refluxing for 4 hr, the starting tetraketone VIIb was largely recovered.

Condensation of Triketone II (R = CH_3) with Diethyl Phthalate by Sodium Hydride.—To a suspension of 11.5 g (0.05 mole) of sodium hydride[11] (52% dispersion in mineral oil) in 50 ml of monoglyme was added 10.2 g (0.05 mole) of triketone II (R = CH_3) dissolved in 50 ml of monoglyme. After the mixture stirred under reflux for 20 min, 11.1 g (0.05 mole) of diethyl phthalate in 50 ml of monoglyme were added. The resulting mixture was refluxed for 6 hr and worked-up as described above for condensations of β-diketones I to give 4.81 g (29%) of XIV, mp 127–127°. The infrared spectrum showed peaks at 760 and 690 (monosubstituted phenyl),[9] 735 (*ortho* disubstitution),[9] and a broad band centered at 1620 cm^{-1} with maxima at 1700, 1650, and 1590 cm^{-1} (β-diketone).[9]

Anal. Calcd for $C_{20}H_{14}O_5$: C, 71.85; H, 4.22. Found: C, 71.55; H, 4.31.

Registry No.—IIIa, 10437-91-9; IIIb, 10437-92-0; IVa, 10437-93-1; IVb, 10481-52-4; V, 10437-94-2; VIIa, 10437-95-3; VIIb, 10437-96-4; X, 1133-72-8; XI, 10464-99-0; XIIIa, 10437-97-5; XIIIb, 10465-00-6; XIV, 10437-98-6; sodium hydride, 7646-69-7.

Ring Enlargements. XII. N-Nitrosolactams as Ring-Enlargement Reagents[1]

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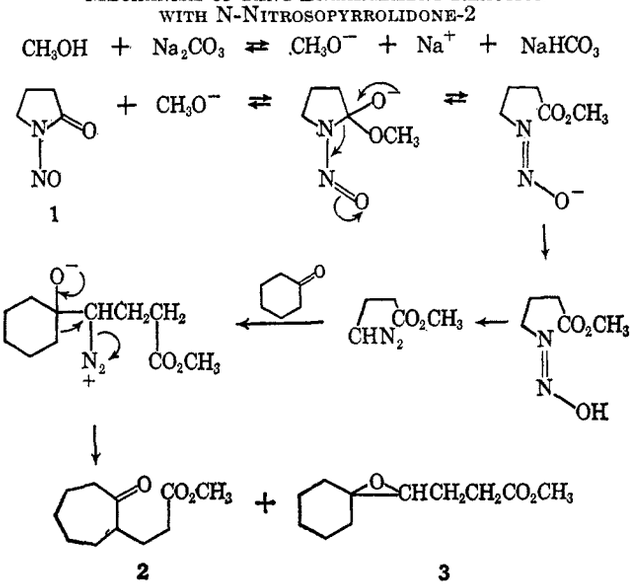
The scope and limitations of reactions involving N-nitrosolactams as ring-enlargement reagents has been investigated. It has been found that (a) cyclohexanone, 2-methylcyclohexanone, 3-methylcyclohexanone, 4-methylcyclohexanone, 4-isopropylcyclohexanone, 4-*t*-butylcyclohexanone, and 4,4-dimethylcyclohexanone all react with N-nitrosopyrrolidone-2 (in methanolic sodium carbonate) to give the corresponding methyl β-(2-ketocycloheptane)propionates in 47–64% yields; (b) cyclohexanone reacts with 3-methyl-N-nitrosopyrrolidone-2 and 4-methyl-N-nitrosopyrrolidone-2 to yield the corresponding ring-enlargement products; (c) cyclopentanone reacts with N-nitrosopyrrolidone-2 to give methyl β-(2-ketocyclohexane)propionate in only 20% yield; and (d) 5-methyl-N-nitrosopyrrolidone-2, N-nitrosopiperidone-2, and N-nitrosocaprolactam-2 fail to yield any ring-enlargement products whatsoever. As a preparative method, therefore, the reaction appears to be limited to N-nitrosopyrrolidones and cyclohexanones as the participants; within this somewhat restricted area, however, it is quite general.

One of the standard methods for effecting the diazoalkane ring enlargement of cycloalkanones involves the *in situ* generation of the diazoalkane by the action of a base on compounds of the general structure $RN<^{NO}_{Y}$ (where Y may be a variety of moieties including CO_2Et, $COCH_3$, $CONH_2$, etc.).[3] Although it has been shown that the mechanism of the conversion of the nitroso compound to the diazo compound is a function of the Y group,[4] the contention that the mechanism of the decomposition of nitrosourethans[5a] and nitrosoamides[5b] involves a nucleophilic attack at the carbonyl group appears to be well founded.[6] The resulting tetrahedral intermediate subsequently collapses to a diazoalkane (*via* an intermediate diazonium hydroxide) with expulsion of the Y group. Ordinarily, the Y group is of no further interest in a ring-enlargement sequence, for only the diazoalkane moiety engages the cycloalkanone. In the special instance, however, in which the Y group is doubly attached to the N-nitroso function, it must appear (as altered by solvolysis) in the ring-enlargement product. To test the preparative applications of this possibility, a series of experiments involving N-nitrosolactams as diazoalkane precursors was carried out.[7] In the simplest example a mixture of cyclohexanone, methanol, and sodium carbonate was treated at room temperature with N-nitrosopyrrolidone-2. Nitrogen was smoothly evolved, and a product was obtained in 60% yield which contained methyl β-(2-ketocycloheptane)propionate (2) contaminated with a small amount of the epoxide 3. The mechanism by which this ring-enlargement reaction presumably proceeds is illustrated in Scheme I.

SCHEME I
MECHANISM OF RING-ENLARGEMENT REACTION WITH N-NITROSOPYRROLIDONE-2



Methyl β-(2-ketocycloheptane)propionate (2) has been prepared by the action of methyl acrylate on the

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(2) Shell Oil Co. Fellow 1960–1961, Wheeler Fellow 1961–1962, and University Fellow 1962–1963.

(3) See C. D. Gutsche, *Org. Reactions*, **8**, 389 (1954).

(4) W. M. Jones, D. L. Muck, and T. K. Tandy, Jr., *J. Am. Chem. Soc.*, **88**, 68 (1966).

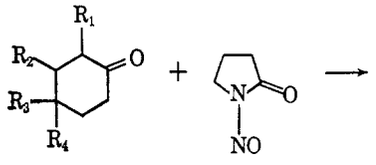
(5) (a) C. D. Gutsche and H. E. Johnson, *ibid.*, **77**, 109 (1955). (b) R. Huisgen, *Ann.*, **573**, 173 (1951); R. Huisgen and J. Reinertshofer, *ibid.*, **575**, 174 (1952).

(6) R. A. Moss, *J. Org. Chem.*, **31**, 1082 (1966).

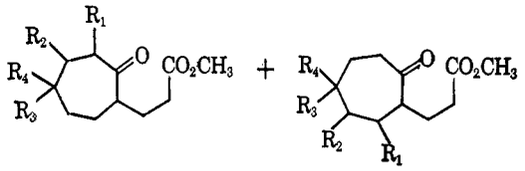
(7) See C. D. Gutsche and I. Y. C. Tao, *J. Org. Chem.*, **28**, 883 (1963), for a preliminary communication of the results of these experiments.

enamine of cycloheptanone,[8] and the corresponding acid has been prepared by several routes involving 2-carbethoxycycloheptanone,[9] 2-cyanocycloheptanone,[10] and 2-dimethylaminomethylcycloheptanone[11] as the starting materials. Thus, the structure of **2** was readily established on the basis of its elemental analysis, its infrared spectrum, and by a comparison of its solid derivatives with those reported in the literature. The structure of the oxide **3** was inferred from its elemental analysis, its infrared spectrum, and its conversion to cyclohexanone *via* acid-catalyzed hydrolysis followed by periodate oxidation.[12] The remainder of the mixture can be accounted for as unreacted cyclohexanone and various solvolysis products from N-nitrosopyrrolidone-2, including γ-butyrolactone and methyl γ-methoxybutyrate. The yield of ring-enlargement product appeared to be relatively insensitive to temperature variations over the range 10–40°, to changes in the cyclohexanone to N-nitrosopyrrolidone ratio over the range of 1.0–2.0, and to changes in the methanol to cyclohexanone ratio over the range of 2.7–1.5.

Having demonstrated the utility of the N-nitrosopyrrolidone ring enlargement with cyclohexanone, the possibility of using variously substituted cyclohexanones was then investigated. All of the substituted cyclohexanones employed (**4a–f**) reacted smoothly to give the corresponding methyl β-(2-ketocycloheptane)-propionates (**5a–f** and **6a–f**) in 47–64% yields. In the case of the 4-substituted cyclohexanones **4c–f** the product consists of a single structural isomer, although the possibility for epimers exists. The presence of the carbonyl group adjacent to one of the chiral centers, however, allows the epimers to be easily interconverted under the conditions of the ring enlargement thereby



4

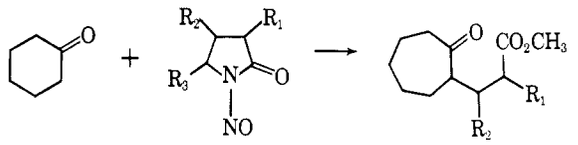


5 **6**

Series a, R_1=CH_3; R_2, R_3, R_4=H
b, R_2=CH_3; R_1, R_3, R_4=H
c, R_3=CH_3; R_1, R_2, R_4=H
d, R_3=$CH(CH_3)_2$; R_1, R_2, R_4=H
e, R_3=$C(CH_3)_3$; R_1, R_2, R_4=H
f, R_3, R_4=CH_3; R_1, R_2=H

permitting the more stable one to predominate. In the case of the unsymmetrically substituted cyclohexanones **4a** and **b** the product may consist of a mixture of structural isomers, **5** and **6**, each of which may also exist in epimeric forms. Unfortunately, vapor phase chromatography (vpc) failed to separate the components of these mixtures, and the composition could not be ascertained.

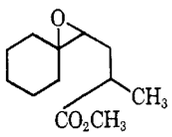
To further explore the scope and limitations of the method, N-nitrosopyrrolidones substituted with methyl groups in the 3, 4, and 5 positions were also investigated. Although the 5-methyl compound **7c** failed to react with cyclohexanone and yielded only low boiling products of solvolysis, the 3-methyl **7a** and 4-methyl **7b** compounds both reacted smoothly with cyclohexanone. From the 3-methyl compound **7a** a mixture containing three components was obtained. Two of the components were identified, on the basis of elemental analysis, saponification equivalents, and infrared spectra, as epimeric forms of methyl α-methyl-β-(2-ketocycloheptane)propionate (**8a**). When a mixture con-



7a, R_1 = CH_3; R_2, R_3 = H
b, R_2 = CH_3; R_1, R_3 = H
c, R_3 = CH_3; R_1, R_2 = H

8a, R_1 = CH_3; R_2 = H
b, R_1 = H; R_2 = CH_3

taining these compounds in a ratio of 3:2 was treated with base, the ratio changed to 1:1, indicating the two epimers to be of comparable stability. The third member of the mixture is tentatively identified as the epoxide **9** on the basis of its elemental analysis and infrared spectrum. From the 4-methyl isomer **7b** an apparently homogeneous fraction (as indicated by a single, sharp peak in the vpc) was obtained in 49% yield. On the basis of its elemental analysis, saponification equivalent, and infrared spectrum it is identified as methyl β-(2-ketocycloheptane)butyrate (**8b**).



9

The N-nitrosopyrrolidone method appears to be of only limited utility for the preparation of cyclohexanone derivatives as indicated by one experiment with cyclopentanone which yielded only 20% of methyl β-(2-ketocyclohexane)propionate. Extension of the method to N-nitrosopiperidone and N-nitrosocaprolactam failed in our hands, to yield any ring-enlargement product whatsoever, although it has been reported that the latter yields a small amount of product at −40°.[13] Thus, the major utility of the method lies in those reactions involving N-nitrosopyrrolidones and cyclohexanones, and the present investigation has shown it to be general with respect to both of these participants.

(8) Z. Eckstein, A. Sacha, and W. Sobotka, *Roczniki Chem.*, **34**, 1329 (1960).
(9) Pl. A. Plattner, A. Fürst, and K. Jirasek, *Helv. Chim. Acta*, **29**, 730 (1946).
(10) C. Ivanoff, *Chem. Ber.*, **87**, 1600 (1954).
(11) W. Treibs and M. Mühlstaedt, *ibid.*, **87**, 407 (1954).
(12) We are indebted to Mr. G. D. Stelling for carrying out the structure determination of the oxide.
(13) W. Pritzkow and P. Dietrich, *Ann.*, **665**, 88 (1963).

Experimental Section[14]

Methyl β-(2-Ketocycloheptane)propionate (2).—Following the nitrosation procedure of White,[15] a mixture containing 0.546 mole of dinitrogen tetroxide and 1.5 moles of anhydrous sodium acetate in 150 ml of carbon tetrachloride was prepared at Dry-Ice temperature. To this rapidly stirred mixture was added, over a period of 1 hr, a solution of 46.5 g (0.546 mole) of 2-pyrrolidone in 50 ml of methylene chloride. The mixture was allowed to stand at −60° for 1 hr and at −20° for 0.5 hr, during which time a color change from blue to green to yellow took place.[16] At this point the reaction mixture was again cooled to −30° and treated with 138 g (1 mole) of potassium carbonate in 150 ml of water, maintaining the temperature at *ca.* −20°. The methylene chloride and water layers were then separated, the water layer was washed several times with methylene chloride, and the combined methylene chloride solution was dried over anhydrous sodium sulfate. Evaporation of the solvent yielded 85–93% of N-nitrosopyrrolidone-2 as a deep red oil which has been reported to have a boiling point of 86° (0.3 mm).[6b] It is susceptible to detonation of attempted distillation, however, and was used without purification. On the basis of the nitrogen evolution observed in more than 30 experiments, the product is estimated to be 80–90% pure. The preparation of N-nitrosopyrrolidone-2 was capricious upon occasion, particularly when being carried out for the first time by a particular exprimenter. The difficulty appears to be associated with the carbonate washing operation, but the precise specification of the problem has been elusive.

To a stirred mixture containing 36.6 g (0.37 mole) of cyclohexanone and 1 g of anhydrous sodium carbonate in 40 ml of absolute methanol was added, over a period of 3 hr, 40 g (0.35 mole) of N-nitrosopyrrolidone-2. During the addition the temperature was maintained at 20–25° by means of an ice bath. At the end of the addition the reaction mixture was filtered, and the filtrate was concentrated and distilled through a 10-in. Vigreux column to give 42 g (60%) of a colorless oil consisting mainly of methyl β-(2-ketocycloheptane)propionate (**2**), bp 103–105° (0.3 mm), $\tilde{\nu}^{\text{liquid}}$ 1740 (ester carbonyl) and 1705 cm^{-1} (cycloheptanone carbonyl).

Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15; sapon equiv, 198. Found: C, 66.87; H, 9.27; sapon equiv, 195.

The semicarbazone of methyl β-(2-ketocycloheptane)propionate was obtained, after three recrystallizations from aqueous ethanol, as white plates, mp 114.5–115°.

Anal. Calcd for $C_{12}H_{21}N_3O_3$: C, 56.43; H, 8.29. Found: C, 56.62; H, 8.45.

The 2,4-dinitrophenylhydrazone of methyl β-(2-ketocycloheptane)propionate was obtained as yellow-orange needles after recrystallization from ethanol, mp 75.5–76.5°.

Anal. Calcd for $C_{17}H_{22}N_4O_6$: C, 54.00; H, 5.83. Found: C, 54.36; H, 5.70.

Base-catalyzed hydrolysis of **2** yielded β-(2-ketocycloheptane)-propionic acid as a viscous oil, $\tilde{\nu}^{\text{liquid}}$ 3520 (hydroxyl) and 1720 cm^{-1} (carbonyl), from which a semicarbazone was obtained as very fine, white needles, mp 192–193° dec (lit.[11] mp 192–193°).

Methyl β-[2-(1-Oxaspiro[2.5]octane]propionate (3).—A vpc analysis of the product from N-nitrosopyrrolidone-2 and cyclohexanone revealed the presence of a small amount (5–10%) of a material other than the keto ester **2**. Fractional distillation through an 18-in. spinning-band column yielded a sample of this component as a colorless oil, bp 87° (0.2 mm), $\tilde{\nu}^{\text{liquid}}$ 1745 (ester carbonyl), 1250, 907, and 898 cm^{-1} (epoxide moiety[17a]).

Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.50; H, 9.37.

A 1.5-g sample of this material was treated with a solution of 20.6 g of sodium hydroxide in 80 ml of water, and the mixture was refluxed for 1.5 hr. The mixture was cooled, neutralized with 12.5 ml of sulfuric acid, and extracted with ether to remove any unreacted starting material and hydroxylactone. To the aqueous solution was added 2.5 g of sodium periodate in 50 ml of water, and the mixture was stirred for 3.5 hr at room temperature. The product, obtained in the usual manner, consisted of a pale yellow liquid which showed carbonyl bands at 1715 and 1800 cm^{-1} (no hydroxyl band). The former arises from cyclohexanone (see below) and the latter possibly from 3-butenolactone.[17b] Upon treatment of the crude product with 2,4-dinitrophenylhydrazine reagent a compound identical with the 2,4-dinitrophenylhydrazone of cyclohexanone was obtained, mp 159–160°, and admixture with an authentic sample gave no depression in the melting point.

Methyl β-(x-Alkyl-2-ketocycloheptane)propionates.—Following the same general procedure that is described above for the ring enlargement of cyclohexanone with N-nitrosopyrrolidone-2, the alkylated cyclohexanones **4a–f** can be converted to the corresponding cycloheptanones. Table I records the experimental data for these reactions.

Methyl β-(2-Ketocyclohexane)propionate.—To a stirred mixture of 15.5 g (0.18 mole) of cyclopentanone, 1 g of anhydrous sodium carbonate, and 20 ml of absolute methanol was added, over a period of 2 hr 20 g (0.18 mole) of N-nitrosopyrrolidone-2. The temperature was maintained at 20–25° during the course of the addition. The reaction mixture was worked up in the usual fashion to give 7.9 g (20%) of distilled product as a colorless oil, bp 76–78° (0.2 mm) [lit.[18] bp 134–137° (11 mm)], $\tilde{\nu}^{\text{liquid}}$ 1740 (ester carbonyl) and 1720 cm^{-1} (cyclohexanone carbonyl). The semicarbazone of methyl β-(2-ketocyclohexane)propionate was obtained as colorless crystals, mp 121.5–123° (lit.[19] mp 123°).

Methyl β-Methyl-β-(2-ketocycloheptane)propionate (8b).—Using the method of Leonard and Felley,[20] a solution of 278 g (4.56 moles) of nitromethane and 70 g of benzyltrimethylammonium hydroxide (40% solution in methanol) was added, over a period of 10 min, to 114 g (1.14 mole) of methyl crotonate. The mixture was heated at 80–85° for 15 hr during which time an additional 24-g portion of base was added. The product obtained from this reaction consisted, after distillation through a 10-in. Vigreux column, of 137 g (74%) of methyl β-methyl-γ-nitrobutyrate as a pale yellow oil, bp 87–88° (4 mm). A 78.4-g (0.48 mole) portion of this matrial was dissolved in 75 ml of absolute ethanol, treated with 4 g of Raney nickel catalyst, and hydrogenated at 100° and 1300 psi. The resulting product was distilled through a 4-in. Vigreux column to yield 41.7 g (86%) of 4-methylpyrrolidone-2, bp 92–100° (0.3–0.5 mm). Three recrystallizations from petroleum ether gave colorless needles, mp 54.5–56° (lit.[21] 43°).

Anal. Calcd for C_5H_9NO: C, 60.58; H, 9.15. Found: C, 60.76; H, 9.03.

Nitrosation of 4-methylpyrrolidone-2 was carried out as described previously, and a 24.3 g (0.19 mole) of the nitroso compound was added over a period of 2 hr to a stirred mixture of 18.6 g (0.19 mole) of cyclohexanone, 1 g of anhydrous sodium carbonate, and 20 ml of absolute methanol, the temperature being maintained at 20–25°. The reaction product consisted, after distillation through a 4-in. Vigreux column, of 21 g (49% based on 4-methylpyrrolidone-2) of methyl β-(2-ketocycloheptane)butyrate (**8b**) as a colorless oil, bp 98° (0.1 mm), $\tilde{\nu}^{\text{liquid}}$ 1740 (ester carbonyl) and 1705 cm^{-1} (cycloheptanone carbonyl).

Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50; sapon equiv, 212. Found: C, 68.02; H, 9.53; sapon equiv, 211.

(14) All melting points are corrected; all boiling points are uncorrected. The infrared spectra were measured with a Perkin-Elmer Infrared spectrometer. The vapor phase chromatographic analyses were performed on (a) an F & M Model 710 instrument containing a 0.25 in. × 16 ft column packed with 0.5% by weight of Dow-Corning No. 710 silicone oil on 110 mesh Superbrite glass beads (Minnesota Mining and Manufacturing Co., St. Paul, Minn.) or (b) a homemade unit containing a 0.25 in. × 16 ft column packed with 15% by weight of A3 neopentylglycol sebacate on 40–50 mesh firebrick (Anakrom type ABS sold by Analytical Engineering Laboratory, Inc., Hamden, Conn.). The percentages quoted for the components of the mixtures analyzed by vpc were calculated from area measurements under the peaks and are uncorrected for relative heat capacities. The short-path distillation apparatus consisted of a two-bulb unit blown from 8- to 10-mm-diameter glass tubing, the end bulb containing the sample and being heated in an electrically controlled air bath and the second bulb acting as a collector and being cooled by air or by pieces of wet cotton wrapped around it. The microanalyses were performed by Dr. Josef Zak, Mikroanalytisches Laboratorium, Vienna, Austria.

(15) E. H. White, *J. Am. Chem. Soc.*, **77**, 6008 (1955).

(16) The low temperatures, however, are not essential, and it is possible to carry out the nitrosation even at room temperature. It has also been found to be advantageous to remove the precipitate by filtration at this point before treatment with potassium carbonate. We are indebted to Mr. Hans Zandstra for this information.

(17) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958: (a) p 118 and (b) p 186.

(18) G. Stork and H. K. Landesman, *J. Am. Chem. Soc.*, **78**, 5128 (1956).

(19) R. Bertocchio and J. Dreux, *Compt. Rend.*, **248**, 1533 (1959).

(20) N. J. Leonard and D. L. Felley, *J. Am. Chem. Soc.*, **71**, 1758 (1949).

(21) J. Colonge and J.-M. Pouchol, *Bull. Soc. Chim. France*, 598 (1962).

TABLE I

RING ENLARGEMENT OF ALKYLCYCLOHEXANONES WITH N-NITROSOPYRROLIDONE-2

Alkylcyclohexanone	Product	Yield, %	Bp, °C (mm)	Calcd, % C	Calcd, % H	Calcd, % Sapon equiv	Found, % C	Found, % H	Found, % Sapon equiv
2-Methylcyclohexanone	Methyl β-[2-keto-3- (and -7-) methylcycloheptane]propionate (**5a, 6a**)	47	90–96 (0.3)	67.89	9.50	212	67.75	9.39	214
3-Methylcyclohexanone	Methyl β-[2-keto-4- (and -6-) methylcycloheptane]propionate (**5b, 6b**)	64	88–80 (0.1)	67.89	9.50	212	67.45	9.51	212
4-Methylcyclohexanone	Methyl β-(2-keto-5-methylcycloheptane)propionate (**5c**)	51	133–138 (10)	67.89	9.50	212	67.97	9.65	210
4-Isopropylcyclohexanone	Methyl β-(2-keto-5-isopropylcycloheptane)propionate (**5d**)	64	97–109 (0.2)	69.96	10.07	240	70.11	10.24	243
4-*t*-Butylcyclohexanone	Methyl β-(2-keto-5-*t*-butylcyclopentane)propionate (**5e**)	47	127–134 (0.5)	70.83	10.30	254	70.76	10.63	257
4,4-Dimethylcyclohexanone	Methyl β-(2-keto-4,4-dimethylcycloheptane)propionate (**5f**)	54	114–116 (0.08)	68.99	9.80		69.21	10.08	

Methyl α-Methyl-β-(2-ketocycloheptane)propionate (8a).—Following the precedure described above, 1.39 g (2.28 moles) of nitromethane was condensed with 57 g (0.57 mole) of methyl methacrylate to give 23.7 g (26%) of methyl α-methyl-γ-nitrobutyrate, bp 90–92° (5 mm), which was hydrogenated and distilled (bp 82–90° at 0.7 mm) to yield 10.7 g (73%) of 3-methylpyrrolidone-2. Recrystallization of the crude solid yielded colorless needles, mp 54–55° (lit. mp 50[21] and 58–59°[22]).

The nitrosation and ring enlargement with cyclohexanone were carried out as described above to yield, from 9.2 g of the nitroso compound, 8.95 g of a colorless liquid which was indicated by vpc to contain three components. The two major components (42% yield), present in a ratio of 3:2, were separated by preparative-scale vpc into the two epimers of α-methyl-β-(2-ketocycloheptane)propionate (**8a**), bp 89–91° (0.1 mm), $\tilde{\nu}^{\text{liquid}}$ 1740 (ester carbonyl) and 1705 cm^{-1} (cycloheptanone carbonyl).

Anal. (for α isomer). Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50; sapon equiv, 212. Found: C, 67.98; H, 9.72; sapon equiv, 214.

Anal. (for β isomer). Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50; sapon equiv, 212. Found: C, 68.00; H, 9.67; sapon equiv, 215.

(22) R. Adams and D. Fleš, *J. Am. Chem. Soc.*, **81**, 4946 (1959).

Treatment of a mixture containing the α and β isomers of **8a** in a ratio of 3:2 with methanolic sodium methoxide for 3 days at room temperature yielded a mixture in which the ratio had changed to 1:1.

Methyl α-Methyl-β-[2-(1-oxaspiro[2.5]octane)]propionate (9).—The third component in the product mixture described above (8% yield) was separated by preparative-scale vpc and obtained as a colorless oil, bp 89–91° (0.1 mm), $\tilde{\nu}^{\text{liquid}}$ 1740 cm^{-1} (ester carbonyl).

Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.77; H, 9.64.

Registry No.—**2**, 10407-26-8; semicarbazone of **2**, 10407-45-1; 2,4-dinitrophenylhydrazone of **2**, 10407-46-2; β-(2-ketocycloheptane)propionic acid, 10407-47-3; **3**, 10407-48-4; **5a**, 10407-49-5; **5b**, 10407-50-8; **5c**, 10407-51-9; **5d**, 10407-52-0; **5e**, 10407-53-1; **5f**, 10407-38-2; **6a**, 10407-55-3; **6b**, 10407-56-4; **8a**, 949-32-6; **8b**, 10407-58-6; **9**, 10407-59-7; methyl β-(2-ketocyclohexane)propionate, 10407-33-7; 4-methylpyrrolidone-2, 2996-58-9.