hydrochloric acid was refluxed for 7 hr. The reaction mixture was diluted with 50 ml. of water and extracted with 200 ml. of ether. After drying the ethereal solution over magnesium sulfate, the ether was removed and the residue was distilled through a semimicrocolumn, yielding 0.92 g. (80%) of 5-phenylcyclooctanone, b.p. 110–111° (0.3 mm.), $n^{25}\text{D}$ 1.5378.

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.12; H, 8.95.

The semicarbazone, recrystallized from aqueous ethanol, melted at 188.2–189.4° dec.

Anal. Calcd. for $C_{15}H_{21}N_3O$: C, 69.46; H, 8.16; N, 16.12. Found: C, 69.30; H, 8.05; N, 16.19.

A solution of 0.18 g. of 5-phenylcyclooctanone, 0.5 g. of potassium hydroxide, and 1.0 ml. of 85% hydrazine hydrate in 10 ml. of diethylene glycol was refluxed for 1 hr. The solution was heated to 200–210° for 3 hr. and approximately 1 ml. of distillate was collected. The distillate was returned to the cooled reaction mixture, which was then treated with 50 ml. of water and extracted with a total of 75 ml. of ether. The ethereal solution was washed with water, dried over magnesium sulfate, and concentrated by slow distillation through a semimicrocolumn. The residue was purified by filtration through 5 g. of alumina with 75 ml. of benzene. After the benzene was removed, short-path distillation of the residue under reduced pressure (0.3 mm.) with a heating block temperature of 100° yielded 0.113 g. (68%) of phenylcyclooctane, $n^{25}\text{D}$ 1.5288, m.p. 5.9–9.0°, which did not depress the melting point of an authentic sample.[19]

1,5-Diphenylcyclooctanol (VIII).—A solution of 0.94 g. of 5-phenylcyclooctanone in 10 ml. of anhydrous ether was added dropwise to a solution of phenyllithium prepared from 0.15 g. of lithium wire and 1.31 g. of bromobenzene in 35 ml. of anhydrous ether. The reaction mixture was refluxed for 1 hr. and treated with 25 ml. of water. The resulting two-phase mixture was separated and the aqueous layer was extracted with 100 ml. of ether. The combined ethereal solutions were dried over magnesium sulfate. After distillation of the ether there remained 0.93 g. (72%) of a crystalline residue. Two crystallizations from 95% ethanol followed by sublimation yielded a mixture of *cis*- and *trans*-1,5-diphenylcyclooctanol, m.p. 149.8–154.2°.

Anal. Calcd. for $C_{20}H_{24}O$: C, 85.66; H, 8.63. Found: C, 85.72; H, 8.62.

1,5-Diphenylcyclooctene (IX).—Short-path distillation at 0.5 mm. with a heating block temperature of 200° of the 1,5-diphenylcyclooctanol from 2.29 g. of 5-phenylcyclooctanone yielded 2.52 g. of a mixture of 1,5-diphenylcyclooctanol and 1,5-diphenylcyclooctene. This mixture was dissolved in 110 ml. of dry benzene to which a few crystals of iodine had been added. The solution was refluxed with an attached water trap[22] for 23 hr. The reaction mixture was washed with sodium thiosulfate solution and with two small portions of water. The residue, after distillation of the benzene, was passed over 8.0 g. of silica gel and eluted with 250 ml. of petroleum ether (b.p. 35–60°). After distillation of the petroleum ether, short-path distillation of the residue at 0.4 mm. with a heating block temperature of 180° yielded 2.04 g. (69% from the ketone) of 1,5-diphenylcyclooctene, $n^{25}\text{D}$ 1.5937.

Anal. Calcd. for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.42; H, 8.09.

***cis*- and *trans*-1,5-Diphenylcyclooctane (X).**—Catalytic hydrogenation of 0.282 g. of 1,5-diphenylcyclooctene over 0.239 g. of 10% palladium on Norit in 10 ml. of 1:1 ethyl acetate–methanol required 48 min. and 101% of 1 molar equiv. of hydrogen was absorbed. The catalyst was separated by filtration and washed with methanol. Distillation of the solvent from the filtrate and sublimation of the residue at 100° (0.3 mm.) yielded a mixture of *cis*- and *trans*-1,5-diphenylcyclooctane, m.p. 57.0–66.2°.

Anal. Calcd. for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 91.15; H, 9.07.

Separation of the *cis* and *trans* isomers was effected by chromatography of a 0.42-g. sample on 127 g. of alumina (Merck, Brockmann grade I)[23] in a 72 × 1.9 cm. column. The hydrocarbons were eluted with *n*-hexane; a total of 380 ml. was passed through the column before any hydrocarbon was found in the effluent. The next three 10-ml. fractions contained a total of 44 mg. of the higher melting isomer, which, after one recrystallization from methanol, melted at 80–81°.

Anal. Calcd. for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 91.13; H, 9.33.

Fourteen 10-ml. fractions containing a mixture of the isomers, m.p. 52.8–72.4°, were then collected. The next four fractions contained 54 mg. of the lower melting isomer, which was rechromatographed and recrystallized from dry methanol and then melted at 62.0–62.5°.

Anal. Calcd. for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 90.85; H, 9.19.

The higher melting isomer was also obtained in a fairly pure state by repeated recrystallization of the original mixture from ethanol and methanol.

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[22] E. W. Dean and D. D. Stark, *Ind. Eng. Chem.*, **12**, 486 (1920).

[23] H. Brockmann and H. Schodder, *Ber.*, **74B**, 73 (1941).

Highly Strained Bicyclic Systems. X.[1-3] The Chemistry of 6-Substituted *exo*-5-Chlorobicyclo[2.1.1]hexanes

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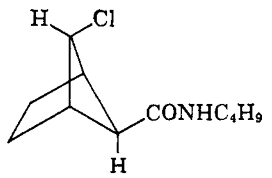
Received August 6, 1964

The synthesis of the epimeric *exo*-5-chlorobicyclo[2.1.1]hexane-6-carboxylic acids and related compounds is described. Dehalogenation of the *exo* acid gives the previously unavailable bicyclo[2.1.1]hexane-*exo*-5-carboxylic acid.

exo-5-Chlorobicyclo[2.1.1]hexane-*exo*-6-*t*-butylcarboxamide (1) has recently been shown to be a compound of considerable interest; it has provided the first example of a large, long-range, spin–spin coupling ($^4J_{AB}$ = 7 c.p.s.) between distant protons of known geometry,[4] and it was found to cyclize to give the first known example of a tricyclo[3.1.0.0^{2,6}]hexane (2) upon treatment with *n*-butyllithium.[5] In fact, neither of



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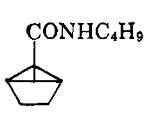

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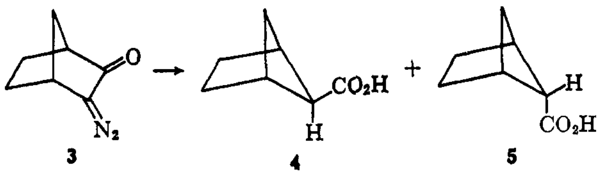
[1] The partial support of this work by a grant from the National Science Foundation is acknowledged with pleasure.

[2] Presented in part before the Division of Organic Chemistry at the 139th National Meeting of the American Chemical Society, St. Louis, Mo., March, 1961, Abstract, p. 390.

[3] For Part IX of this series, see J. Meinwald and P. G. Gassman, *J. Am. Chem. Soc.*, **85**, 57 (1963).

[4] J. Meinwald and A. Lewis, *ibid.*, **83**, 2769 (1961); F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961); K. B. Wiberg, B. R. Lowry, and B. J. Nist, *J. Am. Chem. Soc.*, **84**, 1594 (1962); J. Meinwald and Y. C. Meinwald, *ibid.*, **85**, 2514 (1963); A. Rassat, C. W. Jefford, J. M. Lehn, and B. Waegell, *Tetrahedron Letters*, **No. 5**, 233 (1964).

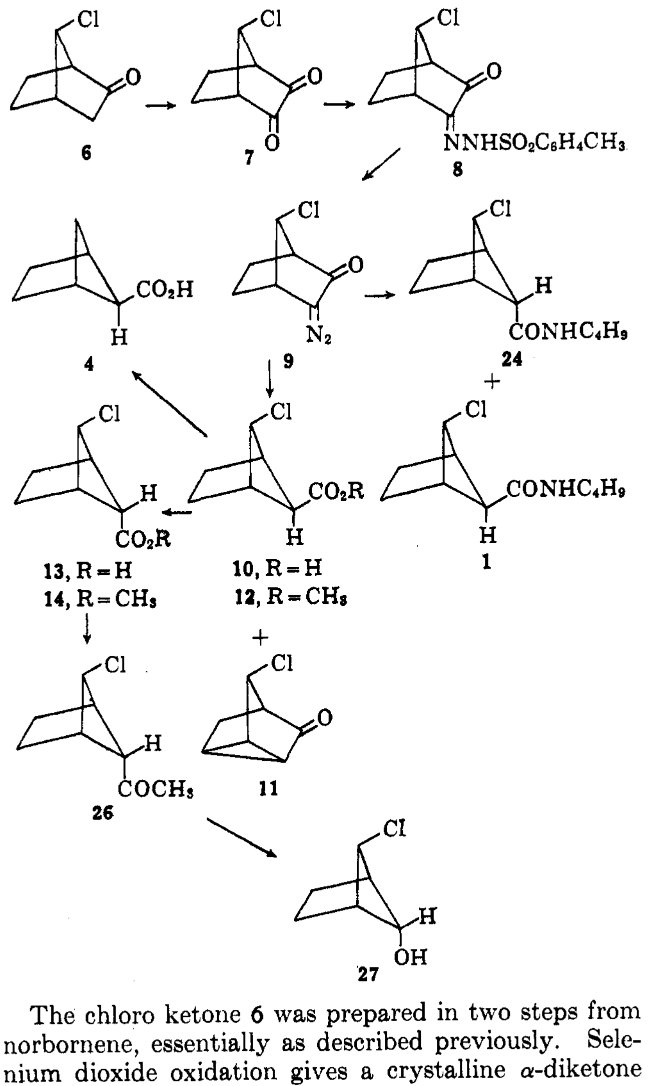
[5] J. Meinwald, C. Swithenbank, and A. Lewis, *J. Am. Chem. Soc.*, **85**, 1880 (1963).



these properties was anticipated, and the actual motivation for preparing compounds related to **1** is presented below.

In studying the photochemical ring contraction of the diazo ketone **3**, Wiberg and his co-workers found that the resultant bicyclic acid was a mixture of the *exo* and *endo* isomers (**4** and **5**, with **5** predominating) which resisted all attempts at separation, a circumstance which made subsequent work difficult.[6] The synthesis of the *exo*-5-chlorobicyclo[2.1.1]hexanes was undertaken partly to resolve this problem, as it was expected that the chlorine substituent at C-5 would provide sufficient directive influence at C-6 to make reactions at this site stereospecific. We now report on synthetic work which shows this to be the case. The over-all reaction sequence is summarized in Chart I.

CHART I

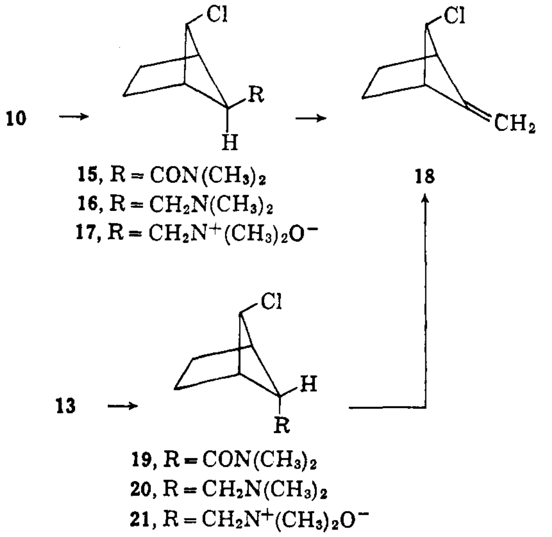


The chloro ketone **6** was prepared in two steps from norbornene, essentially as described previously. Selenium dioxide oxidation gives a crystalline α-diketone (**7**) whose configuration is confirmed by its dipole moment (5.33 D.).[7] Although this oxidation may be carried out in the usual way using either toluene or xylene as solvent, the procedure given here using bromobenzene followed by an aqueous work-up gives purer product in comparable yields. In general, this series of compounds is considerably more stable than the nonchlorinated analogs.[8] No difficulty was experienced in converting **7** into the corresponding monotoluenesulfonylhydrazone (**8**), and then into the α-diazo ketone (**9**), which could be recrystallized from hexane and stored without decomposition.

Photolysis of **9** in aqueous dioxane yielded chiefly the *exo*-5-*exo*-6-chloro acid **10**, whose stereochemistry has been established by dipole moment measurements.[7] The preference for formation of *endo* acid in the photolysis of **3** is therefore reversed in **9**. A neutral by-product in this reaction proved to be 7-chloronortricyclanone (**11**), the expected carbene insertion product.[9]

Treatment of the methyl ester of the *exo*-5-*exo*-6-chloro acid (**12**) with aqueous alcoholic base yielded the epimeric acid (**13**), whose dipole moment is consistent with the assigned stereochemistry.[7] The conversion of both of these epimers by a series of reactions terminating in an amine oxide pyrolysis into 6-methylene-*exo*-5-chlorobicyclo[2.1.1]hexane (**18**), notable for its intense olefinic stretching band at 5.9 μ, provides chemical proof of their relationship (Chart II).

CHART II



Treatment of the acid chloride derived from the *endo* acid (**13**) with methyllithium gave the acetyl compound (**26**), Baeyer–Villiger oxidation of which gave a mixture of *endo* esters which was reduced with lithium aluminum hydride to *exo*-5-chlorobicyclo[2.1.1]hexan-*endo*-6-ol (**27**). Attempts to prepare the *exo* alcohol by this route failed.

In exploring the synthetic possibilities for preparing acid derivatives directly from **9**, an unexpected dependence of the steric course of the addition of nucleophiles to the ketene **22** produced in this photochemical Wolff

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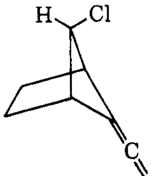
[6] K. B. Wiberg, B. R. Lowry, and T. H. Colby, *J. Am. Chem. Soc.*, **83**, 3998 (1961).

[7] W. D. Kumler, A. Lewis, and J. Meinwald, *ibid.*, **83**, 4591 (1961).

[8] K. Alder, H. K. Schafer, H. Esser, H. Krieger, and R. Reubke, *Ann.*, **593**, 23 (1955).

[9] This observation finds analogy in the formation of isocyclenone from α-diazocamphor [J. Meinwald, A. Lewis, and P. G. Gassman, *J. Am. Chem. Soc.*, **84**, 977 (1962)].

rearrangement was encountered. The stereochemistry of the acid **10** is determined by the direction of "ketonization" of the acid enol **23**, which in turn should proceed by donation of a proton by water from the less hindered (*endo*) side, giving the thermodynamically less stable (*exo*) acid.[10] In contrast, when the diazo ketone is irradiated in ethereal *t*-butylamine, a mixture of epimeric amides in which the *endo* epimer predominates by a ratio of 5:1 was obtained. In this case, the enolic intermediate analogous to **23** would be **25**, and the proton donor would be *t*-butylamine rather than water. At first sight this much more hindered proton donor might be considered especially sensitive to steric effects in the enol. The observed result, however, requires a different explanation. One possibility might be that the transition state in this case lies further toward products than that involved in the reaction of **22** with water, so that the relative stability of the epimeric products can come into play. Independent of the validity of this rationalization, the possibility of being able to control the steric course of analogous reactions by variation of the ketene coreactant is an interesting one.



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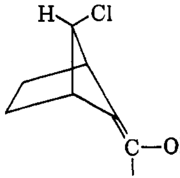

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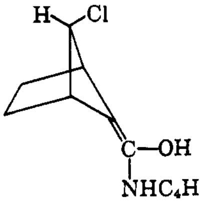

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The characterization of the pure epimeric chloro acids (**10** and **13**) opens the way to the preparation of pure epimers of the nonchlorinated parent acids. Thus, we have found that treatment of the 5-*exo*-6-*exo*-chloro acid (**10**) with lithium and *t*-butyl alcohol[11] yielded bicyclo[2.1.1]hexane-*exo*-5-carboxylic acid (**4**), a compound previously unavailable except as the minor component in a mixture.[6]

Experimental

syn-**7-Chloronorcamphorquinone** (**7**).—Selenium dioxide (164 g.) was suspended in a solution of chloro ketone **6**[12] (200 g.) in bromobenzene (1.5 l.) and the mixture was vigorously stirred and heated in an oil bath to 150–155° for 12 hr. The water slowly generated in the reaction was removed by distillation. After cooling, the solution was decanted from the precipitated selenium and filtered. Boiling water (3.5 l.) was added to the filtrate and steam was passed into the mixture until no more bromobenzene was carried over. The hot, aqueous solution was filtered, cooled, and continuously extracted with ether for 24 hr. The ether solution, when dried and cooled to −78°, yielded **7** as bright yellow crystals (129 g., 58%), m.p. 110–111°, after sublimation or recrystallization (ethyl acetate–hexane). Characteristic infrared maxima (CCl_4) appeared at 5.61 and 5.70 μ.

Anal. Calcd. for $C_7H_7Cl_2O_2$: C, 53.01; H, 4.45; Cl, 22.36. Found: C, 53.10; H, 4.56; Cl, 22.22.

syn-**7-Chloronorcamphorquinone Monotosylhydrazone** (**8**).—A solution of *p*-toluenesulphonylhydrazine (61.5 g.) in glacial acetic acid (180 ml.) at *ca.* 55° was added to a solution of **7** (50 g.) in glacial acetic acid (80 ml.) at *ca.* 75° and the mixture was immediately cooled to room temperature in an ice bath and allowed to stand overnight. The tosylhydrazone which separated was collected by filtration to give an off-white powder, suitable, (after drying) for the next experiment. Recrystallization from ethanol gave 85 g. (85% yield) of fine white needles, m.p. 149.5–151°.

Anal. Calcd. for $C_{14}H_{15}ClN_2O_3S$: C, 51.45; H, 4.63; Cl, 10.85; N, 8.57; S, 9.81. Found: C, 51.68; H, 4.66; Cl, 10.89; N, 8.66; S, 10.17.

syn-**7-Chlorodiazonorcamphor** (**9**).—To a solution of sodium hydroxide (10.5 g.) in water (1 l.) at 0° was added tosylhydrazone **8** (80 g.). The suspension was vigorously stirred with pentane (300 ml.) for 2 hr. The layers were separated and the aqueous phase was repeatedly extracted with fresh pentane until the organic layer no longer became yellow. Evaporation of the pentane yielded the diazo ketone (31 g., 94%) as yellow crystals, m.p. 67.5–68° after recrystallization from hexane. Characteristic infrared (CCl_4) maxima appeared at 4.8 and 5.88 μ; ultraviolet absorption at $\lambda_{\max}^{\mathrm{EtOH}}$ 249 mμ (log ϵ 4.04), $\lambda_{\max}$ 298 mμ (log ϵ 3.54).

Anal. Calcd. for $C_7H_7ClNO_2$: C, 49.29; H, 4.14; Cl, 20.78; N, 16.43. Found: C, 49.01; H, 4.26; Cl, 20.64; N, 16.37.

exo-**5-Chlorobicyclo[2.2.1]hexane**-*exo*-**6-carboxylic Acid** (**10**).—A solution of **9** (13 g.) in Spectrograde dioxane (370 ml.) and water (130 ml.) was irradiated with a Hanovia 450-w. mercury lamp using a water-cooled quartz immersion vessel and a Pyrex filter. After 26 hr., the solution was evaporated to about one-tenth of its volume, ether was added, and the acid was extracted with bicarbonate solution Acidification precipitated the desired acid, which was extracted into ether. The ether solution was dried and the solvent was removed to give the acid (8.0 g., 65%) as colorless crystals, m.p. 147.5–148° after recrystallization from ethyl acetate. V.p.c. analysis of the methyl esters derived from the *total* acidic fraction showed the *exo*–*endo* ratio to be 4:1, using a 0.5% polyethylene glycol column on glass beads at 128°.

Anal. Calcd. for $C_7H_9ClO_2$: C, 52.37; H, 5.65; Cl, 22.08. Found: C, 52.39; H, 5.78; Cl, 21.84.

Work-up of the neutral ether fraction from the photolysis yielded a liquid (3.0 g., 27%), b.p. 62–64° (0.1 mm.), n^{26}D 1.5115, whose infrared (CS_2) absorption at 5.68 and 12.4 μ was consistent with the formulation of the compound as *syn*-7-chloronortricyclanone (**11**).

Anal. Calcd. for C_7H_7ClO: C, 58.96; H, 4.95; Cl, 24.86. Found: C, 59.20; H, 5.17; Cl, 24.77.

A 2,4-dinitrophenylhydrazone was formed in the usual way; recrystallization from ethanol gave an analytical sample, m.p. 148°.

Anal. Calcd. for $C_{13}H_{11}ClNO_4O_4$: C, 48.39; H, 3.41; Cl, 10.99; N, 17.37. Found: C, 48.21; H, 3.77; Cl. 10.85; N, 17.28.

Methyl *exo*-**5-Chlorobicyclo[2.2.1]hexane**-*exo*-**6-carboxylate** (**12**).—An ethereal solution of **10** (10.0 g.) was treated with an ethereal solution of diazomethane until the yellow color persisted. Removal of the solvent yielded the ester (9.5 g., 88%), b.p. 96–98° (5.5 mm.), n^{30}D 1.4834. V.p.c. analysis on a S.E. 30 column at 193° indicated >99.5% purity.

Anal. Calcd. for $C_8H_{11}ClO_2$: C, 55.04; H, 6.35; Cl, 20.31. Found: C, 55.14; H, 6.36; Cl, 20.12.

exo-**5-Chlorobicyclo[2.1.1]hexane**-*endo*-**6-carboxylic Acid** (**13**).—A solution of **12** (5.0 g.) and sodium hydroxide (3.75 g.) in ethanol (60 ml.) and water (15 ml.) was heated under reflux for 2 hr. The solution was diluted with water (75 ml.) and extracted with ether. The aqueous phase was acidified and extracted with ether. The extract was washed and dried, and the solvent was removed to give **13** (3.72 g., 81%), m.p. 95.5–96° after sublimation and recrystallization from pantane.

Anal. Calcd. for $C_7H_9ClO_2$: C, 52.37; H, 5.65; Cl, 22.08. Found: C, 52.51; H, 5.82; Cl, 22.43.

Methyl *exo*-**5-Chlorobicyclo[2.1.1]hexane**-*endo*-**6-carboxylate** (**14**).—An ethereal solution of **13** (1.0 g.) was treated with an ethereal solution of diazomethane until the yellow color persisted. Removal of the solvent yielded **14** (0.83 g., 85%), b.p. 93–95° (5 mm.), n^{25}D 1.4762. V.p.c. analysis on an S.E. 30 column indicated >99.5% purity.

Anal. Calcd. for $C_6H_{11}ClO_2$: C, 55.04; H 6.35; Cl, 20.31. Found: C, 55.10; H, 6.45; Cl, 20.42.

exo-**5-Chlorobicyclo[2.2.1]hexane**-*exo*-**6**-*t*-**butylcarboxamide** (**1**).—A solution of **10** (1.5 g.) in benzene (25 ml.) was treated with oxalyl chloride (1.5 g.) overnight. The solvent and excess oxalyl chloride were removed under reduced pressure, and anhydrous ether (25 ml.) was added. This solution was added dropwise to a solution of *t*-butylamine (2 g.) in ether (25 ml.).

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[10] *Cf.* ref. 9.

[11] This experiment was carried out by Mr. Jack K. Crandall, using the general procedure of P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind.* (London), 405 (1960).

[12] J. D. Roberts, F. O. Johnson, and R. A. Carboni, *J. Am. Chem. Soc.*, **76**, 5692 (1954); R. R. Sauers and J. A. Beisler, *J. Org. Chem.*, **29**, 210 (1964).

After stirring for 30 min., the reaction mixture was filtered and the solvent was removed. The residue was sublimed to give **1** (1.65 g., 93%), m.p. 163.5–164°, $\lambda_{\max}^{\mathrm{EtOH}}$ 200 mμ (log ϵ 3.735).

Anal. Calcd. for $C_{11}H_{18}ClNO$: C, 61.25; H, 8.41; Cl, 16.44; N, 6.50. Found: C, 61.07; H, 8.30; Cl, 16.77; N, 6.82.

***exo*-5-Chlorobicyclo[2.2.1]hexane-*endo*-6-*t*-butylcarboxamide** (**24**).—This amide was prepared as described above for the *exo* compound. The acid **13** (1.0 g.) yielded **24** (1.14 g., 85%), purified by sublimation or recrystallization (hexane), m.p. 120–120.5°, $\lambda_{\max}^{\mathrm{EtOH}}$ 200 mμ (log ϵ 3.735).

Anal. Calcd. for $C_{11}H_{18}ClNO$: C, 61.25; H, 8.41; Cl, 16.44; N, 6.50. Found: C, 61.41; H, 8.37; Cl, 16.34; N, 6.44.

***exo*-5-Chlorobicyclo[2.2.1]hexane-*exo*-6-dimethylcarboxamide** (**15**).—This amide was prepared in the same way as **1**, using dimethylamine in place of *t*-butylamine. The acid **10** (5.0 g.) yielded the amide (4.67 g., 80%), m.p. 75.5–76°, purified by sublimation.

Anal. Calcd. for $C_9H_{14}ClNO$: C, 57.59; H, 7.52; Cl, 18.89; N, 7.46. Found: C, 57.71; H, 7.54; Cl, 18.99; N, 7.52.

***exo*-5-Chlorobicyclo[2.2.1]hexane-*endo*-6-dimethylcarboxamide** (**19**).—This amide was prepared in the same way as **15**. The acid **13** (5.0 g.) yielded **19** (5.08 g., 87%), m.p. 43–43.5°, purified by sublimation.

Anal. Calcd. for $C_9H_{14}ClNO$: C, 57.59; H, 7.52; Cl, 18.89; N, 7.46. Found: C, 57.71; H, 7.71; Cl, 18.88; N, 7.24.

***exo*-5-Chloro-*exo*-6-dimethylaminomethylbicyclo[2.1.1]hexane** (**16**).—A solution of **15** (4.00 g.) in ether (40 ml.) was added dropwise to a stirred suspension of lithium aluminum hydride (3.00 g.) in ether (20 ml.). After stirring at room temperature for 24 hr., the reaction mixture was cooled to 0° and excess hydride was decomposed by the cautious addition of water (12 ml.). The resultant mixture was stirred vigorously for 3 hr. and then filtered. The precipitated salts were washed thoroughly with ether, the combined ether extracts were dried, and the solvent was removed. Fractionation of the residue gave **16** (3.44 g., 93%), b.p. 90–92° (16 mm.), n^{24}D 1.4825.

Anal. Calcd. for $C_9H_{16}ClN$: C, 62.24; H, 9.30; Cl, 20.40; N, 8.07. Found: C, 61.98; H, 9.60; Cl, 20.11; N, 8.17.

A picrate of **16** was prepared in ethanol. Three recrystallizations gave yellow needles, m.p. 165.5–166°.

Anal. Calcd. for $C_{15}H_{19}ClN_4O_7$: C, 44.74; H, 4.75; Cl, 8.80; N, 13.91. Found: C, 44.90; H, 4.95; Cl, 8.80; N, 13.92.

***exo*-5-Chloro-*endo*-6-dimethylaminomethylbicyclo[2.1.1]hexane** (**20**).—This amine was prepared in the same way as **16**. Amide **19** (4.00 g.) yielded **20** (3.36 g., 91%), b.p. 88–90° (16 mm.), n^{25}D 1.4778.

Anal. Calcd. for $C_9H_{16}ClN$: C, 62.24; H, 9.30; Cl, 20.4; N, 8.07. Found: C, 62.02; H, 9.56; Cl, 20.05; N, 7.94.

The picrate formed as described above had m.p. 156–156.5°.

Anal. Calcd. for $C_{15}H_{19}ClO_7N_4$: C, 44.74; H, 4.75; Cl, 8.80; N, 13.91. Found: C, 44.91; H, 4.97; Cl, 8.63; N, 13.70.

***exo*-5-Chloro-*exo*-6-dimethylaminomethylbicyclo[2.1.1]hexane N-Oxide** (**17**).—To a stirred solution of **16** (2.50 g.) in methanol (10 ml.) was added hydrogen peroxide (30%, 6 ml.) with cooling. The reaction mixture was stirred for 20 hr., further hydrogen peroxide (30%, 1 ml.) was added, and the solution was stirred for another 12 hr. Excess hydrogen peroxide was then destroyed by stirring for 12 hr. with a little platinum black. The solvent was evaporated to yield the N-oxide as a waxy solid (2.46 g., 90%), which was used without further purification. The picrate, m.p. 152–153°, was prepared in the usual way and recrystallized from ethanol.

Anal. Calcd. for $C_{15}H_{19}ClN_4O_8$: C, 43.03; H, 4.57; Cl, 8.47; N, 13.38. Found: C, 43.12; H, 4.68; Cl, 8.52; N, 13.27.

***exo*-5-Chloro-*endo*-6-dimethylaminomethylbicyclo[2.1.1]hexane N-Oxide** (**21**).—This oxide was prepared in the same way as **17**. Amine **20** (2.50 g.) yielded crude **21** (2.52 g., 92%), whose picrate had m.p. 145–147°.

Anal. Calcd. for $C_{15}H_{19}ClN_4O_8$: C, 43.03; H, 4.57; Cl, 8.47; N, 13.38. Found: C, 43.19; H, 4.68; Cl, 8.57; N, 13.31.

***exo*-5-Chloro-6-methylenebicyclo[2.1.1]hexane** (**18**). **A.**—The N-oxide **17** (2.46 g.) was pyrolyzed at 130–135° at 20 mm. The pyrolysis products were trapped at −50°, then were diluted with ether and the ethereal solution was washed well with water until all basic material was removed. The ethereal solution was dried and the solvent was removed. The residue was fractionally distilled to give **18** (0.99 g., 73%), b.p. 69–70°, infrared (film) at 5.90 μ.

Anal. Calcd. for C_7H_9Cl: C, 65.37; H, 7.05; Cl, 27.57. Found: C, 65.14; H, 7.31; Cl, 27.36.

B.—Similar treatment of **21** (2.52 g.) yielded an olefin (0.92 g., 68%) possessing the same physical constants and giving an identical infrared spectrum.

***exo*-5-Chloro-*endo*-6-acetylbicyclo[2.1.1]hexane** (**26**).—A solution of methyllithium prepared from methyl iodide (2.82 g.) and lithium (0.28 g.) in ether (25 ml.) was added dropwise to a solution of **13** (1.61 g.) in ether (25 ml.) over a 1-hr. period. After stirring for an additional hour, the reaction mixture was poured onto ice (75 g.) and extracted with ether. The extract was dried and the solvent was removed under reduced pressure. The residue was distilled to give **26** (1.10 g., 70%), b.p. 83–85°, n^{21}D 1.4895. V.p.c. analysis (0.5% polyethylene glycol 400 on glass beads) showed a single peak of retention time 1.60 min. at 128°.

Anal. Calcd. for $C_8H_{11}ClO$: C, 60.52; H, 6.99; Cl, 22.36. Found: C, 60.32; H, 7.05; Cl, 21.98.

A 2,4-dinitrophenylhydrazone was prepared and recrystallized from ethanol to give an analytical sample, m.p. 221.5–222°.

Anal. Calcd. for $C_{14}H_{15}ClN_4O_4$: C, 49.64; H, 4.46; Cl, 10.47; N, 16.54. Found: C, 49.51; H, 4.74; Cl, 10.51; N, 16.27.

A semicarbazone was prepared and recrystallized from ethanol, giving an analytical sample, m.p. 174–175°.

Anal. Calcd. for $C_9H_{14}N_3ClO$: C, 50.11; H, 6.54; Cl, 16.44. Found: C, 49.87; H, 6.49; Cl, 16.60.

***exo*-5-Chlorobicyclo[2.1.1]hexan-*endo*-6-ol** (**27**).—A solution of trifluoroperacetic acid prepared from trifluoroacetic anhydride (3.4 ml.) and hydrogen peroxide (90%, 0.52 ml.) in methylene chloride (6.6 ml.) was added dropwise to a mixture of **26** (0.65 g.) and anhydrous dibasic sodium phosphate (3.90 g.) in methylene chloride (20 ml.) with stirring. The reaction mixture was stirred and heated under reflux for 16 hr., cooled, and filtered; the inorganic salts were washed thoroughly with methylene chloride. The combined filtrates were dried and the solvent was removed under reduced pressure to give the crude acetate (0.82 g.) containing some trifluoroacetate.

This ester mixture was dissolved in anhydrous ether (10 ml.) and added dropwise to a stirred solution of lithium aluminum hydride (1.0 g.) in ether (20 ml.). After stirring at room temperature for 8 hr., the reaction mixture was cooled to 0° and excess hydride was destroyed by the cautious addition of water (4 ml.). The organic layer was decanted and the salts were washed thoroughly with ether. The combined ether fractions were dried and the solvent was removed under reduced pressure. Distillation of the residue (bath temperature of 85–100° at 3 mm.) gave the alcohol (0.34 g., 62%).

Anal. Calcd. for C_6H_9ClO: C, 54.30; H, 6.84. Found: C, 53.92; H, 7.17.

Photolysis of 9 with *t*-Butylamine.—Diazo ketone **9** (11 g.) and *t*-butylamine (20 ml.) were dissolved in ether (350 ml.) and the solution was irradiated using a bank of Sylvania Blacklite tubes for 14 days. Removal of the solvent gave a crude crystalline residue (13 g.), whose infrared spectrum revealed it to be a mixture of **24** and **1** with an *exo–endo* ratio of 5:1. This mixture was taken up in hot aqueous methanol and yielded 7 g. of **24**, m.p. 124–125° after recrystallization and sublimation. The mother liquors were decolorized with Norit and evaporated to dryness. Crystallization of the residue from hot hexane gave 1 g. of a mixture of **1** and **24**, which was not further separated.

Bicyclo[2.1.1]hexane-*exo*-5-carboxylic Acid (**4**).—Lithium metal (0.5 g.), cut in small pieces, was added to a solution of **10** (0.5 g.) in anhydrous *t*-butyl alcohol (4.5 ml.) and tetrahydrofuran (20 ml.). After the initial exothermic reaction had subsided, the reaction mixture was heated under reflux for an additional hour, then was cooled and poured into ice–water (100 ml.) to decompose the excess lithium. The tetrahydrofuran was removed on a flash evaporator and the cold aqueous solution was carefully acidified with concentrated hydrochloric acid and extracted thoroughly with ether. The combined extracts were washed with water and dried, and the solvent was removed to give crude **4** (0.31 g., 79%), m.p. 45–50°. Two sublimations gave an analytical sample, m.p. 51–52°.

Anal. Calcd. for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.95; H, 8.07.

Methyl Bicyclo[2.1.1]hexane-*exo*-5-carboxylate.—Acid **4** (0.1 g.) was treated with excess ethereal diazomethane, and the methyl ester (0.071 g., 64%) was isolated by preparative v.p.c., n^{25}D 1.4549. Analytical v.p.c. on 20% LAC-446 at 85° showed a single peak with a retention time identical with that of the *minor* component from the mixture of epimeric esters prepared according to the method of Wiberg.[6]

The nuclear magnetic resonance spectrum of this ester had a sharp three-proton singlet at τ 6.37 (OCH_3), a partially resolved doublet at 7.27 ($J = 2.5$ c.p.s.), accounting for two bridgehead protons, a broad one-proton doublet centered at *ca.* 7.8 (*exo* C-6 hydrogen) which is partially obscured by a sharp one-proton doublet at 7.88 ($J = 7.5$ c.p.s., *endo* C-5 hydrogen). A four-proton singlet at τ 8.62 (C-2 and C-3 hydrogens) and a one-proton triplet centered at 9.00 ($J = 7.5$ c.p.s.) for the *endo* C-6 hydrogen complete the spectrum.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.41; H, 8.76.

Isomerizations of 1-Chloro-2-butene and 3-Chloro-1-butene[1]

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Received August 3, 1964

The average equilibrium constant for the isomerization of 3-chloro-1-butene to 1-chloro-2-butene in toluene at 80.2° was 2.32. The isomerization was catalyzed by Pyrex glass wool and by diethylamine hydrochloride. The kinetics of the isomerization was pseudo zero order, and the ratio of the rate constants for the forward and reverse reactions gave the same value (within experimental error) of the equilibrium constant as that determined from the composition of butenyl chlorides at equilibrium. The isomerization may be interpreted as occurring by way of ion pairs produced on the surface of electrophilic catalysts. Isomerization is inhibited if the butenyl chloride is stored at 0° in quartz flasks.

The rearrangement of allylic compounds is well known and may occur by way of a displacement reaction (SN2′)[4] or by ionization to ion pairs.[5]

Young and Winstein had shown that an equilibrium mixture of 3-bromo-1-butene and 1-bromo-2-butene (neat) at 100° consisted of about 15% of the former and 85% of the latter.[6] Lewis acids were found to catalyze the interconversion of 3-chloro-1-butene and 1-chloro-2-butene,[7a,b] and the equilibrium mixture at 60° was reported to consist of 26% of the former and 74% of the latter when cuprous chloride was the catalyst.[7b]

In studies on the SN2′ reaction of amines with 3-chloro-1-butene it was shown that the latter did not isomerize significantly under the conditions of the reaction.[8] At late stages of the relatively slow reaction of 3-chloro-1-butene with N-methylaniline some isomerization of the chloride could be detected by gas chromatography.[9] In the reaction of 3-chloro-3-phenyl-1-butene with triethylamine or with dimethylamine, isomerization of the halide was an important complication.[10]

The purpose of our investigation was to determine the rates of isomerization of 1-chloro-2-butene and 3-chloro-1-butene and the conditions under which isomerization may be a complicating factor in SN2′ reactions especially with relatively unreactive amines such as N-methylaniline.

Results

The equilibrium constant (based on concentrations) for the isomerization of 3-chloro-1-butene to 1-chloro-2-butene in toluene at 80.2° was obtained by gas chromatographic determination of the concentrations of the two isomers at equilibrium. The constant, K, ob-

$$CH_2{=}CHCH(CH_3)Cl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3CH{=}CHCH_2Cl$$

$$K = k_1/k_{-1}$$

tained in this way had values ranging from 2.19 to 2.34. The equilibrium constant was determined also by the ratio of rate constants for the forward and reverse reactions. The rate of isomerization was catalyzed by diethylamine hydrochloride and by Pyrex glass wool and the rate actually observed was zero order, independent of the concentration of allylic chloride. A derivation of the pseudo zero order kinetics based on a surface-catalyzed isomerization is given in the Experimental section. Isomerization of 1-chloro-2-butene occurs readily when it is stored in a glass vessel; the isomerization is inhibited when it is stored in a quartz flask at 0°.

TABLE I

COMPOSITION OF EQUILIBRIUM MIXTURE OF 1.113 *M* 3-CHLORO-1-BUTENE AND 1.113 *M* 1-CHLORO-2-BUTENE IN TOLUENE AT 80.2°

Time, hr.	3-Chloro-1-butene, mole %	1-Chloro-2-butene, mole %	K
0	100.0	0.0	. . .
3137	30.3	69.7	2.30[a]
3884	31.3	68.7	2.19[a]
0	0.0	100.0	. . .
3465	31.2	68.8	2.21[a]
4238	29.9	70.1	2.34[a]
0	100.0	0.0	. . .
3573	29.8	70.2	2.36[b]
3978	30.1	69.9	2.33[b]
0	0.0	100.0	. . .
2325	30.9	69.1	2.24[b]
3067	29.0	71.0	2.45[b]

[a] $(C_2H_5)_2NH_2Cl$ (0.1 g.) added/5 ml. of solution. [b] $(C_2H_5)_2NH_2Cl$ (0.1 g.) and Pyrex glass wool (0.4 g.) added/5 ml. of solution.

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[1] For experimental details, see A. F. Marcantonio, Ph.D. Thesis, University of Pennsylvania, 1961.

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