phenyl isocyanate,[9] m.p. 85–86°, after recrystallization twice from petroleum ether. A known sample of cyclohexanol was similarly converted, m.p. 82–84°, mixed m.p. 82–84.5°.

6-(1-Hydroxycyclohexyl)-hexene-1.—By omitting the sodium bisulfite wash during the isolation of the crude alcohol mixture above, spontaneous dehydration was minimized, and it was possible to isolate two high boiling compounds. The first was a colorless liquid which weighed 15 g., b.p. 86° (0.125 mm.), $n^{25}\mathrm{D}$ 1.4774. It was tentatively identified as 6-(1-hydroxycyclohexyl)-hexene-1.

Anal. Calcd. for $C_{12}H_{22}O$: C, 79.05; H, 12.16. Found: C, 78.96; H, 12.19.

The second compound was a thick, colorless oil which slowly crystallized and which weighed 8.0 g., b.p. 125° (0.10 mm.). The crystalline material was recrystallized from ethyl acetate, then from ether, m.p. 97.5–99°. This compound has not been identified.

Anal. Calcd. for $C_7H_{14}O$: C, 73.63; H, 12.36. Found: C, 73.49, 73.56; H, 12.24, 11.95.

6-Ketoundecane-1,11-dioic Acid.—A mixture of 3.28 g. (0.02 mole) of IV, 40 ml. of acetone and 4 ml. of water was cooled in an ice-bath. Potassium permanganate (13.0 g., 0.85 mole) which had been previously ground to a fine powder was added to the stirred mixture over a period of four hours. The thick, brown paste was washed into a beaker with 100 ml. of water and treated with small portions of sodium bisulfite and concentrated hydrochloric acid until the solution cleared. A small amount (0.2 g.) of colorless solid was removed by filtration, m.p. 93–113°. The filtrate was extracted with two 150-ml. portions of ether and the ether was removed by evaporation. The solid residue (0.5 g. (11%), m.p. 109–114°) which remained was recrystallized twice from a mixture of chloroform and petroleum ether and twice from benzene, m.p. 113.2–113.8°; reported for 6-ketoundecane-1,11-dioic acid, m.p. 109°[3] and 111°.[4]

Anal. Calcd. for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88; neut. equiv., 115.1. Found: C, 57.63; H, 8.12; neut. equiv., 114.3.

6,13-Diketoöctadecane-1,18-dioic Acid, III ($m = 3$, $n = 6$).—II ($m = 3$, $n = 6$) (4.97 g., 0.02 mole) was oxidized in the same manner as described for IV and yielded 1.77 g. (25.8%) of a colorless solid, m.p. 125–131°. The product was recrystallized once from water, dried and digested with chloroform, m.p. 135–136°. An authentic sample of III ($m = 3$, $n = 6$),[2] m.p. 134–135°, was mixed with a portion of the product, mixed m.p. 136–137.5°.

1,6-Bis-(1-cyclopenten-1-yl)-hexane, II ($m = 2$, $n = 6$).—This compound was prepared in the same manner as described for II ($m = 3$, $n = 6$). Cyclopentanone (84 g., 1.0 mole, twice theoretical amount) was used as the ketone component. The crude mixture of alcohols was distilled, and the fraction boiling from 120–180° (4 mm.), (37.2 g.) was dehydrated over aluminum sulfate.

The crude product obtained after dehydration was fractionated through a 40-cm. Podbielniak column. II ($m = 2$, $n = 6$) was collected at 143–146° (4 mm), 6.6 g., $n^{25}\mathrm{D}$ 1.4980, 12.1% over-all yield.

Anal. Calcd. for $C_{16}H_{26}$: C, 88.00; H, 12.00. Found: C, 87.61; H, 11.67.

5,12-Diketohexadecane-1,16-dioic Acid, III ($m = 2$, $n = 6$).—II ($m = 2$, $n = 6$) (2.18 g., 0.01 mole) was oxidized in the same manner as described for IV. A colorless solid was obtained which weighed 1.5 g., m.p. 130–136°, 47.7%. The compound was recrystallized from water, methanol, ligroin and acetic acid, m.p. 142.2–143.4°; reported for III ($m = 2$, $n = 6$), m.p. 141–141.5°.[5] An authentic sample, m.p. 141.4–142.6°,[2] was mixed with a portion of product. The mixed m.p. was 141.2–142.6°.

1,10-Bis-(1-cyclohexen-1-yl)-decane, II ($m = 3$, $n = 10$).—This compound was prepared in the same manner as described for II ($m = 3$, $n = 6$). The di-Grignard reagent was prepared from 75.0 g. (0.25 mole) of 1,10-dibromodecane.[2] The crude mixture of alcohols was distilled with the expected partial dehydration, and the fraction boiling from 185–215° (4 mm.) (18.1 g.) was dehydrated over aluminum sulfate.

The crude product obtained after dehydration was fractionated through a 40-cm. Podbielniak column. Two fractions were collected: 2.5 g., b.p. 187–195° (2 mm.), $n^{25}\mathrm{D}$ 1.4900; 6.4 g., b.p. 195–198° (2 mm.), $n^{25}\mathrm{D}$ 1.4909. The over-all yield of II ($m = 3$, $n = 10$), based on these two fractions, was 11.8%.

Anal. Calcd. for $C_{22}H_{38}$: C, 87.34; H, 12.66. Found: C, 87.04; H, 12.65.

CAMBRIDGE, MASS.

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[9] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 226.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE GLIDDEN COMPANY—NAVAL STORES DIVISION]

Nopol. IV. Synthesis of 1(7),8-*p*-Menthadiene and 1(7)-*p*-Menthene

BY ROBERT L. WEBB AND JOSEPH P. BAIN

RECEIVED FEBRUARY 27, 1953

The alcohols, dipentene-7-carbinol and carvomenthene-7-carbinol, slowly decompose at their boiling points with loss of formaldehyde to form 1(7),8-*p*-menthadiene and 1(7)-*p*-menthene, respectively. The reverse reaction, condensation of the hydrocarbons with formaldehyde to form the carbinols, takes place in sealed tubes at 175°.

The condensation of β-pinene (I) and formaldehyde to form the dicyclic alcohol nopol (II) was recently shown to be reversible[1] under the influence of heat though the decomposition of nopol was complicated by its racemization and its simultaneous isomerization to the acyclic alcohol, alloöcimene-carbinol and the monocyclic alcohol, 1,8-*p*-menthadiene-7-carbinol (dipentene-7-carbinol) (III).

It is the purpose of this paper to report that 1,8-*p*-menthadiene-7-carbinol (III) also decomposes slowly near its boiling point at atmospheric pressure, and that there is formed formaldehyde and a hydrocarbon which has been identified as 1(7),8-*p*-menthadiene (pseudo- or ψ-limonene) (IV). Further, its partial reduction product, 1-*p*-menthene-7-carbinol (carvomenthene-7-carbinol) (V), decomposes similarly to yield 1(7)-*p*-menthene (VI). These decompositions are reversible since the hydrocarbons IV and VI may be caused to react with formaldehyde at 175° in sealed tubes to re-form the corresponding alcohols III and V.

The general applicability of this decomposition to the synthesis of compounds of structure $R^1(R^2CH_2)C{=}CH_2$ from carbinols of structure $R^1(R_2CH{=})C{-}CH_2CH_2OH$ and the reverse condensation of the olefin with formaldehyde to yield the carbinol has not yet been studied in a large number of cases, though other work in these laboratories has shown[2] that the reaction is applicable to the de-

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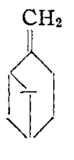
[1] J. P. Bain, A. H. Best and R. L. Webb, THIS JOURNAL, **74**, 429 (1952).

[2] Unpublished work.

composition of pyronene carbinols formed by cyclization of alloöcimenecarbinol.[1]

1(7),8-*p*-Menthadiene (IV) and 1(7)-*p*-menthene (VI) have been reported[3] as dehydration products of dihydro and tetrahydroperillyl alcohols, respectively. Both the method of synthesis employed and the physical properties reported for the hydrocarbons make the validity of that report most doubtful.

The identity of the hydrocarbon formed by thermal decomposition of 1,8-*p*-menthadiene-7-carbinol is indicated by its infrared spectrum which shows the presence of the $CH_2{=}C<$ grouping by the strong absorptions at about 6.1 and 11.3 μ. Further, the optical densities of these absorptions are roughly double those exhibited by compounds such as 1(7)-*p*-menthene (IV), limonene[1] and β-pinene[1] (I) which contain only one $CH_2{=}C<$ group thus indicating the presence of two such groups in IV. The hydrocarbon can therefore only be 1(7),8-*p*-menthadiene (IV) in the absence of a very highly improbable rearrangement. That no such unexpected rearrangement has taken place is evident from results of hydrogenation and isomerization experiments described below as well as by the fact that the hydrocarbon reforms the starting carbinol when treated with formaldehyde. As expected, IV shows no absorption maximum in the ultraviolet at wave lengths greater than 220 mμ.



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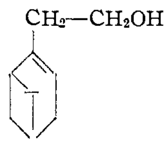

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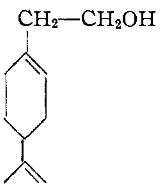

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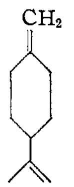

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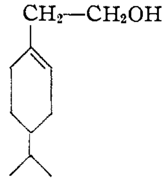

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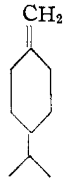
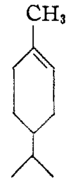


VI



VII

Attempts at selective hydrogenation of 1(7),8-*p*-menthadiene (IV) with one molar equivalent of hydrogen produced a mixture of unchanged IV and *cis*- and *trans*-*p*-menthanes. Neither 1(7)-*p*-menthene nor 8-*p*-menthene, both of which might be expected, could be detected. Complete hydrogenation yielded a mixture consisting of about equal parts of *cis*- and *trans*-*p*-menthane.

Under mild isomerization conditions 1(7),8-*p*-menthadiene yielded 1,8-*p*-menthadiene (dipentene) as expected. More vigorous isomerization produced in addition those isomeric *p*-menthadienes which are more stable under acidic conditions, α-terpinene, γ-terpinene and 2,4(8)-*p*-menthadiene as well as cymene.

The conversion of nopol to 1,8-*p*-menthadiene (dipentene) may be performed in a single operation by heating nopol with a very mild isomerizing agent to about 250°. Such a mild isomerizing agent is rosin which is known[4] to cause the shift of the double bond in β-pinene into the ring to form α-pinene without otherwise affecting the molecule. When nopol is heated with rosin at 250°, apparently thermal isomerization of nopol first occurs then the 1,8-*p*-menthadiene-7-carbinol (III) formed decomposes to 1(7),8-*p*-menthadiene which isomerizes in the presence of the rosin to 1,8-*p*-menthadiene (dipentene).

The structure of the hydrocarbon produced by thermal decomposition of 1-*p*-menthene-7-carbinol (V) is indicated by its infrared spectrum which shows the presence of a single $CH_2{=}C<$ grouping by measurement of the optical density of the bands characteristic of this grouping at 6.1 and 11.3 μ. Identification of the hydrocarbon as 1(7)-*p*-menthene was completed when it was isomerized readily to 1-*p*-menthene (carvomenthene) (VII) and also was caused to react with formaldehyde to reform 1-*p*-menthene-7-carbinol (V).

Experimental

Spectra.—Infrared spectra of the homogeneous compounds and the reaction products involved in this work were recorded using a Perkin-Elmer 12-C instrument equipped with sodium chloride optics. Characteristic absorption bands for IV, VI and VII are listed in the appropriate sections below. Strong bands are indicated by (S) following the wave length at which the band occurs. Spectra of these compounds as recorded with a Baird spectrophotometer are available from Samuel Sadtler & Son, Philadelphia.

1(7),8-*p*-Menthadiene (IV).—To a flask equipped with a short Claisen type distilling head, there was added 680 g. of 1,8-*p*-menthadiene-7-carbinol (III).[1] Upon heating to boiling, initially about 265°, the carbinol slowly decomposed with appearance of solid paraformaldehyde. The rate of heating was maintained so that the temperature of the distilling material remained at about 170 to 180° throughout the slow decomposition. There was required a total of about 30 hours of heating which was conducted intermittently over a period of four days. At the end of this time, there remained in the pyrolysis flask only 89 g. of a resinous material which solidified on cooling. The paraformaldehyde was filtered from the distillate. The crude IV weighed 493 g. (88% of theory) and contained only traces of III and other impurities. It was fractionated at 10:1 reflux at 100 mm. pressure through a 75 by 2.5 cm. Stedman column to provide pure IV as fractions possessing almost constant physical properties including infrared spectra, b.p. 105° at 100 mm., $n^{25}D$ 1.4714 and d^{27}_4 0.8301. Characteristic infrared absorption bands occur at 6.08(S), 8.42, 9.21, 9.69, 10.03, 10.44, 11.26(S), 12.09 and 12.37 μ.

All fractions had an absorption peak in the ultraviolet region at 232 mμ and the maximum extinction coefficient ($\alpha = E^{g/l.}_{1\ cm.}$) of the fractions in isoöctane varied from about 2 to 0.3 without noticeable variation in the infrared spectra of the samples. The material absorbing in the ultraviolet was therefore an impurity and probably did not exceed about 1% in the better fractions. This impurity, a conjugated diene, is thought to be a pyronene resulting from loss of formaldehyde from a pyronene carbinol present as an impurity in the III used.

To a solution of 5 g. of IV in 15 ml. of chloroform there was added bromine at such a rate that the temperature did not exceed 30° and until free bromine was evident by the color of the solution. About 92% of the bromine required for two double bonds was absorbed. Storage of the solution for two days at −20° produced no crystalline bromides nor when the solvent from part of the solution was evaporated could crystalline bromides be obtained from the resulting oil even after storage for several days at −20°.

Hydrogenation of 1(7),8-*p*-menthadiene (IV) with platinum oxide catalyst at room temperature and 20 to 40 pounds

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[3] M. A. Iskenderov, *J. Gen. Chem.* (*USSR*), **7**, 1435 (1937); *C. A.*, **32**, 126 (1938).

[4] G. Austerweil, *Bull. soc. chim. France*, **39**, 1643 (1926).

pressure yielded a mixture shown by infrared analysis to consist of approximately 50% unchanged IV, 25% *cis-p*-menthane and 25% *trans-p*-menthane when only enough hydrogen was absorbed to correspond to one double bond. When IV was fully saturated with hydrogen, the product was a mixture of *cis*- and *trans-p*-menthanes in about equal parts. The hydrogen required for complete saturation was 2.0 moles per mole of IV.

Isomerization of 1(7),8-*p*-Menthadiene (IV). (A) With Rosin.—A mixture of 75% by weight gum rosin and 25% IV was heated at reflux, about 195–205°, for nine hours. The volatile oil was then steam distilled and infrared analysis showed it to consist of 54% 1,8-*p*-menthadiene, the remainder being unchanged IV.

(B) With Clay.—When 5 ml. of IV was heated at reflux with 50 mg. of 30/60 mesh Florex-S[5] there was obtained a mixture which was shown by infrared analysis to consist of 20% cymene, 5% dipentene, 2% 2,4(8)-menthadiene, 2 to 4% α-terpinene, 2 to 4% γ-terpinene and traces of other volatile products. The remainder consisted of high boiling polymeric material.

Conversion of nopol to 1,8-*p*-menthadiene was accomplished by heating a mixture of 350 g. of gum rosin and 166 g. nopol at 250–260° for 4 hours. The volatile oil obtained on steam distillation weighed 77 g. and infrared analysis showed that it consisted of about 80% 1,8-*p*-menthadiene and 20% alcohols. The resinous non-volatile residue possessed a softening point of 79° (Ball and Ring Method, A.S.T.M. Designation: E28-42T) and acid number 123.

Condensation of 1(7),8-*p*-menthadiene (IV) with formaldehyde was accomplished by heating equimolar quantities of IV and paraformaldehyde in a sealed tube at 175° for 4 hours. The infrared spectrum of the product could not be analyzed because of the strong blanketing influence on the spectrum of unreacted formaldehyde or its hemiformals with the alcohol formed. The product was therefore refluxed with excess aqueous 50% sodium hydroxide and ethylene glycol at 150° for one hour. Extraction of this reaction product with pentane and evaporation of the pentane produced a sample of oil free of formaldehyde which was shown by infrared analysis to consist of a mixture of 35 to 40% III and 60 to 65% unreacted IV.

1(7)-*p*-Menthene (VI) was obtained on heating 74 g. of V[1] at atmospheric pressure and 245–314° for about 8 hours a day for 10 days and employing the same type of equipment as for the preparation of IV. The decomposition of V was considerably slower than in the case of III. Aside from paraformaldehyde, there was obtained as distillate 27 g. (44% of theory) of crude VI of 90% or higher purity. It was purified by fractionation, the purest fraction as judged by infrared analysis boiled at 174° at 760 mm. pressure, and showed $n^{25}\text{D}$ 1.4575, d^{25}_4 0.8212. Bromine titration showed the presence of one double bond (88.6% of theory), but a crystalline bromide could not be obtained employing the same procedure as was employed for IV. Examination of the infrared spectrum shows VI to contain the characteristic $CH_2{=}C<$ absorptions at about 6.1 and 11.3 μ, but of only about one-half the optical density of those possessed by IV. Infrared absorption bands characteristic of VI include those occurring at 6.08(S), 8.98, 9.37, 9.62, 9.85, 10.07, 10.22, 11.07, 11.26(S) and 12.52 μ.

Isomerization of 1(7)-*p*-menthene (VI) was accomplished by heating about one ml. of the hydrocarbon with about 10 mg. of 30/60 mesh Florex-S[5] brand fuller's earth at reflux for 30 minutes.

Infrared analysis of the filtered, isomerized sample showed it to contain about 80% 1-*p*-menthene (VII) and 20% unchanged VI. Infrared absorption bands characteristic of VII include those occurring at 9.82(S), 10.18, 10.39, 10.50, 10.98(S), 11.66, 12.50(S), 12.73 and 13.16 μ.

Condensation of 1(7)-*p*-menthene (VI) with formaldehyde and removal of unreacted formaldehyde from the reaction product was accomplished by the same procedure outlined for synthesis of III. The formaldehyde-free reaction product was shown by infrared analysis to consist of 50 to 55% V and 45 to 55% unreacted VI.

JACKSONVILLE, FLORIDA

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[5] Floridin Company, Warren, Pennsylvania.

[CONTRIBUTION FROM THE SCIENTIFIC DEPARTMENT, ISRAELI MINISTRY OF DEFENCE]

Syntheses of Macrocyclic Compounds

BY ERNST D. BERGMANN AND ZVI PELCHOWICZ[1]

RECEIVED MARCH 16, 1953

The reaction between lithium phenyl and 2,2′-bis-(bromomethyl)-diphenylmethane and -dibenzyl leads to about equal parts of polymeric materials and 1,2,4,5,8,9,11,12-tetrabenzocyclotetradeca-1,4,8,11-tetraene and 1,2,5,6,9,10,13,14-tetrabenzocyclohexadeca-1,5,9,13-tetraene, respectively. By successive treatment of the latter with NBS and pyridine, *all-trans*-1,2,5,6,9,10,13,14-tetrabenzocyclohexadeca-1,3,5,7,9,11,13,15-octaene, a colorless hydrocarbon, was obtained. The three macrocyclic compounds are strainless but not planar. The mechanism of the synthesis is discussed. Reaction of 2-benzylbenzyl bromide with lithium phenyl gives 2,2′-dibenzyldibenzyl, reaction of 2-(*o*-methylbenzyl)-benzyl bromide with lithium phenyl 2,2′-di-(*o*-methylbenzyl)-dibenzyl. The formation of an olefin by successive treatment of an ethane with NBS and pyridine appears to be characteristic for *sym*-diarylethanes. Thus, also 2,2′-dibenzyldibenzyl is converted into 2,2′-dibenzylstilbene (*cis*-form), 1,1,2,2-tetraphenylethane into tetraphenylethylene.

The removal of the bromine atoms from 2,2′-bis-(bromomethyl)biphenyl (I) by means of lithium phenyl[2] leads to dihydrophenanthrene (II), thus to intramolecular cyclization. The question arose whether analogously 2,2′-bis-(bromomethyl)-diphenylmethane (III) or -dibenzyl (V) would permit the synthesis of seven- and eight-membered ring systems such as 1,2,4,5-dibenzocyclohepta-1,4-diene (IV) and 1,2,5,6-dibenzocycloöcta-1,5-diene (VI). This did not seem impossible in spite of the greater spatial mobility of III and V as compared with I; according to Wittig and Witt,[3] the above synthesis would proceed in the case of I *via* an organo-lithium compound of the structure VII which evidently attracts preferentially the bromine atom *in the same molecule*, an effect which could well be anticipated also in the case of the analogous derivative of III or V. Moreover, the synthesis of VI from V would be analogous to its formation from *o*-xylylene dibromide and metallic sodium.[4]

As a model experiment, the reaction of lithium phenyl with 2-benzylbenzyl bromide (X) was studied. The latter was synthesized by reduction of methyl 2-benzylbenzoate (VIII) with lithium

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[1] Part of a Thesis submitted by Z. Pelchowicz to the Hebrew University, Jerusalem, in partial fulfillment of the requirements for the degree of Ph.D.

[2] D. M. Hall and E. E. Turner, *Nature*, **163**, 537 (1949); D. M. Hall, S. M. Lesslie and E. E. Turner, *J. Chem. Soc.*, 711 (1950); D. M. Hall and E. E. Turner, *ibid.*, 3072 (1951); E. Bergmann and J. Szmuszkowicz, THIS JOURNAL, **73**, 5153 (1951); E. Bergmann and Z. Pelchowicz, *ibid.*, **75**, in press (1953).

[3] G. Wittig and H. Witt, *Ber.*, **74**, 1474 (1941).

[4] W. Baker, R. Banks, D. R. Lyon and F. G. Mann, *J. Chem. Soc.*, 27 (1945).