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α-METHYLENEOXETANE

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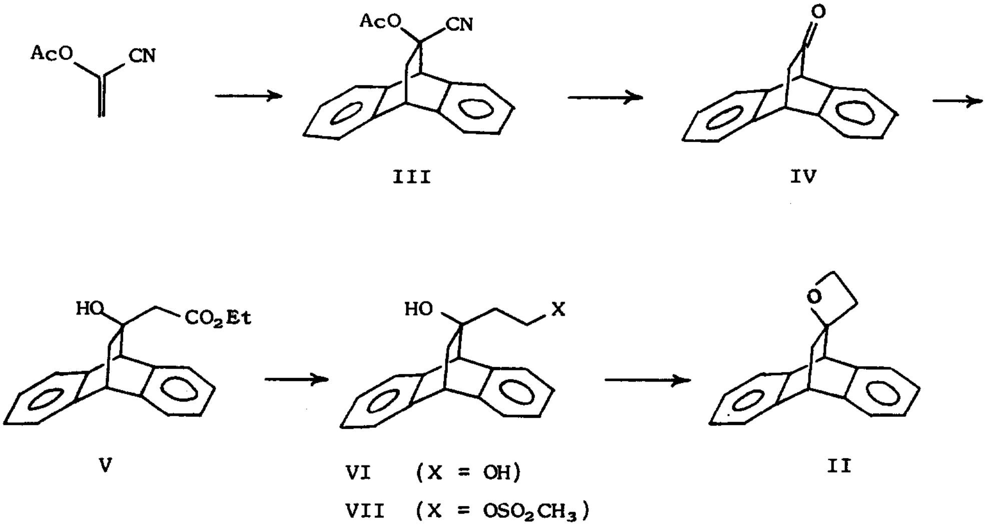
We wish to report the synthesis of α-methyleneoxetane (I). Compounds having this ring system have been prepared by photochemical cycloadditions of carbonyl compounds with allenes[1] and from the reaction of certain ketenes with olefins.[2] The parent compound (I) has not previously been reported, although the isomeric 3-methyleneoxetane is known.[3]

α-Methyleneoxetane was obtained by pyrolyzing[3,4] the anthracene adduct (II) which was prepared by the sequence of steps described below.

The reaction of anthracene (2 equivalents) with α-acetoxyacrylonitrile[5] (8 hours in xylene at 145-150°) produced the Diels-Alder adduct III (81%) as an oil after chromatography on Florisil (a portion was crystallized, m.p. 97.5-99° (methylene chloride- hexane)[6a,b]). The oily adduct (III) was hydrolyzed[7] to the known ketone IV (91%, m.p. 152-153° (ether-hexane)[6a,8]), which was reacted with zinc and ethyl bromoacetate in benzene-ether, giving the hydroxy-ester V (92%, m.p. 119-120° after chromatography on Florisil;[6a,b] The analytical sample[6c] had m.p. 121.5-122° (ether)). The hydroxy-ester (V) was reduced with lithium aluminum hydride (3 hours reflux in THF) to give diol VI (65%, m.p. 87-89.5° (ether)[6a,d]). The diol (dried by distilling off benzene from a solution) was treated with 1.5 equivalents of methane sulfonyl chloride (16 hours at 0° in pyridine) to produce an oily monomesylate (VII)[6a] which, without purification, was treated with potassium t-butoxide in t-butanol (2 hours, 60-70°), giving the crystalline oxetane II (73% yield from VI, m.p. 129-130°, after chromatography



on Florisil and recrystallization from ether.[6a,b] The analytical sample[6c] had m.p. 130-130.5°).

Pyrolyses of II were carried out on a small scale (50-200 mg) by heating to 330-350° in a slow stream of nitrogen for 5-25 minutes and collecting the volatile products in a receiver cooled in dry ice.[*] The oxetane (I) was obtained as a colorless liquid[**] which could be identified by its IR, NMR, and mass spectrum, and its reaction with phenyllithium.

The infrared spectrum (in CCl_4) of α-methyleneoxetane (I) showed strong

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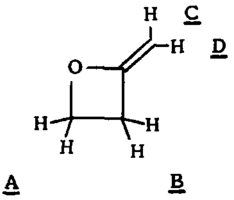
[*] It was found that the success of the pyrolyses was critically dependent on the purity of the starting oxetane (II). Also, in some cases, methyl vinyl ketone was formed as an impurity. On two occasions the yield of I was measured (by integrating the NMR spectrum using cyclohexane as an internal standard) to be 10%. The composition of the nonvolatile residue from the pyrolyses is being investigated.

[**] The oxetane appeared to be stable for several days at room temperature (in solution) and was stable to gas chromatography (SE-30 column at 40°, injector at 100°) (The retention time was comparable to that of THF).

peaks at 1689, 1185, and 957 cm^{-1}. Mass spectrum: m/e 39, 42, 55, 70. The NMR spectrum[9,10] (in CCl_2CCl_2) showed a triplet (J = 6.5 cps) at δ 4.50, and multiplets at 4.03, 3.63, and 3.16, in the ratio of 2:1:1:2. The assignments[11] and coupling constants are shown below.



I

$\delta_A = 4.50$ $J_{AB} = 6.5$ cps

$\delta_B = 3.16$ $J_{BC} = 2.4$ cps

$\delta_C = 4.03$ $J_{BD} = 1.8$ cps

$\delta_D = 3.63$ $J_{CD} = 3.5$ cps

The reaction of excess phenyllithium[12] (in THF) with the oxetane (I) produced 4-phenyl-2-butanone (VIII)[13] after workup, which was purified by preparative VPC and shown to be identical by IR, NMR, and VPC retention time with an authentic sample.[15] This ring opening reaction illustrates the potential synthetic utility of α-methyleneoxetane as a 3-ketobutyl group, e.g. in the Robinson annelation sequence. We are exploring further the reactions of α-methyleneoxetane as well as investigating alternative methods for its synthesis.[16]

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4. For related examples see (a) P. D. Bartlett and F. A. Tate, J. Amer. Chem. Soc., 75, 91 (1953); (b) H. Kwart and K. King, Chem. Rev., 68, 415 (1968).

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6. (a) The IR and NMR spectra were consistent with the structure assigned. (b) The mass spectrum of this compound showed a parent molecular ion and a base peak at m/e 178 (anthracene). (c) Elemental Analysis (C, H) was

within 0.2% of the calculated value. (d) Recrystallization of the diol VI from ether or benzene produced crystals of m.p. 92.5-93.5°. The C, H analyses were unsatisfactory. The mass spectrum showed no molecular ion but did show a peak at m/e 248 ($M-H_2O$) and a base peak at m/e 178 (anthracene).

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9. The chemical shifts are in ppm downfield from tetramethylsilane. The corresponding chemical shifts in CCl_4 solution are at δ 4.53, 3.96, 3.60, 3.18.

10. We thank Dr. D. Z. Denney for obtaining the 100 Mc spectrum.

11. For NMR spectra of related compounds, see reference 1c and L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd Edition, Pergamon Press, 1969; pp. 186-7, 278-9.

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13. 2-Phenyl-3-buten-2-ol (IX)[14] and 2,4-diphenyl-2-butanol (X)[15] were also formed in this reaction. They were isolated by preparative VPC and shown to be identical (IR, NMR, VPC) with samples prepared independently. Whether IX was formed from a possible methyl vinyl ketone impurity or from I has not yet been determined. The reaction of phenyllithium with methyl vinyl ketone (giving IX) did not form VIII.

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16. We thank Research Corporation and The Research Council of Rutgers University for financial support.