flask there was a light deposit of polymer, with a satisfactorily analysis (in the case of an experiment with deuterium oxide) for $(C_4D_4)_x$.

The reactions of the diene samples with maleic anhydride were conducted in tared screw-capped, 0.5 ounce bottles. The bottles were sealed with a short rubber stopper held in place with the cap in which a hole had been drilled for sampling and, occasionally, for charging with a needle and syringe. The reaction of butadiene (0.02 mole) of high purity was usually conducted with about 10% excess maleic anhydride and with low purity samples with at least 100% excess dienophile. For inhibiting polymerization 0.01 g. of picric acid and 0.01 g. of di-*n*-amylamine were added just prior to the addition of the sample which was usually charged last and at about −50°. The main reaction was allowed to start at about 30° behind a barricade. After the main part of the reaction, which is vigorous for high purity samples, had occurred the reaction was completed by heating in a 100° oven, usually for 1 hr. For recovery of unchanged hydrocarbon the bottle was evacuated to constant weight at room temperature to a refrigerated trap and the per cent of the sample reacted calculated as the butadiene content.

Acknowledgment. D. W. Beesing and Caroline A. McKalen carried out the vapor phase chromatography studies reported here; the mass spectrometry was done by E. H. Rowe and Dwain E. Diller. The support of these specialists often went beyond their particular skills.

BRECKSVILLE, OHIO

[CONTRIBUTION FROM THE CHEMICAL DIVISION, DENVER RESEARCH INSTITUTE, UNIVERSITY OF DENVER]

Heptyl and Nonyl Derivatives of Bicyclohexyl and *m*-Tercyclohexyl[1]

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The syntheses and properties of four alkylpolycyclohexyls are reported.

Work in this laboratory, resulting in the synthesis of many new alkylbiphenyls and alkylterphenyls, has made available a potential source of numerous alkylbicyclohexyl and alkyltercyclohexyl compounds. Accordingly we have synthesized gallon quantities of four new hydrocarbons for use as experimental fuels, namely, 4-*n*-heptylbicyclohexyl, 4-*n*-nonylbicyclohexyl, 4′-*n*-heptyl-*m*-tercyclohexyl, and 4′-*n*-nonyl-*m*-tercyclohexyl.

The literature contains only a few references to alkylbicyclohexyl compounds, the most extensive being the work of Goodman and Wise,[2] who prepared a series of 2-alkylbicyclohexyls by the hydrogenation of the corresponding 2-alkylbiphenyls. No alkyltercyclohexyls compounds have been reported.

The alkylbicyclohexyls were obtained by acylating biphenyl with the appropriate acid chloride according to the method of Long and Henze,[3] hydrogenating the resulting ketone to an alkylbiphenylylcarbinol, dehydrating the alcohol to the alkenylbiphenyl, and finally hydrogenating the alkenylbiphenyl to the desired alkylbicyclohexyl. As the acylation of biphenyl has been established as occurring in the 4-position,[4] the 4-alkylbicyclohexyls were thus prepared.

It is interesting to note that whereas the preparation of phenylmethylcarbinol by the hydrogenation of acetophenone can yield large amounts of ethylbenzene unless conditions are carefully controlled,[5] a similar reaction was not noted during the hydrogenation of 4-heptanoyl- or 4-nonanoylbiphenyl.

The alkyl-*m*-tercyclohexyls were prepared by the hydrogenation of the 4′-alkenyl-*m*-terphenyls, the preparation of which has already been described.[6]

The complete hydrogenation of alkylbiphenyls and alkylterphenyls to the desired alkylbicyclohexyls and alkyltercyclohexyls was difficult and was never accomplished in a single step. In practice, the alkenylpolycyclohexyl compound was hydrogenated until no more hydrogen was absorbed. The product showed evidence for incomplete saturation by a slight fluorescence under ultraviolet light irradiation and by the formation of a light red color when treated with aluminum chloride and chloroform, this color becoming more intense and shifting towards blue or purple as the degree of unsaturation increased. The product was rehydrogenated until the final hydrocarbon showed no ultraviolet light fluorescence and gave only a slight yellow color when treated with aluminum chloride and chloroform. It is estimated that the hydrogenation was at least 98% completed in the first step.

All of the four alkylpolycyclohexyl compounds prepared could exist in *cis-trans* configurations. However, no attempt was made to isolate the var-

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[1] This research was supported in whole by the United States Air Force under contract AF 33(600)-37474, monitored by the Propulsion Laboratory, Wright Air Development Division, Wright-Patterson Air Force Base, Ohio.

[2] I. A. Goodman and P. H. Wise, *J. Am. Chem. Soc.*, **73**, 850 (1951).

[3] L. M. Long and H. R. Henze, *J. Am. Chem. Soc.*, **63**, 1939 (1941).

[4] S. L. Silver and A. Lowy, *J. Am. Chem. Soc.*, **56**, 2429 (1934).

[5] V. N. Ipatieff and B. B. Corson, *J. Am. Chem. Soc.*, **61**, 3292 (1939).

[6] J. J. E. Schmidt, J. A. Krimmel, and T. J. Farrell, Jr., *J. Org. Chem.*, **25**, 252 (1960).

ious isomers. Examination by gas chromatographic analysis indicated that all of the compounds were of 99+% purity.[7]

Evidence for the existence of *cis-trans* isomers for the two bicyclohexyl derivatives could be seen from the gas chromatograph charts which showed two overlapping peaks. No isomer separation was noted for the alkyl-*m*-tercyclohexyl derivatives both showing but one peak.

EXPERIMENTAL[8]

4-n-Heptanoylbiphenyl.[9] To a well stirred slurry of 293 g. (2.2 moles) of anhydrous aluminum chloride and 750 ml. of carbon disulfide was added dropwise a solution composed of 328 g. (2.2 moles) of *n*-heptanoyl chloride and 308 g. (2.0 moles) of biphenyl dissolved in 750 ml. of carbon disulfide. The rate of addition was adjusted so as to maintain a gentle reflux. The addition required about 3 hr. The reaction mixture was stirred and refluxed for an additional 4 hr. After removing the carbon disulfide by distillation, the viscous red residue was poured into ice water with vigorous stirring. The yellow precipitate was filtered and washed with cold water until the washings were neutral. The product was vacuum dried at 50°. The crude product was distilled through a Vigreux column (25 × 600 mm.) to give 560 g. of 4-*n*-heptanoylbiphenyl, b.p. 194–195°/0.2 mm., m.p.[10] 85° (lit.[9] m.p. 85.5–86.5°), yield 95%, 2,4-dinitrophenylhydrazone, m.p.[10] 141°.

4-n-Nonanoylbiphenyl. In a similar manner, 308 g. (2.0 moles) of biphenyl was treated with 389 g. (2.2 moles) of nonanoyl chloride to form 410 g. of 4-*n*-nonanoylbiphenyl, b.p. 213–215°/0.4 mm., m.p.[10] 91°, yield 75%, 2,4-dinitrophenylhydrazone m.p.[10] 131.5°.

n-Hexyl-4-biphenylylcarbinol. 4-*n*-Heptanoylbiphenyl, 700 g. was hydrogenated in a 2-l. rocking autoclave,[11] using 25 g. of copper chromite catalyst (Harshaw Chemical Co.), for a period of 1 hr. at 175° and a minimum pressure of 1000 p.s.i. Approximately a quantitative yield of crude *n*-hexyl-4-biphenylylcarbinol was obtained. Usually the alcohol was dehydrated without further purification, however a sample was recrystallized from 95% ethanol, m.p. 55–57°.

n-Octyl-4-biphenylylcarbinol. In a similar manner, 4-nonanoylbiphenyl was hydrogenated to *n*-octyl-4-biphenylylcarbinol. A recrystallized sample (95% ethanol) melted at 40–42°.

4-n-Heptenylbiphenyl. Crude *n*-hexyl-4-biphenylylcarbinol, 1115 g. (4.16 moles) was heated with 40 g. of anhydrous copper sulfate. Dehydration began at a pot temperature of 145°, and continued for a period of 2 hr. during which time the pot temperature rose to 240°. Water was removed as formed, a total of 55 g. (73% of the theoretical amount) being collected. Additional water was lost through the condenser. The dehydration product was filtered through a layer of potassium carbonate. The crude olefin was distilled in a Vigreux column (20 × 120 mm.) to give 905 g. of 4-*n*-heptenylbiphenyl, b.p. 171–173°/0.2 mm., representing a yield of 87%.

Anal. Calcd. for $C_{19}H_{22}$: C, 91.14; H, 8.86. Found: C, 90.53; H, 8.64.

4-n-Nonenylbiphenyl. In a similar manner, *n*-octyl-4-biphenylylcarbinol, 1185 g. (4.0 moles), gave 990 g. of 4-*n*-nonenylbiphenyl, b.p. 184–185°/0.3 mm., representing a yield of 89%.

Anal. Calcd. for $C_{21}H_{26}$: C, 90.59; H, 9.41. Found: C, 90.43; H, 9.31.

4-n-Heptylbicyclohexyl. The hydrogenation of 4-*n*-heptenylbiphenyl for 8 hr. at 200°, using (Universal Oil Products) nickel catalyst and minimum pressures of 1000 p.s.i., gave approximately a quantitative yield of 4-*n*-heptylbicyclohexyl. Hydrogenation of the side-chain occurred during the heating process at about 125°, and hydrogenation of the biphenyl nucleus started at about 150°. At the completion of the hydrogenation, the product was filtered and tested with aluminum chloride and chloroform.[12] Usually a light red color, indicating incomplete hydrogenation, was obtained within 5 min. The product was returned to the autoclave and hydrogenated under the same conditions using fresh catalyst. After this treatment, a negative test (light yellow after 5 min.) with aluminum chloride and chloroform was obtained.

In a typical preparation, the second hydrogenation required 0.4 mole of hydrogen whereas the calculated amount of hydrogen to be absorbed for complete conversion of 4-*n*-heptenylbiphenyl into 4-*n*-heptylbicyclohexyl was 20.0 moles. Instead of a second hydrogenation, the incompletely hydrogenated material could be removed by passing the product through a silica gel column, the unsaturated material being retained on the column. In either case, the hydrocarbon was finally purified by fractional distillation using a vacuum jacketed column, 25 × 600 mm., packed with $^1/_8$″ multiturn glass helicies. Column b.p. 119°/0.3 mm., m.p. 24°, n_D^{25}1. 4765, d_{25}^{25} 0.8697, viscosities 18.8 cs./100° F., 2.96 cs./210° F. Infrared bands[7]: 2.38 (w), 3.48 (s), 3.71 (m), 6.89 (s), 7.21 (m), 7.40 (w), 7.90 (w), 10.20 (m), 10.50 (w), 11.21 (s), 11.79 (m), 13.81 (m) μ.

Anal. Calcd. for $C_{19}H_{36}$: C, 86.17; H, 13.83; mol. wt., 264.8. Found: C, 86.42; H, 13.52; mol. wt. 252.

4-n-Nonylbicyclohexyl. In a similar manner, the hydrogenation of 4-*n*-nonenylbiphenyl gave 4-*n*-nonylbicyclohexyl, column b.p. 138°/0.25 mm., n_D^{25} 1.4762–1.4764, d_{25}^{25} 0.8676, pour point 5° F. (at which temperature crystalline material is present),[13] viscosities 25.1 cs./100° F., 3.65°/210° F., heat of combustion 19,763 Btu./lb.[7] Infrared bands: 2.42 (w), 3.50 (s), 3.73 (m), 6.89 (s), 7.24 (m), 7.41 (w), 7.93 (m), 10.03 (w), 10.24 (w), 11.24 (s), 11.81 (w), 13.86 (s) μ.

Anal. Calcd. for $C_{21}H_{40}$: C, 86.22; H, 13.78; Mol. Wt. 292.5. Found: C, 86.54; H, 13.66; Mol. Wt. 285.

4′-n-Heptyl-m-tercyclohexyl. The hydrogenation of 4′-*n*-heptenyl-*m*-terphenyl,[6] using techniques already described and temperatures up to 230°, gave 4′-*n*-heptyl-*m*-tercyclohexyl, column b.p. 175°/0.3 mm., n_D^{25} 1.4939–1.4950,[13] d_{25}^{25} 0.9080, pour point 15° F., viscosities 257 cs./100° F., 11.1 cs./210° F., heat of combustion 19,450 Btu./lb. Infrared bands: 2.45 (w), 3.48 (s), 3.76 (m), 6.92 (s), 7.26 (m), 7.42 (m), 7.93 (m), 9.66 (w), 10.25 (m), 11.22 (m), 11.79 (m), 13.85 (m) μ.

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(7) We thank Messrs. G. E. Bohner, F. S. Bonomo, and W. D. Schnackenberg for the gas chromatographic and infrared analyses and the Paar oxygen bomb determinations of heats of combustion respectively.

(8) All melting points and boiling points are uncorrected unless otherwise noted. Microanalyses by Huffman Microanalytical Laboratories, Wheatridge, Colo.

(9) Although sufficient amounts of this and other compounds were prepared to furnish gallon quantities of the desired final hydrocarbon, only a smaller typical run is reported.

(10) Corrected m.p. determined on a Kofler microheating stage.

(11) For all hydrogenations, an American Instrument Co. rocking high pressure autoclave was used. By modifying this apparatus to rock at a rate of 11 cycles per minute, the time required for hydrogenation was greatly diminished.

(12) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, John Wiley & Sons, Inc., New York, Fourth Edition, p. 99, 1956.

(13) The indefinite melting point of this compound as as well as the refractive index range of this and other products are attributed to the presence of *cis-trans* isomers.

Anal. Calcd. for $C_{25}H_{46}$: C, 86.62; H, 13.38. Found: C, 86.87; H, 13.26.

4′-n-Nonyl-m-tercyclohexyl. In a similar manner, hydrogenation of 4′-*n*-nonenyl-*m*-terphenyl[6] gave 4′-*n*-nonyl-*m*-tercyclohexyl, column b.p. 188°/0.25 mm., n_D^{25} 1.4933–1.4937,[13] d_{25}^{25} 0.9044, pour point 15° F., viscosities 222 cs./100° F., 11.6 cs./210° F., heat of combustion 19,667 Btu./lb. Infrared bands: 2.41 (w), 3.48 (s), 3.73 (m), 6.90 (s), 7.24 (m), 7.40 (m), 7.92 (m), 9.64 (w), 10.23 (m), 11.20 (m), 11.78 (m), 13.84 (m) μ.

Anal. Calcd. for $C_{27}H_{50}$: C, 86.55; H, 13.45; Mol. Wt., 374.7. Found: C, 86.87; H, 13.28; Mol. Wt., 371.

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DENVER 10, COLO.

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

The Synthesis and Properties of Some α,β-Unsaturated Valerolactams[1]

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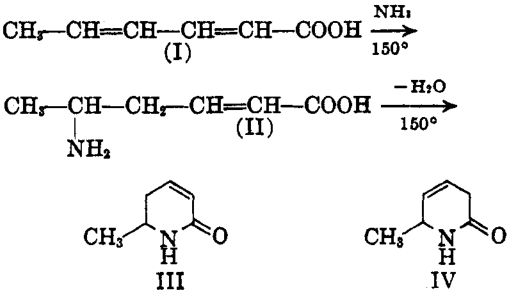
The condensation of sorbic acid (I) and 2-styrylacrylic acid (IX) with a variety of aliphatic and aromatic primary amines led to the formation of 1-substituted 6-methyl-5,6-dihydro-2-pyridone derivatives and 1-substituted 6-phenyl-5,6-dihydro-2-pyridone derivatives, respectively. Reduction of these cyclic lactams with lithium aluminum hydride, lithium aluminum hydride–aluminum chloride, or mixed aluminum hydrides yielded the corresponding substituted piperidines.

Fischer and Schlotterbeck[2] reported in 1904 that the condensation of sorbic acid (I) with ammonia led to the formation of an amino acid (II) which was isolated by means of its mercuric chloride complex. The free amino acid (II) upon heating readily eliminated water and cyclized to yield an unsaturated lactam (III) which had an analysis corresponding to C_6H_9NO. On the basis of a carbon hydrogen analysis, Fischer and Schlotterbeck assigned structure III to the lactam. No degradative studies were undertaken by them to ascertain the position of the double bond and, in a fairly recent review article, Mosher[3] assigned structure IV to the lactam.

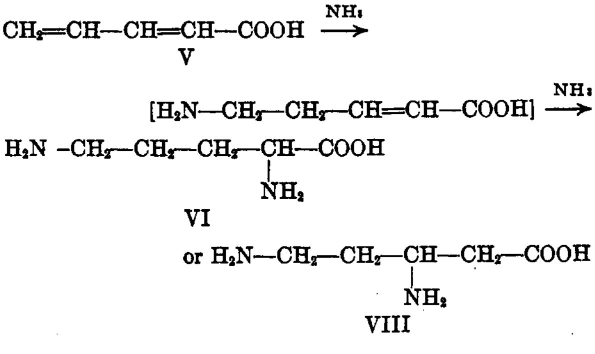


$$\underset{\text{(I)}}{CH_3{-}CH{=}CH{-}CH{=}CH{-}COOH} \xrightarrow[150^\circ]{NH_3}$$

$$CH_3{-}\underset{\substack{|\\ NH_2}}{CH}{-}\underset{\text{(II)}}{CH_2{-}CH{=}CH{-}COOH} \xrightarrow[150^\circ]{-H_2O}$$

III IV

In 1905, Fischer and Raske[4,5] also reported that the addition of ammonia to vinylacrylic acid (V) produced a diaminovaleric acid (VI). Subsequently, Riesser[6] claimed that the melting points of the mono- and dipicrates of the diaminovaleric acid (VI) corresponded to those of ornithine (VII). The structure of these products cannot be considered as definitely established, however, for there are substantial theoretical arguments that could predict that VI is actually 3,5-diaminovaleric acid (VIII).



$$\underset{\text{V}}{CH_2{=}CH{-}CH{=}CH{-}COOH} \xrightarrow{NH_3}$$

$$[H_2N{-}CH_2{-}CH_2{-}CH{=}CH{-}COOH] \xrightarrow{NH_3}$$

$$\underset{\text{VI}}{H_2N{-}CH_2{-}CH_2{-}CH_2{-}\underset{\substack{|\\ NH_2}}{CH}{-}COOH}$$

$$\text{or } \underset{\text{VIII}}{H_2N{-}CH_2{-}CH_2{-}\underset{\substack{|\\ NH_2}}{CH}{-}CH_2{-}COOH}$$

Finally, Riedel[7] reported that the methyl ester of 2-styrylacrylic acid (IX) does not react with amines or ammonia.

In the light of the confusion which existed in the literature concerning the 1,6-addition of amines and ammonia to doubly unsaturated conjugated acids it was of interest to repeat and enlarge the scope of the reported reaction of sorbic acid (I) with ammonia and extend it to 2-styrylacrylic acid (IX).

In the present investigation the method of Fischer and Schlotterbeck was slightly modified. Sorbic acid (I) was condensed with aqueous ammonia to yield the amino acid II which was cyclized, without isolation, to form the monoaddition product III. Little or no reaction occurred between sorbic acid (I) and ammonia at temperatures below 150°, and it was therefore necessary to employ a

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(1) This research was supported by Grant No. G5105 from the National Science Foundation.

(2) E. Fischer and F. Schlotterbeck, *Ber.*, **37**, 2357 (1904).

(3) H. S. Mosner, *Heterocyclic Compounds*, R. C. Elderfield, Editor, John Wiley and Sons, Inc., New York, N. Y., 1950, Vol. I, p. 651.

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(7) A. Riedel, *Ann.*, **361**, 96 (1908).