Formation of a Perhydroindanedione by Reductive Intramolecular β-Acylation of a Cyclohexenone[1]

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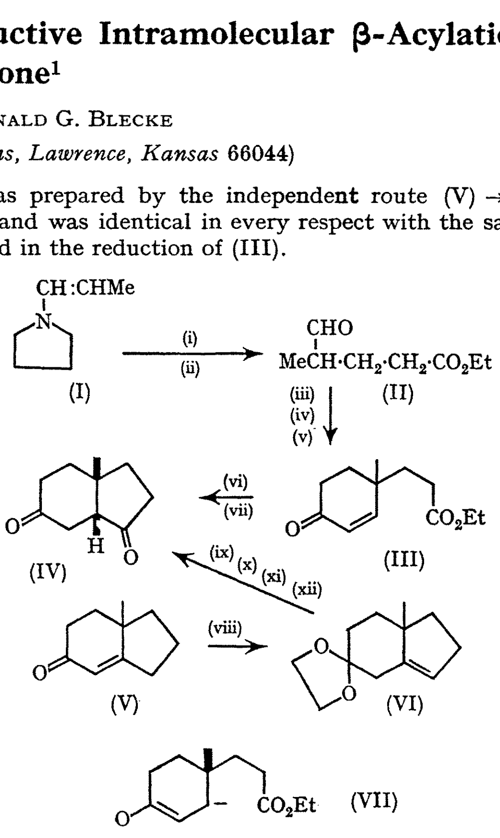
As part of a general study aimed at the development of new, general methods for the construction of carbocyclic systems we have examined the possibility of effecting ring closure by intramolecular β-acylation of the radical anion intermediate produced in the alkali metal–ammonia reduction of αβ-unsaturated ketones. Such intermediates have been successfully employed for the formation of three-membered rings by intramolecular alkylation,[2,3] but an attempt to effect ring closure to a five-membered ring was unsuccessful.[3] One example of an intramolecular β-acylation of an αβ-unsaturated ketone on reduction with lithium–ammonia has been reported in the reduction of a steroidal 11α-acetoxy-3-keto-1,4-diene,[4] but this represents a case in which the electrophilic centre is held very close to the carbanionic centre at C-1 and intramolecular acylation might be expected to compete favourably with protonation by solvent. We report a novel application of this method of ring closure to the formation of a perhydroindanedione in a case in which the electrophilic centre is not rigidly held close to the β-carbon.

The αβ-unsaturated ketone (III) was prepared by the sequence (I) → (II) → (III).[5] Treatment of (III) with an excess of lithium in liquid ammonia followed by oxidation of the crude product with Jones' reagent and chromatography on silica gel gave the dione (IV), m.p. 72—73°, in 50% overall yield. Dione (IV) exhibits i.r. absorption at 1750 and 1710 cm.$^{-1}$ and the angular methyl group appears in the n.m.r. spectrum at δ 1·40. An authentic sample of (IV) was prepared by the independent route (V) → (VI) → (IV) and was identical in every respect with the sample obtained in the reduction of (III).



(i) $CH_2{:}CH{\cdot}CO_2Et$; (ii) H_3O^+; (iii) Tetrahydropyrrole; (iv) Methyl vinyl ketone; (v) H_3O^+; (vi) M–NH_3; (vii) [O]; (viii) Ethylene glycol–TsOH/benzene; (ix) B_2H_6; (x) NaOH, H_2O_2; (xi) CrO_3–H_2SO_4; (xii) H_3O^+.

The use of other reducing conditions for accomplishing the transformation (III) → (IV) has been briefly examined, and so far reduction with potassium–ammonia has given the best results, dione (IV) being obtained in 60% yield. We are currently examining the generality of this novel type of ring closure, which presumably proceeds *via* the radical anion (VII).

We thank the National Science Foundation for support of this work.

(*Received, December 11th,* 1968; *Com.* 1695.)

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[1] Previous paper in this series: R. G. Carlson and Ronald G. Blecke, *J. Org. Chem.*, 1967, **32**, 3538.

[2] G. Stork and J. Tsuji, *J. Amer. Chem. Soc.*, 1961, **83**, 2783.

[3] G. Stork, P. Rosen, N. Goldman, R. V. Coombs, and J. Tsuji, *J. Amer. Chem. Soc.*, 1965, **87**, 275.

[4] M. Tanabe, J. W. Chamberlin, and P. Nishiura, *Tetrahedron Letters*, 1961, 601.

[5] *Cf.* G. Stork and J. E. Dolfini, *J. Amer. Chem. Soc.*, 1963, **85**, 2872.