

Δ^3 -5 β -Cholestenylacetic Acid (XVII) and the Iodolactone XXI.—Silver oxide oxidation of the cholestenylacetaldehyde XVI provided, in 40% yield, the corresponding acid (XVII), which crystallized from ethanol-ethyl acetate in fine, short needles, m.p. 217–219° (cap.) and 209–212° (H.S.), $\alpha_D +97^\circ$.

Anal. Calcd. for $C_{29}H_{48}O_2$ (428.67): C, 81.25; H, 11.29. Found: C, 81.38; H, 11.51.

The methyl ester of XVII (diazomethane) deposited from methanol-ethyl acetate in plates, m.p. 116–118°, $\alpha_D +98^\circ$.

Anal. Calcd. for $C_{30}H_{50}O_2$ (442.70): C, 81.39; H, 11.38. Found: C, 81.44, H, 11.54.

Catalytic hydrogenation of this derivative in ethanol over platinum oxide furnished the methyl ester of XIX, m.p. and mixed m.p. 111–112°.

Application of the iodolactonization reaction^{26,27} to the sodium salt of XVII in dilute solution afforded, in 60% yield, the corresponding δ -iodo- γ -lactone (XXI), which

crystallized from methanol-ethyl acetate in short needles, m.p. 230–231°, $\alpha_D +35^\circ$, λ_{max} 5.65 μ .

Anal. Calcd. for $C_{29}H_{47}O_2I$ (554.61): C, 62.80; H, 8.54; I, 22.91. Found: C, 62.70; H, 8.61; I, 23.06.

Δ^3 -5 α -Cholestenylacetaldehyde (XXIV).—Vinylolation of 800 mg. of Δ^4 -cholestene-3 α -ol,⁵⁶ m.p. 81–84°, $\alpha_D +119^\circ$ (lit.⁵⁶ m.p. 84°, $\alpha_D +121^\circ$ benzene) furnished, by the procedure used for the preparation of XV, ca. 60 mg. of oily chromatographed vinyl ether XXIII, λ_{max} 6.1, 6.2 and 8.4 μ , which appeared to contain some conjugated impurity (λ_{max} 265–270 $m\mu$). Rearrangement of the crude ether in decalin at 190–195° for 3 hr. afforded an aldehydic product (λ_{max} 5.81 μ), from which a crystalline semicarbazone was prepared. Recrystallized from benzene-ethanol, this derivative weighed 13 mg. and melted at 227–229° (depressed to 222–226° on admixture with the semicarbazone, m.p. 230–232°, of XVI).

Anal. Calcd. for $C_{30}H_{51}ON_3$ (469.74): C, 76.70; H, 10.94; N, 8.95. Found: C, 76.94; H, 11.09; N, 8.69.

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Cycloheptatrienes from the Solvolysis of 1,4-Dihydrobenzyl *p*-Toluenesulfonates¹

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The conversion of aromatic carboxylic acids to 1,4-dihydrobenzyl *p*-toluenesulfonates is described. Solvolysis of the *p*-toluenesulfonates in acetic acid containing sodium dihydrogen phosphate gives chiefly cycloheptatrienes with lesser amounts of esters and aromatic hydrocarbons. The preparations of cycloheptatriene, 1-, 2- and 3-methylcycloheptatriene and 1,2-benzo-3-methylcycloheptatriene are described.

The unusual properties and uses of cycloheptatrienes has led to a variety of methods for the preparation of the parent compound.⁴ While some of these methods are capable of being extended to the preparation of substituted cycloheptatrienes, little work has been done in this direction. In a preliminary communication,⁵ we reported briefly a synthesis of cycloheptatriene and three of the four possible methylcycloheptatrienes. This paper discloses the details of this new method for preparing cycloheptatrienes.

The availability of 1,4-dihydrobenzoic acids by metal-ammonia reduction of the aromatic acids⁶ and of 1-alkyl-1,4-dihydrobenzoic acids by alkylation of the 1,4-dihydrobenzoic acids^{6a} led us to investigate the possibility of utilizing these materials for the preparation of cycloheptatrienes. The method we envisioned was to consist of (1) reduction of the dihydro acid with lithium aluminum hydride to a 1,4-dihydrobenzyl alcohol, (2) preparation of the corresponding *p*-toluenesulfonate derivative and (3) solvolysis of the sulfonate in

acetic acid in the presence of a buffer, sodium dihydrogen phosphate monohydrate.^{4d,e}

The solvolysis of 1,4-dihydrobenzyl *p*-toluenesulfonate (Ia) can lead theoretically to a number of products.⁷ An SN2 displacement of the sulfonate group by solvent would give 1,4-dihydrobenzyl acetate (IIa) which may or may not react further under the conditions of the solvolysis. Reaction of Ia by an SN1 process would give the primary carbonium ion IIIa which can rearrange in a number of ways. Toluene could be formed by migration of hydride and aromatization of the resulting cation IVa or *via* protonation-deprotonation reactions of an intermediate methylenecyclohexadiene formed by loss of a proton from IIIa. A direct ring expansion of the ion IIIa would lead to the lower energy allylic carbonium ion VIa which, by loss of a proton, would give cycloheptatriene (VIIa). A more likely route to VIa would involve participation of the π -electrons of IIIa giving the homoallylic cation Va which can now expand to the cycloheptadienyl ion.⁸ Still another route to cycloheptatriene could involve loss of a proton from the homoallylic cation

(1) This work was supported in part by a Frederick Gardner Cottrell Grant of the Research Corporation.

(2) Research Laboratories of the Upjohn Co., Kalamazoo, Mich.

(3) National Science Foundation Summer Fellow, 1959.

(4) (a) R. Willstätter, *Ann.*, **317**, 204 (1901); (b) E. P. Kohler, M. Tishler, H. Potter and H. T. Thompson, *THIS JOURNAL*, **61**, 1057 (1939); (c) W. von E. Doering and L. H. Knox, *ibid.*, **72**, 2305 (1950); **73**, 828 (1951); (d) H. L. Dryden, Jr., *ibid.*, **76**, 2841 (1954); (e) H. L. Dryden, Jr., and E. E. Burgert, *ibid.*, **77**, 5633 (1955); (f) W. G. Woods, *J. Org. Chem.*, **23**, 110 (1958); (g) H. E. Winberg, *ibid.*, **24**, 264 (1959), and other references contained therein.

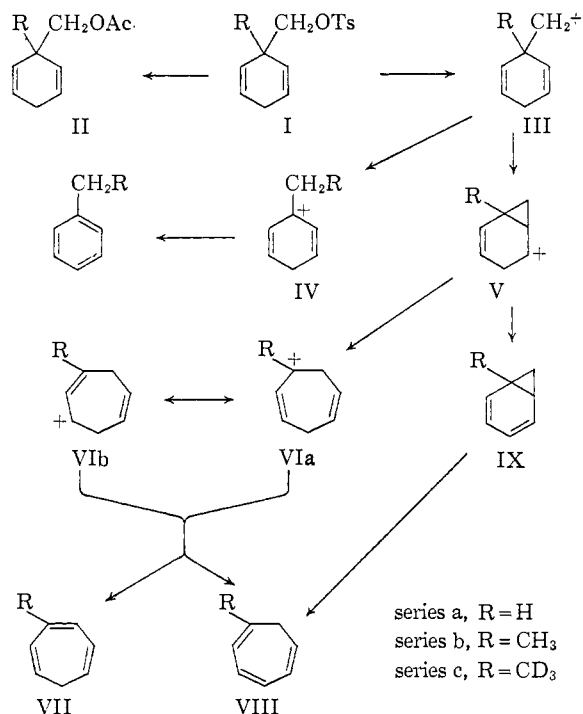
(5) N. A. Nelson, J. H. Fassnacht and J. U. Piper, *THIS JOURNAL*, **81**, 5009 (1959).

(6) (a) A. J. Birch, *J. Chem. Soc.*, 1551 (1950); (b) H. Plieninger and G. Ege, *Angew. Chem.*, **70**, 505 (1958); (c) M. E. Kuehne and B. F. Lambert, *THIS JOURNAL*, **81**, 4278 (1959), and references contained therein; (d) see also E. L. Eliel and T. E. Hoover, *J. Org. Chem.*, **24**, 938 (1959).

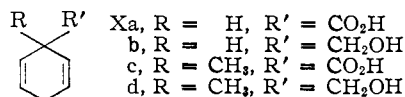
(7) The formation of products is described in terms of discrete intermediates purely for the sake of clarity. It should be understood that some of the intermediates may not exist because of several steps occurring concertedly.

(8) This mode of reaction finds many analogies in the solvolysis of sulfonates and halides having γ,δ -unsaturation, the classical example being the conversion of cholesteryl *p*-toluenesulfonate to *i*-cholesteryl derivatives. See, for example, (a) M. Simonetta and S. Winstein, *THIS JOURNAL*, **76**, 18 (1954); (b) E. M. Kosower and S. Winstein, *ibid.*, **78**, 4347 (1956); (c) R. D. Haworth, J. McKenna and R. G. Powell, *J. Chem. Soc.*, 1110 (1953); (d) C. W. Shoppee, H. C. Richards and G. H. R. Summers, *ibid.*, 4817 (1956); (e) W. G. Dauben and G. J. Fonken, *THIS JOURNAL*, **78**, 4736 (1956); (f) J. W. Rowe, A. Melera, D. Arigoni, O. Jeger and L. Ruzicka, *Helv. Chim. Acta*, **40**, 1 (1957); and (g) P. Bruylants and A. Dewael, *Bull. Sci. Acad. Roy. Belg. [V]* **14**, 140 (1928); *C. A.*, **22**, 3883 (1928).

to give norcaradiene (IXa) which, by valence tautomerism, would give cycloheptatriene.⁹ Reaction of the various cations with solvent could lead to esters; however, ions such as IVa would not be expected to behave in this way.



1,4-Dihydrobenzoic acid (Xa), prepared from benzoic acid in excellent yield by the method of Plieninger and Ege,⁸ was reduced with lithium aluminum hydride to 1,4-dihydrobenzyl alcohol (Xb). The product Xb was shown to contain about 4% of an impurity whose gas chromatographic retention time was identical to that of benzyl alcohol. There is little doubt that this impurity would not influence the subsequent reactions; however, for the sake of simplifying the evaluation of results of the solvolysis reaction, small samples of Xb were purified by gas chromatography before being converted to 1,4-dihydrobenzyl *p*-toluenesulfonate (Ia). The product Ia was obtained as a viscous oil in 90% yield.



The solvolysis of 1,4-dihydrobenzyl *p*-toluenesulfonate at 90° in acetic acid containing two molecular equivalents of sodium dihydrogen phosphate monohydrate gave a crude product which was separated by elution chromatography into a hydrocarbon fraction (70%) and an ester fraction (16%).¹⁰ Analysis of the hydrocarbon fraction by

(9) For a discussion concerning valence tautomerism in this system see E. J. Corey, H. J. Burke and W. A. Remers, *THIS JOURNAL*, **77**, 4941 (1955), and W. von E. Doering, G. Laber, R. Vonderwahl, N. F. Chamberlain and R. B. Williams, *ibid.*, **78**, 5448 (1956).

(10) R. S. Bly, Jr., and H. L. Dryden, Jr., *Chemistry & Industry*, 1287 (1959), have reported that the solvolysis of cyclohexylmethyl methanesulfonate (i) and 4-cyclohexenylmethyl methanesulfonate (ii) in buffered acetic acid leads to the formation of cyclohexylmethyl

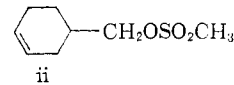
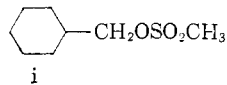
gas chromatography showed the presence of 12% toluene and 88% cycloheptatriene which were collected and identified by comparison of their infrared spectra with those of authentic samples. The ester fraction was hydrogenated and then purified by gas chromatography. Fractions of hexahydrobenzyl acetate (63%) and cycloheptyl acetate (37%) were obtained, the infrared spectra of which were essentially identical to those of authentic samples. The precursor of the cycloheptyl acetate is presumably a cycloheptadienyl acetate which could be formed during rearrangement of the *p*-toluenesulfonate Ia or possibly by acid-catalyzed addition of acetic acid to cycloheptatriene.

In a preliminary solvolysis of 1,4-dihydrobenzyl *p*-toluenesulfonate under less favorable conditions, an ester fraction (24%) was obtained as the main product which, after hydrogenation, appeared to be cycloheptyl acetate on the basis of its infrared spectrum. In this instance, little if any hexahydrobenzyl acetate was detected in the ester fraction.

The dehydration of 1,4-dihydrobenzyl alcohol (Xb) at 175–190° using as catalysts phosphoric acid, potassium bisulfate or Dowex-50 sulfonic acid resin was investigated briefly. The latter two catalysts gave small yields of hydrocarbons (17–24%) which consisted chiefly of cycloheptatriene with lesser amounts of toluene and other low boiling materials. While the formation of cycloheptatriene under these conditions does not appear promising from a preparative standpoint, the formation of small quantities for comparison purposes is rapid and convenient provided equipment is available to effect purification of the mixture.

The alkylation of 1,4-dihydrobenzoic acid with potassium amide and methyl iodide in liquid ammonia by the method of Birch⁶ gave 1,4-dihydro-1-methylbenzoic acid (Xc) in good yield. It is necessary to use freshly prepared 1,4-dihydrobenzoic acid and to work quickly under mild conditions in order to minimize side reactions. Lithium aluminum hydride reduction of Xc gave 1,4-dihydro-1-methylbenzyl alcohol (Xd). Conversion of the alcohol to 1,4-dihydro-1-methylbenzyl *p*-toluenesulfonate (Ib) proceeded in good yield. In initial experiments, the *p*-toluenesulfonate derivative was purified by chromatography on silica gel with considerable loss of material. In later work it was found that the crude product was sufficiently pure to be used directly in the next step.

Subjecting the *p*-toluenesulfonate derivative Ib to solvolytic conditions similar to those described above could result in the formation of ethylbenzene, 1-methylcycloheptatriene (VIIIb), 3-methylcycloheptatriene (VIIb) and possibly a methylenecycloheptadiene by loss of a methyl proton from VIa (R acetate (68%) and 4-cyclohexenylmethyl acetate (71%), respectively; no hydrocarbon fraction was isolated in either instance. These results, albeit obtained under different conditions from ours, further justify our contention that the solvolysis of a *p*-toluenesulfonate such as I is assisted by homoallylic delocalization of charge (III → V). Otherwise, it would be predicted that Ia, being less sterically hindered than i or ii, would give mainly IIa by an S_N2 process rather than the observed rearranged products.



= CH₃). As indicated earlier, a number of esters could be formed, for example, 1,4-dihydro-1-methylbenzyl acetate (IIb), two methylcycloheptadienyl esters derived from VIa and VIb and possibly a bicyclic ester derived from Vb.

The solvolysis of 1,4-dihydro-1-methylbenzyl *p*-toluenesulfonate (Ib) was carried out at 80° in acetic acid buffered with sodium dihydrogen phosphate. A work-up procedure similar to that already described gave a 56% yield of a hydrocarbon fraction and essentially no ester fraction (however, see below). The hydrocarbon fraction appeared to be homogeneous when subjected to gas chromatography on a silicone oil-packed column. However, when a column containing 4-methyl-4-nitropimeloni-trile as the stationary liquid was used, three materials were observed to be present in approximate concentrations of 2% (fraction 1), 50% (fraction 2) and 48% (fraction 3). The material present as fraction 1 was not identified; however, it is perhaps significant to note that its retention time is the same as that for 2-methylcycloheptatriene, described later.

The other two materials were collected as they were eluted from the gas chromatographic column and each was assigned a structure on the basis of spectral evidence. Under the conditions of gas chromatography, it was found that ethylbenzene had the same retention time as fraction 2, but the infrared spectrum of fraction 2 indicates that there is little or no ethylbenzene present since, for example, there is no absorption band at 1495 cm.⁻¹ which is present in the spectrum of ethylbenzene. Catalytic hydrogenation of the distilled hydrocarbon mixture using a palladium-on-carbon catalyst gave one material identified as methylcycloheptane by comparison with an authentic sample of this material.

Of the various hydrocarbons which might be formed during the solvolysis, ethylbenzene is not a product and methylenecycloheptadienes can be excluded on the basis of the infrared and n.m.r. spectra of the two major hydrocarbon products. For example, the infrared spectra of these products have absorption bands attributable to the presence of methyl groups, but no absorption bands characteristic of terminal methylene groups. Bicyclic compounds of the norcaradiene type, while possibly being formed initially, would likely be transformed to the corresponding cycloheptatrienes through valence tautomerism. Therefore, the two major hydrocarbons must represent 1- and 3-methylcycloheptatriene. It is possible to distinguish between these substances on the basis of their n.m.r. spectra. The spectrum of material from fraction 3 exhibits two peaks of nearly equal intensity which can be attributed to methylene hydrogens being split by one adjacent vinyl hydrogen; this material must therefore be 1-methylcycloheptatriene. The n.m.r. spectrum of material from fraction 2 has the expected appearance for 3-methylcycloheptatriene, with an exception. One would expect the methylene hydrogens to be split into a triplet by coupling with the two adjacent vinyl hydrogens, and the bands of the triplet to have relative intensities of 1:2:1. The spectrum of fraction 2 reveals two

peaks having the expected relative intensities, but the nearby methyl hydrogen absorption band hides the third peak of the triplet.

Although the spectra are regarded as sufficient evidence to allow structural assignments of VIIb and VIIIb, the element of doubt in the spectrum of VIIb led us to the preparation and solvolysis of 1,4-dihydro-1-methyl-*d*₃-benzyl *p*-toluenesulfonate (Ic). Solvolysis of Ic should lead to the trideuterio-methylcycloheptatrienes VIIc and VIIIc in the same proportions as for the undeuterated examples. Lack of methyl hydrogens in VIIc and VIIIc would give a clear view of the pattern for the methylene hydrogen absorption in the n.m.r. spectra of these compounds.

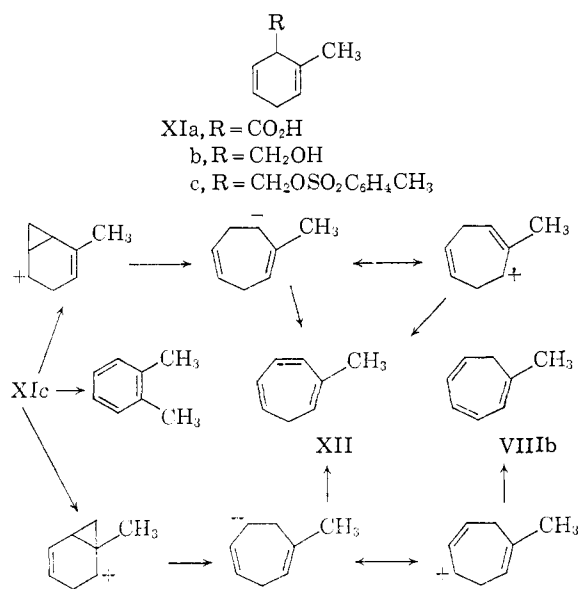
The preparation of 1,4-dihydro-1-methyl-*d*₃-benzyl *p*-toluenesulfonate (Ic) was accomplished by the same series of reactions described for the preparation of Ib, except methyl-*d*₃ iodide¹¹ was used in place of methyl iodide. Solvolysis of Ic for 36 hours in acetic acid containing sodium dihydrogen phosphate monohydrate gave 73% of a hydrocarbon fraction and 11% of an ester fraction. The hydrocarbon fraction, which contained three components in essentially the same percentages as observed before in the undeuterated series, was separated by gas chromatography. The nuclear magnetic resonance spectra of the two major products still showed methyl hydrogen absorption, but of greatly diminished intensity relative to the undeuterated samples. The loss of deuterium from the deuterio-methyl group was confirmed by mass spectrometric data which showed that the 1-substituted isomer contained 61.3% of CD₃, 7.5% of CHD₂, 7% of CH₂D and 24% of CH₃ and the 3-substituted isomer contained 79.5% of CD₃, 7.8% of CHD₂, 2.4% of CH₂D and 10% of CH₃.¹² The loss of deuterium suggests that the methylcycloheptatrienes are interconvertible through protonation-deprotonation reactions under the conditions of the solvolysis. If this is the case, the 2% of material which was not identified above could possibly be one of the other methylcycloheptatrienes. It will be pointed out below that isomerization of the methylcycloheptatrienes does, in fact, occur under the conditions of the solvolysis reaction. The ester fraction obtained from the solvolysis of Ic appears to be a single substance (by gas chromatography) whose retention time, infrared spectrum and refractive index are identical with those of an authentic sample of 1,4-dihydro-1-methyl-*d*₃-benzyl acetate (IIc) prepared by acetylation of 1,4-dihydro-1-methyl-*d*₃-benzyl alcohol.

By a mechanistic interpretation similar to that used above for the solvolysis of Ib, one would predict that the solvolysis of 1,4-dihydro-2-methyl-

(11) F. A. Cotton, J. H. Fassnacht, W. D. Horrocks, Jr., and N. A. Nelson, *J. Chem. Soc.*, 4138 (1959).

(12) It is difficult to visualize a mechanism which can account for this distribution of deuterium. The percentages were calculated from the intensities of the molecular ion peaks of the unfragmented parent hydrocarbons, and are based on the assumption that all of the deuterium present is located on the methyl groups. This assumption is reasonable for the trideuterio species, but can be questioned for the mono- and dideuterio species. In this regard, the similarity of the vinyl hydrogen absorption in the n.m.r. spectra of the deuterated and undeuterated materials suggests that there can be very little vinyl deuterium present.

benzyl *p*-toluenesulfonate (XIc) would give 2-methylcycloheptatriene (XII) as the predominant product together with lesser amounts of 1-methylcycloheptatriene and *o*-xylene.



The same procedure as in the preparation of 1,4-dihydrobenzoic acid was used for the reduction of *o*-toluic acid to 1,4-dihydro-2-methylbenzoic acid (XIa). Lithium aluminum hydride reduction of XIa gave good yields of 1,4-dihydro-2-methylbenzyl alcohol (XIb) which then was converted into the *p*-toluenesulfonate derivative XIc. Solvolysis of XIc gave 73% of a hydrocarbon fraction and 12% of an ester fraction. The hydrocarbon fraction was shown by gas chromatography to consist of four materials: 2-methylcycloheptatriene (31%), 3-methylcycloheptatriene (7%), 1-methylcycloheptatriene (54%) and *o*-xylene (7.5%) eluted in that order. The assignment of structure XII (2-methylcycloheptatriene) to the material in the first fraction of the gas chromatogram was based partly on spectral evidence and partly on the previous structural assignments. The infrared spectrum of XII exhibits a methyl absorption band while the n.m.r. spectrum exhibits methylene hydrogen absorption split into a triplet by the two adjacent vinyl hydrogens (in this case the third band of the triplet appears as a shoulder on the methyl hydrogen absorption band when operating at a frequency of 40 Mc. and is resolved at a frequency of 60 Mc.).

The hydrocarbon mixture consisted of 1- and 2-methylcycloheptatrienes in relative percentages which would not have been predicted and contained 3-methylcycloheptatriene which should not form, at least as a primary product. To help clarify these anomalies, a pure sample of 2-methylcycloheptatriene was heated for 12 hours in acetic acid to which was added one molecular equivalent of *p*-toluenesulfonic acid and two molecular equivalents of sodium dihydrogen phosphate monohydrate (to approximate the solvolytic conditions). Gas chromatography of the crude hydrocarbon product showed the presence of 35% of 2-methylcycloheptatriene, 14% of 3-methylcycloheptatriene and 51%

of 1-methylcycloheptatriene. It was not determined whether this mixture really represented an equilibrium condition; however, the results clearly indicate that isomerization of products can occur by protonation-deprotonation reactions during solvolysis—a fact indicated earlier in the solvolysis of 1,4-dihydro-1-methyl-*d*₃-benzyl *p*-toluenesulfonate (Ic).

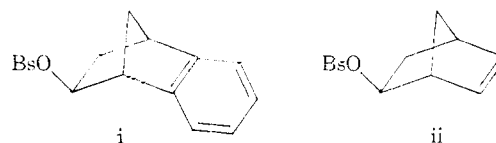
The ester fraction from the solvolysis of 2-methyl-1,4-dihydrobenzyl *p*-toluenesulfonate (XIc) was separated by gas chromatography and shown to consist of 1,4-dihydro-2-methylbenzyl acetate (58%) by comparison of its retention time and infrared spectrum with those of an authentic sample, and 38% of an ester which is presumably a methylcycloheptadienyl acetate (inferred from a mechanistic interpretation of the solvolysis reaction, its infrared spectrum and elemental analysis). An unidentified mixture of three materials amounting to 4% of the ester fraction was eluted early in the chromatographic separation.

We completed our work with the preparation and solvolysis of 1,4-dihydro-1-methyl-1-naphthylmethyl *p*-toluenesulfonate (XIIIc). A knowledge of the products from this solvolysis would allow one to ascertain the relative importance of homoallylic delocalization involving the π -electrons of an olefinic bond (see XIV) or the π -electrons of an aromatic ring (see XVII).¹³

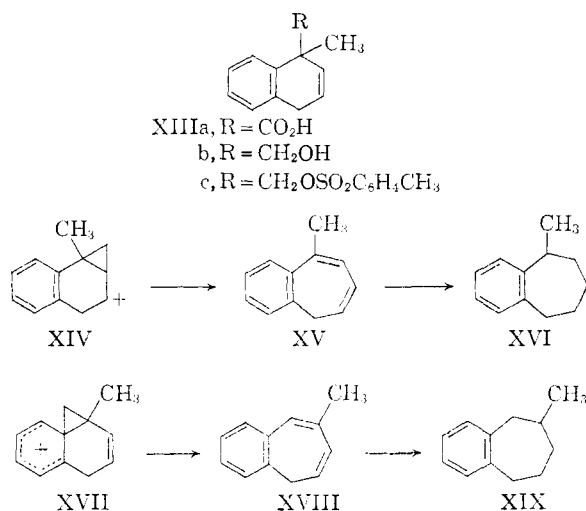
Reduction of 1-naphthoic acid by the method of Birch¹⁴ gave a 77% yield of 1,4-dihydro-1-naphthoic acid. Methylation of this acid by the method described above gave a mixture of products from which 1,4-dihydro-1-methyl-1-naphthoic acid (XIIIa) was obtained in poor yield. Lithium aluminum hydride reduction of the acid XIIIa and treatment of the resulting alcohol XIIIb with *p*-toluenesulfonyl chloride gave the desired *p*-toluenesulfonate XIIIc.

Solvolysis of 1,4-dihydro-1-methyl-1-naphthylmethyl *p*-toluenesulfonate gave 70% of a hydrocarbon fraction and 6% of an ester fraction. Gas chromatography of the hydrocarbon portion gave two fractions corresponding to 97 and 3%. The infrared and ultraviolet spectra of the larger fraction were consistent for either XV or XVIII (or double-bond isomers of these structures) and excluded the presence of 1-ethylnaphthalene. The larger fraction was believed to be homogeneous; however, subsequent work indicated that this fraction must have contained two compounds which are inseparable under the chromatographic conditions employed. Hydrogenation of the hydrocarbon fraction from the solvolysis using a palladium-on-carbon catalyst resulted in the uptake of two molecular equivalents of hydrogen. Gas chroma-

(13) P. D. Bartlett and W. P. Giddings, *THIS JOURNAL*, **82**, 1240 (1960), have recently reported a similar study in which they found that the acetolysis (*k*₁) of i at 25° in glacial acetic acid containing sodium acetate was 0.16 that of ii.



(14) A. J. Birch, *J. Chem. Soc.*, 430 (1944).



tography of the product gave 14% of an unidentified substance [believed to be 1,2-benzo-4-methylcycloheptene (XIX)] and 86% of 1,2-benzo-3-methylcycloheptene (XVI) which was identified by comparison of its retention time and infrared spectrum with those of an authentic sample. The components of the ester fraction obtained in the solvolysis of XIIIc were not completely separated by gas chromatography and remain unidentified.

The isolation of the hydrocarbon XVI as the major ultimate product clearly demonstrates the preferred interaction of the π -electrons of the olefinic bond in XIIIc for homoallylic resonance.¹³

Experimental^{15, 16}

1,4-Dihydrobenzyl Alcohol (Xb).—To a slurry of 12.8 g. of lithium aluminum hydride in 400 ml. of ether was added dropwise with stirring a solution of 20.5 g. of dihydrobenzoic acid (prepared in 84% yield, m.p. ca. 10°; lit.^{6b} m.p. 10–15°) in 200 ml. of ether at such a rate as to cause gentle refluxing of the ether. The mixture was heated under reflux for an additional hour, cooled to 0° and hydrolyzed by the cautious addition of water (40 ml.) followed by 20% by weight sulfuric acid (300 ml.). The ether extract of the product was washed with water, dried and distilled giving 10.2 g. (56%) of 1,4-dihydrobenzyl alcohol, b.p. 95–97° (20 mm.), n_D^{25} 1.5043, $\nu_{\text{max}}^{\text{OH}}$ 3350 (s, OH) and 1632 (w, C=C) cm^{-1} .

(15) Melting points and boiling points are uncorrected. The infrared spectra were determined with a Baird (model B) or Perkin-Elmer (model 21) spectrophotometer fitted with a sodium chloride prism. In reporting infrared spectra, (s) denotes strong, (m) medium and (w) weak absorption. Ultraviolet spectra were determined with a Cary recording spectrophotometer (model 11MS). We are indebted to Prof. J. S. Waugh for the n.m.r. spectra which were determined with a Varian V-4300B spectrometer and stabilized magnetic system operating at a frequency of 40.0 Mc., and to Prof. K. Biemann and Dr. J. Seibl for mass spectrometric analyses which were determined with a CEC 21-103 instrument with a heated inlet at 140°.

(16) Columns for gas chromatography were 8 mm. Pyrex tubes 190 cm. long containing 30% by weight of a stationary liquid on 50–100 mesh firebrick support. Helium at 10–15 p.s.i. was used as the carrier gas and thermistors were employed for the detection of the sample peaks. The following stationary liquids and temperatures were employed: (a) Dow-Corning Silicone oil No. 550 at temperatures of 150° for the alcohols, 175° for the esters and 100° for the hydrocarbons; (b) a solution of silver nitrate (30–40% by weight) in polyethylene glycol at 70°; (c) Caribide and Carbon Carbowax 600 at 160°; (d) 4-methyl-4-nitropimelonitrile at 70°; (e) Dow-Corning Silicone oil No. 550 at temperatures of 230° for the esters, 190–220° for the alcohols and 195° for the hydrocarbons; and (f) 1,2,3-tricyanoethoxypropane at 195°.

The composition of reaction mixtures was calculated using integrated areas from the chromatogram and no correction was made for slight differences in the thermal conductivity of the components.

Anal. Calcd. for $\text{C}_7\text{H}_{10}\text{O}$: C, 76.32; H, 9.15. Found: C, 76.19; H, 9.19.

The product was shown by gas chromatography^{16a} to contain about 4% of a substance whose retention time was identical to that of benzyl alcohol.

In another run, the crude 1,4-dihydrobenzoic acid obtained from the reduction of 30 g. of benzoic acid was reduced directly with 11 g. of lithium aluminum hydride. The reaction mixture was treated successively with 11 ml. of water, 11 ml. of 15% sodium hydroxide solution and 33 ml. of water.¹⁷ Removal of the precipitate by filtration and distillation of the filtrate gave 19.6 g. (72%) of 1,4-dihydrobenzyl alcohol, b.p. 94–98° (20 mm.). The ultraviolet absorption spectrum of the product showed the presence of about 4% of a mixture of conjugated dihydro alcohol and benzyl alcohol.

1,4-Dihydrobenzyl 3,5-dinitrobenzoate, prepared in 81% yield by the method of Brewster and Ciotti,¹⁸ was crystallized from ethanol, m.p. 89–90.5°.

Anal. Calcd. for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_6$: C, 55.26; H, 3.98; N, 9.21. Found: C, 55.26; H, 4.14; N, 9.28.

Preparation and Solvolysis of 1,4-Dihydrobenzyl *p*-Toluenesulfonate (Ia).—To a solution of 4.0 g. of 1,4-dihydrobenzyl alcohol (purified by gas chromatography) in 100 ml. of anhydrous redistilled pyridine was added with swirling 6.8 g. of *p*-toluenesulfonyl chloride. The tightly sealed mixture was allowed to stand at 0–5° for 43 hours and was then diluted with ether. The mixture was washed with ice-cold 1 *N* hydrochloric acid, dilute sodium bicarbonate solution, water and dried. Concentration of the solution on a rotary evaporator under reduced pressure gave 8.7 g. (90%) of crude 1,4-dihydrobenzyl *p*-toluenesulfonate as a light yellow oil, $\nu_{\text{max}}^{\text{OH}}$ 1370 (s) and a doublet at 1180–1190 (s, sulfonate group) cm^{-1} . The infrared spectrum of the product indicated that it was essentially free of unchanged alcohol and solvents. Chromatography of a portion of the product on 50 times its weight of silica gel using pure ether as the eluent gave analytically pure 1,4-dihydrobenzyl *p*-toluenesulfonate (Ia).

Anal. Calcd. for $\text{C}_{14}\text{H}_{16}\text{O}_3\text{S}$: C, 63.63; H, 6.10. Found: C, 63.50; H, 6.15.

A mixture of 8.7 g. (0.033 mole) of crude 1,4-dihydrobenzyl *p*-toluenesulfonate, 100 ml. of purified acetic acid (distilled from triacetyl borate) and 8.9 g. (0.065 mole) of sodium dihydrogen phosphate monohydrate was stirred at 90° for 36 hours in a flask fitted with a magnetic stirrer, reflux condenser and drying tube. The mixture was then cooled to 0°, neutralized with sodium hydroxide solution and extracted with ether. The ether extracts were combined, dried and concentrated by distillation of the ether through a 2-foot Vigreux column and finally a semi-micro column.¹⁹ The residue (3.5 g.) was chromatographed on 200 g. of Merck acid-washed alumina using 400 ml. of pentane to elute the hydrocarbons and 400 ml. of ether-pentane (1:1) to elute the esters. Both of these solutions were concentrated as described above. The crude hydrocarbon fraction weighed 2.1 g. (70%), and the ester fraction weighed 0.8 g. (16%).

Separation of a portion of the hydrocarbon fraction by gas chromatography^{16b} showed it to contain 12% of toluene and 88% of cycloheptatriene (eluted in that order). The identification of the products was made by comparison of retention times and infrared spectra with those of authentic materials. By assigning toluene a relative retention time of 1.0, the retention time of cycloheptatriene was found to be 3.7.

The crude ester fraction was distilled, b.p. 130° (20 mm.), and hydrogenated in acetic acid at atmospheric pressure using 10% palladium-on-carbon catalyst. Gas chromatography^{16c} of the hydrogenated ester fraction resulted in the elution of two fractions in the following order: 63% of hexahydrobenzyl acetate and 37% of cycloheptyl acetate. The retention times and infrared spectra of the esters were essentially identical to those of authentic samples of these materials.

(17) Cf. V. M. Micovic and M. L. Mihailovic, *J. Org. Chem.*, **18**, 1190 (1953).

(18) J. H. Brewster and C. J. Ciotti, Jr., *THIS JOURNAL*, **77**, 6214 (1955).

(19) Of a type similar to that described by C. W. Gould, Jr., G. Holzman and C. Niemann, *Anal. Chem.*, **20**, 361 (1948).

In an earlier solvolysis of 1,4-dihydrobenzyl *p*-toluenesulfonate (Ia) using less optimum conditions, 22.1 g. (0.08 mole) of Ia in 300 ml. of glacial acetic acid was heated at 80° for 40 hours in the presence of 16 g. (0.12 mole) of sodium dihydrogen phosphate monohydrate. The ether extract of the product, obtained as described above, was distilled giving 1.3 g. of hydrocarbons and 5.3 g. (24%) of an ester fraction, b.p. 85–90° (14–15 mm.). Hydrogenation of 4.1 g. of the crude ester as described above gave 2.7 g. of product, b.p. 198–199°. The retention time^{16a} and infrared spectrum of the hydrogenated product are essentially the same as those of an authentic sample of cycloheptyl acetate (b.p. 199–200.5°).

Dehydration of 1,4-Dihydrobenzyl Alcohol.—A mixture of 6.0 g. of the alcohol Xb and 400 mg. of potassium bisulfate was heated to 180–190° in a distilling flask for 90 minutes. The liquid which had distilled was dried over calcium chloride and distilled from a Hickman flask²⁰ yielding 1.2 g. (24%) of a mixture of hydrocarbons. The infrared spectrum of the mixture is very similar to that of cycloheptatriene, but contains additional absorption bands at 1605, 1497, 1080, 1030 and 695 cm.⁻¹ attributable to the presence of not more than 25% toluene.

In a similar run, 19.5 g. of 1,4-dihydrobenzyl alcohol was heated at 175–180° for 60 minutes in the presence of 0.9 g. of Dowex-50 resin. Isolation of the product as described above gave 2.8 g. (17%) of a mixture of hydrocarbons, b.p. 104–111° (with a trace of material distilling at 80–85°). Gas chromatographic analysis^{16b} of the product indicated the presence of several minor constituents (totaling 10%), 25% toluene and 65% cycloheptatriene.

1,4-Dihydro-1-methylbenzoic Acid (Xc).—Approximately 1200 ml. of liquid ammonia (dried in a separate flask with a slight excess of sodium) was distilled into a 2-l. flask equipped with a stirrer and Dry Ice-cooled condenser with a Drierite drying tower attached. The entire reaction and most of the workup was carried out with vigorous stirring under a nitrogen atmosphere. Potassium amide was prepared by adding 75 mg. of ferric chloride to the liquid ammonia followed by 22.6 g. (0.58 mole) of potassium. To the gray reaction mixture was added 34 g. (0.26 mole) of 1,4-dihydrobenzoic acid in 100 ml. of ether as quickly as control of the reaction permitted, followed 15 minutes later by the cautious addition of 42 g. of methyl iodide over a 40-minute period. Toward the end of the methyl iodide addition the vigorous reaction subsided and the yellow partially-soluble carbanion disappeared. Solid ammonium chloride (160 g.) was then added followed by the dropwise addition of 160 ml. of water. Most of the ammonia was allowed to evaporate before adding more water and removing additional ammonia at about 50° using a rotary evaporator. The resulting solution was washed once with ether, neutralized at –5 to –10° with dilute hydrochloric acid and the product extracted with ether. The ether extract was dried and concentrated under reduced pressure using a rotary evaporator to give 34.5 g. (91%) of crude product. A gas chromatographic analysis^{16a} of an aliquot of the product, which had been converted to the methyl ester with diazomethane, indicated that the product was 95% pure and contained about 5% methyl benzoate (identified by retention time only).

An analytical sample of 1-methyl-1,4-dihydrobenzoic acid was obtained by recrystallization of the crude product from pentane at low temperatures, m.p. 35–37°, $\nu_{\text{max}}^{\text{C=O}}$ 1700 (s, C=O) and 1635 (w, C=C) cm.⁻¹ and no ultraviolet absorption maxima above 215 m μ .

Anal. Calcd. for C₈H₁₀O₂: C, 69.54; H, 7.30. Found: C, 69.80; H, 7.28.

1,4-Dihydro-1-methylbenzyl Alcohol (Xd).—By a procedure similar to that used in the preparation of 1,4-dihydrobenzyl alcohol, 28 g. of crude 1,4-dihydro-1-methylbenzoic acid was reduced with 17.1 g. of lithium aluminum hydride to give a crude sample of 1,4-dihydro-1-methylbenzyl alcohol which was purified by distillation through a Nester spinning band column²¹ to give 15.5 g. (62%) of material, b.p. 105–110° (100 mm.). Gas chromatographic analysis^{16a} of the various fractions indicated 1–5% of an impurity whose retention time was identical to that of benzyl alcohol. An analytical sample of 1,4-dihydro-1-methylbenzyl alcohol was

obtained through hydrolysis of the purified *p*-nitrobenzoate derivative (described below) and gas chromatographic purification^{16a} and redistillation of the alcohol. The infrared spectrum of the analytical sample was essentially the same as the spectrum of the distilled material above, $\nu_{\text{max}}^{\text{C=O}}$ 3500 (m, OH) and 1620 (w, C=C) cm.⁻¹.

Anal. Calcd. for C₈H₁₀O: C, 77.37; H, 9.74. Found: C, 77.27; H, 9.78.

1,4-Dihydro-1-methylbenzyl *p*-nitrobenzoate was prepared from 2.1 g. of 1,4-dihydro-1-methylbenzyl alcohol, 2.67 g. of *p*-nitrobenzoic acid, 6.1 g. of *p*-toluenesulfonyl chloride and 40 ml. of pyridine by the method of Brewster and Ciotti¹⁸ and gave 3.1 g. (67.5%) of product, m.p. 92–94.5° (from aqueous ethanol) raised to 93.5–95° by additional recrystallizations.

Anal. Calcd. for C₁₅H₁₅NO₄: C, 65.93; H, 5.53; N, 5.14. Found: C, 66.00; H, 5.78; N, 4.89.

Preparation and Solvolysis of 1,4-Dihydro-1-methyl-Toluenesulfonate (Ib).—The method used in the preparation of 1,4-dihydrobenzyl *p*-toluenesulfonate gave, from 6.6 g. of 1,4-dihydro-1-methylbenzyl alcohol and 9.9 g. of *p*-toluenesulfonyl chloride, 13.0 g. of crude 1,4-dihydro-1-methylbenzyl *p*-toluenesulfonate as a light yellow oil, $\nu_{\text{max}}^{\text{C=O}}$ 1370 (s) and a doublet at 1190–1180 (s, sulfonate group) cm.⁻¹. The spectrum shows that the product was essentially free of unchanged alcohol and solvents.

The solvolysis was carried out by mixing 8.1 g. of the crude *p*-toluenesulfonate and 8.5 g. of sodium dihydrogen phosphate monohydrate in 100 ml. of purified acetic acid, and stirring the mixture at 80° for 24 hours. Isolation of the products as described above gave a crude hydrocarbon fraction which was distilled to give 1.6 g. (56%) of material, b.p. 135–136°, and a very small yield of an ester fraction.

Purification of the hydrocarbon fraction by gas chromatography^{16d} showed the presence of three materials. The first fraction (2%) was of a compound of undetermined structure. The second fraction amounting to 50% was 3-methylcycloheptatriene (VIIb): $\lambda_{\text{max}}^{\text{EtOH}}$ 260 m μ (ϵ 3,880); $\nu_{\text{max}}^{\text{C=C}}$ 1625 (m) and 1615 (w, C=C) 1385 (w, C–CH₃) cm.⁻¹ and no absorption at 890 cm.⁻¹ characteristic of terminal methylene groups (other main bands occur at 1400, 1368, 1292, 1200, 1155, 1075, 1040, 1013, 910, 859 (m) and 700 (s) cm.⁻¹). The n.m.r. spectrum^{15,22} exhibits peaks at 1006, 1013, 1017, 1023, 1036, 1042, 1053 and 1058 c.p.s. for vinyl protons; 1163 and 1169 c.p.s. for methylene protons (the third band of the triplet is presumably obscured by absorption due to methyl protons at 1176 c.p.s.).

Anal. Calcd. for C₈H₁₀: C, 90.50; H, 9.50. Found: C, 90.50; H, 9.35.

The third fraction, which amounted to 48% of the total, was 1-methylcycloheptatriene (VIIIb): $\lambda_{\text{max}}^{\text{EtOH}}$ 269 m μ (ϵ 3,400); $\nu_{\text{max}}^{\text{C=C}}$ 1632 (m, C=C) 1375 (m, C–CH₃) cm.⁻¹ and no appreciable absorption at 890 cm.⁻¹ characteristic of terminal methylene groups (other main bands occur at 1330, 1290, 1190, 1080, 1008, 920, 855 (m) and 703 (s) cm.⁻¹). The n.m.r. spectrum^{15,22} exhibits peaks at 972, 1001, 1019, 1035, 1041, 1048 and 1055 c.p.s. for vinyl protons; 1162 and 1168 c.p.s. for methylene protons; and 1176 c.p.s. for methyl protons.

Anal. Calcd. for C₈H₁₀: C, 90.50; H, 9.50. Found: C, 90.36; H, 9.47.

Catalytic hydrogenation of a portion of the distilled hydrocarbon mixture in acetic acid using a 10% palladium-on-carbon catalyst at atmospheric pressure gave a product which was isolated by gas chromatography,^{16a} n_{D}^{27} 1.4394. The retention time, infrared spectrum and refractive index of this material and those of an authentic sample of methylcycloheptane (b.p. 134–136°, n_{D}^{27} 1.4396) were essentially identical.

Preparation and Solvolysis of 1,4-Dihydro-1-methyl-*d*₃-benzyl *p*-Toluenesulfonate (Ic).—Using procedures described above, the alkylation of 20 g. of 1,4-dihydrobenzoic acid with 24 g. of methyl-*d*₃ iodide¹¹ gave 19.6 g. (90%) of crude 1,4-dihydro-1-methyl-*d*₃-benzoic acid which was reduced with lithium aluminum hydride to give 17.0 g. (94%) of crude 1,4-dihydro-1-methyl-*d*₃-benzyl alcohol. Gas chromatographic analysis^{16a} of the crude alcohol showed the

(20) Similar to that described in F. Schneider's "Qualitative Organic Microanalysis," John Wiley and Sons, Inc., New York, N. Y., 1946, p. 34, Fig. 34.

(21) Available from Labglass, Inc., Vineland, N. J.

(22) Determined in carbon tetrachloride solution using tetramethylsilane as an internal standard. Positions of maximum absorption are expressed in cycles per second relative to the proton resonance band of benzene at 1000 c.p.s. or the band of tetramethylsilane at 1255 c.p.s.

presence of 3% of an impurity whose retention time is identical to that of benzyl alcohol. The 1,4-dihydro-1-methyl-*d*₃-benzyl alcohol used in subsequent work was purified by gas chromatography.

Anal. Calcd. for C₈H₉D₃O: % excess D, 25.0. Found: % excess D, 22.0.

A quantitative mass spectrometric analysis of the alcohol was unsuccessful because of the complicated spectrum arising from complete decomposition of the substance under the conditions of the determination.

The method used in the preparation of the previously obtained *p*-toluenesulfonates gave from 3.3 g. of 1,4-dihydro-1-methyl-*d*₃-benzyl alcohol and 4.6 g. of *p*-toluenesulfonyl chloride, 6.5 g. (96%) of crude 1,4-dihydro-1-methyl-*d*₃-benzyl *p*-toluenesulfonate, $\nu_{\text{max}}^{\text{CCl}_4}$ 2200 (w, C—D), 1370 (s) and a doublet at 1180–1190 (s, sulfonate group) cm.⁻¹.

Solvolysis of 6.5 g. of the *p*-toluenesulfonate Ic for 36 hours at 90° in a solution of 80 ml. of purified acetic acid containing 6.9 g. of sodium dihydrogen phosphate monohydrate, after work-up, gave 1.8 g. (73%) of a crude hydrocarbon mixture and 0.85 g. (22%) of a crude ester which was distilled to give 0.42 g. (11%) of a colorless liquid, b.p. 105–108° (35 mm.).

Purification of the hydrocarbon fraction by gas chromatography^{16d} showed it to consist of a substance of undetermined structure (2%), deuterated 3-methylcycloheptatriene (50%) and deuterated 1-methylcycloheptatriene (48%). The n.m.r. spectra of the latter two compounds have essentially the same patterns for vinyl proton and methylene proton absorption as the undeuterated compounds described above, but have greatly diminished absorption near 1176 c.p.s. (due to methyl proton absorption). The presence of methyl hydrogen was verified by mass spectrometric analyses¹⁵: the partially deuterated 1-methylcycloheptatriene contained 61.3% CD₃, 7.5% CHD₂, 7% CH₂D and 24% CH₃; the partially deuterated 3-methylcycloheptatriene was shown to contain 79.5% CD₃, 7.8% CHD₂, 2.4% CH₂D and 10.3% CH₃.

Purification of the ester fraction by gas chromatography^{16a} gave one compound whose retention time, infrared spectrum [$\nu_{\text{max}}^{\text{CCl}_4}$ 2200 (w, C—D) and 1740 (s, C=O) cm.⁻¹] and refractive index (n_D^{25} 1.4652) were essentially identical to those of an authentic sample of 1,4-dihydro-1-methyl-*d*₃-benzyl acetate (see below). Redistillation of the chromatographed sample through a Hickman still gave an analytical sample.

Anal. Calcd. for C₁₀H₁₁D₃O₂: C, 70.97; H and D, 10.12. Found: C, 71.24; H and D, 10.36.

One gram of 1,4-dihydro-1-methyl-*d*₃-benzyl alcohol was dissolved in 2 g. of acetic anhydride and treated with one drop of sulfuric acid. The solution was heated for 2 hours at 60°, then cooled and neutralized with sodium carbonate solution. The product was extracted with ether and the ether extract was washed, dried and distilled giving 0.75 g. (58%) of 1,4-dihydro-1-methyl-*d*₃-benzyl acetate (IIc), b.p. 106–108° (35 mm.), n_D^{25} 1.4654. The same product was obtained when 1,4-dihydro-1-methyl-*d*₃-benzyl alcohol was acetylated using pyridine as the catalyst. The various samples of IIc were shown to be identical by comparison of their infrared spectra.

1,4-Dihydro-2-methylbenzyl Alcohol (XIb).—By the method described above, 15.9 g. of 1,4-dihydro-2-methylbenzoic acid (prepared by the method of Plieninger and Ege^{6b} in 64% yield, m.p. 74–76°, lit.^{6a} m.p. 74–75°) was reduced with 9.85 g. of lithium aluminum hydride, giving 12.1 g. of crude product which was purified by distillation giving 10.8 g. (77%) of pure 1,4-dihydro-2-methylbenzyl alcohol, b.p. 109° (26 mm.), n_D^{25} 1.5019, $\nu_{\text{max}}^{\text{CCl}_4}$ 3200 (m, OH) and 1640 (w, C=C) cm.⁻¹, with essentially no ultraviolet absorption above 215 m μ .

Anal. Calcd. for C₈H₉O: C, 77.37; H, 9.74. Found: C, 77.29; H, 9.97.

1,4-Dihydro-2-methylbenzyl *p*-Toluenesulfonate (XIc).—By the method described above for the preparation of Ia, 5.8 g. of 1,4-dihydro-2-methylbenzyl alcohol and 8.9 g. of *p*-toluenesulfonyl chloride gave crude 1,4-dihydro-2-methylbenzyl *p*-toluenesulfonate which on recrystallization from ethanol gave 8.1 g. (62%) of pure XIc, m.p. 42–43°.

Anal. Calcd. for C₁₂H₁₃O₃S: C, 64.72; H, 6.53; S, 11.53. Found: C, 64.82; H, 6.59; S, 11.67.

Solvolysis of 1,4-Dihydro-2-methylbenzyl *p*-Toluenesulfonate (XIc).—The solvolysis was carried out for 36 hours at

90° using 12 g. of 1,4-dihydro-2-methylbenzyl *p*-toluenesulfonate and 12.5 g. of sodium dihydrogen phosphate monohydrate in 125 ml. of purified acetic acid. The usual work-up procedure gave 3.3 g. (73%) of a mixture of hydrocarbons and 0.90 g. (12%) of a mixture of esters.

Purification of the hydrocarbon fraction by gas chromatography^{16d} showed it to consist of four materials. The first material eluted (31%) was 2-methylcycloheptatriene (XII): $\lambda_{\text{max}}^{\text{EtOH}}$ 258 m μ (ϵ 2,600); $\nu_{\text{max}}^{\text{CCl}_4}$ 1630 (w) and 1612 (w, C=C), 1375 (m, C—CH₃) cm.⁻¹ and only weak absorption at 890 cm.⁻¹ (indicating the absence of a terminal methylene group) (other main bands occur at 1318, 1295, 1145, 1080, 1040, 1023, 940, 915, 820 (m) and 720(s) cm.⁻¹; the band occurring at 820 cm.⁻¹ may not be real since the solvent begins to absorb strongly at this point). The n.m.r. spectrum^{15,22} has significant peaks at 1000, 1008, 1017, 1020, 1030, 1037, 1045, 1052 and 1059 c.p.s. for vinyl protons; 1164, 1170 and a shoulder at 1175²³ c.p.s. for methylene protons; and 1180 c.p.s. for methyl protons.

Anal. Calcd. for C₈H₁₀: C, 90.50; H, 9.50. Found: C, 90.36; H, 9.47.

The other materials, in order, were 7% of 3-methylcycloheptatriene (VIIb), 54% of 1-methylcycloheptatriene (VIIb) and 8% of *o*-xylene. These materials were identified by comparison of their retention times and infrared spectra with those of 1- and 3-methylcycloheptatriene obtained from the solvolysis of Ib and of an authentic sample of *o*-xylene. The relative retention times of the first three fractions (cycloheptatrienes) relative to the *o*-xylene (fraction 4), taken as 1, are: 2-methylcycloheptatriene (fraction 1), 0.50; 3-methylcycloheptatriene (fraction 2), 0.57; and 1-methylcycloheptatriene (fraction 3), 0.67.

The crude ester fraction was purified by gas chromatography.^{16a} The first fraction eluted was 4% of an unidentified mixture of three materials. The second fraction (58%) was 1,4-dihydro-2-methylbenzyl acetate, n_D^{25} 1.4754, $\nu_{\text{max}}^{\text{CCl}_4}$ 1720 (s, C=O) cm.⁻¹, whose infrared spectrum was essentially identical to that of an authentic sample described below.

Anal. Calcd. for C₁₀H₁₄O₂: C, 72.28; H, 8.49. Found: C, 72.50; H, 8.23.

The third fraction (38%) is presumably a methylcycloheptadienyl acetate, $\nu_{\text{max}}^{\text{CCl}_4}$ 1720 (s, C=O) cm.⁻¹.

Anal. Calcd. for C₁₀H₁₄O₂: C, 72.28; H, 8.49. Found: C, 72.32; H, 8.57.

1,4-Dihydro-2-methylbenzyl Acetate.—To 1.0 g. of 1,4-dihydro-2-methylbenzyl alcohol in 2 g. of acetic anhydride was added 1 drop of pyridine and the solution was heated at 80° for 2.5 hours, then cooled and neutralized with sodium carbonate solution. The product was extracted with ether, and the ether extract was washed with water, dried and distilled giving 0.77 g. (59%) of 1,4-dihydro-2-methylbenzyl acetate, b.p. 115° (30 mm.), n_D^{25} 1.4793, whose infrared spectrum was identical to that of the analytical sample of this material obtained from the solvolysis of XIc.

Isomerization of 2-Methylcycloheptatriene.²⁴—To a solution of 120 mg. (0.001 mole) of pure 2-methylcycloheptatriene in 2.5 ml. of purified acetic acid was added 172 mg. (0.001 mole) of *p*-toluenesulfonic acid and 300 mg. (0.002 mole) of sodium dihydrogen phosphate monohydrate. The mixture was stirred and heated at 90° for 12 hours, after which it was cooled to 0°, neutralized with sodium hydroxide solution and the product extracted with ether. The ether extract was dried and concentrated to a low volume by careful distillation of the ether. Analysis of this crude mixture by gas chromatography^{16d} showed the presence of three fractions, in the order 35, 14 and 51% whose retention times were identical to 2-, 3- and 1-methylcycloheptatriene, respectively. There was no further confirmation of these structures.

1,4-Dihydro-1-methyl-1-naphthylmethyl *p*-Toluenesulfonate (XIIIc).—The reduction of 8.0 g. of 1,4-dihydro-1-methyl-1-naphthoic acid, m.p. 102–113.5° (lit.^{6a} m.p. 116–

(23) When the n.m.r. spectrum is run at a frequency of 60 Mc. this shoulder appears as a well defined peak at 1262 c.p.s. relative to the proton resonance band of benzene at 1000 c.p.s.

(24) The isomerization of 7-methylcycloheptatriene in acetonitrile solution has been found to give an equilibrium mixture of 7-, 2-, 3- and 1-methylcycloheptatriene (4.2, 9.5, 15.7 and 70.6%, respectively); see K. Conrow, Abstracts of papers presented at the New York Meeting of the American Chemical Society, September 11–16, 1960, p. 6P.

117°), with lithium aluminum hydride using the procedure described above for the preparation of Xb gave 7.6 g. of crude product which on redistillation yielded 5.73 g. (71%) of 1,4-dihydro-1-methyl-1-naphthylmethanol, b.p. 102–104° (0.15 mm.). Gas chromatographic analysis^{16a} of the first fraction (3.43 g.) showed the presence of 3% of an impurity while the second fraction (2.3 g.) had 7% of the same impurity.

The reaction of 3.4 g. of 1,4-dihydro-1-methyl-1-naphthylmethanol and 3.8 g. of *p*-toluenesulfonyl chloride, using the procedure described above for the preparation of Ia, gave 6.0 g. (94%) of crude 1,4-dihydro-1-methyl-1-naphthylmethyl *p*-toluenesulfonate, m.p. 49–54°. Several recrystallizations of the crude product from ethanol gave an analytical sample of XIIIc, m.p. 58–59°, $\nu_{\text{max}}^{\text{Cl}}$ 1370 (s) and a doublet at 1190–1180 (s, sulfonate group) cm^{-1} .

Anal. Calcd. for $\text{C}_{19}\text{H}_{20}\text{O}_2\text{S}$: C, 69.50; H, 6.14; S, 9.74. Found: C, 69.46; H, 6.14; S, 9.91.

Solvolysis of 1,4-Dihydro-1-methyl-1-naphthylmethyl *p*-Toluenesulfonate (XIIIc).—The solvolysis was carried out as described above for Ic using 6.0 g. of 1,4-dihydro-1-methyl-1-naphthylmethyl *p*-toluenesulfonate and 4.6 g. of sodium dihydrogen phosphate monohydrate in 70 ml. of purified acetic acid. The usual work-up procedure gave 2.0 g. (70%) of a hydrocarbon fraction, b.p. 136° (25 mm.), and 0.19 g. (6%) of an ester fraction.

Purification of the hydrocarbon fraction by gas chromatography^{16f} showed the presence of two materials. The first fraction eluted accounted for 97% of the crude product, and was presumably a mixture of 2-benzo-3-methylcycloheptatriene (XV) and 1,2-benzo-4-methylcycloheptatriene (XVIII) (or double bond isomers of these compounds), $\lambda_{\text{max}}^{\text{OH}}$ 274 μ (ϵ 6790). The infrared spectrum (CCl_4 solution) of the product shows a weak band at 1385 cm^{-1} ($\text{C}-\text{CH}_3$).

Anal. Calcd. for $\text{C}_{12}\text{H}_{12}$: C, 92.26; H, 7.74. Found: C, 92.05; H, 7.92.

The second material to be eluted from the column consisted of 3% of an unidentified material.

Attempted purification of the ester fraction by gas chromatography^{16e} failed to effect complete separation of the three components which appeared to be present in the mixture.

Hydrogenation of the Hydrocarbon Mixture from the Solvolysis of 1,4-Dihydro-1-methyl-1-naphthylmethyl *p*-Toluenesulfonate.—A solution of 0.50 g. of the distilled

hydrocarbon mixture and 5 ml. of glacial acetic acid was hydrogenated at atmospheric pressure in the presence of 75 mg. of 10% palladium-on-carbon catalyst. The hydrogenation stopped when 100% of two molecular equivalents of hydrogen had been absorbed. The catalyst was removed by filtration and the filtrate was cooled and neutralized with sodium hydroxide solution. The product was extracted with ether and the ether extract was dried and concentrated giving 0.48 g. (96%) of product which, when purified by gas chromatography,^{16e} showed the presence of two materials. The first fraction eluted amounted to 15% of an unidentified hydrocarbon, presumably 1,2-benzo-4-methylcycloheptene (XIX), and the second fraction was 85% of 1,2-benzo-3-methylcycloheptene (XVI), $\lambda_{\text{max}}^{\text{OH}}$ 257 (ϵ 230), 261 (shoulder), 264 (ϵ 300), 267 (ϵ 230) and 271 μ (ϵ 270), whose retention time and infrared spectrum are essentially identical to those of an authentic sample (see below).

Anal. Calcd. for $\text{C}_{12}\text{H}_{16}$: C, 89.94; H, 10.06. Found: C, 89.81; H, 10.15.

1,2-Benzo-3-methylcycloheptene (XVI).—To the Grignard reagent prepared from 5.2 g. of methyl iodide and 0.86 g. of magnesium in 40 ml. of ether was added, with stirring, 5 g. of benzosuberone²⁵ in 20 ml. of ether at such a rate as to maintain gentle refluxing of the ether. When the addition was complete, the mixture was allowed to stand overnight, and then poured into dilute sulfuric acid and ice. The product was extracted with ether, dried over magnesium sulfate and filtered. The ether was removed, and the product heated on the steam-bath for 1 hour in the presence of a 50% (by volume) aqueous sulfuric acid solution. The product was then extracted with ether, and the ether extract was dried. Removal of the solvent gave 5 g. (95%) of crude olefin which was distilled to give 3.1 g. of material in two fractions, b.p. 128° (30 mm.). The first fraction contained a red-colored impurity which came over in the early stages of the distillation. The structure of this red material has not been investigated. A portion of fraction 2 (0.5 g.) was hydrogenated as in the previous experiment to give 0.5 g. of crude 1,2-benzo-3-methylcycloheptene which on gas chromatographic purification^{16e} showed only one material to be present, whose retention time and infrared spectrum were essentially identical to those of the XVI obtained from the hydrogenated solvolysis product above.

(25) We are indebted to Roger L. Thorton for supplying a sample of this compound.

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Ethylidenimines by the Reaction of Acetylene with Primary Aliphatic Amines

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The reaction of acetylene with primary aliphatic amines in the presence of zinc and cadmium acetates has been shown to yield ethylidenimines, $\text{CH}_2\text{CH}=\text{NR}$, instead of the *N*-vinylamines, $\text{CH}_2=\text{CH}-\text{NHR}$, as reported by Reppe and co-workers. Infrared, ultraviolet and mass spectral data indicated the presence of higher boiling vinyls, $\text{CH}_2(\text{CH}=\text{CH})_n\text{CH}=\text{NR}$ ($\text{R} = \text{ethyl or cyclohexyl}$) in the distillation residues and in heat-treated samples of the ethylidenimines. *N*-Cyclohexyl-2-butenylideneimine was isolated, and its structure was established by reduction to *N*-*n*-butylcyclohexylamine.

Although vinylamines are postulated to be intermediates in several reactions, including the synthesis of 2-methyl-5-ethylpyridine, they have seldom been isolated and have been considered to be very unstable. However, Reppe recently reported the preparation of *N*-vinylamines in low or unspecified yields by the reaction of acetylene with certain primary and secondary amines over cadmium and zinc acetates.¹ *N*-Vinylethylamine (24% theoretical yield) and *N*-vinylcyclohexylamine were two of the products claimed to have been isolated, but the only supporting data were elemental analyses and boiling points. In addition,

(1) W. Reppe, *et al.*, *Liebig's Ann. Chem.*, **601**, 81 (1956).

the formation of *N,N*-divinylcyclohexylamine was reported.

It is well known that water adds to acetylenic bonds to produce aldehydes and ketones, not vinyl alcohols (eq. A). Similarly, as shown in eq. B, nitromethane adds to acetylene to produce 1-nitropropene, not 3-nitropropene.²

By analogy, the addition of ammonia or a primary amine to acetylene would be expected to produce an ethylidenimine, $\text{CH}_2\text{CH}=\text{NR}$, not a vinylamine $\text{CH}_2=\text{CHNHR}$ (eq. C). In the light of these reactions it is surprising that the earlier work did

(2) E. M. Vanderbilt and H. B. Hass, *Ind. Eng. Chem.*, **32**, 34 (1940).