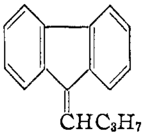
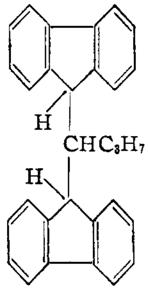
was obtained which had an unexpectedly low boiling point. It was identified as 9-butylidenefluorene[3a] by comparing with a sample prepared from 9-butylfluorenol by dehydrating with a mixture of concentrated hydrochloric and glacial acetic acids.

A second product of the reaction was a hydrocarbon $C_{30}H_{26}$ of m.p. 186–187°, which exhibited the spectrum of fluorene[4] (Fig. 1). It is assumed that this compound is 1,1-di-(9′-fluorenyl)-butane (III) and that it had been formed by a Michael reaction between 9-butylidenefluorene and excess fluorene. Such a reaction has been observed in the case of dibiphenylene ethylene and benzylidenefluorene[5]; it is made possible by the polar character of the semicyclic double bond in fulvenes and their benzologs.[3,6] As the central carbon atom of the fluorene system constitutes the negative end of these dipoles, it is likely that II adds fluorene to form III.

Whilst it was known that aldols[7] and ketols[8] revert to the constituent carbonyl compounds from which they are formed, no such reversion appears to be known generally for the α,β-unsaturated aldehydes and ketones which result from the dehydration of these aldols and ketols.[9] It must, therefore, be assumed, that either 2-ethylhex-2-enal (I) or its condensation product with fluorene, primarily formed, undergo hydration at the original α,β-double bond, followed by formation of two moles of butyraldehyde or one mole each of 9-butylidenefluorene (II) and butyraldehyde, respectively.



II



III

Experimental

9-Butylidenefluorene (II) (a) From 2-Ethylhex-2-enal (I).—A mixture of fluorene (33.2 g., 0.20 mole) and 2-ethylhex-2-enal (27 g., 0.21 mole) was refluxed azeotropically and with stirring for 6 hours with toluene (100 cc.) in the presence of freshly fused and powdered potassium hydroxide (14 g., 0.25 mole). A small amount (0.7 cc.) of water was liberated. The dark mixture was treated with water and the toluene layer separated, washed with dilute sulfuric acid and water and dried. High-vacuum distillation yielded fluorene (in the fraction b.p. 105–110° (0.08 mm., 11 g.) and a main fraction, b.p. 135–150° (0.08 mm.) (22 g.), which soon started to crystallize. By crystallization from hexane at low temperature, the crystalline part was isolated; yield 5 g. The m.p. (52°) was raised to 55° by recrystallization from alcohol. A second crop of 5 g. was obtained by evaporating the hexane mother liquor, dissolving the residue in alcohol and cooling the solution to −20°; the crystals formed were freed from adherent oil by washing with ice-cold alcohol.

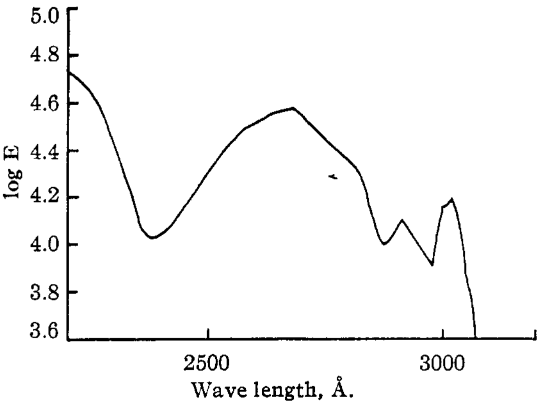


Fig. 1.—Absorption spectrum of the presumed 1,1-di-(9-fluorenyl)-butane in dioxane.

Anal. Calcd. for $C_{17}H_{16}$: C, 92.7; H, 7.3; mol. wt., 220. Found: C, 92.8; H, 7.4; mol. wt., 213 (Rast), 220 (benzene).

(b) A solution of fluorenone (8 g.) in ether (100 cc.) was added to the Grignard solution prepared from butyl bromide (6.4 g.) and magnesium (1.3 g.) in ether (75 cc.). The reaction product was refluxed for 30 minutes and decomposed by means of ice and ammonium chloride. The residue of the ether solution crystallized spontaneously (7 g., 66%). Recrystallization from alcohol gave **9-butylfluorenol**, m.p. 129–131°.[10]

Concentrated hydrochloric acid (2.5 cc.) was added to a boiling solution of 9-butylfluorenol (1 g.) in glacial acetic acid (12.5 cc.). The crystals formed on cooling were filtered, washed with water and alcohol and recrystallized from heptane; m.p. 55°. The products of the two syntheses (a) and (b) did not depress the melting points of each other.

9-Butylidenefluorene (III) is autoxidized easily, turning gradually yellow and soft and developing the odor of butyraldehyde.[11] No deterioration was observed in a sample kept under nitrogen for four months.

9-Butylidenefluorene dibromide was prepared in carbon tetrachloride and recrystallized from alcohol; m.p. 93–94°.

Anal. Calcd. for $C_{17}H_{16}Br_2$: Br, 42.1. Found: Br, 42.5.

1,1-Di-(9′-fluorenyl)-butane (III).—The residue of the distillation of the reaction product from fluorene and (I) (10 g.) was triturated with warm petroleum ether, which left a white powder (2.3 g.) undissolved, m.p. 183–186°. After recrystallization from heptane, it had m.p. 186–187°.

Anal. Calcd. for $C_{30}H_{26}$: C, 93.3; H, 6.7; mol. wt., 386. Found: C, 93.2; H, 6.3; mol. wt., 378 (benzene).

[3a] Schultz and Smullin, THIS JOURNAL, **62**, 2904 (1940).

[4] W. V. Mayneord and E. M. F. Roe, *Proc. Roy. Soc.* (*London*), **A158**, 634 (1937).

[5] L. A. Pinck and G. E. Hilbert, THIS JOURNAL, **68**, 2014, 2739 (1946): the structure of the condensation product with benzylidenefluorene has been determined by E. Bergmann and D. Lavie, *ibid.*, **74**, in press (1952).

[6] A. Pullman, G. Berthier and B. Pullman, *Bull. soc. chim. France*, 1097 (1950) (also for previous literature); E. Bergmann and E. Fischer, *ibid.*, 1084 (1950).

[7] See, *e.g.*, for acetaldol: Beilstein, 2nd Suppl., Vol. I, p. 868.

[8] See, *e.g.*, H. Hammarsten, *Ann.*, **421**, 293 (1920).

[9] L. Claisen (*Ber.*, **7**, 1168 (1879)) and C. Harries (*ibid.*, **32**, 1326 (1899)) have described the reversion of mesityl oxide to acetone by boiling dilute sulfuric acid and alkali, respectively.

[10] W. Schlenk, Jr., *Ber.*, **64**, 742 (1931).

[11] Compare, for 9-ethylidenefluorene: M. Daufresne, *Bull. soc. chim. France*, [4] **1**, 1233 (1907).

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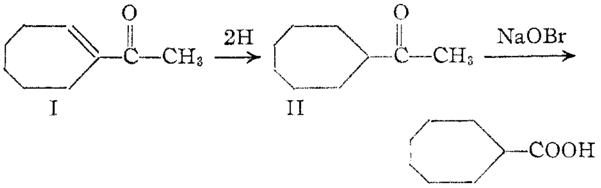
RECEIVED AUGUST 3, 1951

Synthesis of Acetylcycloheptene

BY WILLIAM TAUB AND JACOB SZMUSZKOVICZ

RECEIVED DECEMBER 10, 1951

In connection with experiments directed toward the synthesis of tricyclic compounds containing seven-membered rings, acetylcycloheptene (I) has been prepared by the condensation of cycloheptene and acetyl chloride in carbon disulfide in the presence of aluminum chloride; it is the only defined product of the reaction and is obtained in 22% yield, isolated as the semicarbazone. (I) had been previously prepared[1] by treatment of 1-ethinylcycloheptanol with formic acid; the reported ultraviolet spectrum of the product and the melting point of its semicarbazone are in good agreement with our observations. Friess and Pinson[2] have found that under the condition of Nenitzescu and Cioranescu[3] for the condensation between cycloheptene and acetyl chloride rearrangement and hydrogen transfer took place, and a mixture of acetylmethylcyclohexanes is obtained. The structure of (I) was, therefore, rigidly demonstrated. Hydrogenation led to acetylcycloheptane (II); the melting point of its semicarbazone agreed with that reported[2] for the product obtained through the reaction between cycloheptylmagnesium bromide and acetic anhydride.



Furthermore, hypobromite oxidation of (II) afforded cycloheptanecarboxylic acid which was characterized as its amide.

Experimental[4,5]

Cycloheptene was prepared by reduction of technical cycloheptanone[6] with aluminum isopropoxide,[7] and distillation at atmospheric pressure of the crude cycloheptanol over β-naphthalenesulfonic acid, b.p. 113–115° (756 mm.); yield 74%.

Acetylcycloheptene (I).—Aluminum chloride (166 g., 1.25 moles) was added in small portions over a period of 2.5 hours to a stirred solution of cycloheptene (120 g., 1.25 moles) and acetyl chloride (100 g., 1.27 moles) in 650 ml. of dry carbon disulfide. The temperature of the reaction mixture was maintained between −5 to 0°. Practically no hydrogen chloride was evolved. Stirring was continued for an additional hour at the same temperature; then the reaction mixture was poured into a vigorously stirred mixture of concentrated hydrochloric acid and crushed ice. The organic layer was washed with water and sodium bicarbonate solution and dried over calcium chloride. The solvent was evaporated and the residue distilled from 150 g. of anhydrous sodium carbonate at atmospheric pressure. The oil (75 g.) which came over at 208–215°, was distilled again from 50 g. of anhydrous sodium carbonate and yielded then 60 g. of a colorless liquid, b.p. 208–211° (756 mm.).

This product (57 g.) was treated with semicarbazide acetate and afforded 34 g. of a semicarbazone, melting at 194–195° (dec.) after two recrystallizations from ethanol; ultraviolet λ_{max} 264 mμ (log ϵ 4.39).

Anal. Calcd. for $C_{10}H_{17}N_3O$: C, 61.5; H, 8.8. Found: C, 61.5; H, 8.7.

A second crop of 17 g. (m.p. 188–190°) was isolated from the mother liquor.

Decomposition of the semicarbazone was carried out by refluxing with an aqueous solution of oxalic acid, b.p. 103.5° (20 mm.); ultraviolet λ_{max} 236 mμ (log ϵ 4.01); 308 mμ (log ϵ 1.66).

Anal. Calcd. for $C_9H_{14}O$: C, 78.3; H, 10.2. Found: C, 78.4; H, 9.9.

Acetylcycloheptane (II).—(I) (6.9 g.) was dissolved in 50 ml. of 95% ethanol and hydrogenated in the presence of 0.2 g. of 5% Pd–charcoal in an Adams hydrogenation apparatus. The theoretical amount of hydrogen was absorbed during 16 minutes. The mixture was filtered and concentrated to 10 ml. The semicarbazone was prepared as before; m.p. 177–178°; unchanged on recrystallization, yield 9.0 g. (97%).

Anal. Calcd. for $C_{10}H_{19}ON_3$: C, 60.9; H, 9.6. Found: C, 60.6; H, 9.3.

The semicarbazone (6.7 g.), oxalic acid (30 g.) and 150 ml. of water were refluxed for three hours, and the product worked up as usual. (II) (3.8 g., 80%) boiled at 101–102° (29 mm.).

Anal. Calcd. for $C_9H_{16}O$: C, 77.1; H, 11.5. Found: C, 77.3; H, 11.7.

Cycloheptanecarboxylic Acid.—The hypobromite oxidation of (II) was carried out according to the known procedure.[8] The alkaline reaction mixture was steam distilled, acidified and extracted with ether. The ethereal solution was washed with water, dried on sodium sulfate and evaporated. The resulting oily acid was converted into the acid chloride with thionyl chloride and the latter treated, without further purification, with a concentrated aqueous ammonia solution. The crude amide, m.p. 150–165°, was recrystallized from boiling water, which left some brown, oily impurity undissolved. The amide crystallized in large colorless plates, m.p. 191–193.5°. After one further recrystallization from water it melted at 193.5–194.5°.[9]

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[1] I. Heilbron, E. R. H. Jones, J. B. Toogood and B. C. L. Weedon, *J. Chem. Soc.*, 1827 (1949).

[2] S. L. Friess and R. Pinson, Jr., This Journal, **73**, 3512 (1951).

[3] C. D. Nenitzescu and E. Cioranescu, *Ber.*, **69**, 1820 (1936).

[4] All melting points are uncorrected.

[5] The ultraviolet absorption spectra were determined by Dr. Y. Hirshberg, with a Beckman quartz spectrophotometer; 95% ethanol was employed as solvent.

[6] Courtesy of Messrs. J. R. Geigy, Ltd., Basle.

[7] H. Lund, *Ber.*, **70**, 1520 (1937).

[8] L. T. Sandborn and E. W. Bousquet in "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 526.

[9] E. Buchner and A. Jacobi, *Ber.*, **31**, 2008 (1898); W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Ann.*, **560**, 1 (1948); R. Willstaetter, *Ber.*, **31**, 2498 (1898).

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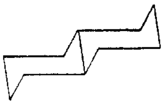
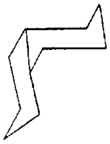
Energy Differences in the *cis*- and *trans*-Decalins

BY RICHARD B. TURNER

Barton's[1] semi-theoretical treatment of the non-bonded repulsive interactions in *trans*-decalin (I) and in the two constellations, II and III,[2] of *cis*-decalin gives I > II > III as the stability order of these forms. Uncertainties in van der Waals radius for hydrogen and in the magnitude of the repulsion term appearing in Barton's calculations, however, vitiate any quantitative estimate of the energy differences in this system, at least within an order of magnitude of ten. Thus, depending upon the choice of the above parameters, a series of values ranging from 0.52 to 8.23 kcal. was obtained for the energy difference between I and II. Estimation of the rotational barrier in ethane by the same procedure gave energy values, 0.09 to 0.39 kcal., appreciably lower than the gener-


I


II


III

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[1] D. H. R. Barton, *J. Chem. Soc.*, 340 (1948).

[2] Electron diffraction data of O. Bastiansen and O. Hassel, *Nature*, **157**, 765 (1946), verify II as the stable structure of *cis*-decalin. Structure III is therefore to be regarded as hypothetical.