[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, REED COLLEGE]

The Structure of Lagidze's Cyclobutadiene Derivatives. Part II.[1] The Hydrocarbon Produced in the Reaction of 2,5-Diacetoxy-2,5-dimethyl-3-hexyne with Benzene in the Presence of Aluminum Chloride[2]

BY J. E. H. HANCOCK AND DORIS R. SCHEUCHENPFLUG

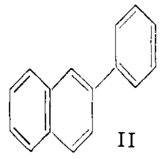
RECEIVED JANUARY 23, 1958

The hydrocarbon obtained by the reaction indicated is shown to possess the structure IX, and not that of the benzocyclobutadiene derivative XII. Some discussion of the mechanism of formation is included.

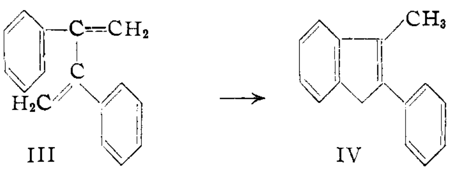
A possible pathway by which benzene, aluminum chloride and I might react to give 2-phenylnaphthalene (II) was outlined very briefly in part I of this series. The details of the mechanism of this reaction have been discussed in preliminary fashion elsewhere,[3] and an experimental investigation of the postulated conversion of 2-phenyl-3-methylindene (IV) to II, together with a complete discussion of the mechanism will constitute part III of this series. It will be recalled that the intermediary formation of 2,3-diphenylbutadiene (III) was postulated to be responsible for the chain of events leading to the final production of II in the studies described earlier.

$CH_3COOCH_2C\equiv CCH_2OCOCH_3$

I



II

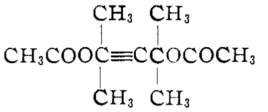


III IV

The present paper describes the reaction carried out with the tetramethyl analog V of I, to give a hydrocarbon $C_{20}H_{22}$, m.p. 83°, the structure of which has been alleged[4] to be XII. Following the previous case, an intermediate VI may be postulated, or some species closely resembling it, and a Lewis acid L may attack this at a benzyl position, to produce VII, which may then cyclize to VIII by elimination of a proton. If two such operations take place, IX is formed: thus either or both of the hydrocarbons IX and X would be expected as products of the reaction.[5]

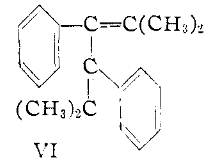
Amongst other possibilities entertained at the outset was XI, arising from the attack of L at the carbon atom bearing the *gem*-dimethyl group.

It was possible to check some of the alternatives presented by this reasoning. Compounds with structures IX, X and XI have been reported, and melting points and ultraviolet data are available.[6]

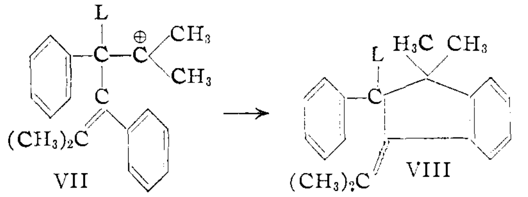


$$CH_3COO\overset{CH_3}{\underset{CH_3}{C}}\equiv C\overset{CH_3}{\underset{CH_3}{C}}OCOCH_3$$

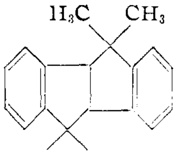
V



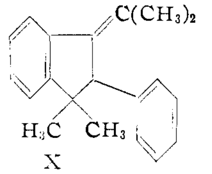
VI



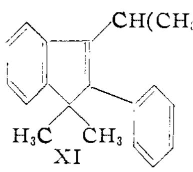
VII VIII



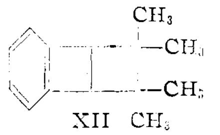
IX



X



XI



XII

Comparison of the relevant data suggested to us that the 83° hydrocarbon described by Lagidze and Loladze was most probably identical with Wright's hydrocarbon, the structure of which was presumably IX; the Russian workers had suggested the structure XII for their hydrocarbon. A sample of the 83° hydrocarbon kindly furnished by Professor Wright (and prepared by his synthesis) did not depress the m.p. of that prepared by Lagidze's synthesis. The ultraviolet absorption data were in good accord, and finally the infrared spectra in carbon tetrachloride were identical.

Even with this information, it was still possible to write an alternative structure, XIII, for the 83° hydrocarbon. This was derivable from VIII as follows: the analogy to part I—production of 2-phenylnaphthalene from a possible tetradesmethyl (VIII)—may be clearly seen.

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[1] Part I, J. E. H. Hancock and Harry W. Taber, *Tetrahedron*, in press (1958): *cf.* also J. E. H. Hancock, H. W. Taber and Doris R. Scheuchenpflug, *Chemistry & Industry*, 437 (1958).

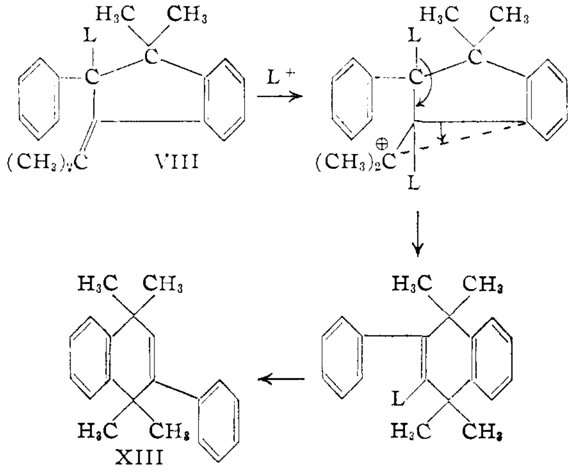
[2] Presented at the 133rd Meeting of the American Chemical Society in San Francisco, Calif., April, 1958.

[3] Harry W. Taber, B.A. thesis, Reed College, 1957.

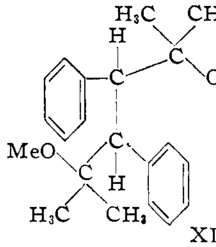
[4] R. M. Lagidze and N. R. Loladze, *Soobshchenya Akademii Nauk Gruzin. S.S.R.*, **16**, 607 (1955); *C. A.*, **50**, 11960b (1956). These workers ascribed a molecular formula $C_{14}H_{16}$ to this hydrocarbon. Compare reference 1.

[5] It may be noted that the stereochemistry in IX about the carbon–carbon bond common to the two five-membered rings is most probably *cis*, since cyclization in this fashion is sterically far easier than for a *trans* product (compare cyclizations carried out in base, J. W. Barrett and R. P. Linstead, *J. Chem. Soc.*, 436 (1935); C. T. Blood and R. P. Linstead, *ibid.*, 2255 (1952)). This has proved to be important in explaining the nuclear magnetic resonance spectrum of the hydrocarbon.

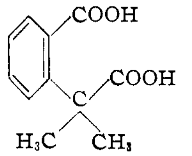
[6] J. G. Smith and G. F Wright, *Can. J. Chem.*, **32**, 729 (1954).



This structure (XIII) would also not be inadmissible for the product of Wright's synthesis, which essentially consisted of the cyclization of XIV in liquid HF or concentrated sulfuric acid.



XIV



XV

The problem therefore narrowed down to a choice between structures IX and XIII for the 83° hydrocarbon. The latter, according to the Canadian workers, furnishes XV on oxidation with chromic acid, and is resistant to the action of perbenzoic acid, ozone, and to hydrogen over Raney nickel at 80° and 100 atm. pressure. Some of these data could have been ascribed to steric hindrance, but the balance was in favor of IX.

The final convincing piece of evidence was the fact that the nuclear magnetic resonance spectrum of the hydrocarbon showed peaks at much too high a frequency for those corresponding to a hydrogen atom in a vinyl position, as is possessed by XIII: two peaks were found corresponding to hydrogens in methyl groups, and this may be explained by the fact that in models of IX two methyl groups are directed essentially in the plane of the molecule taken as a whole, while the other pair is almost perpendicular to this plane, much as axial and equatorial bonds in the cyclohexane series are directed. We interpret the two peaks mentioned above to this difference in the environment of the hydrogen atoms in the methyl groups. There was also present in the spectrum one peak not misplaced for tertiary allylic hydrogen, and one corresponding to hydrogens attached to an aromatic ring.

We feel that IX expresses the necessary structural elements to explain all these data better than any other so far advanced.

Experimental

Melting points are uncorrected.

2,5-Diacetoxy-2,5-dimethyl-3-hexyne (V).—(1) The corresponding diol was acetylated with acetic anhydride in pyridine–benzene using the method described in part I. The yield of diacetate was rather poor (27%) and no diol could be recovered, despite careful evaporation of all aqueous liquors involved; b.p. 106–107° (18 mm.), $n^{20}\text{D}$ 1.4458. The diacetate was a clear, colorless liquid with a viscosity somewhat less than that of glycerol at room temperature.

(2) Acetylation of the diol was carried out with acetyl chloride in pyridine–benzene at 5°; yield of diacetate 54%, b.p. 105.5° (16 mm.), $n^{19}\text{D}$ 1.4430.

(3) A commercial sample of V which had been prepared by treatment of the corresponding diol with isopropenyl acetate and sulfuric acid[7] was received as a mobile liquid with a rather sharp odor: the color and odor were still present after fractionation[8] (b.p. 105° (16 mm.), $n^{20}\text{D}$ 1.4482).

Hydrolysis of the Diacetate V to the Diol.—Owing to the above discrepancies in the properties of samples of diacetate prepared by different methods, a mild basic hydrolysis of this ester was carried out. Treatment of the diacetate (prepared by method 2, above) with a slight excess of sodium hydroxide solution at room temperature gave a quantitative yield of the original diol, m.p. and mixed m.p. 95–96°.

Condensation of 2,5-Diacetoxy-2,5-dimethyl-3-hexyne (V) with Benzene in the Presence of Aluminum Chloride.—Using the general method described in part I, 40.0 g. of the diacetate (prepared by method 1, above) was added slowly, with stirring at 10°, to a suspension of freshly-sublimed aluminum chloride (47.1 g.) in benzene (Baker reagent grade, redistilled, 150 g.). The mixture became yellowish-orange, and later dark red in color. The addition of the diacetate required 80 minutes; the very viscous, almost jelly-like dark brown mixture was gradually warmed to 76° (thermometer in liquid) over a period of 3 hours (much HCl evolved) and held at this temperature for 7 hours. After this time the cooled mixture was slowly siphoned into a stirred mixture of ice (200 g.) and 2 *N* hydrochloric acid (250 cc.). The resulting system (dark blue-green top layer and a mustard-yellow aqueous layer) was separated, the aqueous layer extracted with ether (5 × 50 cc.) and the combined ether and benzene extracts washed with 10% sodium bicarbonate solution (4 × 100 cc.) and saturated sodium chloride solution (2 × 25 cc.). The organic layer was dried ($MgSO_4$) under nitrogen, filtered, and concentrated at room temperature on the water aspirator.

The remaining dark green oil was distilled to give two fractions: (1) 1.7 g., b.p. 78–124° (0.1 mm.); (2) 3.03 g., b.p. 126–129° (0.1 mm.). Much dark tarry residue remained.

On standing at 0° for several days, fraction 2 deposited crystals on the stopper of the flask. Both fractions were seeded and kept at 0° for one week, after which centrifugation (Skau tube) gave 1.74 g. of solid from fraction 1 and 1.2 g. from fraction 2; recrystallization of the latter from 2 cc. of ethanol (Skau tube) gave 1.1 g. of crystals, m.p. 65–76°. After two further similar recrystallizations, 1.0 g. of prisms, m.p. 81.5–83.4°, was obtained; mixed m.p. with the sample provided by Professor G. F Wright, 81.5–83.1°, m.p. of Wright's sample 80.8–81.4°. The yield of crude hydrocarbon amounted to 7%.

In a second attempt, no solid was obtained. This behavior is reminiscent of that in part I, where the fifth attempt was the first successful one.

Infrared Spectra of IX.—The spectra were run in carbon tetrachloride solution, using a micro-cell and a Perkin–Elmer model 21 infrared recording spectrophotometer. The following peaks were observed: the figures given refer to wave lengths in μ, and the intensities of absorption are indicated by the abbreviations s = strong, m = medium, w = weak; 3.4(s). 6.3(w), 6.74(s), 6.86(s), 7.23(s), 7.33(s), 7.56(w), 7.70(w), 7.77(m-s), 7.96(w), 8.11(w), 8.37(w), 8.51(w), 8.66(w), 8.84(w), 8.97(w), 9.23(m-s), 9.75(s), 10.68(w), 11.31(w), 14.5(w). The spectra of the hydrocarbon prepared by Wright's method and Lagidze's method were identical. There was also some evidence of the presence of a large peak near 13.0 μ; a spectrum run in carbon disulfide showed a very strong peak at 13.23 μ, with associated peaks at 13.41(s) and 13.59(w) μ.

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(7) Air Reduction Chemical Co., New York: new product data.

(8) A separate investigation into the nature of this material is in progress.

Nuclear Magnetic Resonance Spectrum of IX.—The sample used had been prepared by Lagidze's method, and the determination was carried out by Professor W. von E. Doering and Dr. Martin Saunders, Yale University, on a Varian model V-4300B high resolution nuclear magnetic resonance spectrometer. There were clearly four types of hydrogen: using benzene as a reference, there was one peak at −20 cycles corresponding to hydrogens attached to an aromatic ring, one smaller peak at 130 cycles (tertiary allylic hydrogen) and two of essentially equal area at 210 and 240 cycles, which appear to be due to the hydrogens in the methyl groups, two of which in models jut out in the plane of the molecule; the two remaining ones are essentially perpendicular to the latter, using a model with a *cis* ring junction in the center.

Acknowledgments.—We wish to thank several people for their most useful assistance: Professor W. von E. Doering, Dr. Horst Prinzbach and Dr. Martin Saunders, Yale University, and Mr. W. J. Potts, Spectroscopy Laboratories, The Dow Chemical Co., Midland, Mich., kindly determined the nuclear magnetic resonance spectra and the infrared spectra; we also thank them for discussions regarding this material. Professor R. M. Lagidze, Tbilisi State University, Georgia, U.S.S.R. has most kindly made several manuscripts available to us, including the ultraviolet absorption spectrum of the 83° hydrocarbon. The Air Reduction Chemical Co. of New York generously donated a large quantity of 2,5-dimethyl-3-hexyne-2,5-diol and a sample of the diacetate prepared according to reference 7. The project has been financially supported by the Research Corporation of New York, to whom we are greatly indebted.

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Grignard Reagents and Unsaturated Ethers. VI. The Cleavage of Diallyl Ethers by Aliphatic and Aromatic Grignard Reagents

BY CARL M. HILL, LONNIE HAYNES, DORIS E. SIMMONS AND MARY E. HILL

RECEIVED JANUARY 13, 1958

The behavior of several diallyl ethers toward aliphatic and aryl Grignard reagents has been investigated. Ethyl-, *n*-butyl- and phenylmagnesium bromides cleave allyl 2-allylphenyl ether and γ-phenyl-γ'-methyl diallyl ether to yield normal cleavage products. *n*-Butyl-, *t*-butyl- and phenylmagnesium bromides cleave diallyl ether to give both normal and abnormal cleavage products.

Previous papers[1,2] have shown that Grignard reagents at the reflux temperature of diethyl ether react with unsubstituted and alkyl and aryl substituted allyl ethers to yield olefins, alcohols and phenols. Formation of these products might be explained on basis of 1,2- and 1,4-addition or various combinations of the S_N2, S_N2′ and S_N1 mechanisms. Because of the relatively high reactivity of the allyl system, it was postulated that the presence of two allyl groups might impart to the ether molecule additional reactivity. Further, it was anticipated that the reaction of such an ether molecule with tertiary and primary alkyl and aryl Grignard reagents might yield products unlike those obtained from unsaturated ethers which contain only one allyl group. This prediction has been borne out by experiment. When diallyl ether was allowed to react with *n*-butylmagnesium bromide, the reaction products were propenal (8%), allyl alcohol (55%) and 1-heptene (24%). The two latter products would be expected if the Grignard reagent cleaved the ether by a 1,2-addition mechanism. The propenal appears to be an abnormal cleavage product. An obvious source of the propenal would be the allyl alcohol. However, the fact that the reaction of diallyl ether with phenylmagnesium bromide gave a 16% yield of propenal and that all reactions were carried out under an atmosphere of nitrogen suggest propenal to be a product resulting from interaction of the ether and the Grignard reagent. Moreover, when a freshly distilled sample (30 g.) of allyl alcohol was dissolved in 150 ml. of dry diethyl ether and treated under experimental conditionss imilar to those used in the reaction of diallyl ether with *n*-butylmagnesium bromide, only 0.5 ml. of propenal was isolated.

$$CH_2{=}CHCH_2OCH_2CH{=}CH_2 + n\text{-}C_4H_9MgBr \longrightarrow CH_2{=}CHCHO + CH_2{=}CHCH_2OH + CH_2{=}CH(CH_2)_4CH_3$$

From the reaction of *t*-butylmagnesium bromide with diallyl ether various products were obtained. The nature and number of the reaction products seem to depend upon length of the heating period. For example, when the reaction was heated two hours, 4,4-dimethyl-1-pentene (7.5%), allyl alcohol (56%), 1-*t*-butoxy-1-propene (5%) and propylene were isolated; when heated 24 hours, 4,4-dimethyl-1-pentene (10%) and allyl alcohol (60%) were the reaction products.

$$\begin{tikzcd}
CH_3C(CH_3)_2CH_2CH{=}CH_2 + CH_2{=}CHCH_2OH \\
(CH_2{=}CHCH_2{-})_2O + t\text{-}C_4H_9MgBr \arrow[u, "24\text{ hr.}"'] \arrow[d, "2\text{ hr.}"] \\
CH_3C(CH_3)_2CH_2CH{=}CH_2 + CH_2{=}CHCH_2OH + CH_3CH{=}CH_2 + CH_3CH{=}CHOC(CH_3)_3
\end{tikzcd}$$

Formation of the propylene and *t*-butoxy-1-propene could result from an abnormal reaction of *t*-butylmagnesium bromide with diallyl ether. Displacement of the π-pair of electrons from the olefinic bond during or after cleavage of the ether, accompanied by reductive action of the Grignard

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(1) C. M. Hill, L. Haynes, D. E. Simmons and M. E. Hill, THIS JOURNAL, **75**, 5408 (1953).

(2) C. M. Hill, D. E. Simmons and M. E. Hill, *ibid.*, **77**, 3889 (1955).