filtration and washed with several portions of ether. The combined filtrates were distilled through a 10-in. packed column to give 65.1 g. (71%) of 2-ethyl-3-piperidinocyclobutanol, b.p. 98° (0.8 mm.), $n^{20}D$ 1.4930.

The rearrangement of VIII to a mixture of 2-ethyl-1-piperidino-1-buten-3-one and 1-piperidino-1-hexen-3-one was followed by infrared spectra. A small sample of the ether solution of VIII described previously was allowed to stand for a few days at room temperature. Periodic examination by infrared spectroscopy showed a gradual disappearance of the band at 5.65 μ and a corresponding appearance of bands at 6.05, 6.25, and 6.38 μ.

2-Ethyl-1-piperidino-1-buten-3-one (IX) and 1-Piperidino-1-hexen-3-one (X).—Ketene was added to a stirred solution of 139 g. (1 mole) of 1-(1-butenyl)piperidine in 400 ml. of benzene to a weight increase of 42 g. (1 mole). Frequent cooling was required to maintain the reaction temperature at 10 to 25°. The solution was stirred for 1 hr. after the addition, and then distilled through a 10-in. packed column to give 109.2 g. (60%) of a mixture of IX and X, b.p. 137° (0.3 mm.), $n^{22}D$ 1.5544.

Anal. Calcd. for $C_{11}H_{19}NO$: C, 72.9; H, 10.5; N, 7.8. Found: C, 72.7; H, 10.5; N, 7.7. N.m.r. spectrum (50% solution in CCl_4): IX, singlet at −301 (C═CH—N), broad peaks at −150 and −85 ($C_5H_{10}N$), −100 ($CH_3C{=}O$), −108 (CH_2), −60 c.p.s. (CH_3); X, doublets centered at −308 and −216 (CH═CH—N), broad peaks at −150 and −85 ($C_5H_{10}N$), −108 ($CH_2C{=}O$), −85 (CH_2), −60 c.p.s. (CH_3). Relative areas of peaks corresponding to C═CH—N protons indicated the ratio of IX to X was approximately 1:2.

Acknowledgment.—We wish to thank Mr. P. G. Gott for the preparation of some compounds involved in this work, Mr. A. L. Thompson for interpretation of infrared spectra, Dr. Wilson Goodlett for interpretation of n.m.r. spectra, and Dr. K. C. Brannock for many helpful discussions.

An Unusual Fragmentation–Rearrangement under Acyloin Reaction Conditions[1,2c]

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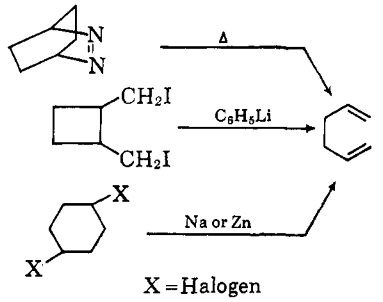
Received December 28, 1962

Attempted acyloin ring closure on *cis*-1,2-dicarbethoxycyclobutane leads, by an apparent fragmentation reaction, to 2-carbethoxycyclopentanone.

The bicyclo[2.2.0]hexane skeleton has eluded most attempts toward its synthesis.[3] The result of many previous investigations has been a fragmentation reaction[3c] as the following examples indicate.

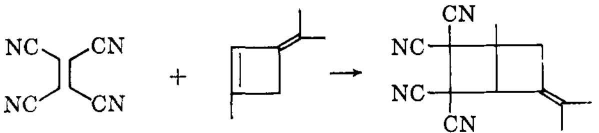


(1)[3a]

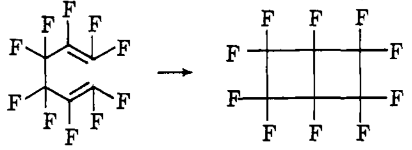
(2)[3b]

(3)[3c]

Only unusual reagents or combinations of reagents, *e.g.*, tetracyanoethylene and 1-methyl-3-isopropylidenecyclobutene,[4] the isomerization of perfluoro-1,5-hexadiene,[5] or photochemical reactions[6] have been successful in producing the bicyclo[2.2.0]hexane system. In fact, the first example of "Dewar benzene," a bicyclo[2.2.0]hexadiene, has been produced by a photochemical reaction.[7]



(4)



(5)

Cope and Herrick,[8] in their synthesis of bicyclo[4.2.0]octane-7-ol-8-one from 1,2-dicarbethoxycyclohexane, demonstrated that the acyloin reaction can produce a four-membered ring. Because the generally accepted mechanism for the acyloin reaction involves the dimerization of intermediate radical ions[9] and because the fragmentation reactions known to us when this work was started involved purely ionic intermediates[3c,10] it was felt that bicyclo[2.2.0]hexane-2-ol-3-one might be prepared simply from 1,2-dicarbethoxycyclobutane following the example of Cope and Herrick.

When this reaction was conducted in liquid ammonia,[11] the major product (40%) was 2-carbethoxycyclopentanone, identical in all respects with an authen-

(1) This paper was presented before the Division of Organic Chemistry at the 143rd National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963.

(2)(a) To whom inquiries concerning this communication should be addressed; (b) Participant in the National Science Foundation supported Research Participation for College Teachers program in the Summer of 1962. (c) NOTE ADDED IN PROOF.—After this paper was accepted, we learned, by personal communication, that the observations reported here had been made independently *(and prior to our work)* by Dr. H. Ogura and Dr. J. Meinwald at Cornell University. Dr. P. G. Gassman at Ohio State University has also independently observed this rearrangement.

(3) (a) S. G. Cohen and R. Zand, *J. Am. Chem. Soc.*, **84**, 586 (1962); (b) R. Criegee and K. Matterstock, unpublished results quoted by E. Vogel, *Angew. Chem.*, **72**, 4 (1960); (c) C. A. Grob and W. Baumann, *Helv. Chim. Acta*, **38**, 594 (1955).

(4) J. K. Williams, *J. Am. Chem. Soc.*, **81**, 4013 (1959).

(5) A. H. Fainberg and W. T. Miller, *ibid.*, **79**, 4170 (1957).

(6) (a) S. Cremer and R. Srinivasan, *Tetrahedron Letters*, No. **21**, 24 (1960); (b) W. G. Dauben and G. J. Fonken, *J. Am. Chem. Soc.*, **81**, 4060 (1959).

(7) E. E. van Tamelen and S. P. Pappas, *ibid.*, **84**, 3789 (1962).

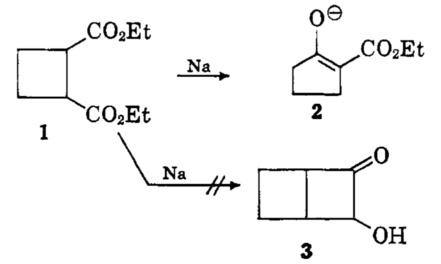
(8) A. C. Cope and E. C. Herrick, *ibid.*, **72**, 983 (1950).

(9) S. M. McElvain, "Organic Reactions," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 256.

(10) C. A. Grob, *Experentia*, **13/3**, 126 (1957).

(11) *Cf.*, J. C. Sheehan, R. A. Coderre, and P. A. Cruickshank, *J. Am. Chem. Soc.*, **75**, 6231 (1953).

tic sample.[12] When toluene was the solvent, the yield of keto ester was only 9–20%. In both solvents, particularly toluene, other, unidentified, substances were produced in varying amounts. There was no evidence for acyloin products.[2c]

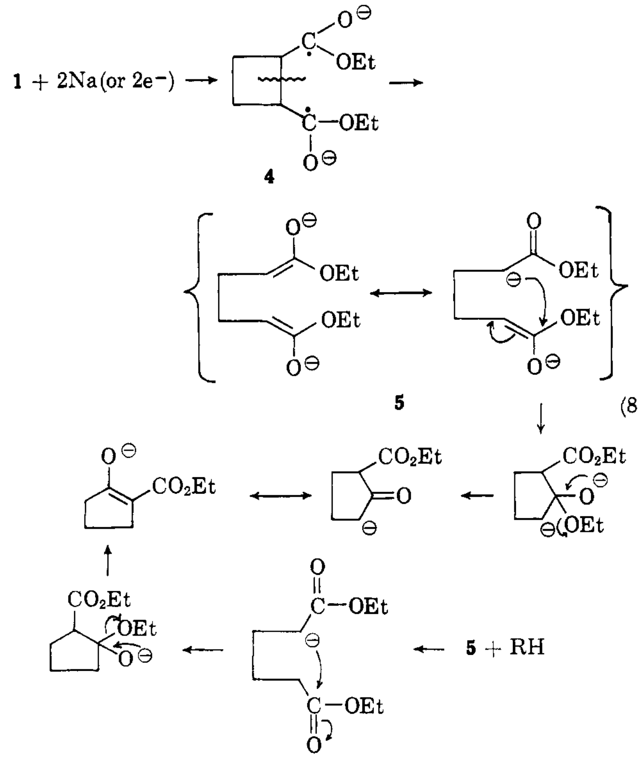


(6)

(7)

Sheehan has shown that sodium dispersion in toluene will produce adipoin from adipic ester.[13] We find that under the liquid ammonia conditions adipoin also is produced, but in lower yield than in the toluene reaction.

Two general mechanisms seem possible. In the first, a diradical intermediate, 4, homolyzes to produce the fragmentation product, a bisenolate, 5, of diethyl adipate. The enolate may react directly to produce an anion of 2-carbethoxycyclopentanone or it may abstract a proton from either the solvent or an unreacted molecule of ester to produce the monoenolate of adipic ester which subsequently undergoes the Dieckmann reaction in the usual way. The second mechanism involves the rearrangement of a 1,2-dianion to give 5.



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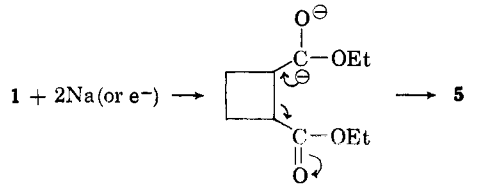
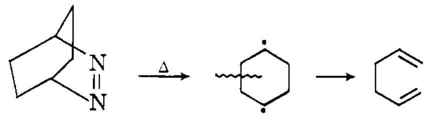


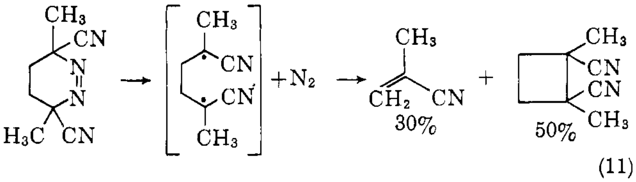
(9)

It does not seem possible at this time to choose between these alternatives. The dianion mechanism has been proposed in the past,[14] in modified form, to explain the results obtained in acyloin reactions. Recent work of Hauser[15] shows the plausibility of the 1,2-dianion. On the other hand, the formation of 1,5-hexadiene from 2,3-diazabicyclo[2.2.0]oct-2-ene[3a] follows a free radical path.[16]

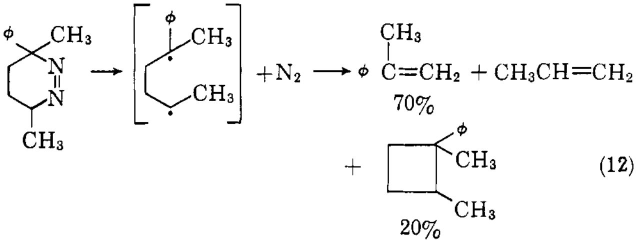


(10)

Fragmentations have been observed in other decompositions of azo compounds.[17]



(11)



(12)

Experimental

***cis*-1,2-Dicarbethoxycyclobutane.**—This starting ester was prepared by Fischer esterification of *cis*-1,2-cyclobutane dicarboxylic acid anhydride.[18]

Acyloin Reactions in Liquid Ammonia.[11]—The reactions were carried out under dry, oxygen-free nitrogen in a three-neck flask fitted with a dropping funnel, Dry Ice condenser, and a Trubore stirrer and insulated by a heating mantle. In a typical reaction, sodium, 4.65 g. (0.20 g.-atom), was added to 1.0 l. of liquid ammonia and 100 ml. of anhydrous ether. Ten grams (0.05 mole) of the diester in 400 ml. of anhydrous ether was added over 5 hr. Anhydrous ether, 200 ml., was added and the ammonia and ether evaporated under a stream of nitrogen over 24 hr. To the reaction mixture, which was a light creamy paste, was added a further 200 ml. of ether and this also was evaporated. The procedure was repeated (two to three times) until the exit gas was no longer basic to wet litmus. This left a yellow paste which was worked up by adding 250 ml. of ether and then (rapidly) excess dilute 3–5% hydrochloric acid solution while the flask and contents were cooled in an ice bath. The ether layer was separated, dried over anhydrous magnesium sulfate, evaporated, and the residue was distilled at 3.0 mm., b.p. 81–84°. The yield of 2-carbethoxycyclopentanone was 40–42%, $n^{25}\text{D}$ 1.4484–1.4488; semicarbazone, m.p. 141–144°. The infrared spectrum was

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[12] P. S. Pinkney, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 116.

[13] J. C. Sheehan, R. C. O'Neill, and M. A. White, *J. Am. Chem. Soc.*, **72**, 3376 (1950).

[14] (a) H. Scheibler and F. Emden, *Ann.*, **434**, 265 (1923); (b) F. F. Blicke, *J. Am. Chem. Soc.*, **47**, 229 (1925).

[15] (a) C. R. Hauser, T. M. Harris, and T. G. Ledford, *ibid.*, **81**, 4099 (1959); (b) W. G. Kofron, W. R. Dunnavant, and C. R. Hauser, *J. Org. Chem.*, **27**, 2737 (1962).

[16] It may be, however, that the bicyclo-(2.2.0)-hexane *was* formed from the diradical, 7, but, that at the high temperature of pyrolysis, it rearranged.[6a]

[17] (a) C. G. Overberger, G. Kesslin, and N. R. Byrd, *J. Org. Chem.*, **27**, 1568 (1962); (b) C. G. Overberger and G. Kesslin *ibid.*, **27**, 3898 (1962).

[18] E. R. Buchman, A. O. Reims, T. Skei, and M. J. Schlatter, *J. Am. Chem. Soc.*, **64**, 2696 (1942).

identical with an authentic sample prepared in 65% yield according to the method of Pinkney,[12] n^{25}_{D} 1.4491, b.p. 75–84° at 2.9 mm.; semicarbazone, m.p. 141–144°; m.m.p. with "acyloin" product, 141–144°.

In one reaction starting with 29.25 g. of diester there was obtained 10.2 g. (41%) of keto ester, 1.22 g. of a liquid, b.p. 86–95° at 0.01–0.02 mm., n^{25}_{D} 1.4557, and 1.1 g. of a yellow liquid, b.p. 120–133° at 0.01 mm., n^{25}_{D} 1.4681. Both of these liquids had infrared spectra indicative of ketones, but no further attempts have been made to characterize them.

Acyloin Reaction in Toluene.—Into a 2-l., three-neck flask, fitted with a Hershberg dropping funnel, Trubore stirrer, and condenser was distilled 650 ml. of toluene (from calcium hydride), under dry, oxygen-free nitrogen. The toluene was brought to a boil and sodium, 5.95 g. (0.259 g.-atom), was added. With vigorous stirring (not high speed) the diester, 12.80 g. (0.064 mole) in 210 ml. of dry toluene, was added over 1.5 hr. The solution turned yellow within 10 min. The reaction mixture was cooled to 0° and then 14.7 ml. of glacial acetic acid was added. The presence of unchanged sodium was noted, and it was destroyed by stirring, under nitrogen, with 30 ml. of dry ethanol. The reaction mixture was quite red at this point. The solvent was evaporated under reduced pressure and the residue was filtered. The organic layer was washed repeatedly with 5% sodium bicarbonate solution, then with saturated sodium chloride solution, dried over anhydrous sodium sulfate, filtered, and distilled to give 2.05 g. (20.5%) of 2-carbethoxycyclopentanone, n^{25}_{D} 1.4484, b.p. 60–66° at 0.9 mm. In a similar, subsequent run the yield was only 8.7%.

Adipoin.—Under the conditions for acyloin reactions in liquid ammonia described previously, there was obtained 0.60 g. (8.3%) of adipoin, b.p. 71–72.5° at 7.0 mm., n^{25}_{D} 1.4658, from 12.8 g. of diethyl adipate. The adipoin readily solidified. No keto ester was obtained.

Elimination Reactions of α-Halogenated Ketones. XI.[1a] Kinetic and Product Studies of Amine-Promoted Elimination from 2-Bromo-2-benzyl-4,4-dimethyl-1-tetralone in Benzene

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Received July 16, 1962

Dehydrobromination of 2-bromo-2-benzyl-4,4-dimethyl-1-tetralone (I) by piperidine or morpholine in dilute benzene solution at elevated temperatures has been found to give largely 2-benzal-4,4-dimethyl-1-tetralone (II) accompanied by lesser amounts of 2-benzyl-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (III). The kinetics suggest that a substitution reaction initially accompanies elimination but the intermediate formed in the substitution subsequently undergoes an elimination reaction to yield the α,β-unsaturated ketones.

Amine-promoted elimination from 2-bromo-2-benzyl-4,4-dimethyl-1-tetralone (I) in the absence of solvent or in a variety of solvents[2] previously has been shown to yield a mixture of two α,β-unsaturated ketones: 2-benzal-4,4-dimethyl-1-tetralone (II) by exocylic elimination and 2-benzyl-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (III) by endocyclic elimination. This first investigation[2] and also subsequent investigations[3-6] involving various elimination promoting reagents all led to largely or completely endocyclic elimination.

In this investigation it has been found that elimination as promoted by piperidine or preferably by morpholine in dilute benzene solution at elevated temperatures leads to high yields of the exocyclic isomer II.

During the initial stages of reaction in both the piperidine- and the morpholine-promoted elimination, the second-order rate coeffficients for amine neutralization were about 50% greater in value than the second-order rate coefficients for bromide ion production. It follows that during the initial stages of reaction, amine is being consumed faster than the rate at which bromide ions are being produced. It is known that the two amines are stable in benzene[7] and further during amine-promoted elimination from 4-biphenylyl 1-bromocyclohexyl ketone in benzene, the values for the two sets of second-order rate coefficients were identical in value.[7]

It follows that the nonidentity of values results from interaction of the amine with either the reactant bromotetralone I, other than to produce the α,β-unsaturated ketones, or alternatively the α,β-unsaturated ketones are first formed and then a relatively rapid addition of amine occurs with establishment of an equilibrium between the α,β-unsaturated ketones and the 1:4 addition product; elimination–addition reactions of this nature previously have been observed.[8] An explanation in terms of 1:4 addition is, however, invalidated by the absence of any addition product when the reaction is completed; also the extent of subsequent addition would be dependent upon the concentration of amine and would not be consistently about 50% of the extent of bromide production. At 100% bromide ion formation it is found that only an equivalent quantity of amine has been consumed; for example, a solution 0.0200 *M* in bromotetralone I and 0.0400 *M* in piperidine had reacted to 98% after 138 hr. at 90.6° and remaining was 44% of the initial piperidine concentration.

Since the additional consumption of amine cannot be explained in terms of elimination–addition it follows that substitution must initially accompany the elimination. If these substitution products are in themselves unstable then over longer periods of time, they subsequently can undergo elimination reaction to yield the isolated α,β-unsaturated ketones. Both elimination and substitution lead to the formation of one molecule of amine hydrobromide but in the substitution reaction

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[1] (a) For paper X in this series see D. N. Kevill, G. A. Coppens, and N. H. Cromwell, *J. Org. Chem.*, **28**, 567 (1963); (b) to whom communications concerning this article should be addressed.

[2] A. Hassner and N. H. Cromwell, *J. Am. Chem. Soc.*, **80**, 901 (1958).

[3] N. H. Cromwell, R. P. Ayer, and P. W. Foster, *ibid.*, **82**, 130 (1960).

[4] D. N. Kevill and N. H. Cromwell, *ibid.*, **83**, 3812 (1961).

[5] D. N. Kevill and N. H. Cromwell, *ibid.*, **83**, 3815 (1961).

[6] G. Coppens, D. N. Kevill, and N. H. Cromwell, *J. Org. Chem.*, **27**, 3299 (1962).

[7] D. N. Kevill, P. H. Hess, P. W. Foster, and N. H. Cromwell, *J. Am. Chem. Soc.*, **84**, 983 (1962).

[8] N. H. Cromwell and P. H. Hess, *ibid.*, **83**, 1237 (1961).