1,3-Diethoxy-1,3-dienes from β-Diketones

By EZIO RIZZARDO

(*Research School of Chemistry, Australian National University, P.O. Box 4, Canberra ACT 2600, Australia*)

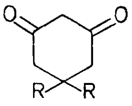
Summary Alkylation of dimedone or cyclohexane-1,3-dione with 1 equiv. of triethyloxonium fluoroborate yielded mono-enol ethers whereas excess of alkylating agent gave 1,3-diethoxy-1,3-dienes.

THE potential usefulness of the Diels–Alder reaction with dienes containing 1,3-oxygenated functions has been demonstrated,[1–3] involving *in situ* reactions with 1,3-diacetoxy-1,3-dienes generated from cyclic β-diketones,[1] with 1-methoxy-3-trimethylsilyloxybuta-1,3-diene from 4-methoxybuten-2-one,[2] and with 1,3-dialkoxy-1,3-dienes. Thus far however, the availability of the 1,3-dialkoxydienes has been limited to those accessible *via* Birch reduction of 1,3-dialkoxybenzenes.[3]

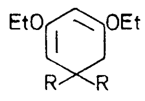
This report shows that cyclohexane-1,3-diones such as (I) and (II) can be converted into the di-enol ethers (III) and (IV) by alkylation of the appropriate β-diketone with triethyloxonium fluoroborate[4] in the presence of a hindered base. These transformations are examples of a novel and potentially flexible approach to the synthesis of 1,3-dialkoxy-1,3-dienes.

Treatment of dimedone or cyclohexane-1,3-dione with triethyloxonium fluoroborate (3 equiv.†) and Pr$^i_2$NEt (3·2 equiv.) in CH$_2$Cl$_2$ at 5 °C gave an essentially quantitative yield of 1,3-diethoxy-5,5-dimethylcyclohexa-1,3-diene (III)‡ [δ(CDCl$_3$) 5·08 (1H, m, 2-H) and 4·34 (1H, d, *J* 1·5 Hz, 4-H)] or 1,3-diethoxycyclohexa-1,3-diene (IV) [δ 4·94 (1H, d, *J* 2 Hz, 2-H and 4·44 (1H, m, 4-H)].

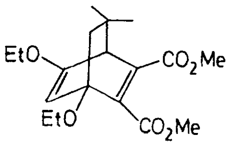
These dienes showed the expected high reactivity towards dienophiles. For example, the reaction of (III) with dimethyl acetylenedicarboxylate or maleic anhydride at room temperature yielded > 80% of cycloaddition products (V) and (VI) respectively.



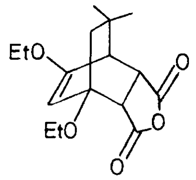
(I) R = Me
(II) R = H



(III) R = Me
(IV) R = H



(V)



(VI)

The reaction of (I) or (II) with triethyloxonium fluoroborate (1 equiv.) and Pr$^i_2$NEt (1·1 equiv.) in CH$_2$Cl$_2$ at 5 °C produced quantitative yields of the *O*-alkylated products: 5,5-dimethyl-3-ethoxycyclohex-2-en-1-one and 3-ethoxycyclohex-2-en-1-one respectively.[5] This constitutes a new simple procedure for the conversion of enolisable β-diketones cleanly and rapidly into mono-enol ethers and should prove to be a useful alternative to the existing methods.[6]

The helpful discussions with Professor A. J. Birch and Dr. I. Jenkins are gratefully acknowledged.

(*Received, 5th May* 1975; *Com.* 511.)

---

† < 3 equiv. resulted in incomplete conversion owing to a slow reaction between Pr$^i_2$NEt and triethyloxonium fluoroborate.

‡ All compounds showed the expected spectral characteristics and the crystalline products gave satisfactory elemental analyses.

[1] C. M. Cimarusti and J. Wolinsky, *J. Amer. Chem. Soc.*, 1968, **90**, 113; J. Wolinsky and R. B. Login, *J. Org. Chem.*, 1970, **35**, 1986.

[2] S. Danishefsky and T. Kitahara, *J. Amer. Chem. Soc.*, 1974, **96**, 7807; *J. Org. Chem.*, 1975, **40**, 538.

[3] A. J. Birch, D. N. Butler, and J. B. Siddall, *J. Chem. Soc.*, 1964, 2932; I. Alfaro, W. Ashton, L. D. McManus, R. C. Newstead, K. L. Rabone, N. A. J. Rogers, and W. Kernick, *Tetrahedron*, 1970, **26**, 201.

[4] H. Meerwein, G. Hing, P. Hofmann, E. Kroning, and E. Pfeil, *J. Prakt. Chem.*, 1937, **147**, 257.

[5] Identical with samples prepared by the method of R. B. Frank and H. K. Hall, *J. Amer. Chem. Soc.*, 1950, **72**, 1645.

[6] G. J. Heiszwolf and H. Kloosteriel, *Chem. Comm.*, 1966, **51**; E. G. Meek, J. H. Turnbull, and W. Wilson, *J. Chem. Soc.*, 1953, **811**; B. Eisert, F. Arndt, L. Loewe, and E. Ayca, *Chem. Ber.*, 1951, **84**, 156.