[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, STANDARD OIL COMPANY (INDIANA), AND THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY]

Action of Alkali Metals and Metal Hydrides on Deuterated Alkylaromatics and the Mechanism of Side-chain Alkylation

BY HAROLD HART[1]

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When alkylaromatics containing deuterium in the side-chain were heated with catalytic amounts of alkali metals or metal hydrides, exchange occurred involving, specifically, hydrogen atoms on the α-carbon. Ethylbenzene-d_α disproportionated to ordinary ethylbenzene and ethylbenzene-$d_{\alpha,\alpha}$ and transferred deuterium to the α-carbon of *sec*-butylbenzene. Ethylbenzene-d_β showed no loss of deuterium under similar conditions. Inorganic hydride replaced organically bound α-hydrogens. Optically active 2-phenylpentane, when alkylated on the side-chain with ethylene, gave inactive 3-methyl-3-phenylhexane, but recovered unreacted 2-phenylpentane was only slightly racemized. Under similar conditions but in the absence of ethylene, 2-phenylpentane was rapidly racemized. The mechanisms of deuterium exchange and side-chain alkylation are interpreted in terms of carbanion intermediates.

The alkali metal-catalyzed addition of alkylaromatics to olefins offers unusual possibilities for synthesis in hydrocarbon chemistry.[2-4] Thus sodium, phenylsodium or sodium and a variety of "promoters" readily convert toluene and ethylene to *n*-propylbenzene, 3-phenylpentane and related products in excellent yield and high purity.[5] The ease of replacement of the α-hydrogen by an ethyl group decreased in the order tertiary > secondary > primary.[4] Orientation with unsymmetrical olefins is shown by propylene which, with toluene, gave mainly isobutylbenzene. A chain mechanism was tentatively proposed[4] in which a benzyl-type organosodium compound adds to ethylene, and the resulting organometallic abstracts a benzylic proton from a hydrocarbon molecule to continue the chain.

$$C_6H_5CH_2Na + CH_2{=}CH_2 \longrightarrow C_6H_5CH_2CH_2CH_2Na$$

$$C_6H_5CH_2CH_2CH_2Na + C_6H_5CH_3 \longrightarrow C_6H_5CH_2CH_2CH_3 + C_6H_5CH_2Na$$

To study the mechanism in more detail,[6] the interaction of alkali metals and their hydrides with deuterated alkylaromatics and the alkylation of an optically active hydrocarbon with ethylene have been investigated. By these methods, information regarding the reactive intermediates and the relative rates of the various steps has been obtained.

The direct metalation of aliphatic side-chains on aromatic compounds by metals,[7] metals and oxides[8] and organometallics[9] has previously been followed largely by carbonation and analysis of the resulting mixtures of acids. The technique of labeling with deuterium and analyzing mass spectrometrically, used in the present work, was more direct and less tedious.

Experimental

Two alkylaromatics, ethylbenzene and *sec*-butylbenzene, were used in the deuterium exchange studies. The content and location of deuterium was determined by the mass spectrometer, extensive use being made of known cracking patterns.[10] The symbols d_0, d_α, $d_{\alpha,\alpha}$ and d_β will signify alkylaromatics with 0, 1 or 2 deuteriums on the α-carbon or 1 deuterium on the β-carbon of the alkyl side-chain. A numerical subscript, as in d_3, indicates the number of deuterium atoms per molecule but not their positions.

Ethylbenzene-d_α was prepared by reduction of α-phenethyl chloride with lithium deuteride and lithium aluminum deuteride[11]; $n^{20}D$ 1.4948, 96% ethylbenzene-d_α and 4% ethylbenzene-d_0.

Ethylbenzene-d_β was prepared by the action at 0° of 12.0 g. (0.60 mole) of D_2O (99.8%) in 100 ml. of tetrahydrofuran, freshly distilled from lithium aluminum hydride, on the Grignard reagent from 92.5 g. (0.50 mole) of β-phenethyl bromide in 400 ml. of anhydrous ether. The mixture was refluxed for 1 hr., allowed to stand overnight, refluxed again for 2 hr. and cooled. A solution of 30 ml. of concentrated sulfuric acid in 150 ml. of water was slowly added. After extraction with pentane, the combined organic layers were dried over calcium chloride and distilled through a packed column. There was obtained 44.5 g. (84%) of ethylbenzene, $n^{20}D$ 1.4950, which consisted of 93.0% ethylbenzene-d_β, 3.3% ethylbenzene-d_α[12] and 3.7% ethylbenzene-d_0.

Disproportionation of ethylbenzene-d_α involved gentle refluxing of 5 ml. of 96% ethylbenzene-d_α and 0.1 g. of potassium for 8 hr. in a nitrogen atmosphere. The metal became coated with a dark deposit which, on shaking, sloughed off and imparted a red color to the solution. The mixture was shaken occasionally during the last 2 hr. of the reaction period. The liquid product was pipetted from the sediment, distilled and analyzed mass spectrometrically.

Other deuterium exchange experiments (see Table I) were carried out in a 100-ml. stainless-steel Magne-Dash autoclave. The autoclave was charged with the reactants, flushed with nitrogen, sealed and heated electrically with automatic temperature control. The magnetic stirrer was operated at moderate speed throughout the reaction period. After an experiment was completed and the bomb had cooled, it was opened in a nitrogen atmosphere. The contents and benzene rinsings were filtered through glass wool and treated with alcohol, then water. The organic layer was dried over anhydrous sodium sulfate and distilled, and selected fractions were analyzed for deuterium content and location mass spectrometrically.

Alkylation and Racemization of (−)-2-Phenylpentane.—All rotations were determined on homogeneous materials in a 1-dm. tube.

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[1] Consultant at Standard Oil Company (Indiana), Laboratories, Summer, 1953.

[2] G. M. Whitman, U. S. Patent 2,448,641 (September 7, 1948).

[3] E. L. Little, Jr., U. S. Patent 2,548,803 (April 10, 1951).

[4] H. Pines, J. A. Vesely and V. N. Ipatieff, THIS JOURNAL, **77**, 554 (1955), H. Pines and V. Mark, paper presented at the 127th National Meeting of the American Chemical Society, Cincinnati, Ohio, 1955.

[5] A reaction that may be related mechanistically to side-chain alkylation is the facile addition of isopropyl or *t*-butyl lithium to ethylene reported by P. D. Bartlett, S. Friedman and M. Stiles, THIS JOURNAL, **75**, 1771 (1953).

[6] We were not aware of Professor Pines' work in 1953, when our studies were made.

[7] A. A. Morton and H. E. Ramsden, THIS JOURNAL, **70**, 3132 (1948).

[8] C. E. Claff, Jr., and A. A. Morton, *J. Org. Chem.*, **20**, 440, 981 (1955).

[9] For recent studies and earlier references, see (a) D. Bryce-Smith, *J. Chem. Soc.*, 1079 (1954); (b) D. Bryce-Smith, V. Gold and D. P. N. Satchell, *ibid.*, 2743 (1954); (c) A. A. Morton, C. E. Claff, Jr., and F. W. Collins, *J. Org. Chem.*, **20**, 428 (1955).

[10] S. Meyerson, *Appl. Spectroscopy*, **9**, 120 (1955).

[11] E. L. Eliel, THIS JOURNAL, **71**, 3970 (1947).

[12] The ethylbenzene-d_α may have arisen from some α-phenethyl bromide formed during preparation of the β-phenethyl bromide from the corresponding alcohol, hydrogen bromide and sulfuric acid.

TABLE I

EXCHANGE EXPERIMENTS WITH ETHYLBENZENE AND *sec*-BUTYLBENZENE AT 165 ± 5°

Ethylbenzene		*sec*-Butylbenzene,[a] ml.	Reagent		Time, hours	Product composition, vol. %[b]	
Ml.	Composition, vol. %		Type	g.		Ethylbenzene	*sec*-Butylbenzene
10	4-d_0 96-d_α	10	..		3	4-d_0 96-d_α	100-d_0
10	4-d_0 96-d_α	10	K	0.4	3	33-d_0 49-d_α 17-$d_{\alpha,\alpha}$ 1-d_3	89-d_0 11-d_α
10	3.7-d_0 3.3-d_α 93.0-d_β	5.6	K	0.4	4	3.8-d_0 2.9-d_α 92.6-d_β 0.7-$d_{\alpha,\beta}$	100-d_0
11.2	4-d_0 96-d_α	..	KH	1.5	3	9.8-d_0 86.9-d_α 3.2-$d_{\alpha,\alpha}$	......
10	3.7-d_0 3.3-d_α 93.0-d_β	..	KH	1.5	4	3.5-d_0 3.5-d_α 93.0-d_β	......
20	100-d_0	..	K LiD	0.4 1.5	3.5	91-d_0 9-d_α	......
..	......	25.5	K LiD	0.4 1.5	3	......	95.5-d_0 4.5-d_α

[a] The mass spectrum of the *sec*-butylbenzene used was indistinguishable from that of API standard non-deuterated *sec*-butylbenzene. [b] Analyses were run on fractionated samples of constant boiling point and constant refractive index, n^{20}D 1.4948 for ethylbenzene and 1.4898 for *sec*-butylbenzene.

A 100-ml. Magne-Dash autoclave was charged with 16.8 g. of 2-phenylpentane (α^{25}D −9.26°),[13] 0.15 g. of potassium and 0.90 g. of sodium hydride. The bomb was flushed with hydrogen, charged with 5.5 g. of ethylene, heated to 190° and maintained at that temperature for 2 hr. (pressure drop, 210 p.s.i.). After cooling, the combined benzene rinsings were washed with water, dried and distilled. The products consisted of 4.9 g. of recovered 2-phenylpentane (α^{25}D −8.82 ± 0.01°, n^{20}D 1.4883) and 9.9 g. of 3-methyl-3-phenylhexane (α^{25}D −0.07 ± 0.01°, n^{20}D 1.4960).[14]

Five ml. of 2-phenylpentane (α^{25}D −9.26°) was refluxed in a nitrogen atmosphere over 0.4 g. of potassium for 2 hr. with occasional shaking. The mixture became reddish-black; a small sample withdrawn from it gave a positive organometallic test.[15] After cooling, the mixture was filtered through glass wool; the filtrate, after distillation, gave 4.2 ml. of 2-phenylpentane (α^{25}D −2.19°). Infrared analysis gave no evidence of isomerization to 3-phenylpentane.

Results and Discussion

(A) Deuterium Exchange Studies.—When 96% ethylbenzene-d_α (4%-d_0) was refluxed over a catalytic amount of potassium, disproportionation to 92%-d_α, 2%-$d_{\alpha,\alpha}$ and 6%-d_0 occurred. There was no evidence of ring or β-deuteration. The specificity of the deuterium migration was further investigated at higher temperatures; pertinent results are summarized in Table I.

In the absence of a catalyst, ethylbenzene-d_α did not exchange deuterium when heated at 165° for 3 hr. with *sec*-butylbenzene-d_0. In the presence of a catalytic amount of metallic potassium, however, extensive but specific exchange occurred. Analysis of the products demonstrated that two processes were involved: (a) self-exchange of ethylbenzene, which resulted in a considerable amount of ethylbenzene-$d_{\alpha,\alpha}$, and (b) exchange between ethylbenzene and the α-hydrogen of *sec*-butylbenzene. The recovery of ethylbenzene-d_β essentially unchanged, from similar experiments, emphasizes that only α-hydrogens were involved.[16]

When potassium hydride was used as the catalyst, a similar specific exchange occurred. When 96% ethylbenzene-d_α was heated with potassium hydride, there was formed 3.2% of ethylbenzene-$d_{\alpha,\alpha}$, which could only have arisen from exchange between two ethylbenzene-d_α moieties. In addition, there was evidence for direct exchange between inorganic hydride and the α-hydrogen of the alkylaromatic; the absolute amount of ethylbenzene-d_0 was greater by 2.6% than could be accounted for by disproportionation. Finally, the latter type of exchange was clearly demonstrated by the formation of ethylbenzene-d_α and *sec*-butylbenzene-d_α when the non-deuterated hydrocarbons were heated with a mixture of potassium and lithium deuteride.

Three processes are clearly distinguishable: (a) initiation of the exchange by the catalyst, (b) the exchange itself, involving two organic moieties, and (c) exchange between inorganic hydride and organically bound hydrogen. Each requires its own mechanistic interpretation.

(a) Because either an alkali metal or a metal hydride will catalyze the exchange process, two initiating mechanisms appear necessary. For the reaction of potassium with the alkylaromatic

$$\mathrm{Ar{-}\underset{|}{\overset{|}{C}}{-}H + K\cdot \longrightarrow Ar{-}\underset{|}{\overset{|}{C}}{}^{-}K^{+} + H\cdot} \qquad (1)$$

seems reasonable. It is rapidly followed by the combination of hydrogen, either as atoms or molecules, with potassium to form potassium hydride,

$$\mathrm{K\cdot + H\cdot \longrightarrow KH}$$

or the two steps may be combined in a concerted process. The sequence is probably irreversible, because potassium hydride is essentially undissociated under the reaction conditions.[17] A positive organometallic test[15] and the usual reddish color of the reaction mixtures constitute evidence for the presence of an organopotassium compound. Attack at the α-carbon is preferred because the resulting carbanion is stabilized by resonance. Indeed, the small amount of ethylbenzene-d_3 that resulted in one experiment may have arisen from nuclear deuteration due to resonance forms of the benzyl-type carbanion in which negative charge is distributed to *ortho* and *para* positions of the ring.

$$\mathrm{Ar{-}\underset{|}{\overset{|}{C}}{-}H + H^{-} \longrightarrow Ar{-}\underset{|}{\overset{|}{C}}{}^{-} + H_2} \qquad (2)$$

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[13] R. L. Burwell, Jr., A. D. Shields and H. Hart, THIS JOURNAL, **76**, 908 (1954).

[14] The slight rotation of this product may have been real but was more likely due to a trace of unreacted 2-phenylpentane. For a complete study, the rotation of optically pure 3-methyl-3-phenylhexane should be determined.

[15] H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).

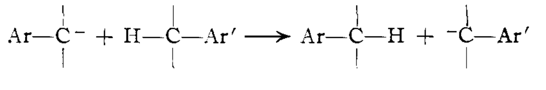
[16] The trace of ethylbenzene-$d_{\alpha,\beta}$ must have arisen from exchange of the 3.3% ethylbenzene-d_α in the charge with ethylbenzene-d_β.

[17] E. F. Sollers and J. L. Crenshaw, THIS JOURNAL, **59**, 2015 (1937). It is possible that hydrogen is a product of the initiation step, in which case (1) would be written $\mathrm{Ar{-}\underset{|}{\overset{|}{C}}{-}H + K\cdot \rightarrow Ar{-}\underset{|}{\overset{|}{C}}{}^{-}K^{+} + {}^{1}/{}_{2}H_2}$. J. dePostis [*Compt. rend.*, **222**, 398 (1946)] has claimed that cesium metal liberates hydrogen from toluene. This point requires further study.

Whereas the metal-initiated exchange involved removal of the α-hydrogen as an atom, hydride-ion initiation is probably the result of proton removal, again producing a benzyl type of carbanion.[18]

(b) A sequence of reactions involving equations 1 or 2 and the reverse could account for the exchange. In each case, however, the formation of dideuterated product would require the recombination of two species, both of which could be present in small concentration. For example, reversal of equation 2 to form ethylbenzene-$d_{\alpha,\alpha}$ would require reaction between HD and $C_6H_5\bar{C}DCH_3$.

The preferred principal exchange path, whether catalysis is by metals or metal hydrides, seems to be a proton transfer from the α-carbon of a hydrocarbon molecule to a carbanion



$$\mathrm{Ar{-}\overset{|}{\underset{|}{C}}{}^{-} + H{-}\overset{|}{\underset{|}{C}}{-}Ar' \longrightarrow Ar{-}\overset{|}{\underset{|}{C}}{-}H + {}^{-}\overset{|}{\underset{|}{C}}{-}Ar'}$$

Ar and Ar′ may be the same or different, and H may be D. Exchange is essentially the result of an acid–base equilibrium in the hydrocarbon system. The particular sequence that would account for the formation of ethylbenzene-$d_{\alpha,\alpha}$ would be

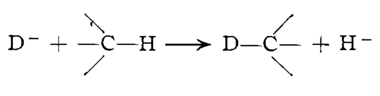
$$C_6H_5CHDCH_3 + K\cdot \longrightarrow C_6H_5\bar{C}DCH_3 + H\cdot$$

$$C_6H_5\bar{C}DCH_3 + C_6H_5CHDCH_3 \longrightarrow C_6H_5CD_2CH_3 + C_6H_5\bar{C}HCH_3$$

This exchange path does not require reaction between two components present in small concentrations.

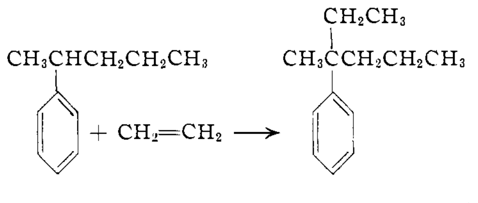
This mechanism is quantitatively consistent with the data. Self-exchange of ethylbenzene was more extensive than exchange between it and *sec*-butylbenzene, presumably because the inductive effect of the ethyl group in the latter makes its α-hydrogen less acidic than that in ethylbenzene. These results are consistent with the observation[9a] that the rate of side-chain metalation with ethyl potassium decreased in the order toluene > ethylbenzene > isopropylbenzene. By measuring competitive rates of deuterium exchange (to avoid the interpretational difficulties of heterogeneous reaction rates), it should be possible to measure quantitatively the acidities of hydrocarbons, particularly those with a benzylic hydrogen.[19]

(c) The direct exchange between inorganic hydride and the alkylaromatic may be explained by a reversal of equation 2 or by a direct hydride-ion displacement



The present data do not permit a clear choice between these alternatives.

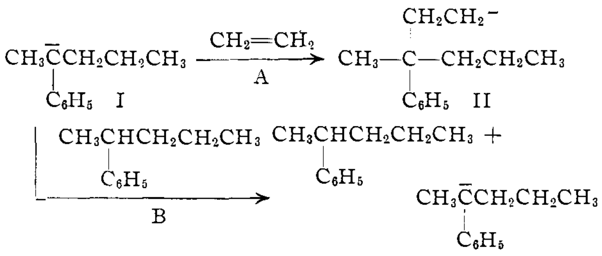
(B) **Alkylation of an Optically Active Hydrocarbon.**—To obtain further information about side-chain alkylation, optically active 2-phenylpentane was alkylated with ethylene



This case was selected because optically active 2-phenylpentane is readily available[13] and because the expected product, 3-methyl-3-phenylhexane, would be theoretically capable of optical activity. Furthermore, the absence of hydrogens on the α-carbon of the side-chain would protect the product from further attack by the catalyst, which might result in racemization.

The 3-methyl-3-phenylhexane obtained from (−)2-phenylpentane and ethylene was essentially inactive, but recovered unalkylated 2-phenylpentane was only slightly racemized. In contrast, 2-phenylpentane was racemized extensively when treated with potassium under essentially the same conditions but in the absence of ethylene.

The reactive intermediate is presumably the carbanion I derived from 2-phenylpentane by removal of the α-hydrogen. This anion may react with ethylene (path A) or may abstract a proton from another 2-phenylpentane molecule (path B)



$$\underset{\mathrm{C_6H_5}\quad \mathrm{I}}{\mathrm{CH_3\bar{C}CH_2CH_2CH_3}} \xrightarrow[\mathrm{A}]{\mathrm{CH_2{=}CH_2}} \mathrm{CH_3{-}\overset{CH_2CH_2^-}{\underset{C_6H_5}{C}}{-}CH_2CH_2CH_3}\quad \mathrm{II}$$

$$\xrightarrow[\mathrm{B}]{\mathrm{CH_3\underset{C_6H_5}{CH}CH_2CH_2CH_3}} \mathrm{CH_3\underset{C_6H_5}{CH}CH_2CH_2CH_3} + \mathrm{CH_3\underset{C_6H_5}{\bar{C}}CH_2CH_2CH_3}$$

In the absence of ethylene, only the latter process is possible, and the 2-phenylpentane racemizes.[20] This type of reaction was clearly demonstrated in the deuterium exchange experiments.

Under alkylating conditions, reaction *via* path A is faster than *via* path B, because recovered unalkylated 2-phenylpentane had lost little activity. On the other hand, anion II, presumably a much more reactive anion than I, abstracts a proton from a 2-phenylpentane molecule more rapidly than it adds to ethylene, for no product corresponding to the latter process was isolated. There is a delicate balance between the proton-abstraction and ethylene-addition reactions of the benzyl-type carbanion I and the primary γ-carbanion II. The relative rates of these processes may depend in part on the degree of covalency of the anion–metal bond.

Postulation of a rapid reaction between a carbanion and an olefin requires comment.[21] Olefins are usually considered nucleophilic and primarily subject to attack by electrophilic reagents.[22] However,

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[18] No assertion is made concerning the ionic or covalent character of the carbon–metal bond; see, however, references 9a and 9c.

[19] See ref. 9a and also G. E. Hall, R. Piccolini and J. D. Roberts, THIS JOURNAL, **77**, 4540 (1955).

[20] For racemization of a similar hydrocarbon with somewhat weaker bases, see E. Eliel, P. H. Wilken and F. T. Fang, Abstracts of the Minneapolis, Minnesota, Meeting of the A.C.S., 1955, p. 43-O.

[21] For an example of a reaction which is kinetically controlled by addition of an anion to a triple bond, see S. I. Miller and G. Shkapenko, THIS JOURNAL, **77**, 5038 (1955).

[22] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 646-675.

by placing strong electron-withdrawing substituents on the double-bonded carbon atoms, susceptibility to attack by nucleophilic species can be enhanced.[23] The same goal may also be reached by increasing the nucleophilicity of the attacking reagent.[24] Carbanions of the type studied must be strongly nucleophilic, and the double bond appears sufficiently polarizable to permit rather rapid attack by such species. Substituted ethylenes should react more slowly than ethylene, because of electron release by the alkyl groups. On the other hand, since when a choice is available the most branched side-chain (with an α-hydrogen) is alkylated,[4] the nucleophilicity of the α-carbanion, and not the acidity of the α-hydrogen, is the dominating factor. In keeping with this, secondary and especially tertiary, but not primary, alkyl lithiums add rapidly to ethylene at −60°.[5]

Acknowledgments.—I owe a special debt to Seymour Meyerson, without whose ingenuity in mass spectrometry the major portion of this work would not have been possible. I acknowledge, also, helpful discussions of this work with Professor Fausto Ramirez of Columbia University, and with members of the research staff of the Standard Oil Company (Indiana).

EAST LANSING, MICHIGAN

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(23) Examples are the addition of Grignard reagents or cyanide ion to α,β-unsaturated ketones or esters and the base-catalyzed addition of alcohols to perfluoro-olefins.

(24) Reference 22, p. 667.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Terpenes. IV.[1] The Acid-induced Cyclization of Dihydro-α-ionone

BY G. BÜCHI, K. BIEMANN, B. VITTIMBERGA AND M. STOLL[1a]

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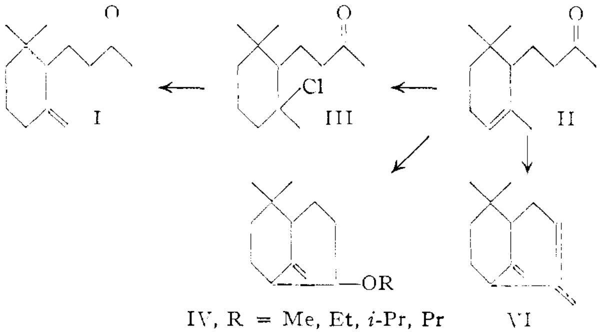
Dihydro-α-ionone (II) undergoes cyclization in the presence of phosphoric acid. Three bicyclic hydrocarbons were isolated and the structures of two of them were elucidated by hydrogenation, dehydrogenation and oxidative degradation and shown to be 1,1,6-trimethyl-1,2,3,7,8,8a-hexahydronaphthalene (VII) and 2,2,6-trimethyl-9-methylene-bicyclo[3,3,1]-6-nonene (XII). A possible mechanism for the formation of the bicyclic hydrocarbons is discussed.

Dihydro-γ-ionone (I), a constituent of the steam-volatile fraction of ambergris[2] has been synthesized from dihydro-α-ionone (II) *via* the tertiary chloride III.[3] The addition of hydrochloric acid to II in ether solution, however, is not quantitative and a considerable amount of non-ketonic material is formed.

The study of this reaction, using hydroxylic solvents, has been continued in the laboratory of Firmenich and Cie.[4] It has been shown that dihydro-α-ionone (II) when treated with anhydrous hydrochloric acid in the presence of lower aliphatic alcohols is converted to bicyclic ethers IV, whereas the corresponding tertiary alcohol V is formed when the reaction is carried out in 2-butanol. In all cases studied small quantities of hydrocarbons were formed for which structure VI had been suggested.



IV, R = Me, Et, *i*-Pr, Pr
V, R = H

VI

In the present communication we wish to report work on the acid-induced cyclization of dihydro-α-ionone (II) in the absence of solvents.

Upon treatment of dihydro-α-ionone (II) with 85% phosphoric acid at 25°, a mixture of isomeric hydrocarbons $C_{13}H_{20}$ was obtained from which the individual components were isolated by chromatography and fractional distillation. Hydrogenation experiments showed that all three hydrocarbons $C_{13}H_{20}$ contain two double bonds and are therefore bicyclic. In the compound formed in largest quantity (VII) the double bonds are conjugated (ultraviolet: λ_{max} 240 mμ, log ε 4.36) and catalytic reduction in the presence of Adams platinum catalyst gave VIII, identical in all respects with authentic 1,1,6-trimethyldecalin.[5] Confirmatory evidence for the carbon skeleton of VII was obtained by catalytic dehydrogenation over palladium–charcoal[6] at 323°; ionene (IX), identical with an authentic sample was obtained.[7] In order to differentiate between structures VII and X, both of which are compatible with the ultraviolet absorption spectrum, the hydrocarbon was oxidized by osmium tetroxide and the resulting tetrol $C_{13}H_{24}O_4$ (XI) cleaved with potassium periodate. No formaldehyde was formed and the hydrocarbon must therefore have structure VII (1,1,6-trimethyl-1,2,3,7,8,8a-hexahydronaphthalene) rather than X.

The infrared spectrum of the second hydrocarbon (XII), formed in the cyclization of dihydro-α-ionone (II), shows bands at 6.07 and 11.35 μ typical for terminal methylene groups. The ultraviolet absorption spectrum indicates the absence of con-

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(1) Paper III, G. Büchi, W. S. Saari and A. Eschenmoser, *Experientia*, in press.

(1a) Firmenich and Cie., Geneva.

(2) L. Ruzicka, C. F. Seidel and M. Pfeiffer, *Helv. Chim. Acta*, **31**, 827 (1948).

(3) L. Ruzicka, G. Büchi and O. Jeger, *ibid.*, **31**, 293 (1948).

(4) M. Stoll, B. Willhalm and G. Büchi, *ibid.*, **38**, 1573 (1955).

(5) V. Prelog and B. Vaterlaus, *ibid.*, **32**, 2082 (1949).

(6) A. G. Anderson, Jr., and J. A. Nelson, THIS JOURNAL, **73**, 232 (1951).

(7) M. T. Bogert and V. G. Fourman, *ibid.*, **55**, 4670 (1933).