move hydride ions from the hydrocarbon to form trimethylcyclohexylcarbonium ions, which then undergo skeletal isomerization. Chromia–alumina does not cause isomerization in this case or in the case of dehydrogenation of the cyclohexene.

Experimental Part

Materials.—(a) Platinum–alumina catalyst was prepared according to the method described previously.[6] (b) Platinum–charcoal catalyst was prepared according to the method described by Linstead and co-workers[10] except that activated Burrell coconut charcoal (10–14 mesh) was used in place of Norit to facilitate its use in a vertical catalyst tube. (c) Chromia–alumina catalyst was prepared according to the method of Archibald and Greensfelder.[11] (d) 1,1,3-Trimethyl-*x*-cyclohexene and 1,1,3-trimethylcyclohexane were prepared by the method described previously.[4]

Apparatus and Procedure.—The apparatus consisted of a graduated buret connected to a Pyrex glass reaction tube containing the catalyst bed, a water-cooled receiver-condenser, and a calibrated gas collecting bottle containing saturated salt solution. The reaction tube was heated in a thermostatically controlled vertical furnace brought to the desired temperature in a slow stream of hydrogen.

The gaseous products formed were analyzed on a mass spectrograph at the laboratory of the Universal Oil Products Company.

The liquid products were distilled and analyzed. It was found that the bottoms of the distillation, amounting to about 1% of the total product had an index of over 1.510, probably indicating the presence of a diaryl hydrocarbon. The distillate was analyzed by infrared absorption. In some instances, the aromatic hydrocarbons were separated chromatographically from the naphthenes and submitted separately to analysis.

The structure of the aromatic hydrocarbons produced, such as *m*-xylene and 1,2,4-trimethylbenzene, was determined by means of solid nitro and bromo derivatives; they did not depress the melting point when mixed with the corresponding derivatives of known compounds.[12] The analyses were made according to the procedure described previously.[6] The wave lengths used for calculating the composition of the various samples are given in Table IV.

TABLE IV

WAVE LENGTHS (λ) OF CHARACTERISTIC INFRARED ABSORPTIONS, IN MICRONS

Hydrocarbon	Major λ, μ	Minor λ or check λ, μ
o-Xylene	13.49	10.75
m-Xylene	13.00	11.42
p-Xylene	12.55	8.2
1,2,3-Trimethylbenzene	13.08	9.2
1,2,4-Trimethylbenzene	12.40	11.45
1,3,5-Trimethylbenzene	11.95	(None)
1,1,3-Trimethylcyclohexene	7.7	8.0, 8.5

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[10] R. P. Linstead, K. O. Michaelis and S. L. S. Thomas, *J. Chem. Soc.*, 1139 (1940).

[11] R. C. Archibald and B. S. Greensfelder, *Ind. Eng. Chem.*, **37**, 356 (1945).

[12] "Infrared Spectral Analysis" (by Ed. Baclawski), Research and Development Laboratories, Universal Oil Products Company, Riverside, Illinois.

EVANSTON, ILL.

[CONTRIBUTION NO. 1802 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Spiro[3.5]nonane[1]

BY E. R. BUCHMAN, D. H. DEUTSCH AND G. I. FUJIMOTO

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Spiro(3.5)nonane (I) has been prepared by two methods. The more practical of these involved the application of the malonic ester synthesis to 1,1-di-(bromomethyl)-cyclohexane (IV) and conventional treatment of the product to give spiro-(3.5)nonane-2-carboxylic acid (VI). The Hunsdiecker degradation of this acid yielded the corresponding bromide (VII) which was catalytically reduced to I. In the second method, spiro(3,5)nonan-2-one (IX) was obtained as a product of the reaction between pentamethyleneketene (VIII) and diazomethane. Reduction of IX *via* the semicarbazone gave I.

Only five of the parent spirane hydrocarbons have been reported in the literature[2]; none of these contains the cyclobutane ring. The present paper describes two independent syntheses of spiro-(3.5)nonane (I), each of which proceeds from a suitable cyclohexane derivative with subsequent closure of the 4-carbon ring.[3]

In the first route to I, use was made of the malonic ester synthesis, a standard means of obtaining cyclobutane acids. The appropriate dibromide, 1,1-di-(bromomethyl)-cyclohexane (IV), had been prepared by Boord and co-workers[2e] by the action of phosphorus tribromide on the glycol II. In the present work, this procedure was advantageously modified; II was converted to the ditosylate III and the latter, on treatment with sodium bromide, gave IV in over-all yield from the glycol of better than 50%. The ester V, resulting from the malonic ester synthesis carried out in isoamyl alcohol,[4] was saponified and decarboxylated in the usual manner. The acid VI when subjected to the Hunsdiecker reaction[5] gave rise to the bromide VII from which spirane I was prepared by catalytic

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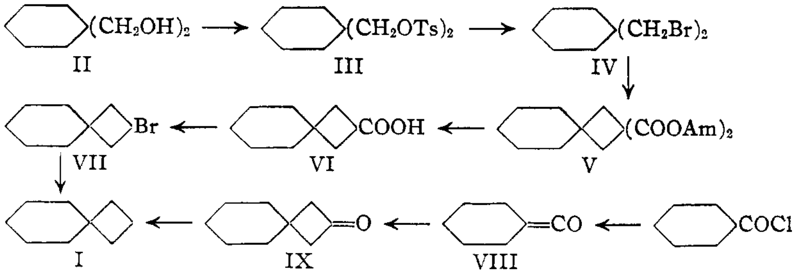
[1] Presented before the Division of Organic Chemistry, American Chemical Society at the San Francisco Meeting, March, 1949. This research received support from the Office of Naval Research.

[2] There are sixteen theoretically possible parent monospirane hydrocarbons having eleven carbon atoms or less. Those reported are: (chronologically) (a) spiro(5.5)undecane, W. S. G. P. Norris, *J. Chem. Soc.*, 245 (1926); (b) spiro(4.5)decane, N. D. Zelinsky and N. I. Schuikin, *Ber.*, **62**, 2180 (1929); *cf.* G. R. Clemo and J. Ormston, *J. Chem. Soc.*, 352 (1933); N. N. Chatterjee, *J. Indian Chem. Soc.*, **13**, 536 (1936); C. S. Marvel and L. A. Brooks, THIS JOURNAL, **63**, 2630 (1941); (c) spiro(4.4)nonane, N. D. Zelinsky and N. V. Elagina, *Compt. rend. acad. sci. (URSS)*, **49**, 568 (1945); *cf.* N. N. Chatterjee, *J. Indian Chem. Soc.*, **14**, 259 (1937); (d) spiro(2.2)pentane, M. J. Murray and E. H. Stevenson, THIS JOURNAL, **66**, 314, 812 (1944); see also V. A. Slabey, *ibid.*, **68**, 1335 (1946); (e) spiro(2.5)octane, R. W. Shortridge, R. A. Craig, K. W. Greenlee, J. M. Derfer and C. E. Boord, *ibid.*, **70**, 946 (1948).

[3] Regarding other syntheses of spiro(3.5)nonane derivatives, see (a) G. A. R. Kon, *J. Chem. Soc.*, **121**, 513 (1922); (b) P. K. Paul, *J. Indian Chem. Soc.*, **8**, 717 (1931); (c) N. N. Chatterjee, *C. A.*, **30**, 5947 (1936); *J. Indian Chem. Soc.*, **14**, 127 (1937).

[4] *Cf.* H. Fecht, *Ber.*, **40**, 3883 (1907).

[5] *Cf.* J. Cason and R. L. Way, *J. Org. Chem.*, **14**, 31 (1949).



reduction[6] in the presence of Raney nickel and alkali. Good yields were obtained at each step.

The second path to I employed a method[7] for formation of the 4-carbon ring which has only seldom found use. The ketene VIII,[8] which resulted from the abstraction of hydrogen chloride from cyclohexanecarbonyl chloride, was treated,[7] without isolation, with diazomethane. A very small yield of spiro(3.5)nonan-2-one[9,10] (IX) was isolated together with still smaller amounts of an isomer, presumably spiro(3.5)nonan-1-one; hexahydroacetophenone was also detected as a reaction product. Wolff–Kishner reduction of IX *via* the semicarbazone[11] gave I.

The close agreement of the infrared spectra of the two specimens of I (made by independent routes), while attesting the purity of the samples, at the same time confirms their structure and the validity of the synthetic methods employed.

Experimental[12]

1,1-Di-(bromomethyl)-cyclohexane (IV).[2e]—1,1-Di-(hydroxymethyl)-cyclohexane (II)[13] (368 g., 2.55 moles) was dissolved in 2100 ml. of dry pyridine and the solution was cooled to 0°; 1075 g. (10% excess) of tosyl chloride (recrystallized from petroleum ether) was then added over a period of 25 minutes while the reaction mixture was cooled in an ice-bath and swirled occasionally. After the mixture had been allowed to stand overnight at room temperature, it was poured into water containing hydrochloric acid. The tosylate separated as an oil which quickly solidified; it was filtered off, washed with dilute hydrochloric acid and recrystallized twice from methanol; large prisms, m.p. 74.0–74.5°, yield 778 g. (67%). On a smaller scale, nearly quantitative yields were obtained.

Anal. Calcd. for $C_{22}H_{28}O_6S_2$: C, 58.38; H, 6.24. Found: C, 58.54; H, 6.39.

Tosylate III (778 g., 1.72 moles), 426 g. (20% excess) of sodium bromide and 1200 ml. of diethylene glycol were heated together for three hours at 150–170° in a 5-liter flask provided with an efficient Hershberg stirrer. Considerable frothing took place. After cooling, 2500 ml. of water was added, the lower organic layer was separated and the aqueous phase was extracted four times with carbon tetrachloride. The combined extracts and dibromide were washed with water, dried over sodium sulfate and distilled, b.p. 110° at *ca.* 5 mm., n^{25}_{D} 1.5355 (lit.[2e] b.p. 117° at 6 mm., n^{20}_{D} 1.5390), yield 366 g. (79%).

Diisoamyl Spiro(3.5)nonane-2,2-dicarboxylate (V).—To a solution of 85.0 g. (3.7 gram-atoms) of sodium in 3.0 l. of absolute isoamyl alcohol, 594 g. (3.7 moles) of diethyl malonate was added and the mixture was refluxed for one hour during which time the ethanol liberated was distilled off. After cooling, 404 g. (1.5 moles) of dibromide IV and some porous chips were added and the mixture was refluxed gently for 44 hours. The flask was again cooled, ice-water was poured in and the system was neutralized with hydrochloric acid. The organic phase was separated and the aqueous portion was extracted with ether and the extracts were combined with the organic phase. After removal of solvent, the residue was distilled at reduced pressure. Refractionation gave 151.5 g. (28%) of V, b.p. 195° at 4–5 mm., n^{25}_{D} 1.4564, d^{22}_{4} 0.961.

Anal. Calcd. for $C_{21}H_{36}O_4$: C, 71.55; H, 10.30. Found: C, 71.65; H, 10.33.

Spiro(3.5)nonane-2-carboxylic Acid (VI).—A solution of 84 g. (1.5 moles) of potassium hydroxide in 500 ml. of absolute ethanol was added with stirring to 133.5 g. (0.38 mole) of V. A heavy white precipitate formed after a few minutes; the mixture was heated on the steam-cone for 20 minutes and the resulting mass was broken up and filtered (sintered glass funnel). The dipotassium salt was triturated with absolute ethanol, filtered, and dried, yield 102 g. (93%). To a solution of the salt in 200 ml. of cold water, 38 g. (0.4 mole) of sulfuric acid in an equal volume of water was slowly added with stirring. The precipitated diacid was filtered off, washed with cold water and dried, yield 89.6 g.; a portion was recrystallized from water and dried *in vacuo*, m.p. *ca.* 200° dec.

Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.24; H, 7.60. Found: C, 62.35; H, 7.76.

Crude diacid (97.5 g.) was heated at 220° until the evolution of carbon dioxide ceased (10 minutes). On distillation *in vacuo*, the main fraction came over at 163–165° at 15 mm., n^{25}_{D} 1.4793, d^{24}_{4} 1.036, m.p. 21°, yield 45.6 g. (65% based on V).

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.42; H, 9.53.

The amide was prepared in the usual manner from the acid with thionyl chloride and ammonium hydroxide; m.p. 157° after recrystallization from water–methanol and drying *in vacuo*, analysis for $C_{10}H_{17}NO$.

2-Bromospiro(3.5)nonane (VII).—An aqueous solution of the potassium salt of VI, adjusted to *ca.* *p*H 6, was added (at 40–50°) slowly with stirring to an equivalent amount of silver nitrate dissolved in water. After cooling, the silver salt was filtered off, washed with water and then with acetone, and finally dried *in vacuo* at 100°; yield 65 g. from 41.6 g. (0.25 mole) of VI. This salt was introduced gradually in a moisture-free system over a period of 45 minutes to a well-stirred dry solution of 40 g. of bromine in 200 ml. of carbon tetrachloride maintained at 0°. After the vigorous evolution of carbon dioxide had subsided, the reaction mixture was refluxed for 15 minutes and, after cooling, silver bromide was filtered off and washed with carbon tetrachloride. The combined filtrates were extracted with aqueous sodium bisulfite and with aqueous sodium bicarbonate and were dried over sodium sulfate. Distillation *in vacuo* gave the bromide, b.p. 103–104° at 13–14 mm., n^{25}_{D} 1.5015, d^{21}_{4} 1.254, yield 28.8 g. (57% from VI).

Anal. Calcd. for $C_9H_{15}Br$: C, 53.21; H, 7.44. Found: C, 53.58; H, 7.69.

Spiro(3.5)nonane (I).—To a cold solution of 4.6 g. of sodium in 150 ml. of absolute methanol were added 28.3 g. (0.14 mole) of VII and 15 g. of Raney nickel.[14] The mixture was shaken with hydrogen at atmospheric pressure; over a six-hour period, 92% of the theoretical amount was absorbed (further 1–2 g. portions of catalyst were added from time to time during the reduction). The reaction product

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(6) *Cf.* L. Ruzicka, P. A. Plattner and H. Wild, *Helv. Chim. Acta*, **28**, 395 (1945); V. Prelog and R. Seiwerth, *Ber.*, **74**, 1769 (1941).

(7) *Cf.* P. Lipp and R. Köster, *Ber.*, **64**, 2823 (1931); M. D. Owen, G. R. Ramage and J. L. Simonsen, *J. Chem. Soc.*, 1211 (1938).

(8) C. M. Hill with J. R. Johnson, Cornell University Ph.D. Thesis, 1941.

(9) Numbering, see Patterson and Capell, "The Ring Index," Reinhold Publishing Corp., New York, N. Y., 1940.

(10) Kon[2a] has reported the preparation of IX in 1% yield by cyclization of cyclohexane-1,1-diacetic ester with alkali metal. The properties of our preparation of IX are in agreement with those listed by Kon.

(11) *Cf.*, for example, A. H. Cook and R. P. Linstead, *J. Chem. Soc.*, 946 (1934).

(12) Melting points are corrected except in the section dealing with the spirononanones IX and X; microanalyses are by Dr. A. Elek, Los Angeles, Calif.

(13) M.p. 97–98°; the preparation of II and of intermediates used in its preparation was based on the directions in the literature[2e]; for details, see the Ph.D. Thesis of D. H. Deutsch, California Institute of Technology, 1950.

(14) A. A. Pavlic and H. Adkins, THIS JOURNAL, **68**, 1471 (1946).

was freed of catalyst by filtration; ether was added and the solution was washed with water and with 6 *N* hydrochloric acid. After drying, first over potassium carbonate and then over sodium, the hydrocarbon was isolated by distillation; 11.8 g. (68% yield) of I was obtained boiling in the range 156–157°. Refractionation gave material with the following constants[15]: b.p. 157.5–157.7° cor. at 753 mm., n^{25}_{D} 1.4581, d^{22}_{4} 0.849.

Anal. Calcd. for C_9H_{16}: C, 87.02; H, 12.98. Found: C, 86.94; H, 13.11.

A mixture of 2.5 g. of IX semicarbazone (see below) and 3.6 g. of powdered potassium hydroxide was placed in a distilling flask and heated with a free flame while slowly swirling the flask; a two-phase distillate was collected. The hydrocarbon layer was separated and washed with saturated sodium bisulfite solution and then with concentrated sulfuric acid. It was distilled over sodium; after a forerun, there was collected 0.5 g. (31%) of I, b.p. *ca.* 155°, n^{25}_{D} 1.4572, d^{24}_{4} 0.846.

Spiro(3.5)nonan-2-one (IX) and Spiro(3.5)nonan-1-one (X).[12]—To a solution of 44.5 g. (0.44 mole) of triethylamine in 150 ml. of dry ether cooled in an ice-bath was added, in a nitrogen atmosphere and with stirring, a solution of 58.5 g. (0.40 mole) of cyclohexanecarbonyl chloride in 100 ml. of dry ether. The dropwise addition required three hours. After standing for 48 hours at 0°, the ether phase was separated from precipitated triethylamine hydrochloride by inverted filtration. To the cold solution was added in small portions an ethereal solution of diazomethane until an excess was present. The mixture was allowed to stand for 48 hours and was then filtered and the filtrate was washed with dilute sulfuric acid, water, sodium bicarbonate solution and water in that order. After drying over anhydrous magnesium sulfate, the ether was removed and the residue distilled *in vacuo;* in an average run of this type, about 10 g. of material was collected, b.p. *ca.* 55–75° at 3 mm.

Preliminary studies indicated the non-homogeneity[16] of this product. Treatment with semicarbazide afforded a mixture, successive recrystallizations of which from methanol gave IX semicarbazone. The semicarbazone of X was obtained with difficulty from the mother liquors by allowing such solutions to evaporate spontaneously in a centrifuge tube; under such conditions, one of the isomeric semicarbazones was preferentially deposited on the sides of the tube.

Crude ketones from several runs were combined and fractionally distilled *in vacuo.* Although IX evidently has a higher b.p. than X, it was not possible effectively to separate the isomers. A fraction, b.p. 63.5–64.5° at 14 mm., contained small amounts of X (demonstrated by semicarbazone formation) and significant amounts of a $C_8H_{14}O$ compound (shown to be hexahydroacetophenone[17]) which, like X, did not readily combine with bisulfite. From this fraction a 2,4-dinitrophenylhydrazone was obtained (analysis for $C_{14}H_{18}N_4O_4$); orange prisms from ethanol, m.p. 134–135° (m.p. depressed when mixed with dinitrophenylhydrazone, m.p. 132.5–133°, see footnote 16; m.p. raised when mixed with authentic hexahydroacetophenone dinitrophenylhydrazone[17]). The *p*-nitrophenylhydrazone crystallized from methanol in long, irregular, deep-orange, needles, m.p. 152.5°, analysis for $C_{14}H_{19}N_3O_2$.

The IX-X containing fractions, resulting from redistillation of the crude ketone mixture, were shaken at room temperature with saturated aqueous sodium bisulfite solution until the separation of solid bisulfite addition compound was complete. The solid was washed with ether and heated with aqueous sodium carbonate to regenerate the 2-keto isomer (IX). From IX purified in this way was prepared the semicarbazone (m.p. 201–202°); the yield was of the order of magnitude of 1% from the acid chloride. From 2.4 g. of semicarbazone, on steam distillation in the presence of oxalic acid, there was obtained[3a] 1 g. of IX as a colorless liquid, b.p. 200–202° at 751 mm., n^{25}_{D} 1.4692, d^{22}_{4} 0.958 (lit.[3a] b.p. 208° (751 mm. (cor.)), n_D 1.4711, $d^{20.7}$ 0.961), analysis for $C_9H_{14}O$. The semicarbazone crystallized from methanol in colorless prisms, m.p. 204–204.5° (lit.[3a] m.p. 204°), analysis for $C_{10}H_{17}N_3O$. The *p*-nitrophenylhydrazone formed large orange prisms from ethanol, m.p. 139.5–140° (lit.[3a] m.p. 137–138°), analysis for $C_{15}H_{19}N_3O_2$. The 2,4-dinitrophenylhydrazone crystallized from ethanol in orange needles, m.p. 161.5–162°, analysis for $C_{15}H_{18}N_4O_4$.

From the portion not reacting with sodium bisulfite, a small yield of the 1-keto isomer (X) was isolated as the semicarbazone and purified by recrystallization from methanol. There were obtained colorless, elongated, needle-like plates melting at 200–201°, which when mixed with IX semicarbazone, m.p. 203–204°, melted at 178–180°.

Anal. Calcd. for $C_{10}H_{17}N_3O$: C, 61.50; H, 8.78. Found: C, 61.36; H, 8.72.

By steam distillation of a mixture of X semicarbazone and oxalic acid, there was obtained a small amount of X which was characterized by derivatives: The *p*-nitrophenylhydrazone crystallized from ethanol in stout, orange-red prisms, m.p. 166.5–168.5°. *Anal.* Calcd. for $C_{15}H_{19}N_3O_2$: C, 65.91; H, 7.01. Found: C, 65.93; H, 6.96. The 2,4-dinitrophenylhydrazone crystallized from ethanol in orange needles, m.p. 108–109°. *Anal.* Calcd. for $C_{15}H_{18}N_4O_4$: C, 56.59; H, 5.70. Found: C, 56.56; H, 5.79.

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(15) Infrared spectrum see D. H. Deutsch, Ph.D. thesis, California Institute of Technology, 1950.

(16) In one experiment, there was obtained an apparently homogeneous 2,4-dinitrophenylhydrazone, clusters of orange needles from ethanol, m.p. 132.5–133°, isomeric with the dinitrophenylhydrazone of IX and X. *Anal.* Calcd. for $C_{15}H_{18}N_4O_4$: C, 56.59; H, 5.70. Found: C, 56.56; H, 5.58.

(17) Hexahydroacetophenone was prepared by addition of methyl Grignard to hexahydrobenzoyl chloride at −25° (*cf.* G. Darzens and H. Rost, *Compt. rend.*, **153**, 773 (1911)). The ketone, b.p. 68–70° at 12 mm., did not combine with bisulfite (confirming J. von Braun, *Ber.*, **40**, 3948 (1907); C. Hell and O. Schaal, *ibid.*, **40**, 4163 (1907), reported a contrary finding). The 2,4-dinitrophenylhydrazone was recrystallized from ethanol–ethyl acetate, m.p. 138–139° (*cf.* C. F. H. Allen, THIS JOURNAL, **52**, 2958 (1930), m.p. 140°; G. K. Hughes and F. Lions, *Chem. Zentr.*, **110, I**, 113 (1939), m.p. 128°; M. Métayer and S. Roumens, *Compt. rend.*, **225**, 1326 (1947), m.p. 132°). The *p*-nitrophenylhydrazone melted at 145.9–150° (from ethanol) (both J. von Braun, above, and O. Wallach, *Ann.*, **360**, 48 (1908), reported m.p. 154°).