of this work could be viewed in another way. If the degree of crystallinity obtained by Price's volume method were accepted and combined with the observed heat of fusion for the slow-cooled sample, the calculated heat of fusion of the pure crystals would be (8.40 ± 0.2)/(0.75 ± 0.05) or 11.2 ± 1.0 cal./g., which is in good agreement with the value 10.3 ± 0.6 obtained by Bueche by application of Flory's theory.

Acknowledgment.—The author is indebted to Dr. A. M. Bueche of this Laboratory for use of data prior to publication and for suggesting the present application of Flory's theory as a basis for crystallinity measurements. Thanks are also due Dr. Defoe C. Ginnings of the Bureau of Standards, and Mr. S. I. Reynolds of the laboratory, for use of data prior to publication.

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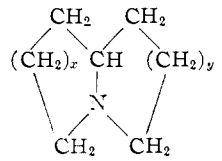
Reductive Cyclization. A Route to 6-Methyl-1-azabicyclo[5.3.0]decane from Methyl Sorbate[1]

BY NELSON J. LEONARD, DONALD L. FELLEY AND ERNEST D. NICOLAIDES

The reductive cyclization reaction of nitro α,ω-diesters, recognized as general for the preparation of pyrrolizidines, has been extended to the formation of 1-azabicyclo compounds containing one five- and one seven-membered ring. As an example, the Michael addition product from methyl γ-nitrobutyrate with methyl sorbate gives 6-methyl-1-azabicyclo[5.3.0]decane when subjected to hydrogenation over copper chromite at high temperature and pressure. The structure of the reductive cyclization product was established by comparison with a sample prepared by an unequivocal method. 1-*n*-Propylpyrrolizidine was also prepared for comparison with the isomeric base.

The reductive cyclization of oximino diesters over copper chromite catalyst at high temperature and high hydrogen pressure has been shown to be a method generally applicable to the synthesis of 1-azabicyclo compounds possessing five-, six- or seven-membered rings (I).[2] Similar conditions



I

applied to γ-nitropimelic esters provide the most convenient route to pyrrolizidine (I, $x = y = 1$) and substituted pyrrolizidines.[3] Thus far, γ-nitropimelic esters, as obtained by the addition of nitroparaffins to acrylic or substituted acrylic esters, constitute the only group of nitro diesters available and successfully applied in the reductive cyclization process. It should be possible to obtain 1-azabicyclo[5.3.0]decane (I, $x = 1$, $y = 3$) and substituted bases possessing this ring system if the requisite precursor $\gamma(\epsilon')$-nitro diesters could be made available by 1,6-addition of a γ-nitro monoester to an $\alpha,\beta;\gamma,\delta$-unsaturated ester.

The model $\gamma(\epsilon')$-nitro diester (II) selected for study would, it was hoped, be available by 1,6-addition of methyl γ-nitrobutyrate to methyl sorbate. The reductive cyclization product from II would then be 6-methyl-1-azabicyclo[5.3.0]-decane (III). By contrast, if the Michael addition of methyl γ-nitrobutyrate to methyl sorbate occurred in the 1,4-manner, the intermediate $\gamma(\gamma')$-nitro diester (IV) would give 1-*n*-propylpyrrolizidine (V) on reductive cyclization. The addition of methyl γ-nitrobutyrate[3] to methyl sorbate was carried out in the presence of diisopropylamine[4] to give, in 32% yield, a nitro diester with the molecular formula, $C_{12}H_{19}NO_6$, requisite for II, IIa or IV. Evidence available from infrared and molar refractivity data favored an unconjugated structure for this diester and therefore, presumably, formula II. Hydrogenation of $C_{12}H_{19}NO_6$ in dioxane at 260° and 300 atmospheres in the presence of copper chromite catalyst produced a tertiary amine, $C_{10}H_{19}N$, in 60% yield. The base was characterized by the formation of picrate (m.p. 188.5–189.5°) and picrolonate (m.p. 200–202°) derivatives.

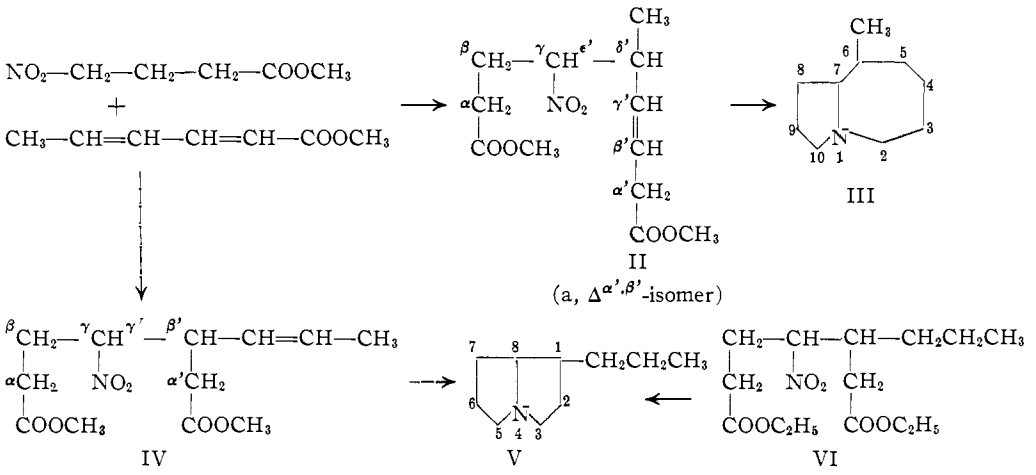
Since a general method exists for the facile preparation of 1-alkylpyrrolizidines,[4] the possibility that the $C_{10}H_{19}N$ reductive-cyclization product might be 1-*n*-propylpyrrolizidine was explored by utilizing this method for the unequivocal synthesis of V. The addition of nitromethane to ethyl 2-hexenoate in the presence of benzyltrimethylammonium butoxide at 80° gave ethyl β-*n*-propyl-γ-nitrobutyrate in 71% yield, and this product, on condensation with ethyl acrylate in the presence of the same catalyst, gave diethyl β-*n*-propyl-γ-nitropimelate (VI) in 53% yield. Reductive cyclization of the nitro diester VI over copper chromite catalyst produced 1-*n*-propylpyrrolizidine (V) in 79% yield. The picrate (m.p. 143–145°) and picrolonate (m.p. 164–166°) formed by V differed from the corresponding derivatives of the $C_{10}H_{19}N$ base obtained by the methyl sorbate route. The physical properties (infrared absorption spectra, refractive indices) of the bases were also substantially different. Such evidence can be considered as eliminating 1-*n*-propylpyrrolizidine (which will exist in two racemic forms) as the structure of the methyl sorbate final product only if it is argued that equivalent racemates should

(1) This work was supported in part by a grant from E. I. du Pont de Nemours and Company, Inc.

(2) N. J. Leonard and W. E. Goode, THIS JOURNAL, **72**, 5404 (1950).

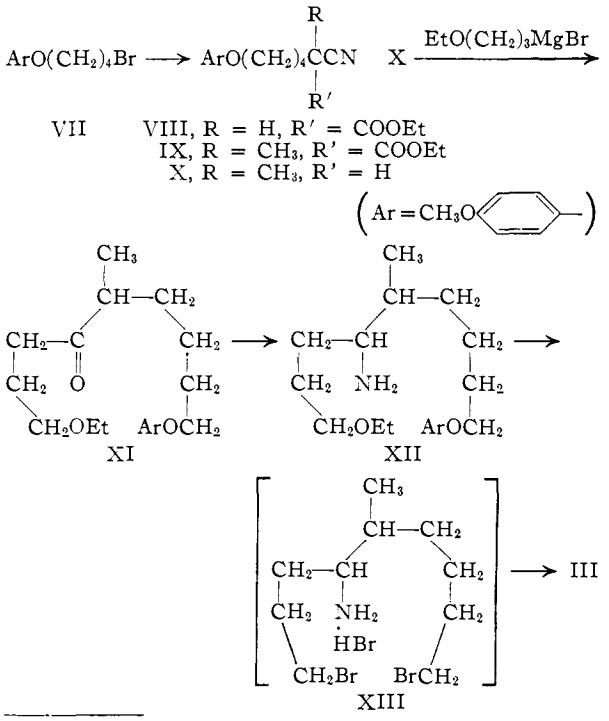
(3) For leading reference, see N. J. Leonard and D. L. Felley, *ibid.*, **72**, 2537 (1950).

(4) N. J. Leonard and D. L. Felley, *ibid.*, **71**, 1758 (1949).



predominate in the analogous formation of the intermediate diesters VI and (IV). While the argument is indeed plausible, a more positive method was sought to establish the structure of the $C_{10}H_{19}N$ compound obtained by hydrogenation of the γ-nitrobutyrate–sorbate condensation product.

6-Methyl-1-azabicyclo[5.3.0]decane (III) was prepared unequivocally by a method adapted from that of Prelog and Seiwerth.[5] 1-Bromo-4-(*p*-methoxyphenoxy)-butane (VII) was condensed with ethyl cyanoacetate to give ethyl α-cyano-ε-(*p*-methoxyphenoxy)-caproate (VIII). Methylation produced ethyl α-cyano-α-methyl-ε-(*p*-methoxyphenoxy)-caproate (IX), and subsequent saponification followed by decarboxylation resulted in the formation of 1-(*p*-methoxyphenoxy)-5-cyanohexane (X). Attempts to bring about the reaction of the nitrile X with either the Grignard reagent or the lithium derivative prepared from 1-bromo-3-(*p*-methoxyphenoxy)-propane to give a ketone were unsuccessful. However, the substitution of γ-ethoxypropyl bromide[6] in the preparation of the Grignard reagent and the subsequent reaction with 1-(*p*-methoxyphenoxy)-5-cyanohexane (X) in di-*n*-butyl ether under a nitrogen atmosphere gave a fair yield of 1-ethoxy-9-(*p*-methoxyphenoxy)-5-methyl-4-nonanone (XI). Catalytic hydrogenation of the ketone in liquid ammonia furnished the corresponding amine XII, which was cyclized to III after hydrobromic acid cleavage of the terminal ether linkages (XIII).



The 6-methyl-1-azabicyclo[5.3.0]decane (III) thus obtained formed a picrate (m.p. 192–193°) which had an infrared absorption spectrum identical with that of the picrate of the $C_{10}H_{19}N$ base obtained by the methyl sorbate route. Thus, all of the evidence on hand indicates that the structure of the methyl γ-nitrobutyrate–methyl sorbate addition product is II (IIa is not ruled out entirely), and that the structure of the base obtained by reductive cyclization of this intermediate nitro diester is 6-methyl-1-azabicyclo[5.3.0]decane (III).[7]

Experimental[8]

Addition of Nitromethane to Methyl Sorbate.—A solution of 25 g. (0.20 mole) of methyl sorbate (prepared from Carbide and Carbon Chemicals Corporation sorbic acid using a methyl ester column and *p*-toluenesulfonic acid as the catalyst), 48.8 g. (0.80 mole) of nitromethane and 20.2 g. (0.20 mole) of diisopropylamine was allowed to stand at 30° for 37 days. The volatile materials were removed by distillation at reduced pressure (to 55° at 20 mm.). The dark residual oil was taken up in an equal volume of ethylene dichloride and the solution was washed with 1 *N* hydrochloric acid followed by two portions of water. The ethylene dichloride was removed by distillation at 30 mm. and the residual oil was fractionally distilled in vacuum, b.p. 81.5–82° (0.25 mm.); $n^{20}D$ 1.4600; d^{20}_4 1.128; yield 7.9 g. (21%).

Anal. Calcd. for $C_8H_{13}NO_4$: C, 51.33; H, 7.00; MR_D (neglecting possibility of exaltation due to conjugation), 45.96. Found: C, 51.15; H, 7.15; MR_D, 45.45.

The structure of this nitro ester, which appeared to be homogeneous, can be assigned tentatively as methyl 5-methyl-6-nitro-3-hexenoate on the basis of molar refrac-

(5) (a) V. Prelog and R. Seiwerth, *Ber.*, **72**, 1638 (1939); see also (b) N. J. Leonard and W. C. Wildman, THIS JOURNAL, **71**, 3089 (1949).

(6) L. I. Smith and J. A. Sprung, *ibid.*, **65**, 1276 (1943).

(7) It should be pointed out that complete characterization has been made of the racemates of III and V which are produced in *predominant* amounts by these reaction schemes (*cf.*, for example, refs. 3 and 4).

(8) All melting points are corrected. The authors are indebted to Miss Elizabeth M. Petersen for determination of the infrared absorption spectra and to Miss Emily Davis, Mrs. Jean Fortney and Mrs. Katherine Pih for microanalyses.

tivity and infrared absorption spectrum, which indicated probable absence of conjugation, and analogy with the established (see below) 1,6-addition of methyl γ-nitrobutyrate to methyl sorbate. When the addition of nitromethane to methyl sorbate was attempted using benzyltrimethylammonium butoxide[4] at 75° or benzyltrimethylammonium hydroxide at 20 or 60°, none of the desired product was isolated and 75–85% of methyl sorbate was recovered.

Addition of Methyl γ-Nitrobutyrate to Methyl Sorbate.—A solution of 24 g. (0.19 mole) of methyl sorbate, 28 g. (0.19 mole) of methyl γ-nitrobutyrate[3] and 19 g. (0.19 mole) of diisopropylamine was allowed to stand at 50° for 12 days. The volatile components were removed by distillation at 35 mm., and the residue was distilled using a short-path apparatus. The yellow, viscous liquid boiling at 155–168° (1.1–1.6 mm.) was redistilled with fractionation, b.p. 142–145° (0.5 mm.); $n^{20}D$ 1.4682; d^{20}_4 1.1526; yield 16.5 g. (32%).

Anal. Calcd. for $C_{12}H_{19}NO_6$: C, 52.73; H, 7.01; N, 5.13; MR_D, 66.09. Found: C, 53.01; H, 7.29; N, 5.20; MR_D, 65.93.

Molar refractivity and infrared absorption indicated the probable absence of conjugation, and this information, together with the proof that the addition was 1,6 (see below), indicated the structure of this compound to be dimethyl 5-methyl-6-nitro-3-nonenedioate (II).

Reductive Cyclization of the Methyl Sorbate–Methyl γ-Nitrobutyrate Condensation Product.—A solution of 10.6 g. (0.039 mole) of the condensation product in 140 ml. of dioxane was hydrogenated at 260° and 250–300 atm. in the presence of 10 g. of copper chromite. After 1.5 hours the theoretical amount of hydrogen had been absorbed. The catalyst and solvent were removed, and the residual oil was fractionally distilled *in vacuo*, b.p. 91–92° (33 mm.); $n^{20}D$ 1.4790; yield 3.6 g. (60%).

Anal. Calcd. for $C_{10}H_{19}N$: C, 78.36; H, 12.50; N, 9.14. Found; C, 78.00; H, 12.59; N, 9.33.

The compound showed strong infrared absorption peaks at 2923–2843, 2769, 1459, 1378, 1333, 896–894 and 861 cm.$^{-1}$, and a medium peak at 1389 cm.$^{-1}$.

The picrate, prepared in ether and recrystallized from 95% ethanol, formed yellow plates, m.p. 188.5–189.5°.

Anal. Calcd. for $C_{16}H_{22}N_4O_7$: C, 50.26; H, 5.80; N, 14.65. Found: C, 50.52; H, 5.96; N, 14.64.

The picrolonate, prepared in ether and recrystallized from methanol, formed yellow-brown prisms, m.p. 200–202°, with decomposition.

Anal. Calcd. for $C_{20}H_{27}N_5O_5$: C, 57.54; H, 6.52; N, 16.78. Found: C, 57.73; H, 6.67; N, 16.71.

Ethyl β-*n*-Propyl-γ-nitrobutyrate.—A solution of 102 g. (1.68 moles) of nitromethane, 48 g. (0.34 mole) of ethyl 2-hexenoate[9] and 16 g. of a 25% butanol solution of benzyltrimethylammonium butoxide was stirred at 80° for 72 hours. The catalyst was replenished during the reaction (12 g. every 24 hours). The reaction mixture was cooled and then acidified with dilute hydrochloric acid.

An equal volume of ethylene dichloride was added and the mixture was shaken. The ethylene dichloride layer was washed with water, and the solvent and volatile materials were removed at reduced pressure. The residue was distilled with fractionation as a colorless oil, b.p. 98–100° (1.5 mm.); $n^{20}D$ 1.4412; d^{20}_4 1.055; yield 48 g. (71%).

Anal. Calcd. for $C_9H_{17}NO_4$: C, 53.18; H, 8.43; N, 6.89; MR_D 51.05. Found: C, 53.38; H, 8.50; N, 6.91; MR_D, 51.23.

Diethyl β-*n*-Propyl-γ-nitropimelate (VI).—To a stirred solution of 47 g. (0.23 mole) of ethyl β-*n*-propyl-γ-nitrobutyrate and 12 g. of benzyltrimethylammonium hydroxide (40% solution in water, Rohm and Haas Company) in 25 ml. of *t*-butyl alcohol was added 23 g. (0.23 mole) of ethyl acrylate. After the initially exothermic reaction had subsided, the reaction mixture was maintained at 55–60° for 72 hours, and 5-g. portions of catalyst were added at 24-hour intervals. The product was isolated in the usual manner and was distilled through a short-path distillation apparatus as a light amber oil, b.p. 150–160° (1.0 mm.); $n^{20}D$ 1.4527; d^{20}_4 1.083; yield 37 g. (53%).

Anal. Calcd. for $C_{14}H_{25}NO_6$: C, 55.43; H, 8.31; N, 4.62; MR_D, 75.80. Found: C, 55.65; H, 8.39; N, 4.60; MR_D, 75.63.

1-*n*-Propylpyrrolizidine (V).—A solution of 27 g. (0.09 mole) of diethyl β-*n*-propyl-γ-nitropimelate in 120 ml. of dioxane with 16 g. of copper chromite catalyst was hydrogenated during 2.25 hours at 260° and 250–300 atm. After removal of the catalyst and solvent, the residual oil was fractionally distilled in vacuum, b.p. 94–95° (30 mm.); $n^{20}D$ 1.4639; d^{20}_4 0.895; yield 10.7 g. (79%).

Anal. Calcd. for $C_{10}H_{19}N$: C, 78.36; H, 12.50; N, 9.14; MR_D, 47.3. Found: C, 77.48; H, 12.45; N, 8.62; MR_D, 48.1.

1-*n*-Propylpyrrolizidine showed strong infrared absorption peaks at 2933–2847 and 1459 cm.$^{-1}$, and a medium peak at 1380 cm.$^{-1}$.

1-*n*-Propylpyrrolizidine Picrate.—Prepared in ether and recrystallized from 95% ethanol, the picrate separated as fine yellow needles, m.p. 143–145°.

Anal. Calcd. for $C_{16}H_{22}N_4O_7$: C, 50.26; H, 5.80; N, 14.65. Found: C, 50.18; H, 5.75; N, 14.80.

1-*n*-Propylpyrrolizidine Picrolonate.—Prepared in ether and recrystallized from 95% ethanol, the picrolonate formed yellow-brown prisms which melted, with decomposition, at 164–166°.

Anal. Calcd. for $C_{20}H_{27}N_5O_5$: C, 57.54; H, 6.52; N, 16.78. Found: C, 57.77; H, 6.48; N, 16.57.

1-Bromo-4-(*p*-methoxyphenoxy)-butane (VII).—A solution of 28 g. (0.5 mole) of potassium hydroxide in 350 ml. of methanol was added over a one-hour period to a stirred solution of 62 g. (0.5 mole) of hydroquinone monomethyl ether and 340 g. (1.57 mole) of 1,4-dibromobutane maintained at 70°. The solution was heated under reflux until neutral (*ca.* 5 hours). Sufficient water was then added to dissolve the inorganic salts, and the organic layer was separated, washed with water, dried and distilled. After a large forerun (250 g.) of 1,4-dibromobutane, the product was collected at 125–130° (1.5 mm.). The 1-bromo-4-(*p*-methoxyphenoxy)-butane solidified upon standing and was recrystallized from ethanol as shiny white platelets, m.p. 42–43°; yield 78 g. (60%).

Anal. Calcd. for $C_{11}H_{15}BrO_2$: C, 51.00; H, 5.79. Found: C, 51.04; H, 5.73.

Ethyl α-Cyano-ε-(*p*-methoxyphenoxy)-caproate (VIII).—A mixture of 104 g. (0.40 mole) of 1-bromo-4-(*p*-methoxyphenoxy)-butane, 226 g. (2.0 moles) of ethyl cyanoacetate and 56 g. (0.40 mole) of anhydrous potassium carbonate was heated at 120° with stirring for 22 hours. The mixture was cooled and 200 ml. of water was added. The organic layer was extracted with ether, and the ethereal solution was thoroughly washed with water and dried. The ether was removed and the product was distilled as a light yellow viscous oil, b.p. 177–180° (0.4 mm.); $n^{20}D$ 1.5087; d^{20}_4 1.1083; yield 72 g. (62%). Compound VIII was used directly for the preparation of IX.

Ethyl α-Cyano-α-methyl-ε-(*p*-methoxyphenoxy)-caproate (IX).—To a solution of sodium ethoxide prepared from 5.1 g. (0.22 gram atom) of sodium in 200 ml. of absolute ethanol was added with stirring 65 g. (0.22 mole) of ethyl α-cyano-ε-(*p*-methoxyphenoxy)-caproate in 25 ml. of absolute ethanol. The solution was heated to reflux temperature and 85 g. (0.60 mole) of methyl iodide was added over a one-half hour period to the stirred solution. The resulting solution was refluxed for 8 hours. The ethanol and methyl iodide were removed by distillation and the residue was taken up in ether, washed with water and dried. After removal of the ether, the residue was distilled *in vacuo* as a light yellow oil, b.p. 166–167° (0.25 mm.); $n^{20}D$ 1.5002; d^{20}_4 1.0918; yield 55 g. (81%).

Anal. Calcd. for $C_{17}H_{23}NO_4$: C, 66.86; H, 7.59; N, 4.59; MR_D, 81.79. Found: C, 66.58; H, 7.38; N, 4.77; MR_D, 82.51.

α-Cyano-α-methyl-ε-(*p*-methoxyphenoxy)-caproic Acid.—To 50 g. (0.16 mole) of ethyl α-cyano-α-methyl-ε-(*p*-methoxyphenoxy)-caproate in 100 ml. of ethanol was added one equivalent of a 30% aqueous solution of potassium hydroxide. The solution was gently warmed on the steam-bath for 12 hours and then allowed to stand at room temperature for an additional 12 hours. The solution was neutralized with 6 *N* hydrochloric acid and sufficient water was added to separate the layers. The organic layer was extracted with

(9) K. von Auwers, *Ann.*, **432**, 46 (1923).

ether, washed with water and dried. After the ether had evaporated, the oily residue crystallized on standing in the ice-box for 24 hours. The α-cyano-α-methyl-ε-(*p*-methoxyphenoxy)-caproic acid was recrystallized from an ethanol–petroleum ether mixture as small colorless needles, m.p. 74–75°; yield 34 g. (75%).

Anal. Calcd. for $C_{15}H_{19}NO_4$: C, 64.96; H, 6.91; N, 5.05. Found: C, 65.12; H, 7.09; N, 5.02.

1-(*p*-Methoxyphenoxy)-5-cyanohexane (X).—Fifty grams (0.18 mole) of crude α-cyano-α-methyl-ε-(*p*-methoxyphenoxy)-caproic acid was heated at 200° for 3 hours. The dark red oil was cooled, washed once with 5% sodium carbonate solution, once with water, dried and distilled. The 1-(*p*-methoxyphenoxy)-5-cyanohexane was distilled at 145–155° (0.20 mm.) as a faint yellow oil which solidified on standing; yield 23 g. (55%). A sample was recrystallized twice from petroleum ether for analysis. The colorless needles melted at 49–50°.

Anal. Calcd. for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.01. Found: C, 72.04; H, 8.14; N, 6.07.

1-Ethoxy-9-(*p*-methoxyphenoxy)-5-methyl-4-nonanone (XI).—To 1.7 g. (0.07 gram atom) of magnesium and 30 ml. of anhydrous diethyl ether was added slowly with stirring under a nitrogen atmosphere 12 g. (0.07 mole) of γ-ethoxypropyl bromide[6] in 50 ml. of anhydrous diethyl ether. The reaction started upon gentle heating. After the addition of the halide was complete, the solution was refluxed for 2 hours. The diethyl ether was then distilled out through the top of the condenser as 100 ml. of di-*n*-butyl ether was added. To this solution at the reflux temperature was added during one hour 14 g. (0.06 mole) of 1-(*p*-methoxyphenoxy)-5-cyanohexane in 100 ml. of di-*n*-butyl ether. The solution was stirred at the reflux temperature for 48 hours. The mixture was decomposed at 0° by the slow addition of 100 ml. of 1.2 *N* hydrochloric acid. The ether layer was separated and the aqueous layer was extracted twice with ether. The combined ethereal solutions were dried and the mixed solvent was removed.

The crude residue was dissolved in 200 ml. of absolute ethanol and to this solution was added 10 g. of Girard Reagent T.[10] The mixture was boiled for 48 hours, cooled and poured into ice-water. The aqueous layer was extracted twice with ether to remove any non-ketonic products. The aqueous layer was then acidified with 6 *N* hydrochloric acid and upon standing at room temperature for 24 hours, an oily layer separated. The organic layer was extracted with ether, the ethereal solution was dried and the ether was removed. The residue, which gave a strong ketone test, was distilled as a yellow oil, b.p. 176–178° (0.25 mm.); $n^{20}D$ 1.4976; d^{20}_4 1.024; yield 3 g. (24%, based on recovered nitrile).

Anal. Calcd. for $C_{19}H_{30}O_4$: C, 70.77; H, 9.38; MR_D, 91.28. Found: C, 71.06; H, 9.48; MR_D, 92.27.

4-Amino-1-ethoxy-9-(*p*-methoxyphenoxy)-5-methylnonane (XII).—A mixture of 4 g. (0.013 mole) of 1-ethoxy-9-(*p*-methoxyphenoxy)-5-methyl-4-nonanone and 50 ml. of liquid ammonia was hydrogenated over Raney nickel catalyst at 150° and 200 atm. for 5 hours. The ammonia was allowed to evaporate and the residue was dissolved in ethanol. The catalyst was removed by filtration and the ethanol was distilled. The crude amine obtained as a residue (yield, *ca.* 60%), was not purified, but was used directly in the subsequent hydrolysis and ring closure.

6-Methyl-1-azabicyclo[5.3.0]decane (III).—The crude amine (3 g.) was dissolved in 100 ml. of glacial acetic acid and the solution was saturated with dry hydrogen bromide. To this solution was added 100 ml. of 48% hydrobromic acid. The solution was then refluxed for 72 hours and at the end of this time the solvents were removed under reduced pressure. The dark red residue was dissolved in 100 ml. of ethanol and the ethanol was removed under reduced pressure. The crude ω,ω′-dibromoamine hydrobromide was not purified, but was dissolved in 250 ml. of water and added over a three-hour period to a stirred solution of 2 l. of 0.1 *N* sodium hydroxide at 50°. The basic solution was steam-distilled and the distillate was made strongly basic with 12 *N* sodium hydroxide solution. The aqueous solution was extracted four times with 50-ml. portions of ether and the combined ethereal extracts were dried and the solution was concentrated to a small volume.

The picrate of 6-methyl-1-azabicyclo[5.3.0]decane was prepared directly from the ether solution and was recrystallized from ethanol as yellow platelets, m.p. 192–193°.

Anal. Calcd. for $C_{16}H_{22}N_4O_7$: C, 50.26; H, 5.80; N, 14.65. Found: C, 50,42; H, 5.92; N, 14.57.

The infrared absorption spectrum of the picrate of 6-methyl-1-azabicyclo[5.3.0]decane was found to be identical with the infrared absorption spectrum of the picrate of the hydrogenated condensation product of methyl sorbate and methyl γ-nitrobutyrate. A mixture of the two picrates melted at 188.5–190°.

1-(*p*-Methoxyphenoxy)-5-hexanol.—To 9.6 g. (0.40 gram atom) of magnesium and 200 ml. of dry ether was added slowly 78 g. (0.30 mole) of 1-bromo-4-(*p*-methoxyphenoxy)-butane in 250 ml. of dry ether. The reaction was initiated by gentle heating and was complete after 2 hours. To the Grignard reagent at 0° was added with stirring during 30 minutes 13 g. (0.30 mole) of freshly distilled acetaldehyde in 50 ml. of dry ether. The mixture was decomposed by pouring onto 150 g. of cracked ice and 100 ml. of dilute hydrochloric acid. The ether layer was separated, washed with water and dried. The ether was removed and the product was distilled as a light yellow oil, b.p. 142–144° (0.6 mm.); $n^{20}D$ 1.5179; d^{20}_4 1.1541; yield 42 g. (70%).

Anal. Calcd. for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99; MR_D, 58.25. Found: C, 69.44; H, 8.93; MR_D, 58.96.

Diethyl γ-Keto-δ-carbethoxyazelate.—To a solution of sodium ethoxide prepared from 3.4 g. (0.15 gram atom) of sodium in 200 ml. of absolute ethanol was added with stirring 35 g. (0.15 mole) of diethyl β-ketoadipate.[11] The solution of the sodio-derivative was heated to reflux temperature and 35 g. (0.16 mole) of ethyl γ-iodobutyrate was added slowly. The solution was heated under reflux until neutral (*ca.* five hours), cooled and sufficient water was added to dissolve the inorganic salts. The organic layer was extracted with ether, the combined ether extracts were dried and the ether was removed. The residue was distilled and following a large forerun the keto diester was obtained as a colorless oil, b.p. 157–157.5° (0.3 mm.); $n^{20}D$ 1.4519; d^{20}_4 1.075; yield 10 g. (19%).

Anal. Calcd. for $C_{16}H_{26}O_7$: C, 58.17; H, 7.93; MR_D, 82.77. Found: C, 58.48; H, 8.05; MR_D, 82.89.

URBANA, ILLINOIS RECEIVED OCTOBER 11, 1951

(10) E. Lederer and G. Nachmias, *Bull. soc. chim. Mem.*, **16**, 400 (1949).

(11) B. Riegel and W. M. Lilienfeld, THIS JOURNAL, **67**, 1273 (1945).