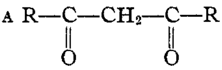
TABLE II

GENERAL FORMULA

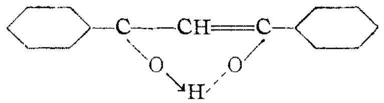


$\mathrm{R{-}\underset{\underset{O}{\|}}{C}{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}R^1}$

VIII, R and R^1 = phenyl
IX, R = *p*-bromophenyl; R^1 = phenyl
X, R = phenyl; R^1 = mesityl
XI, R = *p*-methoxyphenyl; R^1 = mesityl
XII, R = *m*-nitrophenyl; R^1 = mesityl
XIII, R = *p*-nitrophenyl; R^1 = mesityl

These β-diketones like the α-diketones did exhibit absorption at 3.4 and 6.25 μ which is characteristic of CH and phenyl absorption.

Thus we have negative evidence, the disappearance of bands at 2.95 and 6 μ, for the chelated structure of the β-ketones. It is difficult to indicate the presence of the O–H–O band since it too absorbs at about 3.4 μ.



However, the O–D–O band[8] appears at about 4.35 μ, and it is the plan of the authors to prepare β-diketones with the labile hydrogen replaced by deuterium and study them spectroscopically in an attempt to establish definitely that the enols of the β-diketones are chelated.

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(8) R. C. Herman and R. Hofstadter, *J. Chem. Phys.*, **6**, 534 (1938).

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Boiling Point and Composition of Methanethiol–Isobutane Azeotrope

BY F. R. BROOKS AND A. C. NIXON

RECEIVED AUGUST 18, 1952

Recently Denyer, Fidler and Lowry[1] predicted the boiling point and composition of an azeotrope between methanethiol and isobutane by extrapolation from the boiling points and azeotropic compositions of other thiols and hydrocarbons. We recently had occasion to determine the boiling point of this azeotrope and find that the azeotrope has a boiling point of −13.0° and contains 17.5 mole % of the thiol; corresponding values of −16.5° and 12.5 mole % were predicted by Denyer, *et al.* The difference between the observed and predicted values may reflect the deviation which commonly occurs with the first member of a series or it may be due to uncertainty in our determination. Our data were obtained by distillation of mixture of 19.6 mole % methanethiol (Eastman Kodak Co. white label) in isobutane (Phillips 99.9% pure). The distillation was carried out in standard (Podbielniak) low temperature distillation apparatus, which is equivalent to about 25 theoretical plates, at a reflux ratio of about 50:1. Several cuts were taken after the temperature had leveled out and after intermittent periods of total reflux operation. We estimate that the data are good to ±0.5° and ±0.5 mole %.

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(1) Denyer, Fidler and Lowry, *Ind. Eng. Chem.*, **41**, 2727 (1949).

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Eight-membered Carbocycles. IV. Reduction of Cycloöctatetraene

BY L. E. CRAIG, R. M. ELOFSON AND I. J. RESSA

RECEIVED SEPTEMBER 2, 1952

Since it has been shown that cycloöctatetraene can be determined quantitatively by polarographic analysis,[1] the electrolytic reduction of cycloöctatetraene at a mercury cathode was investigated. Reduction was found to proceed smoothly in neutral and alkaline solutions in the presence of the tetramethylammonium ion. Without the tetramethylammonium ion, the reduction was found to be much less efficient, a fact which is in agreement with the polarographic findings.[1]

The product of the electrolytic reduction was shown by elementary analyses and by the absorption of three molar equivalents of hydrogen to give cycloöctane to be cycloöctatriene. Chromatographic examination of the product showed that two materials were present, one to the extent of about three times the other. The ultraviolet absorption spectrum of the material present in the larger amount was essentially identical with that reported by Cope and Hochstein[2] for 1,3,6-cycloöctatriene. The ultraviolet absorption spectrum of the mixture produced by electrolytic reduction indicates that it is a mixture of about 75% 1,3,6-cycloöctatriene and 25% 1,3,5-cycloöctatriene, which is in agreement with the composition indicated by the chromatographic separation.

During the course of the work, isomerization of 1,3,6-cycloöctatriene to 1,3,5-cycloöctatriene during slow distillation was encountered. The alkali-catalyzed isomerization as reported by Cope and Hochstein[2] was confirmed by treating with ethanolic sodium ethoxide and following the isomerization by means of the ultraviolet absorption spectra. The curves of Fig. 2 clearly indicate that the one product is being formed at the expense of the other. It, therefore, seems probable that 1,3,6-cycloöctatriene is the product formed upon electrolytic reduction and that the 1,3,5-cycloöctatriene is formed by isomerization. The formation of bicyclic hydrocarbons in the reduction appears to be negligible because of the high (84%, distilled) yield of cycloöctane obtained on hydrogenation.

Cycloöctatrienes have also been reported to be produced from cycloöctatetraene by the addition of lithium followed by treatment with methanol,[2,3] by reduction with sodium in liquid ammonia,[3] and by reduction with sodium and methylaniline in ether.[4] Ziegler and Wilms[4] suggested that the first product of the reduction with sodium and *m*-ethylaniline in ether is bicyclo[4,2,0]-3,7-octa-

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(1) R. M. Elofson, *Anal. Chem.*, **21**, 917 (1949).

(2) A. C. Cope and F. A. Hochstein, THIS JOURNAL, **72**, 2515 (1950).

(3) W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Ann.*, **560**, 1 (1948).

(4) K. Ziegler and H. Wilms, *ibid.*, **567**, 1 (1950).