benzaldehyde.[18] The crude product was reduced with 25 g. of red phosphorus and 25 g. of iodine in 1200 ml. of glacial acetic acid and 120 ml. of water. The mixture was stirred and heated under reflux for 31 hr. Then the phosphorus was filtered, the mixture cooled, and the acid neutralized with a saturated solution of sodium carbonate. The resulting material was extracted thrice with isopropyl ether, the combined extracts washed with water, twice with 10% sodium hydroxide, and twice again with water, dried over calcium chloride, concentrated, and distilled at 1 mm. The fraction distilling at 119–122° (lit.,[19] b.p. 179–183° (21.5 mm.)) weighed 105 g. (65% based on aldehyde).

2′-Chloro-2-benzylbenzophenone.[20] A Grignard reagent was prepared from 54.5 g. (0.22 mole) of *o*-bromodiphenylmethane and 5.35 g. (0.22 mole) of magnesium in 250 ml. of anhydrous ether. The reaction was initiated by means of a few drops of methyl iodide. After all the solution had been added, reflux was continued until most of the magnesium had dissolved (about 1 hr.). The solution was cooled to room temperature and 40.4 g. (0.22 mole) of anhydrous cadmium chloride was added in one portion. The mixture was then heated under reflux for 40 min. after which the ether was allowed to distil from the mixture as 150 ml. of anhydrous benzene was added to replace it. The mixture was cooled and 34.4 g. (0.22 mole) of *o*-chlorobenzoyl chloride in 150 ml. of anhydrous benzene was added slowly enough to give moderate boiling of the benzene. The mixture was heated under reflux for 1.5 hr, the mixture cooled, poured on an ice–hydrochloric acid mixture, and left overnight. The layers were separated, the aqueous layer extracted thrice with fresh ether, the combined extracts washed with 10% sodium hydroxide and twice with water, dried over calcium chloride, concentrated, and fractionated at 1 mm. The fraction distilling at 201–204° weighed 40 g. (59%). On redistillation an analytical sample was taken at 207° at 0.5 mm.

The other haloketones were prepared in a similar manner.

2′-Chloro-2-benzoylbenzophenone.[21] To a mixture of 1.95 g. (0.006 mole) of 2′-chloro-2-benzylbenzophenone in 8 ml. of glacial acetic acid was added 1.98 g. (0.02 mole) of chromium trioxide in 6.5 ml. of glacial acetic acid and 4 ml. of water. The mixture was heated under reflux with stirring for 48 hr. The hot mixture was poured on 70 g. of ice. A white gum separated which crystallized on standing overnight. This was filtered, washed with water, and air dried. The 2.07 g. melted at 78–83°. Crystallization from methanol gave a m.p. of 87.5–88°.

2′-Bromo-2-benzoylbenzophenone was prepared in a similar manner.

9-(2-Bromophenyl)anthracene. A mixture of 1.47 g. of 2′-bromo-2-benzylbenzophenone, 30 ml. of 48% hydrobromic acid and 60 ml. of glacial acetic acid was heated in a sealed tube in a Carius furnace at 150° for 7 hr. A sticky semisolid separated which was filtered without suction, washed twice with water, and removed from the paper with acetone. The acetone was removed on a steam bath and the residue crystallized from methanol using activated charcoal. Almost white, very small rosettes separated, m.p. 136–137°, 29 g. (21%).

When yields were high the product of cyclization would crystallize in the tube as it cooled. This only needed to be filtered, washed, and weighed. Rates calculated from weights measured in either case were the same for the same compound. Rate calculations were made using at least three and usually four different time intervals. The intervals used were 3 hr., 7 hr., 12 hr., and 29 hr. For the less active ketones the 3 hr. interval gave only an oil from which no crystalline product could be obtained. When this occurred the oil could be oxidized to the corresponding diketone (V) except in the case of the methyl analog (I, X = $2\text{-}CH_3$). The identity of these products was checked by means of mixed melting points with authentic samples.

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[18] R. Adams and E. H. Vollweiler, *J. Am. Chem. Soc.*, **40**, 1737 (1918).

[19] C. K. Bradsher and F. A. Vingiello, *J. Org. Chem.*, **13**, 786 (1948).

[20] This procedure is similar to that developed by Cason[7] for the aliphatic halides and acid halides which are more active than the analogous aromatic halides.

[21] The procedure of Vingiello and Van Oot[6] using sodium dichromate and sulfuric acid on our new ketones often gave dark products which were purified with some difficulty. Yields were also lower than reported in the *para*-substituted compounds.

[CONTRIBUTION FROM THE WHITMORE LABORATORY OF THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

Syntheses of Four Spiro Hydrocarbons

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Synthetic routes to four spiro hydrocarbons are described.

As a portion of a continuing study[3] of hydrocarbon structure and physical properties, spiro[4.5]decane, spiro[5.5]undecane, spiro[5.6]dodecane, and 7-hexadecylspiro[4.5]decane were prepared. The first three of these compounds have been reported previously.[4–9] However, because many of the properties reported were seriously

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[1] American Petroleum Institute Fellow, 1956–58. Esso Research and Development Company Fellow, 1958–59.

[2] Taken in part from the dissertation submitted by P. A. Naro in partial fulfillment of the requirements for the Ph.D. degree at The Pennsylvania State University.

[3] For the previous paper in this series see S. G. Clark II, and J. A. Dixon, *J. Org. Chem.*, **23**, 1628 (1958).

[4] N. D. Zelinsky and N. I. Schuikin, *Ber.*, **62**, 2180 (1929).

[5] R. Ya. Levina, V. R. Skvarchenko, and O. Yw. Okhlobystin, *Zhur. Obshcheĭ Khim.*, **25**, 1466 (1955); *Chem. Abstr.*, **50**, 4797a (1956).

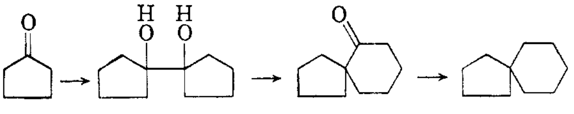
[6] G. A. Laber, *Ann.*, **588**, 79 (1954).

[7] M. Mousseron, R. Jacquier, and H. Christol, *Bull. soc. chim. France*, 346 (1957).

[8] R. Mayer, G. Wenschuh, and W. Topfelman, *Chem. Ber.*, **91**, 1616 (1958).

in error and because significant improvements were made in the syntheses, they are reported here.

Spiro[4.5]decane was prepared from cyclopentanone *via* the pinacol reduction,[10] pinacol rearrangement,[4,10] and Wolff-Kishner reduction.[11] The best yield of diol, 30%, was obtained by letting the reaction proceed very rapidly and vigorously. Only sufficient cooling to keep the reaction in the flask was used. The diol was rearranged to the ketone in 72% yield.[10]

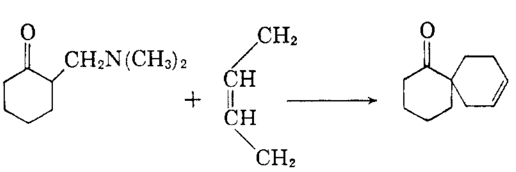


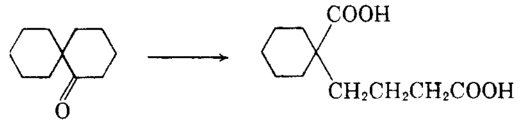
Reduction of the ketone to the hydrocarbon by the Wolff-Kishner reaction[11] gave only a 41% yield of highly purified spiro[4.5]decane. The low yield was due in part to decomposition of the ketone since the amount of gas evolved during the reduction exceeded the theoretical value by 18%. The difficulty may have arisen because 6-ketospiro[4.5]decane is a highly hindered ketone.

Attempts were made to introduce an *n*-hexadecyl group into the spiro[4.5]decane system by addition of the Grignard reagent or alkyllithium reagent to the ketone. All such attempts failed. The products of the Grignard reaction consisted of 6-hydroxyspiro[4.5]decane, normal hexadecene, and traces of ketone and dotriacontane. Apparently the predominant reaction was Grignard reduction. In contrast, treatment of the spiranone with hexadecyllithium yielded chiefly starting ketone (75%) plus smaller amounts of cetyl alcohol and dotriacontane. In contrast, Rowe[12] has observed that upon treatment of 6-ketospiro-[4.5]decane with methylmagnesium bromide, a quantitative yield of the tertiary alcohol was obtained.

Alkylation with hexadecyl bromide and potassium *t*-butoxide at the carbon *alpha* to the carbonyl carbon provided a satisfactory route to 7-hexadecyl-6-ketospiro[4.5]decane. Wolff-Kishner reduction[11] yielded the hydrocarbon.

Spiro[5.5]undecane was prepared by a modification of a synthetic route suggested by Mousseron and co-workers.[7] The Mannich base prepared from cyclohexanone, formaldehyde, and dimethylamine was treated with butadiene at 150–160°. When the reported procedure was followed exactly, the product appeared to be one ketone, and the 2,4-dinitrophenylhydrazone had the same melting point as that previously reported by Mousseron, *et al.*[7] However, when the reaction was run on such a scale that the products could be fractionally distilled through an efficient column, the reaction product proved to be a complex mixture. The properties of the saturated ketone and its 2,4-dinitrophenylhydrazone also were significantly different from those previously reported.[7] By-products (from the reaction of the Mannich base with butadiene) boiling higher and lower than the desired ketone were obtained. The higher boiling fractions from the distillation were green, turned red on standing, and had exceedingly complex infrared spectra. The carbonyl absorptions frequently appeared as doublets. The purified ketone obtained from the fractional distillation had properties which were significantly different from the reported ones.[7] The structure of the ketone was established by its infrared spectrum, carbon and hydrogen analysis, molar refraction, and by hydrogenation of the unsaturated ketone to 1-ketospiro[5.5]undecane followed by oxidation to 1-carboxycyclohexanebutyric acid.





Spiro[5.5]undecane was prepared from the unsaturated ketone by Wolff-Kishner reduction[11] followed by hydrogenation of the olefin.

Preparation of 1-ketospiro[5.5]undeca-8-ene using the morpholine Mannich base in place of the dimethylamine Mannich base was unsuccessful. The desired product could not be isolated from the complex mixture of products which resulted.

An attempt was made to prepare spiro[5.6]-dodecane from cyclohexanone by the synthetic route used for the preparation of spiro[4.5]decane. This failed when all attempts to convert the diol to the ketone yielded 1,1′-bicyclohexenyl, tars, and very small quantities of the desired ketone.

The synthesis of spiro[5.6]dodecane by the route which was used for the preparation of spiro[5.5]-undecane was abandoned also when treatment of cycloheptanone with formaldehyde and dimethylamine produced the Mannich base in very low yields and low purity.

Alkylation of cycloheptanone with 1,5-dibromopentane in the presence of potassium *t*-butoxide, a procedure suggested by Mousseron,[7] was used to prepare 7-ketospiro[5.6]dodecane. However, this reaction, too, leads to a complex mixture of products. The desired ketone could not be isolated by careful fractional distillation. Infrared analyses

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(9) R. Ya. Levina and T. I. Tantsyreva, *Doklady Akad. Nauk S.S.S.R.*, **89**, 697 (1953); *Chem. Abstr.*, **48**, 6792e (1954).

(10) P. A. Naro and J. A. Dixon, *J. Am. Chem. Soc.*, **81**, 1681 (1959).

(11) Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2478 (1946).

(12) J. W. Rowe, A. Melera, D. Arigoni, O. Jeger, and L. Ruzicka, *Helv. Chim. Acta*, **40**, 1 (1957).

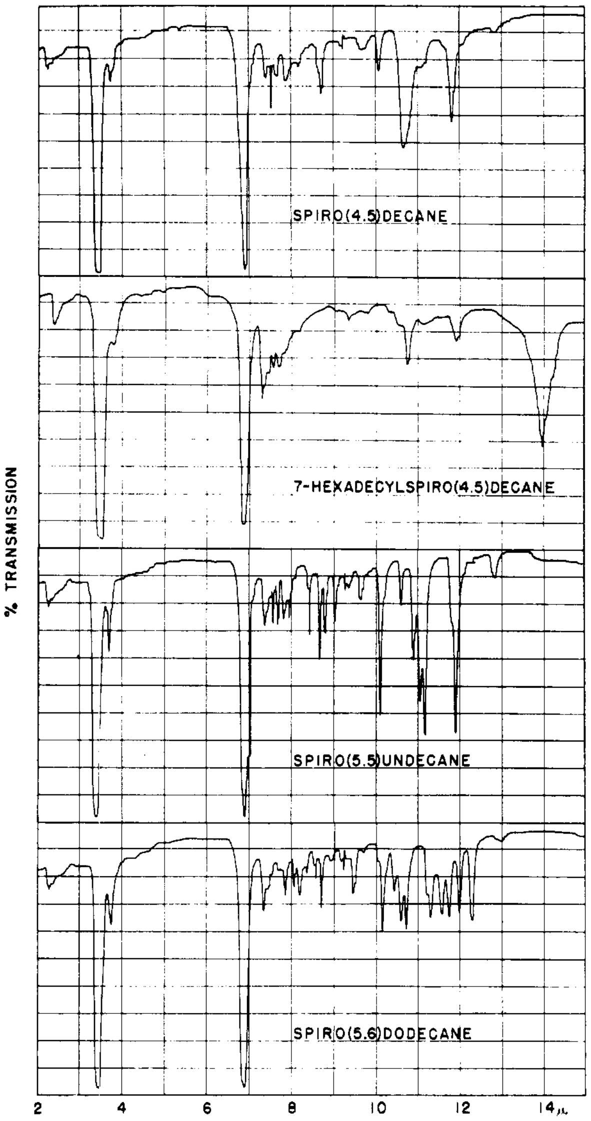

Fig. 1. Infrared absorption spectra (cell thickness, 0.026 mm.)

and vapor phase chromatography suggested that 15–20% of isomeric ketones and olefinic impurities were present. It has been frequently observed in this laboratory that olefins and ketones will azeotrope or co-distill. Conversion of the ketonic material to the semicarbazone, followed by regeneration and fractional distillation gave a 45% yield of high purity 7-ketospiro[5.6]dodecane. This ketone could be isolated also by elution chromatography, but the yield was much lower.

Spiro[5.6]dodecane was prepared (37%) in a state of high purity by Wolff-Kishner reduction[11] of the crude ketone-olefin mixture followed by a high-efficiency fractional distillation. A sample of the mixture of spirane and byproducts obtained from the Wolff-Kishner reduction was analyzed by vapor phase chromatography. At least six products were shown to be present.

The infrared spectra of the spiranes are shown in Fig. 1. An examination of these plus the spectra of ten other compounds containing the spiro system revealed that there is a doublet at 7.30–7.66 μ which may be characteristic of the spiro system.[13] Unfortunately, both *gem*-dimethyl and isopropyl groupings absorb in this region also.

EXPERIMENTAL[14]

Preparation of spiro[4.5]decane. Spiro[4.5]decane. The hydrocarbon was prepared by the modified Wolff-Kishner reduction[15] of 6-ketospiro[4.5]decane.[10] After efficient fractional distillation and repeated passage through silica gel and alumina a 40.9% yield of spirane was obtained, n_D^{25} 1.4687, d_4^{20} 0.8782, M_D calcd. 44.00, found 43.97. Vapor phase chromatographic analysis indicated a purity in excess of 99.5%.

Anal.[16] Calcd. for $C_{10}H_{18}$: C, 86.88; H, 13.12. Found: C, 87.02; H, 13.03.

Preparation of 7-hexadecylspiro[4.5]decane. 7-Hexadecyl-6-ketospiro[4.5]decane. Potassium metal (43.0 g., 1.1 moles, Baker Reagent) was dissolved in anhydrous *t*-butyl alcohol (750 g.). The excess *t*-butyl alcohol was distilled and the white residue treated with anhydrous toluene (1000 ml.), *n*-hexadecyl bromide (305 g., 1 mole; n_D^{25} 1.4602), and 6-ketospiro[4.5]decane (152 g., 1 mole).[10] This mixture was refluxed with stirring under nitrogen for 46 hr., then treated with 500 ml. of water and 100 ml. of 10% hydrochloric acid. The organic product (388 g.) was fractionally distilled. Crystallization from acetone of the fractions having n_D^{25} 1.4700–1.4734 yielded 54% spiroketone, m.p. 29.3–29.8°.

Anal.[17] Calcd. for $C_{26}H_{48}O$: C, 82.91; H, 12.85. Found: C, 83.00; H, 12.88.

7-Hexadecylspiro[4.5]decane. The hydrocarbon was prepared by both the Herr-Whitmore-Schiessler[15] modification and the Huang-Minlon[11] modification of the Wolff-Kishner reduction. The latter gave a higher yield (77% after fractional distillation) of more readily purified product. After an additional fractional distillation and fractional elution from alumina, the hydrocarbon had the following properties: n_D^{25} 1.4704, $d_4^{37.7}$ 0.8482, M_D calcd. 117.92, found 118.37.

Anal.[16] Calcd. for $C_{26}H_{50}$: C, 86.10; H, 13.90. Found: C, 86.08; H, 13.78.

Preparation of spiro[5.5]undecane. 2-(N,N-Dimethylaminomethyl)cyclohexanone.[7] A mixture of cyclohexanone (392 g., 4 moles; n_D^{25} 1.4479), paraformaldehyde (60 g., 0.66 mole, Eastman White Label), dimethylamine hydrochloride (164 g., 2 moles, Eastman White Label), 200 ml. of water, and 4 ml. of concd. hydrochloric acid was rapidly heated with stirring until a vigorous reaction ensued. When the initial reaction had subsided, the homogeneous solution was refluxed for 15 min., cooled in an ice bath, and diluted with 500 ml. of water. After addition of potassium hydroxide, the amine was separated and distilled as rapidly as possible through an 18-inch Vigreux column. The pale yellow oil, 261 g., (84%), b.p. 66° (0.75 mm.), n_D^{25} 1.4630–1.4635, picrate m.p. 164.3–165.3° (reported:[18] m.p. 149°), was used without further purification.

1-Ketospiro[5.5]undeca-8-ene. Small quantities of the unsaturated ketone were prepared in sealed tubes while large quantities were prepared in an Aminco pressure hydro-

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(13) C. Chiurdoglu and B. Tursch, *Bull. soc. chim. Belges*, **66**, 600 (1957).

(14) All melting points are uncorrected.

(15) C. H. Herr, F. C. Whitmore, and R. W. Schiessler, *J. Am. Chem. Soc.*, **67**, 2061 (1945).

(16) Elemental analysis performed by Mr. James Rigas, 470 Eastern Parkway, Brooklyn 25, N. Y.

(17) Elemental analysis performed by Dr. Alfred Bernhardt, Max-Planck Institut, German Federal Republic.

(18) C. Mannich, *Ber.*, **53**, 1874 (1920).

genation apparatus. The procedures used were patterned after the methods of Mousseron.[7]

Into a heavy-walled Pyrex tube (Fisher Carius C, 150-ml. capacity) were placed 2-(*N*,*N*-dimethylaminomethyl)cyclohexanone (23.3 g., 0.15 mole), butadiene (50 ml., Phillips Rubber Grade), anhydrous toluene (50 ml.), and hydroquinone (0.2 g., Eastman White Label). After heating at 150° for 7 hr. the products were distilled through a Claisen head at reduced pressure. The crude product, n_D^{25} 1.4932–1.5002, 14.2 g., 58%, yielded a 2,4-dinitrophenylhydrazone, m.p. 104.5–105.5° (reported,[19] m.p. 107–108°). After efficient fractional distillation the ketone (42%) had the following properties: n_D^{20} 1.5047, d_4^{20} 1.0174, M_D calcd. 48.16, found 47.86.

Anal.[17] Calcd. for $C_{11}H_{16}O$: C, 30.44; H, 9.82. Found: C, 30.34; H, 9.94.

The 2,4-dinitrophenylhydrazone of the high purity ketone melted at 132.5–133.5° after three recrystallizations from ethanol (reported,[19] m.p. 107–108°).

1-Ketospiro[5.5]undecane. Partial hydrogenation of 1-ketospiro[5.5]undeca-8-ene over a kieselguhr-supported nickel catalyst (Universal Oil Products Corp.) at 84–86° and 1400–1700 p.s.i. gave two products which were separated by fractional distillation: 1-ketospiro[5.5]undecane, 60%, and 1-hydroxyspiro[5.5]undecane, 25%. The spiranone was crystallized from hexane and then sublimed; m.p. 39.0–39.6° (reported,[19] m.p. 47°).

Anal.[17] Calcd. for $C_{11}H_{16}O$: C, 79.46; H, 10.91. Found: C, 80.06; H, 11.28.

The 2,4-dinitrophenylhydrazone crystallized as yellow-orange fibrous needles from ethanol, m.p. 133.4–134° (reported,[19] m.p. 123–124°). A mixed melting point with the 2,4-dinitrophenylhydrazone of 1-ketospiro[5.5]-8-undecene was depressed.

The 1-hydroxyspiro[5.5]undecane was not purified. The 3,5-dinitrobenzoate crystallized from alcohol-water, m.p. 112–113°.

1-Carboxycyclohexanebutyric acid. A mixture of concd. nitric acid (45 ml., Baker Analyzed Reagent), water (20 ml.), ammonium metavanadate (0.5 g., Fisher Scientific Co.), and 1-ketospiro[5.5]undecane (1 g., 0.006 mole) was heated to 80°. After the initial reaction had subsided, the heating mantle was removed and the remaining spiranone (9 g., 0.054 mole) was added dropwise with stirring. The crystals which separated on cooling to room temperature were recrystallized from water to yield 5.8 g. (45%) of 1-carboxycyclohexanebutyric acid, m.p. 105.2–106.0°.

Anal.[17] Calcd. for $C_{11}H_{18}O_4$: C, 61.61; H, 8.47; neut. equiv., 107.1. Found: C, 61.42; H, 8.39; neut. equiv., 107.8.

Spiro[5.5]-8-undecene. The olefin was obtained from the keto olefin by the Wolff-Kishner reaction.[11] After fractional distillation the yield was 85%: n_D^{20} 1.4919, d_4^{20} 0.9122, M_D calcd. 48.15, found 47.78.

Anal.[16] Calcd. for $C_{11}H_{18}$: C, 87.93; H, 12.07. Found: C, 88.15; H, 12.00.

Spiro[5.5]undecane. The olefin was hydrogenated over kieselguhr-supported nickel catalyst (15%, Universal Oil Products Corp.) at 123–125° and 300–1600 p.s.i. After separation, fractional distillation, and repeated passage of the individual fractions through activated alumina and silica gel, there was obtained 75% of high purity material, n_D^{25} 1.4760, d_4^{20} 0.8887, b.p. 212° (723 mm.), M_D calcd. 48.62, found 48.51. Analysis by vapor phase chromatography indicated a purity in excess of 99.5%.

Anal.[16] Calcd. for $C_{11}H_{20}$: C, 86.76; H, 13.24. Found: C, 87.03; H, 13.03.

Preparation of spiro[5.6]dodecane. 1,1′-Dihydroxy-1,1′-dicyclohexyl. This diol was prepared by the procedure described above for 1,1′-dihydroxy-1,1′-dicyclopentyl. The yield of diol was 34%, m.p. 130–131° (reported,[20] m.p. 128.5–129.5°).

7-Ketospiro[5.6]dodecane. The spiranone was prepared by a modification of the method of Mousseron.[7] Anhydrous *t*-butyl alcohol (1000 g., 13.5 moles) and potassium metal (82.1 g., 2.1 moles, Fisher Chemical Co.) were stirred overnight under nitrogen and the excess *t*-butyl alcohol removed by distillation.[21] Anhydrous toluene (2.0 l.), cycloheptanone (112 g., 1 mole, Aldrich Chemical Co.), and 1,5-dibromopentane (230 g., 1 mole; n_D^{25} 1.5102) were added to the resulting white solid and the mixture refluxed for 73 hr. After the usual separation procedures the crude ketone was fractionally distilled through a 40-plate column. The ketone so obtained [n_D^{25} 1.4890–1.4895, b.p. 68° (0.6 mm.)] was shown by its infrared spectrum to contain olefinic impurities. Since separation of these olefinic impurities from the spiro[5.6]dodecane is readily accomplished, this material can be used directly for the preparation of the hydrocarbon. However, samples of high purity ketone were prepared by elution chromatography and by a purification sequence involving preparation and purification of the semicarbazone, regeneration, and fractional distillation of the spiranone (45%), b.p. 100° (2.3 mm.), n_D^{25} 1.4922, d_4^{20} 0.9897, M_D calcd. 53.25, found 53.02. Analysis by vapor phase chromatography indicated a purity of 99.7%.

The 2,4-dinitrophenylhydrazone melted at 117–118°. A mixed melting point with the 2,4-dinitrophenylhydrazone of the ketone prepared by the pinacol rearrangement of 1,1′-dihydroxy-1,1′-dicyclohexyl was undepressed.

Anal.[16] Calcd. for $C_{16}H_{24}N_4O_4$: N, 15.55. Found: N, 15.54.

Spiro[5.6]dodecane. The hydrocarbon was prepared from crude 7-ketospiro[5.6]dodecane by the Huang-Minlon modification[11] of the Wolff-Kishner reaction. After careful fractional distillation through a column of forty theoretical plates and elution chromatography a 37% yield of high purity spiro[5.6] dodecane was obtained, n_D^{25} 1.4851, d_4^{20} 0.9031, M_D calcd. 53.24, found 52.98. Analysis by vapor phase chromatography indicated that the material was at least 99.9% pure.

Anal.[17] Calcd. for $C_{12}H_{22}$: C, 86.66; H, 13.34. Found: C, 86.43; H, 13.04.

An additional 8% of 99% pure and 8% of 97–98% pure spiro[5.6] dodecane were also obtained.

Acknowledgment. The authors express their appreciation to the American Petroleum Institute and the Esso Research and Development Company for the grants which made this research possible.

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(19) H. Christol, R. Jacquier, and M. Mousseron, *Bull. soc. chim. France*, 1053 (1957).

(20) E. E. Gruber and R. Adams, *J. Am. Chem. Soc.*, **57**, 2555 (1935).

(21) W. S. Johnson and G. H. Daub, *Org. Reactions*, VI, 42 (1951).