (1962), and P. Bruck, Tetrahedron Letters No. 10, 449 (1962).

[7] This ratio was determined by vapor phase chromatography and by catalytic hydrogenation.

[8] S. Winstein and H. J. Lucas, J. Amer. Chem. Soc. 60, 836 (1938).

gave pure 7,7-dimethoxybicyclo[2.2.1] hept-2-ene[9] (V) in 63 percent yield [b.p. 78° (30 mm.), n_D^{29} 1.4587]. (Found: C, 70.10; H, 9.13; O, 20.91. Calc. for $C_9H_{14}O_2$: C, 70.10; H, 9.15; O, 20.75). Hydrolysis of V could be accomplished with either acetic acid (72 percent yield) or with 10 percent aqueous sulfuric acid (86 percent yield) to give 7-ketonorbornene[9,10] [b.p. 62-63° (30 mm.), n_D^{25} 1.4772, $\lambda_{\text{max.}}^{\text{isooctane}}$ 274 mμ (ε = 31), $\gamma_{\text{max.}}$ 5.37, 5.58, 5.62μ]. (Found: C, 77.56; H, 7.69. Calc. for C_7H_8O: C, 77.75; H, 7.46).

7-Ketonorbornane (II) was prepared from both the saturated ketal and the unsaturated ketone. Catalytic hydrogenation of the mixture of V and VI (from the lithium dechlorination) over 5 percent palladium on carbon gave the saturated ketal, VI, in 87 percent yield [b.p. 78-80° (30 mm.), n_D^{25} 1.4538]. (Found: C, 69.46; H, 10.28; O, 20.45. Calc. for $C_9H_{16}O_2$: C, 69.19;

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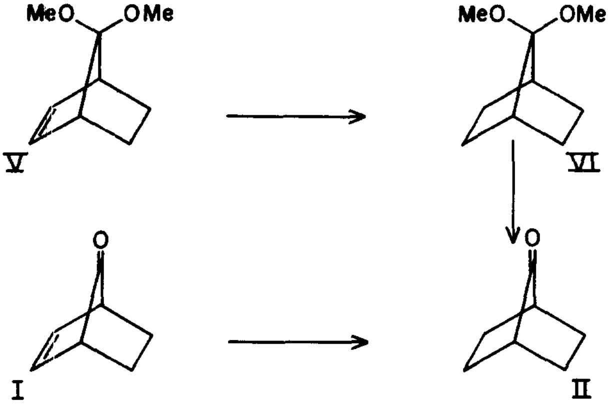
[9] The retention of the norbornene skeleton was established by near infrared spectroscopy. These spectroscopic studies, which will be published separately, were carried out as part of a program supported by the National Science Foundation.

[10] In general the physical constants of 7-ketonorbornene and 7-ketonorbornane agreed well with those of Norton (ref. 3). The major discrepancies were in the ultraviolet spectrum of 7-ketonorbornene (I) and in the melting point of the 2,4-dinitrophenylhydrazone of 7-ketonorbornane. Whereas Norton reported $\lambda_{\text{max.}}^{\text{ethanol}}$ 233 (ε = 1300) for I, we observed no maximum in this region although relatively strong end absorption was noted. The melting point of the 2,4-dinitrophenylhydrazone of 7-ketonorbornane, VII, is confusing. Norton reported that the 2,4-dinitrophenylhydrazones of the saturated and unsaturated ketone melt at 134.5 - 135.6° and 134 - 135° respectively. Walborsky (ref. 3) listed the melting point of VII as 133 - 134°, but described the ketone as being a liquid. Our saturated ketone had physical constants which were identical to Norton's. However, we found VII melted at 158.2 - 158.8°. (Found: C, 53.79; H, 4.87; N, 19.38. Calc. for $C_{13}H_{14}N_4O_4$: C, 53.79; H, 4.86; N, 19.30). The 2,4-dinitrophenylhydrazone of the unsaturated ketone, m.p. 137.2-137.8°, was in fair agreement with Norton's value. (Found: C, 54.23; H, 4.36; N, 19.38. Calc. for $C_{13}H_{12}N_4O_4$: C, 54.16; H, 4.20; N, 19.44).

H, 10.32; O, 20.49). Hydrolysis of VI with acetic acid or with 10 percent aqueous sulfuric acid gave 7-ketonorbornane[11] [m.p. 79.5 - 80.5°, $\lambda_{max.}^{isooctane}$ 292 (ε = 18), $\nu_{max.}$ 5.46, 5.61, 5.73 μ]. (Found: C, 76.40; H, 9.36. Calc. for $C_7H_{10}O$: C, 76.32; H, 9.15). Catalytic hydrogenation of 7-ketonorbornene (I) over 5 percent palladium on carbon gave the saturated ketone, II, in 92 percent yield.[12]



The elucidation of this simple synthetic route to I and II described in this communication makes a study of the reactions of these compounds possible. The results of these investigations will be the topic of future publications.

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[11] 7-Ketonorbornane was shown to be free of impurities by vapor phase chromatography.

[12] The percent yield was determined by isolation of the product as the 2,4-dinitrophenylhydrazone.