Azulenes. Part II. Application of the Pinacone Reduction to the Synthesis of 1-Substituted Azulenes.*

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In a general investigation of the application of the bimolecular reduction of ketones to the synthesis of cyclic compounds, the reduction of a 2-3′-oxobutyl*cyclo*heptanone has been studied. The product obtained was dehydrogenated to 1-methylazulene.

FOLLOWING Kipping and Perkin's suggestion (*J.*, 1889, **55**, 330) that intramolecular reduction of diketones might lead to cyclic 1 : 2-glycols, a number of workers (*e.g.*, Kipping and Perkin, *J.*, 1891, **59**, 214; 1893, **63**, 111; Wislicenus *et al.*, *Annalen*, 1898, **302**, 191, 195, 215, 223, 236; Japp and Michie, *J.*, 1901, **79**, 1010) investigated the preparation of derivatives of *cyclo*pentane, *cyclo*hexane, and *cyclo*heptane by such a method. Japp and Michie (*loc. cit.*), using aluminium amalgam, showed that good yields of the cyclic products were obtainable, but despite this and other recent accounts of good yields obtained by this method, with various reagents (*e.g.*, Bachmann, *J. Amer. Chem. Soc.*, 1932, **54**, 1969; Bachmann and Chu, *ibid.*, 1935, **57**, 1095; 1936, **58**, 1118; Bartlett and Brown, *ibid.*, 1940, **62**, 2927; Pauson, *ibid.*, 1954, **76**, 2187), little attention has been paid to this reaction as a means of effecting ring-closure.

The acyloin condensation has, however, been much studied as a most valuable method for the preparation of macrocyclic compounds (Prelog, Frenkiel, Kobelt, and Barman, *Helv. Chim. Acta*, 1947, **30**, 1741; Stoll and Hulstkamp, *ibid.*, p. 1815).

Prelog *et al.* (*loc. cit.*) explained the high yields by regarding the reduction as taking place at the metal surface. In view of the similarity of the acyloin condensation and pinacone reduction, it seemed possible that the reduction of suitable long-chain diketones might also lead to the formation of macrocyclic compounds, and an investigation of this reaction seemed worth while.

Another neglected study has been the reduction of unsymmetrical diketones, although the bimolecular coupling of two dissimilar carbonyl compounds has been described (*e.g.*, Elagina and Zelinski, *Doklady Akad. Nauk S.S.S.R.*, 1950, **71**, 293).

As part of a general investigation of the application of pinacone reduction to ring-

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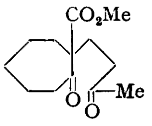
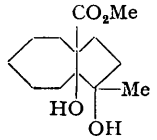
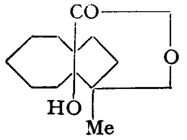
closure, the intramolecular reduction of the unsymmetrical diketone, methyl 2-oxo-1-3′-oxobutyl*cyclo*heptane-1-carboxylate (I), was studied which would lead to the formation of a *bicyclo*[5 : 3 : 0]decane derivative; this exemplifies a possible synthetical route to 1-substituted azulenes. The yield of bicyclic compound was small (9%), but is of interest as the first record of the intramolecular reduction of such an unsymmetrical diketone.



(I)



(II)



(III)

Various reducing agents were tested; aluminium amalgam in aqueous ethanol appeared to be most generally satisfactory. The product obtained was not the glycol (II) but the lactone (III); the latter was hydrolysed slowly by a boiling aqueous methanolic solution of potassium hydroxide.

This lactone was converted into 1-methylazulene by a single-stage dehydration, decarboxylation, and dehydrogenation, the product being identified by means of derivatives and its ultra-violet spectrum.

EXPERIMENTAL

*Methyl 2-Oxo-1-3′-oxobutyl*cyclo*heptane-1-carboxylate* (I).—Prepared by the method of Prelog, Wirth, and Ruzicka (*Helv. Chim. Acta*, **1946**, **29**, 1425) from ethyl 2-oxo*cyclo*heptane-1-carboxylate (16·5 g.), the product (16·6 g., 80%) had b. p. 102—105°/0·02 mm., 99—102°/0·012 mm.

Reduction of (I).—The main methods investigated were magnesium–magnesium iodide (Gomberg and Bachmann, *J. Amer. Chem. Soc.*, **1928**, **50**, 2762), aluminium in anhydrous conditions (Newman, *ibid.*, **1940**, **62**, 1683), and aluminium in aqueous ethanol (Japp and Michie, *loc. cit.*). Other reagents studied included magnesium and calcium in a variety of media, *e.g.*, water, aqueous ethanol, water–benzene. Aluminium in aqueous ethanol proved to be the most satisfactory.

7 : 8-*Dihydroxy-8-methyl*bicyclo[5 : 3 : 0]*decane-1-carboxylic* 1 : 8-*Lactone* (III).—To a solution of 2-oxo-1-3′-oxobutyl*cyclo*heptane-1-carboxylate (12·76 g.) in 50% aqueous ethanol (500 ml.) was added aluminium foil (15 g.) (which previously had been etched by immersion in a concentrated solution of potassium hydroxide), and a small quantity of an ethanolic mercuric chloride solution. The mixture was refluxed for 3 weeks, small quantities of mercuric chloride being added at intervals; the pH of the solution remained about 8. The bulk of the ethanol was then removed, water was added, and the aluminium hydroxide which had been formed was removed by use of a centrifuge. After extraction of the aqueous solution with ether, and evaporation of the ether, a dark gum was obtained which slowly deposited crystals; these were recrystallised from benzene. The product (1·0 g., 9%) had m. p. 157·5° and its behaviour towards methanolic potassium hydroxide indicated a *lactone* (III) (Found: C, 68·7; H, 8·5%; equiv., 210. $C_{12}H_{18}O_3$ requires C, 68·6; H, 8·6%; equiv., 210).

	Present work						P. & H. (*loc. cit.*)					
$\lambda_{max.}$	2410	2820	3000	3380	3460	3650	2400	2800	2990	3380	3470	3640
log ε	4·30	4·66	3·84	3·53	3·65	3·40	4·30	4·61	3·74	3·46	3·68	3·50

1-*Methylazulene.*—The lactone (III) (0·1 g.) was distilled at 0·2 mm. in an atmosphere of nitrogen, over alumina–palladium–charcoal heated to 350°. The product was purified by fractionation over alumina, a deep blue liquid (4 mg.; 4%) being obtained. The ultra-violet spectrum agreed with that previously recorded by Plattner and Heilbronner (*Helv. Chim. Acta*, **1948**, **31**, 804) (see Table). The product formed a picrate, m. p. 135°, and a trinitrobenzene adduct, m. p. and mixed m. p. 155°.

We thank Prof. Plattner and Dr. Fürst for supplying an authentic specimen of the trinitrobenzene adduct of 1-methylazulene. One of us (F. R.) is indebted to the Cheshire County Council Education Committee for a grant.

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