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CYCLOADDITION OF KETENES TO ETHOXYACETYLENE. THE MONOENOLETHER OF CYCLOBUTANE-1, 3-DIONE. [1]

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IT has recently been shown that the reaction of ethoxyacetylene with diphenylketene yields the ethoxycyclobutenone Ia among other products.[2a-d] Alkoxycyclobutenones of this type have also been obtained by the pyrolysis of substituted alkoxyacetylenes, presumably by addition of the ketenes formed *in situ* to the parent acetylene.[3]

During studies on addition reactions of alkoxyacetylenes we have applied the ketene-acetylene cyclization to the synthesis of the novel compound Ic, (the enolether of cyclobutane-1, 3-dione), and to the preparation of alkoxycyclobutenones of type I from acid chlorides.

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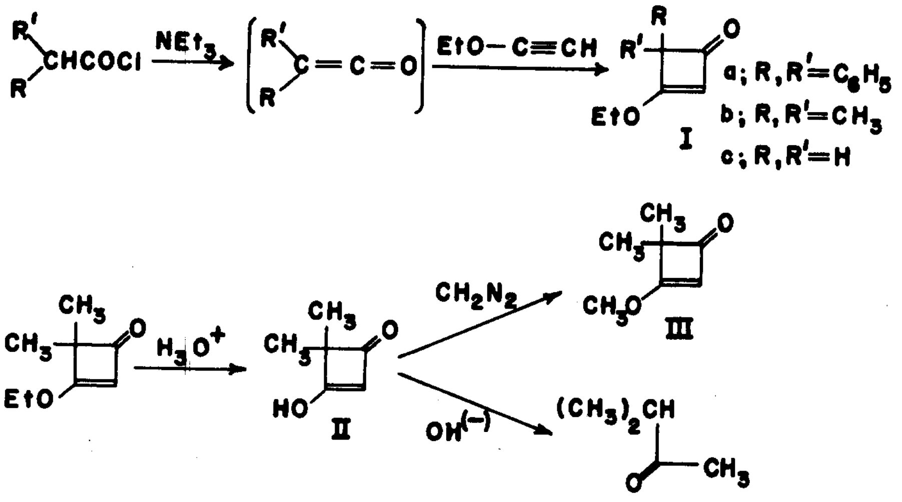
[1] Contribution No. 1710 from the Sterling Chemistry Laboratory, Yale University.

[2] (a) J. Nieuwenhuis and J. F. Arens, *Rec. Trav. Chim. Pays-Bas*. **77**, 1153 (1958); (b) E. F. Jenny, K. Schenker, and R. B. Woodward, *Angew. Chem.*, **73**, 756 (1961); (c) J. Druey, E. F. Jenny, K. Schenker and R. B. Woodward, *Helv. Chim. Acta.*, **45**, 600 (1962); (d) D. H. R. Barton, J. N. Gardner, R. C. Petterson and O. A. Stamm. *Proc. Chem. Soc.*, **21** (1962).

[3] J. Ficini, *Bull. Soc. Chim. Fr.* 1367 (1954); J. Nieuwenhuis and J. F. Arens, *Rec. Trav. Chim. Pays-Bas*, **77**, 761 (1958); J. F. Arens, Ethynylethers and Thioethers as Synthetic Intermediates, in *Advances in Organic Chemistry*, Vol. II, pp. 195-7. Interscience Publishers, Inc., New York (1960).



The latter type of reaction is shown in the above scheme whereby the ketenes, formed _in situ_ by the treatment of acid chlorides with a tertiary amine undergo addition to the alkoxyacetylene. Ketene dimer formation and polymerization are competitive reactions in the presence of the ammonium salt.[4] Thus, isobutyryl chloride and ethoxyacetylene, in the presence of triethylamine at 0°C yield 65% of Ib (Found: C, 68.35; H, 8.69. $C_8H_{12}O_2$ requires: C, 68.54; H, 8.63), b.p. 78-82° /9mm. n_D^{22} 1.4562; U.V. (95% EtOH):λmax 233 mμ, ϵ 12,700; I.R: 1745, 1575, 865 cm^{-1}; N.M.R. $(CH_3)_4Si$): 5.27τ (singlet); 5.78τ (quartet); 8.53τ (triplet), 8.81τ (singlet), areas 1:2:3:6.

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[4] W. E. Hanford and J. C. Sauer, Preparation of Ketenes and Ketene Dimers, in _Organic Reactions_, Vol. III, pp. 124-26 John Wiley & Sons, Inc., New York (1946).

Hydrolysis of Ib in dilute acid leads to II, which, as expected,[5a-b] is a very strong acid (pKa 2.65). (Found: C, 64.04; H, 7.24. $C_6H_8O_2$ requires: C, 64.27; H, 7.19), m.p. 129-130°; U.V. (95% EtOH): 241 mμ, ε 14,100; I.R: 1750, 1575 cm^{-1}. Ib forms a monobromo derivative with bromine, while II gives the methyl ether with diazomethane.[6] On treatment with warm aqueous alcoholic NaOH followed by acidification II is degraded to methyl isobutyl ketone.

Utilizing other aliphatic acid chlorides as sources of the intermediate ketenes, products of structure I were obtained although in lower yields. Thus, from cyclohexane and cyclopentane carbonyl chlorides, 2-ethyl butyryl chloride, and propionyl chloride 10-30% of products were isolated, while from acetyl chloride, only ketene dimer and dehydracetic acid could be obtained.

The formation of alkoxycyclobutenones (I) can be traced in reaction mixtures by the observation of the characteristic, strong infrared bands near 1755 and 1580 cm^{-1},[2c] and a peak of medium intensity at about 870 cm^{-1}. Utilizing this method of assay we were able to detect substantial amounts of Ic in the complex mixture resulting when ketene is bubbled through a solution of ethoxyacetylene in methylene chloride. The separation of Ic from ethoxyacetylene, acetone, diketene, and polymeric products was accomplished by repeated column chromatography and crystallization from ether-pentane at -50°C.

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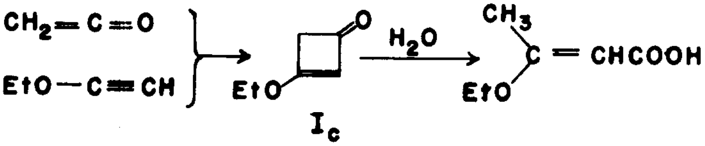
[5] (a) R. B. Woodward and G. Small, Jr., J. Amer. Chem. Soc. 72, 1297 (1950); (b) E. J. Smutny, M. C. Caserio, J. D. Roberts, J. Amer. Chem. Soc. 82, 1793 (1960).

[6] Satisfactory analytical data were obtained for both of these derivatives.

Pure Ic (30% yield) m. p. 26-27.5°, is stable at low temperatures,



but polymerizes exothermically when heated up to 65°C. (Found: C, 64.03; H, 7.21; OC_2H_5, 38.11. $C_6H_8O_2$ requires: C, 64.27; H, 7.19; OC_2H_5, 40.19.) U.V. (anhydrous EtOH) λmax 233 mμ, ϵ, 12450; I.R.: 1760, 1580, 875 cm^{-1}; N.M.R.: 5.12τ (singlet); 5.74τ (quartet); 6.89τ (singlet); and 8.55τ (triplet), areas 1:2:2:3.

When Ic is stirred overnight with moist ether, ring opening takes place with formation of β-ethoxycrotonic acid,[7] while with hot anhydrous ethanol the corresponding ethyl ester is produced. Other aspects of the chemistry of Ic and related products will be reported elsewhere.[8,9]

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[7] M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, E. A. Smith and W. E. Vaughan, J. Amer. Chem. Soc. 60, 440 (1938); L. N. Owen J. Chem. Soc. 385 (1945).

[8] For related syntheses of cyclobutenone ethers from substituted alkoxyacetylenes see B. Rosebeek and J. F. Arens, Rec. Trav. Chim. Pays-Bas 81, 549 (1962).

[9] This work was supported, in part, by U.S. Public Health Service Grant RG-7874 (C1).