[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Synthesis and Deamination of 1-Aminobicyclo[2.2.1]heptan-7-one[1]

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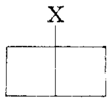
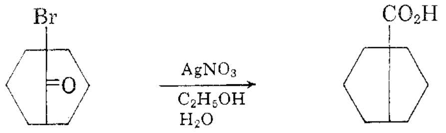
The amine of the title has been prepared by a Curtius degradation and isolated as its hydrated hydrochloride and perchlorate salts. Diazotization of the perchlorate in acetic acid followed by a hydrolytic isolation procedure has given unrearranged 1-hydroxybicyclo[2.2.1]heptan-7-one (as its hydrate) and 4-ketocyclohexanecarboxylic acid. A possible product, bicyclo[2.2.0]hexane-1-carboxylic acid, has not been obtained.

In connection with other studies in progress in this laboratory, it was desired to have a source of 1-substituted bicyclo[2.2.0]hexanes (I).

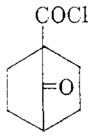


I

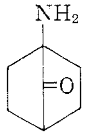
A route to such compounds which appeared promising was a ring contraction similar to contractions of 1-substituted bicyclo[3.3.1]nonan-9-ones which have previously been observed.[2] A typical example is the reaction of 1-bromobicyclo[3.3.1]nonan-9-one (II) with silver nitrate in aqueous ethanol to give the acid III and its ethyl ester.[2b] The possibility of analogous ring contractions in the bicyclo[2.2.1]heptane series has been presented by a recently announced synthesis of bicyclo[2.2.1]heptan-7-one-1-carbonyl chloride (IV).[3] In particular, it appeared probable that amine V would be readily obtainable, and that diazotization of V would be similar enough to the reaction of II with silver nitrate that contraction to the bicyclic acid (I, X = COOH) might occur.



II III

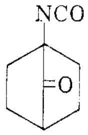


IV

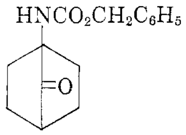


V

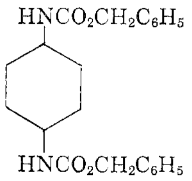
The reaction of IV with activated sodium azide in refluxing benzene gave a product characterized as the isocyanate, VI, by its infrared spectrum, which showed typical 7-keto carbonyl absorption[4] at 1786 cm.$^{-1}$ and isocyanate absorption[5] at 2240 cm.$^{-1}$



VI



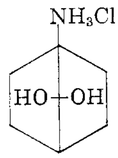
VII



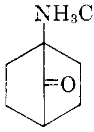
VIII

Reaction of sodium azide with IV in acetone-water and subsequent reaction of the product with benzyl alcohol did not give the expected bicyclic ketobenzyl carbamate, VII, but gave the dibenzyl carbamate, VIII, of *trans*-1,4-diaminocyclohexane. Its identity was established by analysis, infrared spectrum (bands at 3270, 1688, 1678, and 1550 cm.$^{-1}$ which probably can be assigned to the amide group and to the aromatic ring; lack of a carbonyl absorption in the 1775 cm.$^{-1}$ region) and comparison with the literature melting point.[6] The great sensitivity of the 7-ketobicyclo[2.2.1]heptane system toward nucleophilic ring opening, when an electronegative substituent is on the bridgehead, had been observed previously.[3]

Reaction of VI with concentrated hydrochloric acid gave the hydrated amine hydrochloride, IX, rather than the expected V hydrochloride (X). The infrared spectrum of IX showed broad absorptions in the 3000–3450 cm.$^{-1}$ region (OH and NH stretching vibrations) but no carbonyl



IX



X

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[1] Abstracted from the Ph.D. thesis of J. P. Kleiman, University of Illinois, 1960.

[2] (a) A. C. Cope and M. E. Synerholm, *J. Am. Chem. Soc.*, **72**, 5228 (1950); (b) A. C. Cope and E. S. Graham, *J. Am. Chem. Soc.*, **73**, 4702 (1951); (c) A. C. Cope, E. S. Graham, and D. J. Marshall, *J. Am. Chem. Soc.*, **76**, 6159 (1954).

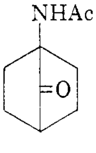
[3] W. R. Hatchard and A. K. Schneider, *J. Am. Chem. Soc.*, **79**, 6261 (1957).

[4] (a) C. F. H. Allen and J. A. VanAllan, *J. Org. Chem.*, **20**, 323 (1955); (b) P. Wilder, Jr., and A. Winston, *J. Am. Chem. Soc.*, **78**, 868 (1956).

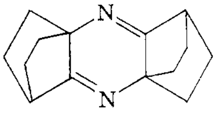
[5] R. N. Jones and C. Sandorfy in A. Weissberger, *Technique of Organic Chemistry*, Vol. IX, Interscience Publishers, Inc., New York, N. Y., 1956, p. 544.

[6] T. Curtius, *J. prakt. Chem.*, **91**, 1 (1915).

absorption, which was expected near 1775 cm.$^{-1}$ When IX was heated at 100° at reduced pressure over phosphorus pentoxide, compound X was obtained, having a strong infrared absorption at 1775 cm.$^{-1}$ and a sharp peak at 3370 cm.$^{-1}$ There was no broad absorption in the OH region. When X was treated with concentrated hydrochloric acid, IX was regenerated, as shown by the identity of the infrared spectra. Reaction of IX with acetic anhydride in pyridine gave the dehydrated amide XI, as shown by elemental analyses and the infrared spectrum (ketone C=O at 1775 cm.$^{-1}$, N—H at 3400 cm.$^{-1}$, and amide C=O at 1665 cm.$^{-1}$). Reaction of IX with aqueous sodium hydroxide gave the dihydropyrazine XII as shown by elemental analysis, molecular weight, and absence of OH, NH, or C=O absorptions in the infrared (C=N appeared at 1697 cm.$^{-1}$ (medium)). Reaction of XII with concentrated hydrochloric acid regenerated IX.

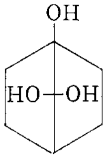


XI

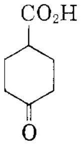


XII

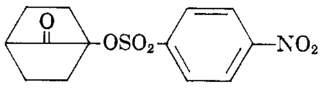
Hydrochloride IX was converted to the perchlorate with silver perchlorate and the perchlorate was diazotized with sodium nitrite in glacial acetic acid at room temperature. An isolation procedure which involved probable saponification of any ester products yielded the triol, XIII, and the keto acid, XIV, the yields being 38% and 21%, respectively. The structure of XIII was assigned on the basis of its analysis, infrared spectrum (broad OH absorption in the 3000–3500 cm.$^{-1}$ region and no carbonyl absorption), reaction with 2,4-dinitrophenylhydrazine to form a 2,4-dinitrophenylhydrazone (C=N absorption at 1685 cm.$^{-1}$ and broad OH absorption in the infrared), and reaction with *p*-nitrobenzenesulfonyl chloride to give the keto *p*-nitrobenzenesulfonate XV (C=O stretching absorption at 1788 cm.$^{-1}$). The acid XIV was identified by comparison with an authentic sample.



XIII

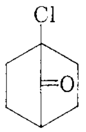


XIV



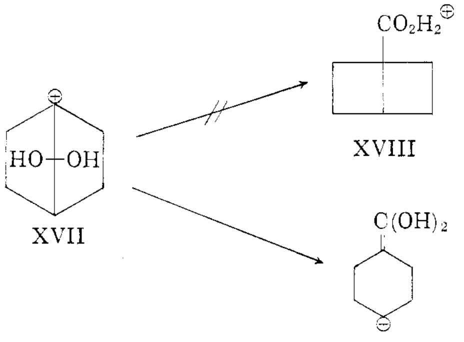
XV

Diazotization of IX in water gave a 52% yield of crude XIII and a small amount of 1-chlorobicycloheptanone (XVI) which was characterized as its dinitrophenylhydrazone. The NMR spectrum of the latter showed signals at 2.58 p.p.m. and 1.64 p.p.m. (from water) in a ratio of 8:1, corresponding to the methylene and bridgehead hydrogens, respectively. The infrared spectrum showed no carbonyl or hydroxyl absorptions. Some acidic material was also obtained in the aqueous diazotization, but no pure substances were isolated from it.



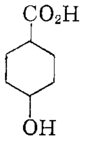
XVI

The formations of XIII and XVI are not without analogy in the deaminations of bridgehead amines, which normally proceed without rearrangement.[7] It was somewhat surprising that the intermediate cation XVII apparently opened up to give XIX rather than to give the contraction product XVIII expected from the analogies in the bicyclo[3.3.1]nonane system.[2] The less favorable locus of positive charge in XIX as compared with XVIII is presumably compensated for by the excessive strain in XVIII. The possibility exists that XVIII was actually formed first, and that ring opening, leading to XIV, took place under the conditions of the reaction or isolation procedure. This possibility lacks analogy at present and appears improbable. Another possibility is that some nonclassical cation, of which XVII, XVIII, and XIX are contributing resonance structures, gives both types of product observed.

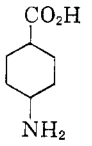


XVII XVIII XIX

The formation of XIX would be expected to lead to the hydroxy acid XX, or its acetate ester under the diazotization conditions reported here.



XX



XXI

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(7) D. E. Applequist and J. D. Roberts, *Chem. Rev.*, **54**, 1065 (1954).

An oxidation is required to obtain the observed keto acid, XIV. Such oxidation may have been caused by some oxidizing species derived from nitrous acid in the diazotization reaction mixture, or may have been a Meerwein-Ponndorf reduction of XIII by XX during the basic extraction in the isolation procedure. That the oxidation was not simply an oxidation of XX by nitrous or perchloric acid was shown by diazotization of 4-aminocyclohexanecarboxylic acid (XXI) as its perchlorate salt in acetic acid under the same conditions of reaction and isolation to give the hydroxy acid, XX, rather than the keto acid, XIV.

EXPERIMENTAL[8]

Hexahydroterephthaloyl chloride.[9] A mixture of 43 g. (0.25 mole) of *cis*- and *trans*-hexahydroterephthalic acid (from hydrogenation of dimethyl terephthalate in acetic acid over platinum oxide at room temperature and 2500 p.s.i.) and 215 g. of thionyl chloride was stirred and heated under reflux for 24 hr. The excess thionyl chloride was removed *in vacuo* and the residue was distilled to give 48 g. of *cis*- and *trans*-hexahydroterephthaloyl chloride, b.p. 85–90° (0.5 mm.).

Bicyclo[2.2.1]heptan-7-one-1-carbonyl chloride (IV).[3] A solution of 29 g. (0.29 mole) of triethylamine in 100 ml. of anhydrous ether was added dropwise over 1 hr. to a stirred mixture of 50 g. (0.24 mole) of *cis*- and *trans*-hexahydroterephthaloyl chloride in 550 ml. of ether at reflux temperature. The reaction mixture was refluxed and stirred for an additional 20 hr. The mixture was then filtered directly into a distillation flask in small portions in an apparatus designed to exclude air and moisture. The ether was removed from each portion at reduced pressure before more ether mixture was added. On distillation of the residue, 18.8 g., b.p. 78–82° (0.5 mm.) (reported[10] b.p. 86.5–88°, 1 mm.) of IV was obtained.

Reaction of bicyclo[2.2.1]heptan-7-one-1-carbonyl chloride with sodium azide in aqueous acetone. To a cooled stirred solution of 3.7 g. (0.0214 mole) of bicyclo[2.2.1]heptane-7-one-1-carbonyl chloride in 200 ml. of reagent-grade acetone was added 1.7 g. (0.0262 mole) of sodium azide in 4.8 ml. of water. The mixture was poured into 32 ml. of water and 30 ml. of benzene. The benzene layer was separated and added to 40 ml. of benzyl alcohol. The mixture was heated to a pot temperature of 70° and then the heat source was removed. Nitrogen evolution proceeded at a steady rate and no heat was necessary to keep the reaction going. The mixture was heated to 75° for a few minutes after nitrogen evolution appeared to cease. On cooling the reaction mixture, 1.59 g., m.p. 239–243°, of a solid precipitated out. A pure sample, m.p. 245–247°, was obtained by recrystallization from benzene and was identified as the bis(benzylcarbamate) of *trans*-1,4-diaminocyclohexane (lit.[6] m.p. 244–245°). Its infrared spectrum had bands at 3270 cm.$^{-1}$, 1688 cm.$^{-1}$, 1678 cm.$^{-1}$, and 1550 cm.$^{-1}$

Anal. Calcd. for $C_{22}H_{.6}N_2O_4$: C, 69:09; H, 6.85; N, 7.33. Found: C, 68.92; H, 6.76; N, 7.30.

Evaporation of the filtrate at reduced pressure gave an additional 3.5 g. of material, m.p. 204–214°, which was not identified.

7-Ketobicyclo[2.2.1]hept-1-yl isocyanate (VI). Activated sodium azide was prepared with 85% hydrazine hydrate.[11] A mixture of 1.0 g. (0.0058 mole) of bicyclo[2.2.1]heptane-7-one-1- carbonyl chloride, 0.41 g. (0.0063 mole) of activated sodium azide, and 50 ml. of benzene was refluxed and stirred for 22 hr. The reaction mixture was cooled and filtered to remove the inorganic material. The benzene was removed by freeze-drying. The infrared spectrum of the residue indicated the product was 7-ketobicyclo[2.2.1]hept-1-yl isocyanate (a carbonyl band at 1786 cm.$^{-1}$ and an isocyanate band at 2240 cm.$^{-1}$). The crude material was used directly in the next step.

7,7-Dihydroxybicyclo[2.2.1]hept-1-ylamine hydrochloride (IX); *Procedure A*. The crude isocyanate was dissolved in 25 ml. of benzene. To this was added 15 ml. of concd. hydrochloric acid and the mixture was heated under reflux for 2.5 hr. The cooled layers were separated and the benzene layer was washed with a little water. The water layers were combined and the water was removed at reduced pressure. The last traces of water were removed in a vacuum desiccator over phosphorus pentoxide to give 0.8 g. of a white solid. Its infrared spectrum had a wide absorption in the 3450–3000 cm.$^{-1}$ region, many small peaks in the 2800–2400 cm.$^{-1}$ region, and peaks at 2020, 1625, 1600, and 1531 cm.$^{-1}$

A sample was heated at 100° for 10 hr. over phosphorus pentoxide at reduced pressure to give a material with a strong carbonyl absorption at 1775 cm.$^{-1}$ and a sharp peak at 3370 cm.$^{-1}$ Addition of concentrated hydrochloric acid to the dried material and then removal of the acid at reduced pressure and drying of the residue over phosphorus pentoxide gave back the original product (IX) as shown by the infrared spectrum. The carbonyl absorption was no longer present.

Procedure B. To a solution of 5 g. (0.029 mole) of bicyclo-[2.2.1]heptane-7-one-1-carbonyl chloride in 100 ml. of benzene was added 2.02 g. (0.0315 mole) of activated sodium azide. The stirred mixture was heated under reflux for 20 hr. The reaction mixture was cooled and filtered directly into another reaction flask. The precipitate was washed with about 50 ml. of benzene. To the combined benzene solutions was added 75 ml. of concd. hydrochloric acid and the mixture was heated under reflux for 6 hr. The cooled mixture was separated and the benzene layer was washed with water. The combined water layers were evaporated at aspirator pressure and the final traces of water were removed by drying over phosphorus pentoxide in a vacuum desiccator. A total of 4.8 g. of amine hydrochloride was obtained.

3,9-Diazapentacyclo[8.2.2.2.^{4,7} 0.^{2,10} 0^{4,8}]hexadecadiene-2,8 (XII). To a solution of 3.2 g. (0.0178 mole) of 7,7-dihydroxybicyclo[2.2.1]hept-1-ylamine hydrochloride in 50 ml. of water was added enough 10% sodium hydroxide to make the *p*H 12. The solution was extracted continuously with ether for 1 day to give 1.6 g. of solid, m.p. 204–208°. Its infrared spectrum had a band at 1697 cm.$^{-1}$ and no absorption in the NH or OH region (3500–3000 cm.$^{-1}$). An analytical sample, m.p. 211.5–212°, was prepared by recrystallization from cyclohexane-ether. Treatment of the condensation product with concentrated hydrochloric acid at room temperature for 10 hr. and evaporation of the acid gave back 7,7-dihydroxybicyclo[2.2.1]hept-1-ylamine hydrochloride as shown by identity of its infrared spectrum with that of an authentic sample.

Anal. Calcd. for $C_{14}H_{18}N_2$: C, 78.46; H, 8.47; N, 13.07; M. W., 214. Found: C, 78.78; H, 8.38; N, 13.18; M. W. 229.

1-Acetamidobicyclo[2.2.1]heptan-7-one (XI). To a solution of 0.2221 g. (0.00123 mole) of 7,7-dihydroxybicyclo[2.2.1]-hept-1-ylamine hydrochloride in 15 ml. of pyridine was

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(8) Melting points and boiling points are uncorrected. Infrared spectra were measured by Mr. James Brader, Mr. Paul McMahon, and their associates using a Perkin-Elmer model 21B spectrophotometer with sodium chloride optics. The NMR spectra were measured by Mr. Ben Shoulders with a Varian high resolution spectrometer (model V-4300B with super stabilizer) at 40 mc. with external methylene chloride as standard. The signal of methylene chloride was taken to be at −0.65 p.p.m. from water. Microanalyses were done by Mr. Josef Nemeth and his associates.

(9) R. Malachowski, J. J. Wasowska, S. Jozkiewicz, J. Adamiczka, and G. Zimmerman-Pasternak, *Ber.*, **71B**, 759 (1938).

(10) W. R. Hatchard, private communication.

(11) P. A. S. Smith, *Org. Reactions*, **3**, 382 (1946).

added 0.413 g. (0.00405 mole) of acetic anhydride. The reaction mixture was refluxed overnight. It was cooled and then poured onto 25 ml. of concd. hydrochloric acid on cracked ice. The solution was extracted continuously with ether for 1 day to give 100 mg. of amide. Several recrystallizations from cyclohexane gave an analytical sample, m.p. 115–117°. Its infrared spectrum had a strong carbonyl band at 1775 cm.$^{-1}$ and amide bands at 3400 and 1665 cm.$^{-1}$.

Anal. Calcd. for $C_9H_{13}NO_2$: C, 64.65; H, 7.84; N, 8.38. Found: C, 64.67; H, 7.89; N, 8.47.

Reaction of 7,7-dihydroxybicyclo[2.2.1]hept-1-ylamine hydrochloride with sodium nitrite in water. To a stirred solution of 4.8 g. (0.0266 mole) of 7,7-dihydroxybicyclo[2.2.1]hept-1-ylamine hydrochloride in 50 ml. of 2.5*N* hydrochloric acid was added a solution of 7.44 g. (0.108 mole) of sodium nitrite in 25 ml. of water over a 30-min. period. The reaction mixture was heated under reflux for 6 hr., cooled, made basic with aqueous sodium hydroxide, and extracted continuously for 3 days with ether. Evaporation of the ether gave 2.5 g. of solid material. Addition of warm benzene to this solid dissolved 0.5 g. The benzene was filtered and on evaporation of the filtrate an oil was obtained that had a strong carbonyl band at 1775 cm.$^{-1}$ A 2,4-dinitrophenylhydrazone was prepared according to the method of Shriner, Fuson, and Curtin.[12] A yield of 500 mg. of crude material was obtained. On chromatography of this material on acid-washed alumina, 290 mg. of the 2,4-dinitrophenylhydrazone of 1-chlorobicyclo[2.2.1]heptan-7-one, m.p. 207.5–208.5°, was obtained. The NMR spectrum of a saturated deuterochloroform solution had signals at 2.58 and 1.64 p.p.m. relative to water, in the ratio of 8:1.

Anal. Calcd. for $C_{13}H_{13}N_4O_4Cl$: C, 48.08; H, 4.03; N, 17.25; Cl, 10.92. Found: C, 48.18; H, 4.07; N, 16.87; Cl, 11.13.

The 2.0 g. of benzene-insoluble material had an infrared spectrum quite similar to the spectrum of 1,7,7-trihydroxybicyclo[2.2.1]heptane (wide OH absorption in 3500–3000 cm.$^{-1}$ region and peaks at 938 and 967 cm.$^{-1}$).

The reaction solution was made acidic to about *p*H 2 with concentrated hydrochloric acid and extracted continuously with ether for 3 days. Evaporation of the ether gave 1.6 g. of an orange oil that had a neutralization equivalent of 94. No pure compound could be isolated. The infrared spectrum had bands at 1700 cm.$^{-1}$ and broad-OH absorption from 3500 to 3000 cm.$^{-1}$ and 2700 to 2600 cm.$^{-1}$

Diazotization of 7,7-dihydroxybicyclo[2.2.1]hept-1-ylamine perchlorate in glacial acetic acid. To a solution of 5.0 g. (0.0278 mole) of 7,7-dihydroxybicyclo[2.2.1]hept-1-ylamine hydrochloride in 100 ml. of water was added a solution of 5.75 g. (0.0278 mole) of anhydrous silver perchlorate in water. The mixture was filtered and the silver chloride cake was washed with water. The combined solution and washings were evaporated at reduced pressure and the last traces of water were removed by drying in a vacuum desiccator over phosphorus pentoxide. The yield was 4.0 g. To a stirred suspension of 4.0 g. (0.0164 mole) of the amine perchlorate in 20 ml. of glacial acetic acid cooled with an ice bath was added 3.41 g. of solid sodium nitrite over a 45-min. period. The reaction mixture was protected with a drying tube except during the addition of the sodium nitrite. The ice bath was removed and the reaction mixture was stirred for an additional 2.5 hr., after which time no sodium nitrite was present (potassium iodide-starch paper). The reaction mixture was diluted with 150 ml. of water and was extracted with 1500 ml. of ether. The ether was dried over Drierite. After removal of the ether and acetic acid at reduced pressure, the residue, 3.43 g., was dissolved in aqueous sodium hydroxide to *p*H 10 to 12 and extracted continuously for 3 days with ether. The ether was evaporated in an air stream to give 0.9 g. of solid XIII, m.p. 114–118°. An analytical sample, m.p. 121.5–122.5°, was prepared by recrystallization from acetone.

Anal. Calcd. for $C_7H_{12}O_3$: C, 58.31; H, 8.39. Found: C, 58.57; H, 8.54.

Its infrared spectrum had a broad —OH absorption at 3500–3000 cm.$^{-1}$ and no carbonyl band in the 1775 cm.$^{-1}$ region. Reaction of the compound with 2,4-dinitrophenylhydrazine gave an immediate precipitate. An analytical sample, recrystallized from ethanol, melted at 216.5–217.5°.

Anal. Calcd. for $C_{13}H_{14}O_5N_4$: C, 50.97; H, 4.61; N, 18.29. Found: C, 51.27; H, 4.38; N, 17.97.

The basic solution was then made acidic with concentrated hydrochloric acid to *p*H 1 or 2 and extracted continuously with ether for 3 days to give 1.6 g. of dark brown acidic material after evaporation of the ether. Sublimation of this material at 70°, 0.05 mm., gave 0.5 g. of solid XIV m.p. 56–63°, which, on drying *in vacuo*, melted at 66–69°. An analytical sample, m.p. 70.5–71.5°, was prepared by two more sublimations. The acid gave a precipitate with 2,4-dinitrophenylhydrazine. It was identified (see below) as 4-ketocyclohexanecarboxylic acid (lit.[13] m.p. 68°).

Anal. Calcd. for $C_7H_{10}O_3$: C, 59.12; H, 7.09; neut. equiv., 142. Found: C, 58.83 H, 7.18; neut. equiv., 143.

A semicarbazone of XIV was prepared according to directions in Shriner, Fuson, and Curtin.[14] After several recrystallizations from ethanol, it decomposed at 196–197° (lit.[13] decomposition point, about 200°).

Anal. Calcd. for $C_8H_{13}N_3O_3$: C, 48.23; H, 6.57; N, 21.10. Found: C, 48.26; H, 6.42; N, 20.96.

7-Ketobicyclo[2.2.1]hept-1-yl p-nitrobenzenesulfonate (XV). A solution of 1.12 g. (0.0078 mole) of 1,7,7-trihydroxybicyclo[2.2.1]heptane and 3.82 g. (0.0172 mole) of *p*-nitrobenzenesulfonyl chloride in 10 ml. of pyridine was stirred at room temperature for 45 hr. The reaction mixture was then poured onto 20 ml. of concd. hydrochloric acid and 50 g. of cracked ice. The solution was extracted with 2 l. of ether and the ether solution was dried over Drierite. After evaporation of the ether and recrystallization from benzene-hexane, 1.41 g. of ester, m.p. 130–132°, was obtained. An analytical sample, m.p. 131–132°, was prepared by several recrystallizations from benzene-hexane.

Anal. Calcd. for $C_{13}H_{13}NO_6S$: C, 50.15; H, 4.21. Found: C, 50.17; H, 4.37.

4-Hydroxycyclohexanecarboxylic acid (XX). A mixture of 60 g. of ethyl *p*-hydroxybenzoate, 600 ml. of glacial acetic acid, and 1.0 g. of platinum oxide was shaken with hydrogen at 1500 p.s.i. at room temperature until the theoretical amount of hydrogen was taken up. The reaction mixture was filtered and the acetic acid was removed at reduced pressure. The product showed no aromatic bands in the infrared region. The reaction mixture was distilled at reduced pressure to give two products, ethyl cyclohexanecarboxylate, b.p. 65–67° (10 mm.), 14.3 g., and ethyl 4-hydroxycyclohexanecarboxylate, b.p. 93–98° (0.3 mm.), 17.4 g. The ethyl 4-hydroxycyclohexanecarboxylate was saponified by boiling with 100 ml. of 10% aqueous sodium hydroxide for 2 hr. The solution was cooled and made acid to *p*H 2 with concentrated hydrochloric acid. The mixture was then extracted continuously with ether for 4 hr. The ether was removed by air blowing and the residue was recrystallized from benzene-ethanol-ether to give 11.7 g., m.p. 120–142°, of a mixture of *cis*- and *trans*-4-hydroxycyclohexanecarboxylic acid.

Reaction of 4-carboxycyclohex-1-ylamine perchlorate with sodium nitrite in glacial acetic acid. To a solution of 3.1 g. (0.0172 mole) of 4-carboxycyclohex-1-ylamine hydrochloride[15] in 50 ml. of water was added a solution of 3.56 g.

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[12] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, John Wiley & Sons, Inc., New York, N. Y., 1956, p. 219.

[13] W. H. Perkin, Jr., *J. Chem. Soc.*, **85**, 416 (1904).

[14] Ref. 12, p. 218.

[15] J. P. Greenstein and J. Wyman, *J. Am. Chem. Soc.*, **60**, 2341 (1938).

(0.0172 mole) of silver perchlorate in 50 ml. of water. After filtration, the solution was evaporated to near dryness at aspirator pressure and last traces of water were removed by drying over phosphorus pentoxide in a vacuum desiccator to give 3.8 g. (0.0156 mole) of 4-carboxycyclohex-1-ylamine perchlorate. To a mixture of 3.8 g. of the amine perchlorate in 20 ml. of glacial acetic acid, cooled in an ice bath, was added 3.24 g. (0.047 mole) of sodium nitrite over a period of about 30 min. The ice bath was removed and the mixture stirred for an additional 6 hr. The mixture was poured into 250 ml. of water and extracted with 1.5 l. of ether. After evaporation of the ether, the residue gave a negative test with 2,4-dinitrophenylhydrazine reagent. Aqueous sodium hydroxide (10%) was added to the residue until the *p*H was 12 and the solution was extracted continuously with ether for 2 days. Evaporation of the ether gave no residue. After acidification of the basic solution with concentrated hydrochloric acid to *p*H 2 and continuous extraction for 2 days with ether, evaporation of the ether and extracted acetic acid gave 90 mg., m.p. 112–127°, of acidic material. Its infrared spectrum had bands at 3440, 2600, and 1705 cm.$^{-1}$ and was almost identical with the spectrum of a mixture of *cis*- and *trans*-4-hydroxycyclohexanecarboxylic acid.

4-Ketocyclohexanecarboxylic acid (XIV). To a stirred suspension of 3.0 g. (0.0208 mole) of 4-hydroxycyclohexanecarboxylic acid in 10 ml. of water and 3.6 g. of sulfuric acid was added 4.23 g. (0.0144 mole) of potassium dichromate in small portions over a 15-min. period, during which time the temperature rose to about 50°. After the addition was complete, the reaction mixture was stirred for 3 hr. The solution was extracted with 1 l. of ether. The ether was dried over sodium sulfate and then was evaporated to give 2.39 g. of solid material. Sublimation of 0.86 g. of this material gave 0.69 g. of 4-ketocyclohexanecarboxylic acid, m.p. 67–70°. Its infrared spectrum had a band at 1705 cm.$^{-1}$ and broad absorptions from 3500–3000 cm.$^{-1}$ and 2700–2600 cm.$^{-1}$ and was identical to the spectrum of the acid obtained from diazotization of 7,7-dihydroxybicyclo[2.2.1]hept-1-ylamine perchlorate. A mixed melting point with the acid obtained from the diazotization was 68–71°.

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Bridged Polycyclic Compounds. XIV. Free-Radical Addition of *p*-Toluenesulfonyl Chloride to Some Norbornenes[1]

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Free-radical addition of *p*-toluenesulfonyl chloride to norbornene (I) and to aldrin (II) led to the formation of *trans* 1,2-addition products (III and IV, respectively) without skeletal rearrangement or *cis-exo* addition products being noted. Addition to norbornadiene (V) gave the rearranged product VII. The results are discussed in terms of classical radical intermediates.

The addition of sulfonyl halides to olefins *via* free-radical paths has been noted by several groups of investigators.[2,3,4] In the course of our work on the stereochemistry of addition and of rearrangements during additions to bridged polycyclic olefins,[1,5–10] we decided to investigate the free-radical additions of arenesulfonyl chlorides to norbornenes to see whether these followed the same general pattern as other free-radical addition reactions.

Exclusive *exo-cis* addition of *p*-thiocresol to 6-chloroaldrin (*endo-exo*-1,2,3,4,6,10,10-heptachloro-1,4,4a,5,8,8a-hexahydro-1,4,5,8-dimethanonaphthalene) has been reported.[7] The free-radical addition of bromine to various substituted norbornenes (and 7-oxa analogs) has also been shown to give considerable *exo-cis* products,[11] and ethyl bromoacetate is reported to give *exo-cis* addition to norbornene.[12] On the other hand, we have now found that *p*-toluenesulfonyl chloride adds to norbornene (I) and to aldrin (II) to give the *trans* addition product.

When norbornene (I) was heated at 75–90° with *p*-toluenesulfonyl chloride in the presence of

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