Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.22; H. 9.31.

A mixture of 1.0 g. of V (R = $-C(=O)-CH_3$) and 0.66 g. of tetracyanoethylene in 20 ml. of benzene was refluxed for two hours, cooled, diluted with 20 ml. of ligroin, and refrigerated. There separated 1.0 g. of product, m.p. 141–143°, which was recrystallized from benzene–petroleum ether and then melted at 144–145°.

Anal. Calcd. for $C_{16}H_{18}N_4O_2$: C, 67.08; H, 5.61; N, 17.29. Found: C, 67.03; H, 5.73; N, 16.95.

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Reactions Catalyzed by Potassium Fluoride. II. The Conversion of Adipic Acid to Cyclopentanone

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A preliminary communication[1] recently reported the apparent function of anhydrous potassium fluoride as a base in the Hofmann reaction converting *N*-chlorobenzamide to phenyl isocyanate. This unexpected behavior of potassium fluoride became the object of further study in an attempt to determine whether the salt behaved similarly in other reactions.

The literature cites a few examples of the use of potassium fluoride which include several catalytic decarboxylation reactions[2] and a series of addition-dehydration reactions of active methylene-containing compounds.[3] Each of the reported reactions is classically base-catalyzed, either to form initially a carboxylate ion or a carbanion, suggesting that hydrogen fluoride is evolved as a by-product. Moreover, each reaction reported employed an essentially equimolar amount of potassium fluoride.

It was decided to study in greater detail the conversion of adipic acid to cyclopentanone because of its relative simplicity. In a series of experiments in which the amount of potassium fluoride was decreased relative to the concentration of adipic acid, it was found that the yield of cyclopentanone increased, although the rate of reaction was slower (Table I).

TABLE I

Affect of Potassium Fluoride Concentration on Yield of Cyclopentanone

Mole Ratio of Adipic Acid/KF	% Yield of Cyclopentanone
1:2	23
1:1	31
2:1	37
4:1	54
20:1	81

The absence of any potassium fluoride in a reaction carried out under the same conditions failed to produce any ketone.

A quantitative examination provided further pertinent data. The determination of the amounts of volatile products, according to Equation 1,

$$HOOC-(CH_2)_4-COOH \longrightarrow C_5H_8O + CO_2 + H_2O \quad (1)$$

indicated that each product was formed in equimolar quantities, the ratio of ketone: carbon dioxide: water being 1:1.19:1.06. This suggests the absence of any appreciable side reactions, such as the formation of cyclopentene, as had been reported in an earlier study,[4] or any appreciable elimination of hydrogen fluoride. This analytical data also precludes the formation of adipic anhydride as an intermediate in the formation of cyclopentanone since it has been shown that the anhydride decomposes spontaneously to a polymer.[5] The small amount of basic catalyst required had already been illustrated, since not only will the reaction occur with much less than a molar equivalent of barium hydroxide,[6] but it proceeds also in high yield when the adipic acid is distilled from jena glass,[4] which contains basic salts of barium and calcium.

A mechanism for this reaction has been postulated by Neunhoeffer and Paschke[4] which requires the abstraction of an α-hydrogen followed by a Dieckmann condensation. Since potassium fluoride, which is capable of abstracting a proton from an acid and still retain bonding,[7] does not appear to be a strong enough nucleophile to react with the α-hydrogen, it was felt that either the cyclopentanone formation using barium hydroxide followed a different path than when potassium fluoride was employed, or that abstraction of the α-hydrogen was not a necessary step. It was of interest, therefore, to attempt the formation of 2,2,5,5-tetramethylcyclopentanone from 2,2,5,5-tetramethyl-

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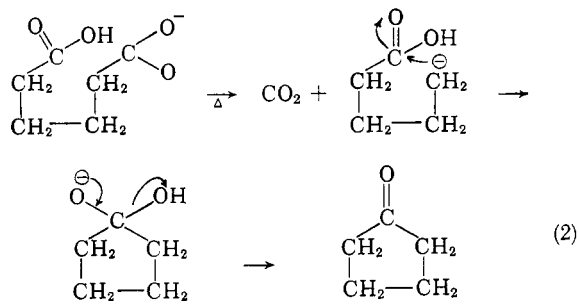
adipic acid since there are no α-hydrogens available. In this case, dry distillation from barium oxide produced 72% of the ketone and from potassium fluoride under the same conditions 52% of the ketone.

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.



(2)

EXPERIMENTAL

2,2,5,5-Tetramethyladipic acid. This compound was prepared in 18% yield following the procedure[8] 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 method[9] 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).

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.

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Elimination Reactions. III. *cis*-Cyclooctene from Cyclooctylbenzyldimethylammonium Bromide[1]

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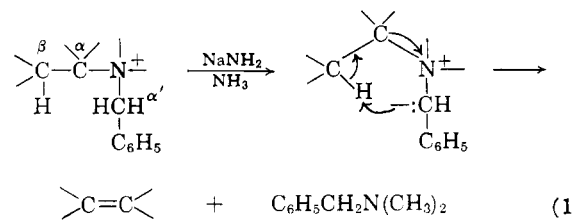
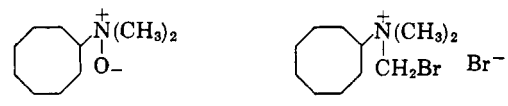
Formation of olefins from alkylbenzyldimethylammonium halides and sodium amide in liquid ammonia has been classified as a α'-β-elimination or intramolecular β-elimination reaction as illustrated in Equation 1.[2] This process resembles, therefore,



(1)

the thermal decomposition of amine oxides[3] 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 cycloöctylbromomethyldimethylammonium bromide (II) with methyllithium[4] gives largely *cis*-cycloöctene. However, thermal decomposition of



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