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Ring Enlargements. IX. The Reactions of Cycloalkanones Carrying Three-carbon Side Chains Containing Potential Diazoalkyl Moieties[1]

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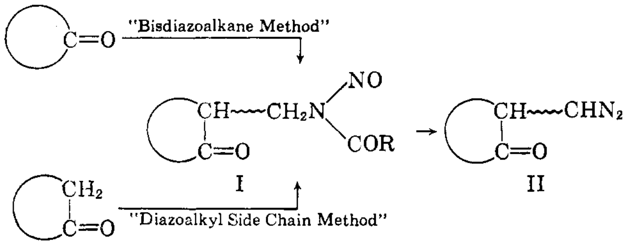
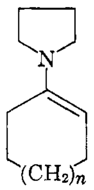
The syntheses of cyclopentanone, cyclohexanone, and cycloheptanone carrying a $—CH_2CH_2CH_2N(NO)COCH_3$ moiety in the 2-position are described. Base-catalyzed decomposition of these compounds converts the nitrosoamide group to a diazo group which reacts intramolecularly with the cycloalkanone to yield the bridged ring ketones 8-ketobicyclo[3.2.1]octane, 9-ketobicyclo[4.2.1]nonane, and 10-ketobicyclo[5.2.1]decane, respectively.

Chemists have long been fascinated by molecules which catch their own tails.[3] This and the following paper[4] add further examples to the collection of such sportive substances and describe cycloalkanones (II) which contain a diazoalkyl tail capable of being intramolecularly caught in the jaws of the carbonyl group and ingested into the ring. To isolate and directly study compounds of type II, however, is difficult because of the facility with which the intramolecular diazoalkane–carbonyl interaction takes place. Consequently, it is necessary to prepare compounds of type I in which a potential diazoalkyl group [*i.e.*, $—CH_2N(NO)COR$] is present from which, under suitable conditions, the free diazoalkanes can be generated *in situ.* One approach to this problem has been outlined in a previous paper of this series[5] which discussed the reaction between bisnitrosourethanes (as sources of bisdiazoalkanes) and cycloalkanones. Although compounds of type I were not isolated from the reaction mixtures encountered in that study, it is almost certain that they were present as transient intermediates. The present paper outlines as an alternative to the "bisdiazoalkane method" the "diazoalkyl side chain method" by means of which compounds of type I can be synthesized and actually isolated.



Compounds of the general type I containing a three-carbon side chain (VII) were synthesized in the following manner. Cyanoethylation of the pyrrolidine-enamine prepared from the appropriate cycloalkanone[6] (III) yielded the 2-(β-cyanoethyl)cycloalkanone (IV); protection of the carbonyl by formation of the ethylene ketal (V) followed by reductive acetylation[7] and selective hydrolysis yielded the (γ-acetylaminopropyl)cycloalkanone (VI) from which the corresponding N-nitroso compound (VII) was obtained by nitrosation with dinitrogen tetroxide.[8] In spite of the several steps involved, the conversion of the cycloalkanone to the ketonitrosoamide (VII) is an easy and efficient one; the intermediates need not be isolated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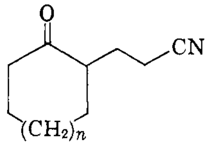
b (n = 1)
c (n = 2)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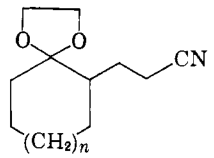
b (n = 1)
b (n = 2)


Va (n = 0)
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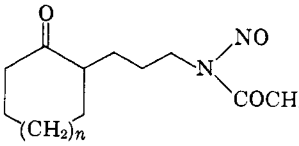
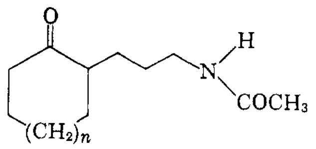
b (n = 2)


VIIa (n = 0)
b (n = 1)
c (n = 2)


VIa (n = 0)
b (n = 1)
c (n = 2)

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[1] This work was supported, in part, by a grant-in-aid from the National Science Foundation (G-6282).

[2] Universal Match Company Fellow, 1959–1961.

[3] See, for instance, A. Kekule, *Ber.*, **23**, 1306 (1890).

[4] D. M. Bailey, J. E. Bowers, and C. D. Gutsche, *J. Org. Chem.*, **28**, 610 (1963).

[5] C. D. Gutsche and T. D. Smith, *J. Am. Chem. Soc.*, **82**, 4067 (1960).

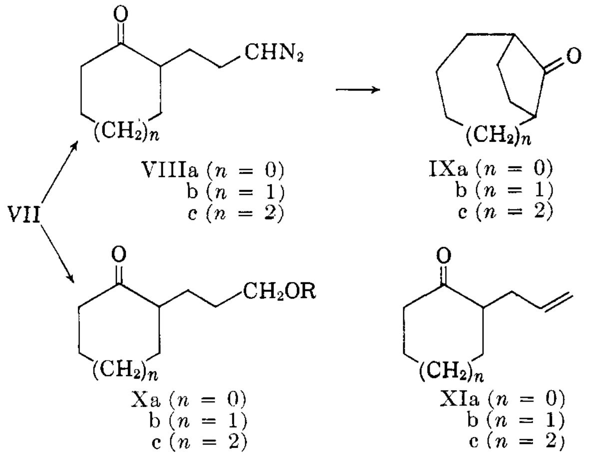
[6] G. Stork, R. Terrell, and J. Szmuszkovicz, *ibid.*, **76**, 2029 (1954); G. Stork and H. K. Landesman, *ibid.*, **78**, 5128 (1956).

[7] F. E. Gould, G. S. Johnson, and A. F. Ferris, *J. Org. Chem.*, **25**, 1658 (1960).

[8] E. J. White, *J. Am. Chem. Soc.*, **77**, 6008 (1955).

and purified, and the over-all yields from cyclopentanone, cyclohexanone, and cycloheptanone to VII are 45–65%.

Since VIIb is the most accessible of the compounds in this series, its behavior on base-catalyzed decomposition was studied in some detail. Employing the previously-described conditions for carrying out the ring enlargement reaction *via* the *in situ* method,[9] *viz.* addition of the nitroso compound to a cold mixture of the ketone, methanol and potassium carbonate, a reaction took place with the quantitative evolution of nitrogen. The volatile product consisted of a mixture (total yield *ca.* 60%) of IXb and Xb in a ratio of 6:1. On the basis of an earlier observation[10] that the ratio of ring enlargement product to solvolysis product increased with decreasing temperature, the decomposition of VIIb at lower temperature was studied. Contrary to expectation, however, the ratio of IXb to Xb decreased somewhat as the temperature was decreased to −30° and −60°. Although it was interesting that the nitroso compound underwent any decomposition at these low temperatures,[11] the product ratio was disappointing from the standpoint of a useful synthesis of IXb. On the other hand, when the reaction temperature was increased to 60°, the ratio of IXb to Xb increased to *ca.* 10:1. The higher reaction temperature also allowed a reduction in the amount of methanol necessary for the decomposition of VIIb, and this led to a further improvement in the ketone to ether ratio. It was subsequently ascertained that sodium methoxide could be used in place of potassium carbonate, that refluxing ethanol containing sodium ethoxide was equally as effective, that refluxing isopropyl alcohol containing sodium isopropoxide was completely ineffective,[12] and that an aqueous–alcoholic solvent gave rise to appreciable amounts of 2-allylcyclohexanone (XIb) in addition to the ketone IX. Under the optimum conditions of decomposition 9-ketobicyclo[4.2.1]nonane (IXb) can be obtained virtually free of Xb and/or XIb in 80% yield from VIIb which corresponds to a better than 50% over-all yield from cyclohexanone. Thus, the method provides a definite advantage over the previously reported procedure whereby IXb was obtained in only 10% yield from the reaction of cyclopentanone with the bisnitrosourethane from butane-1,4-diamine.[5]



VIIIa (*n* = 0)
b (*n* = 1)
c (*n* = 2)

IXa (*n* = 0)
b (*n* = 1)
c (*n* = 2)

VII

Xa (*n* = 0)
b (*n* = 1)
c (*n* = 2)

XIa (*n* = 0)
b (*n* = 1)
c (*n* = 2)

The decomposition of VIIa also proceeded very smoothly in a refluxing solution containing ethanol and sodium ethoxide to provide an 88% yield of 8-ketobicyclo[3.2.1]octane (IXa) contaminated with only a small amount of the keto ether (Xa, $R = OEt$), the identity of which is inferred from the analogy with similar ring enlargement mixtures. In aqueous–alcoholic solvents 2-allylcyclopentanone (XIa) was also produced, its identity being established through an independent synthesis. The structure of the ketone IXa was verified by a comparison with material obtained by another route.[13] In this instance, also, the present method provides a reasonably easy route to the bridged ring ketone XIa.

The decomposition of VIIc in refluxing methanol containing sodium methoxide proceeded smoothly and with quantitative nitrogen evolution, but the product contained mainly the keto ether Xc. The yield of IXc was improved by carrying out the reaction at 10° in methanol containing suspended potassium carbonate but only to the extent that the product, obtained in 80% yield, consisted of 10-ketobicyclo[5.2.1]decane (IXc) and ether (Xc) in a ratio of 3:2. To obtain pure ketone from this mixture is rather difficult and inefficient, and in this instance the synthesis from cyclohexanone and the bisnitroso compound from butane-1,4-diamine[5] is the method of choice.

The base-catalyzed decomposition of compounds of the type VII thus provides a useful method for the synthesis of bridged ring ketones of the type IX. Extensions of this method to compounds of the type VII which are substituted in the cycloalkanone ring and/or the side chain will be reported at a later time. Extensions to compounds carrying side chains of other lengths and to compounds carrying the side chain at other positions in the cycloalkanone ring are reported in the following paper.[4]

Experimental[14]

α-6-3 Series[15] [Synthesis of 9-Ketobicyclo[4.2.1]nonane (IXb)]

N-Acetyl-3-(2′-ketocyclohexyl)propylamine (VIb).—Following published procedures[6] 98 g. (1.0 mole) of cyclohexanone was treated with 100 g. (1.4 moles) of pyrrolidine in 300 ml. of benzene, the mixture was heated until no more water was formed (4 hr.), and the excess solvent and pyrrolidine were removed under vacuum. To the pale yellow residue consisting of IIIb 66 g. (1.25 moles) of acrylonitrile and 400 ml. of benzene was added, and the mixture was refluxed overnight. About two-

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[9] See ref. 4 and C. D. Gutsche, *Org. Reactions*, **VIII**, 364 (1954).

[10] C. D. Gutsche and H. H. Peter, *J. Am. Chem. Soc.*, **77**, 5971 (1955).

[11] Intermolecular diazoalkane–carbonyl reactions in which the diazoalkane is generated *in situ* frequently become very sluggish even at 0°. The much more facile decomposition of compounds of type VII suggests that some sort of intramolecular assistance is provided by the cycloalkanone carbonyl.

[12] A similar failure is recorded for the system of decalone and nitrosomethylurethan in isopropyl alcohol and sodium isopropoxide.[4]

[13] A. C. Cope, J. M. Grisar, and P. E. Peterson, *J. Am. Chem. Soc.*, **82**, 4299 (1960). We are indebted to Professor Cope for the melting point and infrared comparisons of the ketones and derivatives thereof.

[14] Melting points are corrected; boiling points are uncorrected. The infrared spectra were recorded on a Perkin–Elmer Model 21 spectrophotometer; the ultraviolet spectra were recorded on a Cary spectrophotometer. Analytical vapor phase chromatographic determinations were carried out with columns 1/4 in. in diam. packed with firebrick (6-ft. column) or glass beads (16-ft. column) with silicone oil (Dow-Corning 710) as the adsorbed phase. Preparative vapor phase chromatographic separations were carried out on a column 1/2 in. × 10 ft. packed with silicone oil on firebrick. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill., and by Mikroanalytisches Laboratorium, Vienna, Austria.

[15] In this and subsequent designations in the Experimental the Greek letter refers to the point of attachment of the side chain to the cycloalkanone, the first number refers to the ring size of the cycloalkanone, and the second number refers to the number of carbon atoms in the side chain.

thirds of the solvent was then removed under vacuum, 400 ml. of water and 25 ml. of glacial acetic acid were added, and the mixture was refluxed for 6 hr. The product, IVb, consisted of 130 g. (86%) of a colorless oil, b.p. 144–146° (8 mm.) [reported[16] b.p. 138–142° (10 mm.)]. This material (130 g., 0.86 mole) was treated with 62 g. (1 mole) of ethylene glycol, 1.5 g. of *p*-toluenesulfonic acid, and 500 ml. of dry, thiophene-free benzene, and the mixture was refluxed in an apparatus equipped with a water separator until no more water was collected (16–20 hr., 18–20 ml. of water). The product, Vb, consisted of a pale yellow oil which was used directly in the next experiment without purification. Employing the method of Gould, Johnson, and Ferris[7] the ketal Vb from 130 g. of IVb was treated with 300 ml. of acetic anhydride, 25 g. of W-2 Raney nickel,[17] and 25 g. of anhydrous sodium acetate and subjected to hydrogenation at 25 p.s.i. and 100°. When the hydrogen uptake ceased (2.5–3 hr.), the reaction mixture was filtered, most of the solvent was removed under reduced pressure, and the residue was dissolved in 200 ml. of sulfuric acid (1:25) containing sufficient acetic acid for complete solution. After standing at room temperature for 8–12 hr., the mixture was poured into 1 l. of saturated salt solution and worked up in the usual way to yield 135 g. (80%) of VIb as an almost colorless oil, b.p. 142–145°(0.05 mm.). The oil slowly crystallized, and recrystallization from isopropyl ether containing a small amount of ethanol gave colorless needles, m.p. 59–60.5°.

Anal. Calcd. for $C_{11}H_{19}NO_2$: C, 66.97; H, 9.71. Found: C, 67.01; H, 9.74.

The 2,4-dinitrophenylhydrazone of N-acetyl-3-(2′-ketocyclohexyl)propylamine was obtained as orange needles after recrystallization from 95% ethanol, m.p. 190.5–191°.

Anal. Calcd. for $C_{17}H_{23}N_5O_5$: C, 54.10; H, 6.14. Found: C, 54.21; H, 6.19.

N-Nitroso-N-acetyl-3-(2′-ketocyclohexyl)propylamine (VIIb).—Employing the method of White[8] an ice-cold solution of 49.5 g. (0.25 mole) sample of VIb in 200 ml. of dichloromethane was slowly added to a mixture of 37.8 g. (0.41 mole) of dinitrogen tetroxide, 67 g. (0.82 mole) of anhydrous sodium acetate, and 350 ml. of dichloromethane cooled to −30°. The solution, which fairly quickly warmed to *ca.* −10°, was maintained at −10° to 0° over a period of 20–30 min. During this time the initial green color changed to a bright yellow color. The reaction mixture was washed with 500 ml. of an ice-cold solution of 10% potassium carbonate and then with water. After drying over anhydrous potassium carbonate, the solvent was removed to leave 54.5 g. (96%) of a red oil which was not purified but was used directly in the subsequent experiment. On the basis of the nitrogen evolution upon decomposition this material was estimated to be *ca.* 98% pure.

Ring Enlargement of N-Nitroso-N-acetyl-3-(2′-ketocyclohexyl)-propylamine: (A) Reflux Method.—To 25 ml. of absolute ethanol heated at reflux temperature a solution of N-nitroso-N-acetyl-3-(2′-ketocyclohexyl)propylamine (from 0.25 mole of VIb) in 200 ml. of dichloromethane and a 30–40 ml. of a 0.4 M solution of sodium ethoxide in ethanol were simultaneously added over a period of 10–15 min. After an additional 15 min. of refluxing, the reaction mixture was steam distilled until all of the organic layer had been carried into the distillate (*ca.* 1–1.2 l.). The distillate was saturated with sodium sulfate and extracted with five 100-ml. portions of dichloromethane. The combined extract was dried over anhydrous sodium sulfate and evaporated at 52° to leave 28 g. (81%) of 9-ketobicyclo[4.2.1]nonane (IXb) as a mushy solid possessing a strong camphoraceous odor. Vapor phase analysis of this material indicated that it was essentially one compound contaminated with only small amounts of other substances. Like camphor, however, the product appears to have a large cryoscopic constant so that only small amounts of impurities are required to lower drastically its melting point. After one recrystallization from petroleum ether (b.p. 63–69°) 24.2 g. (70%) of material with m.p. 95–103° was obtained and after several additional crystallizations from the same solvent the m.p. could be raised to 108–111° (reported m.p. 109–111°).[4] Admixture with a sample obtained *via* the bisdiazoalkane route[5] showed no depression in m.p. Similarly, the 2,4-dinitrophenylhydrazone of IXb, m.p. 159–160°, showed no depression in m.p. when admixed with the derivative prepared from material obtained by the earlier procedure.[5]

The semicarbazone of 9-ketobicyclo[4.2.1]nonane was obtained after several recrystallizations from aqueous ethanol as lustrous white flakes, m.p. 207–208°.

Anal. Calcd. for $C_{10}H_{17}N_3O$: C, 61.51; H, 8.78. Found: C, 61.77; H, 8.91.

(B) Ice Bath Method.—To a stirred and cooled (0–5°) mixture of 200 ml. of absolute methanol and 0.4 g. of finely powdered potassium carbonate a solution of 0.25 mole of N-nitroso-N-acetyl-3-(2′-ketocyclohexyl)propylamine in 100 ml. of dichloromethane was added over a period of 2 hr. The solution was stirred an additional 30 min. and then worked up as described above to yield 27.5 g. of an oil which was shown by v.p.c. analysis to contain 9-ketobicyclo[4.2.1]nonane (IXb) and 2-(γ-methoxypropyl)cyclohexanone (Xb) in a ratio of *ca.* 6:1.

(C) Aqueous Solvent.—To 50 ml. of a solution of ethanol and water (2:1) heated to reflux, a solution of 0.25 mole of VIIb in 150 ml. of ethanol–water (2:1) and a solution of 14 g. (0.25 mole) of potassium hydroxide in 100 ml. of ethanol–water (2:1) were added simultaneously over a period of 20 min. The solution was refluxed an additional 5 min. and then worked up as described above to yield 22 g. of a yellow oil which contained, in addition to IXb and Xb (R = C_2H_5), 28% of 2-allylcyclohexanone (XIb). An authentic sample of XIb for comparison was prepared by alkylation of cyclohexanone enamine (IIIb) with allyl bromide and was obtained in 55% yield as a colorless oil, b.p. 88–89° (17 mm.) [reported b.p. 90–92° (17 mm.)[18]].

α-5-3 Series[15] [Synthesis of 8-Ketobicyclo[3.2.1]octane (IXa)]

N-Acetyl-3-(2′-ketocyclopentyl)propylamine (VIa).—Cyanoethylation of cyclopentanone enamine (IIIa) from 84 g. (1 mole) of cyclopentanone yielded 63% of 2-cyanoethylcyclopentanone (IVa) as a colorless oil, b.p. 146–148° (8 mm.). The corresponding ketal (Va) was prepared as described above, and the crude product was reduced with hydrogen and Raney nickel in a solution containing acetic anhydride and sodium acetate.[7] Selective hydrolysis by the procedure described above gave 89 g. (77% from IVa) of N-acetyl-3-(2′-ketocyclopentyl)propylamine (VIa) as a colorless oil, b.p. 144–147° (0.05 mm.).

Anal. Calcd. for $C_{19}H_{17}NO_2$: C, 65.54; H, 9.35. Found: C, 65.56; H, 9.26.

The 2,4-dinitrophenylhydrazone of VIa was obtained after recrystallization from 95% ethanol as yellow needles, m.p. 183.5–184°.

Anal. Calcd. for $C_{16}H_{21}N_5O_5$: C, 52.88; H, 5.83. Found: C, 53.12; H, 5.83.

N-Nitroso-N-acetyl-3-(2′-ketocyclopentyl)propylamine (VIIa) was prepared as described above for VIIb and was obtained in 97% yield as a red oil which, on the basis of subsequent nitrogen evolution on decomposition, was indicated to be *ca.* 99% pure.

Ring Enlargement of N-Nitroso-N-acetyl-3-(2′-ketocyclopentyl)propylamine: (A) Reflux Method.—A sample of N-nitroso-N-acetyl-3-(2′-ketocyclopentyl)propylamine (VIIa) prepared from 0.25 mole of VIa was subjected to ring enlargement in a refluxing solution of ethanol containing sodium ethoxide as described above for VIIb. Steam distillation of the reaction mixture yielded 27.2 g. (88%) of 8-ketobicyclo[3.2.1]octane (IXa) as a waxy solid with a strong camphoraceous odor. One recrystallization from petroleum ether (b.p. 63–69°) with cooling to *ca.* −60° provided 20 g. (65%) of IXa as a colorless solid with m.p. 135–138°. Although additional crystallizations raised the m.p. only to 136–138°, passage through a preparative v.p.c. apparatus gave material with m.p. 140–142° (reported m.p. 134–136°,[19] 141.5–143.2°[13]). An infrared spectrum of IXa was identical with that of material obtained by an alternate route, and admixture of the two samples showed no depression in m.p.[13] Similarly, the 2,4-dinitrophenylhydrazone of IXa, m.p. 175–176°, showed no depression in melting point when admixed with material obtained by the alternate method.[13]

The semicarbazone of 8-ketobicyclo[3.2.1]octane was obtained as colorless fine needles after recrystallization from water, m.p. 191–191.5° dec.

Anal. Calcd. for $C_9H_{15}N_3O$: C, 59.64; H, 8.34. Found: C, 59.58; H, 8.31.

(B) Aqueous Solvent.—Decomposition of a 0.125-mole sample of IIa in an aqueous ethanolic solution under the conditions de-

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[16] H. A. Bruson and T. W. Riener, *J. Am. Chem. Soc.*, **64**, 2850 (1942).

[17] R. Mozingo, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons Inc., New York, N. Y., 1955, p. 181.

[18] C. A. Vanderwerf and L. V. Lemmerman, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 44.

[19] R. Mayer, G. Wenschuh, and E. Topelmann, *Ber.*, **91**, 1616 (1958).

scribed above for VIIb gave 13 g. of an oil which was shown to contain, in addition to IXa and Xa (R = C_2H_5), 5–10% of 2-allylcyclopentanone (XIa). An authentic sample of XIa was prepared for comparison by the procedure of Staudinger and Ruzicka[20] and obtained as an oil with b.p. 72–74° (12 mm.) [reported b.p. 86° (12 mm.)[20]]. In view of the discrepancy between the boiling points a *p*-nitrophenylhydrazone was prepared, m.p. 138–139.5° (reported m.p. 139°[20]).

α-7-3 Series[15] [Synthesis of 10-Ketobicyclo[5.2.1]decane (IXc)]

N-Acetyl-3-(2′-ketocycloheptyl)propylamine (VIc).—Cyanoethylation of cycloheptanone enamine (IIIc) from 112 g. (1 mole) of cycloheptanone yielded 84 g. (60% based on 15 g. of recovered cycloheptanone) of 2-cyanoethylcycloheptanone (IVc) as a colorless oil, b.p. 152–154° (9 mm.). The corresponding ketal Vc was prepared as described above, and the crude product was reduced with hydrogen and Raney nickel in a solution containing acetic anhydride and sodium acetate.[7] Selective hydrolysis by the procedure described above gave 82 g. (76% from IVc) of N-acetyl-3-(2′-ketocycloheptyl)propylamine (VIc) as a colorless oil, b.p. 146–148° (0.02 mm.).

Anal. Calcd. for $C_{12}H_{21}NO_2$: C, 68.21; H, 10.02. Found: C, 67.78; H, 9.97.

The 2,4-dinitrophenylhydrazone of VIc was obtained after recrystallization from dimethoxyethane-water as fine orange needles, m.p. 108–108.5°.

Anal. Calcd. for $C_{18}H_{25}N_5O_5$: C, 55.23; H, 6.44. Found: C, 55.09; H, 6.08.

N-Nitroso-N-acetyl-3-(2′-ketocycloheptyl)propylamine (VIIc) was prepared as described above for VIIb and was obtained in 96% yield as a red-orange oil which, on the basis of subsequent nitrogen evolution on decomposition, was indicated to be *ca.* 99% pure.

Ring Enlargement of N-Nitroso-N-acetyl-3-(2′-ketocycloheptyl)propylamine: (A) Reflux Method.—When N-nitroso-N-acetyl-3-(2′-ketocycloheptyl)propylamine (VIIc) was decomposed in a solution of ethanol containing sodium ethoxide heated to reflux under the conditions described above for VIIb only a small amount of bicyclic ketone (IXc) was formed, and the v.p.c. analysis indicated at least eight products to be present.

(B) Ice Bath Method.—To a stirred and cooled (below 10°) mixture of 250 ml. of absolute methanol and 0.4 g. of finely powdered potassium carbonate a solution of 0.25 mole of VIIc in 200 ml. of dichloromethane was added over a period of 2 hr. The mixture was stirred an additional hour and worked up as described above to give 33 g. of a mobile, yellow oil which was shown by v.p.c. analysis to contain *ca.* 60% of 10-ketobicyclo-[5.2.1]decane (IXc). Purification of a 1-g. sample of this material by passage through a preparative v.p.c. column yielded a solid, m.p. 112–115°, which showed no depression in m.p. when admixed with a sample of IXc as obtained *via* the bis-diazoalkane method.[5]

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[20] H. Staudinger and L. Ruzicka, *Helv. Chim. Acta.*, **7**, 442 (1942).

Ring Enlargements. X. The Reactions of Cycloalkanones Carrying Two-carbon and Four-carbon Side Chains Containing Potential Diazoalkyl Moieties[1]

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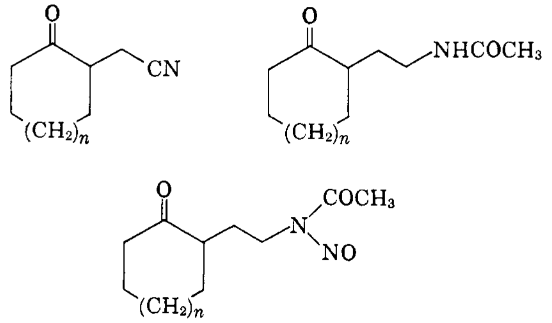
The syntheses of cyclopentanone, cyclohexanone, and cycloheptanone carrying a —$CH_2CH_2N(NO)COCH_3$ moiety in the 2-position, of cyclohexanone carrying a —$CH_2CH_2N(NO)CO_2C_2H_5$ moiety in the 4-position, and of cyclopentanone carrying a —$(CH_2)_4N(NO)COCH_3$ moiety in the 2-position are described. Base-catalyzed decomposition of these compounds results in the formation of solvolysis and elimination products in the case of the cycloalkanones with two-carbon side chains in the 2-position, in the formation of 2-ketobicyclo[3.2 1]octane in the case of cyclohexanone carrying a two-carbon side chain in the 4-position and in the formation of a mixture of 2-ketobicyclo[4.3.0]nonane and 9-ketobicyclo[3.3.1]nonane in the case of cyclopentanone carrying a four-carbon side chain in the 2-position.

The previous paper of this series[4] described the base-catalyzed decomposition of cycloalkanones carrying in the α-position a three-carbon side chain terminating in a potential diazoalkane moiety. The present paper extends the scope of the investigation to include examples of compounds carrying two- and four-carbon side chains in the α-position and a compound carrying a two-carbon side chain in the γ-position.

Ketonitriles of structure I were prepared by treatment of the enamine of cyclopentanone (n = 0) and cyclohexanone (n = 1) with chloroacetonitrile and by ring enlargement (*in situ* method[5]) of cyclohexanone with β-(N-acetyl-N-nitrosoamino)propionitrile for n = 2. Protection of the carbonyl function by formation of the ethylene ketal followed by reductive acetylation[6] and selective hydrolysis yielded the 2-(β-acetylaminoethyl)cycloalkanone (II) from which the corresponding N-nitroso compound III was obtained by nitrosation with dinitrogen tetroxide.[7] Decomposition of the nitrosoamides III resulted in the evolution of 65–85% of the theoretical amount of nitrogen, but the volatile products were obtained in low yield and contained little or none of the fused ring or bridged ring ketones. The only identified products were methoxyethylcyclopentanone (IVa) and vinylcyclopentanone



Ia (n = 0) IIa (n = 0) IIIa (n = 0)
b (n = 1) b (n = 1) b (n = 1)
c (n = 2) c (n = 2) c (n = 2)

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[2] Universal Match Company Fellow, 1959–1961.

[3] Universal Match Company Fellow, 1961–1962; National Science Foundation Summer Research Fellow, 1962.

[4] C. D. Gutsche and D. M. Bailey, *J. Org. Chem.*, **28**, 607 (1963).

[5] See C. D. Gutsche, *Org. Reactions*, **VIII**, 364 (1954).

[6] F. E. Gould, G. S. Johnson, and A. F. Ferris, *J. Org. Chem.*, **25**, 1658 (1960).

[7] E. J. White, *J. Am. Chem. Soc.*, **77**, 6008 (1955).