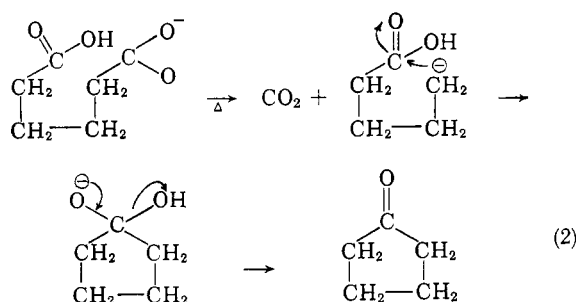


adipic acid since there are no α -hydrogens available. In this case, dry distillation from barium oxide produced 72% of the ketone and from potassium fluoride under the same conditions 52% of the ketone.

A mechanism, consistent with the experimental results, involves the initial formation of a monocarboxylate ion by nucleophilic reaction with the potassium fluoride. Excess salt would hinder the reaction by forming the dicarboxylate ion. The elevated temperature required serves to decarboxylate the ion to form a carbanion which is preferentially cyclized to form the enolate ion. Elimination of the hydroxide ion and its combination with the abstracted proton accounts for the formation of water (Equation 2). The lower yield of 2,2,5,5-tetramethylcyclopentanone with potassium fluoride might be due to the decreased acidity of the acid groups.



EXPERIMENTAL

2,2,5,5-Tetramethyladipic acid. This compound was prepared in 18% yield following the procedure⁸ of Coffman, Jenner, and Lipscomb, m.p. 188–190° (reported, m.p. 188–190°).

Ketone formation. The cyclization of adipic acid to cyclopentanone was carried out using a distillation flask immersed in a Wood's metal bath. The temperature was maintained at 250–280° until the distillation of volatile products ceased, usually about 1 hr. with a 20-g. sample of adipic acid. The cyclopentanone was purified by a standard procedure.⁵ The analytical data for this reaction were determined from a reaction mixture having a 4:1 mole ratio of adipic acid to potassium fluoride. The carbon dioxide was collected on Ascarite in a Nesbitt tower, and the water was determined by a modified Karl Fischer method⁹ after redistillation of the liquid products to remove any adipic acid that had been carried over. Total weight losses on the basis of three trials did not exceed 16 p.p.t.

2,2,5,5-Tetramethylcyclopentanone was obtained by heating a mixture of 4.0 g. (0.02 mole) of 2,2,5,5-tetramethyladipic acid and 0.5 g. (0.003 mole) of barium oxide at 320–330° under distillation conditions for 5 hr. The distillate was extracted with 25 ml. of ether. The ethereal solution, after drying over anhydrous sodium sulfate, yielded upon distillation 2.0 g. (72%) of a colorless liquid, b.p. 153.5–154.5°, n_D^{20} 1.4272. (reported,¹⁰ b.p. 154–155°, n_D^{20} 1.4280).

(8) D. D. Coffman, E. L. Jenner, and R. D. Lipscomb, *J. Am. Chem. Soc.*, **80**, 2864 (1958).

(9) E. D. Peters and J. L. Jungnickel, *Anal. Chem.*, **27**, 450 (1955).

(10) J. M. Conia, *Ann. Chim.*, **8**, 709 (1953); *Chem. Abstr.*, **48**, 13644 (1954).

The 2,4-dinitrophenylhydrazone recrystallized as fine red-orange needles from ethanol, m.p. 205–206°.

Anal. Calcd. for $C_{15}H_{20}N_4O_4$: C, 56.24; H, 6.29; N, 17.49. Found: C, 56.24; H, 5.88; N, 17.50.

The tetramethylketone was prepared also by heating a mixture of 4.0 g. (0.02 mole) of the tetramethyladipic acid with 0.5 g. (0.009 mole) of anhydrous potassium fluoride at 320–340° over an 8-hr. period. In the same manner as above 1.4 g. (52%) of the ketone was obtained.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

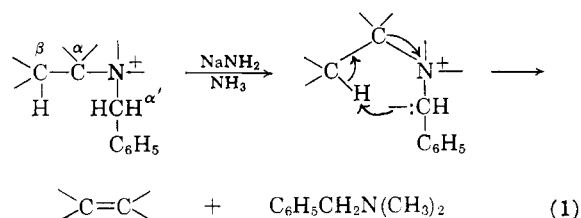
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Elimination Reactions. III. *cis*-Cyclooctene from Cyclooctylbenzyltrimethylammonium Bromide¹

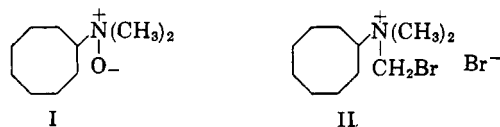
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Formation of olefins from alkylbenzyltrimethylammonium halides and sodium amide in liquid ammonia has been classified as a α' - β -elimination or intramolecular β -elimination reaction as illustrated in Equation 1.² This process resembles, therefore,



the thermal decomposition of amine oxides³ and the elimination reactions of nitrogen ylids formed by halogen-metal interchange.⁴ Interestingly, pyrolysis of cyclooctyldimethylamine oxide (I)⁵ gives pure *cis*-cyclooctene and treatment of cyclooctylbromomethyltrimethylammonium bromide (II) with methylolithium⁴ gives largely *cis*-cyclooctene. However, thermal decomposition of



(1) This work was done under the sponsorship of the U. S. Army Ordnance Corps, Contract No. DA-01-021-ORD-11878.

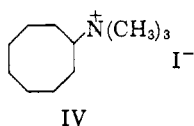
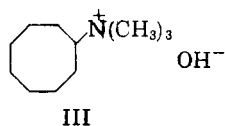
(2) C. L. Bumgardner, *J. Am. Chem. Soc.*, **83**, 4420 (1961).

(3) A. C. Cope and E. R. Trumbull, *Org. Reactions*, **11**, 317 (1960).

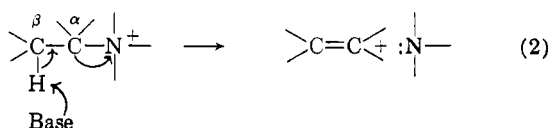
(4) G. Wittig and R. Polster, *Ann.*, **612**, 102 (1958).

(5) A. C. Cope, R. A. Pike, and C. F. Spencer, *J. Am. Chem. Soc.*, **75**, 3212 (1953).

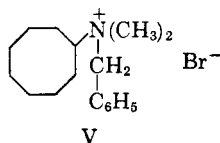
cyclooctyltrimethylammonium hydroxide (III) and treatment of cyclooctyltrimethylammonium iodide (IV) with potassium amide in liquid ammonia yield predominately *trans*-cyclooctene.^{4,5} Wittig and



Polster⁴ concluded that *cis*-cyclooctene comes from α' - β -elimination of the amine function in compounds I and II (and possibly III and IV), whereas *trans*-cyclooctene arises mainly, if not entirely, from pure β -elimination generalized by Equation 2.



If the interpretation depicted in Equation 1 is correct, and if Wittig and Polster's rationalization is valid, the action of sodium amide in liquid ammonia on cyclooctylbenzyltrimethylammonium bromide (V) would be expected to afford *cis*-



cyclooctene. We have carried out this reaction and have obtained *cis*-cyclooctene which infrared analysis indicates is free of the *trans*-isomer.

Therefore, two complementary low temperature methods of forming olefins from quaternary ammonium halides appear to be available: treatment of alkyltrimethylammonium halides with potassium amide in liquid ammonia (the Wittig-Polster procedure), which produces olefins by *trans*- β -elimination (Equation 2); and treatment of alkylbenzyltrimethylammonium halides with sodium amide in liquid ammonia, which yields olefins by the *cis*- α' - β -process (Equation 1).

EXPERIMENTAL⁶

Cyclooctylbenzyltrimethylammonium Bromide. (V). A benzene solution containing 2.64 g. of cyclooctyltrimethylamine⁶ and 5.56 g. of benzyl bromide was stirred and refluxed for 19 hr. The white solid which formed was separated by filtration, washed with benzene, and dried in a vacuum desiccator. Cyclooctylbenzyltrimethylammonium bromide (5.02 g.), m.p. 184–186°, was obtained in 90% yield.

Anal. Calcd. for $C_{17}H_{29}NBr$: C, 62.58; H, 8.59; N, 4.29. Found: C, 62.79; H, 8.73; N, 4.07.

***cis*-Cyclooctene.** Bromide V (4.8 g.) was added during 10 min. to 100 ml. of liquid ammonia containing 0.022 mole

of sodium amide. The mixture was stirred for 3 hr.; then 1.8 g. of ammonium chloride followed by 75 ml. of ether was added. The Dry Ice condenser was replaced by a water condenser and the ammonia was allowed to evaporate overnight. Water was added to the residue and the two resulting liquid phases were separated. The ethereal solution, after being washed with 10% hydrochloric acid solution, water, 5% sodium bicarbonate solution, and water, was dried over magnesium sulfate. Distillation through a semimicro column yielded 0.87 g. (54%) of *cis*-cyclooctene, b.p. 62–63° (47 mm.), n_D^{20} 1.4685. The infrared spectrum was the same as a published spectrum and the absence of bands at 11.8 and 12.6 μ indicated that *trans*-cyclooctene was not present.⁵

From the aqueous acid solution, benzyltrimethylamine, identified by its infrared spectrum, was isolated in 65% yield by adding an excess of 20% potassium hydroxide solution, extracting the liberated amine with ether, and distilling.

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Preparation of Dipivaloylmethane

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As a consequence of our interest in metal chelates derived from sterically hindered β -diketones we have frequently needed to prepare large batches of 2,2,6,6-tetramethylheptan-3,5-dione (dipivaloylmethane). The method of Adams and Hauser¹ does not give high yields when used for the synthesis of sterically hindered β -diketones so a variety of modifications have been investigated. These have included the use of lithium amide as the condensing agent followed by isolation of the lithium chelate by extraction of the reaction mixture with ether and the use of phenyl pivalate rather than ethyl pivalate as the substrate in the condensation with pinacolone. Combination of the two variations has given yields as high as 85%. The method is not reported in detail, however, since isolation of lithium dipivaloylmethide is tedious because of the large volume of ether required. The procedure which we have found most practical for preparation of large batches involves formation of the sodium enolate of pinacolone in dimethoxyethane solution by reaction of the ketone with sodium hydride. The enolate is acylated *in situ* with methyl or ethyl pivalate. Yields in the 60–70% range are very easily obtained. The method should be general for the preparation of hindered diketones.

EXPERIMENTAL

Methyl pivalate (90 g.) and 72 g. of sodium hydride dispersed in mineral oil (52% hydride by weight) were added to 1 l. of dimethoxyethane in a 2-l. flask. The mixture was

(1) J. T. Adams and C. R. Hauser, *J. Am. Chem. Soc.*, **66**, 1220 (1944).

(6) Melting points and boiling points are uncorrected. Infrared spectra were determined with a Perkin-Elmer Infracord spectrophotometer with a sodium chloride prism.