Cleavage of 1,4-Diketones on Reduction with Lithium in Liquid Ammonia. Conversion of Cyclohexenone Photodimers into the Dihydrodimers

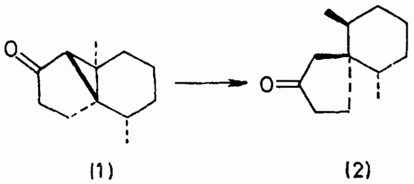
By JAMES GRIMSHAW* and REGINALD J. HASLETT
(*Department of Chemistry, Queen's University, Belfast* BT9 5AG)

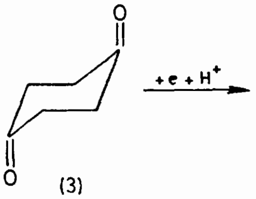
Summary A mechanism is discussed for cleavage of the central carbon–carbon bond in 1,4-diketones, (CO)C–C(CO), when this bond is orthogonal to the planes of the two carbonyl functions; lithium–ammonia–t-butyl alcohol reduction of the 1,4-diketonic photochemical dimers from isophorone and cyclohexenone gave in each case one stereoisomer of the corresponding dihydrodimers.

THE reductive cleavage by lithium in liquid ammonia of a cyclopropyl ring conjugated to a carbonyl function has been known for some time and the stereochemical requirements for the reaction have been investigated.[1] *E.g.*, in the reduction of compound (**1**) to (**2**) the carbon–carbon bond which is broken is the one orthogonal to the plane of the carbonyl group. This allows maximum overlap in the transition state between the carbonyl π-orbitals and one of the carbon p-orbitals which develop during the breaking of the σ-bond.

In the system (CO)C–C(CO) we can envisage an analogous reductive cleavage of the central carbon–carbon bond provided that this bond is orthogonal to the planes of both carbonyl functions so that overlap can occur in the transition state between the carbonyl π-orbitals and the carbon p-orbitals which develop during bond cleavage to give initially a dienolic product. For example, Kariv and Cohen observed 9% of compound (**4**) among the products from electrochemical reduction of cyclohexane-1,4-dione (**3**) while Wenkert and Loder obtained 90% of (**4**) from zinc and acid reduction.[2]

Photochemical dimerisation of isophorone gives a mixture from which the head to head dimer (**5**) can be isolated.[3] The structure of (**5**) has been established by *X*-ray methods.[4] It has the arrangement of bonds as detailed above and a further driving force for cleavage of the carbon–carbon bond β to both carbonyl functions is the added gain in energy from opening of the cyclobutane ring. Reduction of the ketone (**5**), m.p. 188°, with excess of lithium in liquid ammonia, t-butyl alcohol, and tetrahydrofuran gave a diol (20% yield) which on oxidation afforded the diketone (**6**), m.p. 128°. This latter diketone was identical (mixed m.p. and i.r. spectrum) with the lower-melting diketone obtained[5] by reduction of isophorone with lithium in ether and must be the (±)-form. The diketone, m.p. 166°, obtained by reduction of isophorone by lithium in ether[5] or electrochemically[6] is the *meso*-form corresponding to (**6**).


(1) (2)



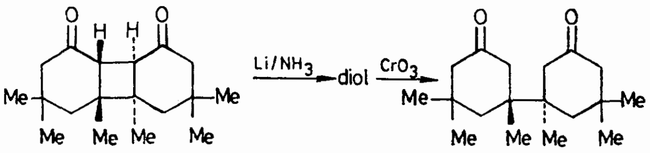
MeCOCH$_2$CH$_2$COMe

(4)

+ other products

(3)

The cyclohexenone dimer (**7**), m.p. 78°,[7] on lithium–ammonia reduction gave a diketone, m.p. 80°, (7% yield) with analytical and m.s. data consistent with the formula $C_{12}H_{18}O_2$ and which is not identical with the starting diketone. This new diketone must be the (±)-compound (**8**).



(5) (6)

(7) (8)

Reduction of cyclohexenone either electrochemically or by sodium amalgam gives two diketones, m.p. 63—65° and m.p. 97°, which are thought to be (**8**) and the corresponding *meso*-form respectively.[8] We find by v.p.c. on two columns (2 m, 2½% silicone gum rubber, *t* 160° and 2 m, antarox CO-990, temp. 215°) that the material with m.p. 63—65° is a mixture of the form with m.p. 97°, and our diketone obtained by the lithium–ammonia reduction. The diketone with m.p. 97°, is therefore the *meso*-isomer of (**8**).

(*Received*, 12*th December* 1973; *Com.* 1686.)

---

[1] E. Piers and P. N. Worster, *J. Amer. Chem. Soc.*, 1972, **94**, 2895; and references cited therein.
[2] E. Kariv and B. J. Cohen, *J.C.S. Perkin II*, 1972, 509; E. Wenkert and J. E. Loder, *J. Org. Chem.*, 1970, **35**, 2986.
[3] D. J. Trecker, A. A. Griswold, and O. L. Chapman, *Org. Photochem. Synth.*, 1971, **1**, 62.
[4] R. E. Koning, G. J. Visser, and A. Vos, *Rec. Trav. chim.*, 1970, **89**, 920.
[5] J. P. Morizur, B. Furth, and J. Kossanyi, *Bull. Soc. chim. France*, 1967, 1422.
[6] J. Simonet, *Compt. rend.* (*C*), 1968, **267**, 1548.
[7] E. Y. Y. Lam, D. Valentine, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1967, **89**, 3482.
[8] E. Touboul, F. Weisbuch and J. Wiemann, *Bull. Soc. chim. France*, 1967, 4291; *Compt. rend.* (*C*), 1969, **268**, 1170.