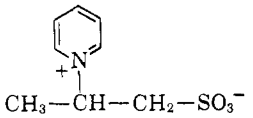
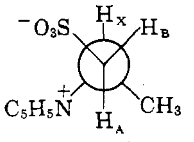
(III or IV) because a carbocyclic system is not necessarily a good model for a similar ring with four hetero atoms.

In the original report of the disultone[10] the reaction with pyridine was postulated to give a zwitterionic product, the correct structure of which must be V. Since the conformational analysis of ethane derivatives has been studied successfully by n.m.r. techniques, it is of interest to report the spectrum of V. In particular, comment on the question of internal rotation is afforded by the nonequivalence of the methylene protons in compounds such as V. The observed chemical shifts (in c.p.s. from internal acetonitrile) and coupling constants (in c.p.s.) are $\nu_A = -95.2$, $\nu_B = -91.8$, $\nu_X = -192.5$, and $\nu_{CH_3} = +15.5$; $J_{AB} = 15.2$, $J_{AX} = \pm 11.3$, $J_{BX} = \pm 2.7$, and $J_{CH_3X} = 6.9$. The methylene–methine coupling constants are of the same sign, but differ significantly in magnitude. One is larger than normal for a vicinal acyclic system, but any error in the assumption that the single line in the AB spectrum is completely degenerate would tend to decrease this. Nevertheless it strongly indicates an *anti*-type coupling in a conformation that is practically locked (VI). One would expect the sulfonate group to be near the pyridinium ring to minimize charge separation and *anti* to the methyl group to avoid steric interaction. The above conformation (VI) satisfies both this and the values of the coupling. The large difference between J_{AX} and J_{BX} indicates that other conformations play only a small part in the weighted mean.



$$\mathrm{CH_3-\overset{\overset{C_5H_5\overset{+}{N}}{|}}{C}H-CH_2-SO_3^-}$$

V



VI

Experimental

Melting points are uncorrected. Analyses were made by Galbraith Laboratories, Inc., Knoxville 21, Tenn.

4,8-Dimethyl-1,5-dioxa-2,6-dithiacyclooctane 2,2,6,6-Tetraoxide (I).—Samples of the disultone described previously were used.[2]

2-(N-Pyridinium)propane 1-Sulfonate (V).—A solution of the disultone (0.476 g., 0.00195 mole) in dry pyridine (5 ml.) was refluxed for 2.5 hr. Turbidity developed within 15 min.; white solid was present after 0.5 hr. The solid was collected, washed four times with acetone, and dried in a vacuum desiccator to give 0.347 g. (44.3%) of product, sintering at 278°, m.p. 297.5–298.5° dec. (lit.[10] m.p. 278° dec).

Anal. Calcd. for $C_8H_{11}NO_3S$: C, 47.75; H, 5.51; N, 6.96; S, 15.93. Found: C, 47.73; H, 5.54; N, 6.73; S, 16.06.

N.m.r. Spectra.—Measurements were obtained with a Varian HR-60 instrument at 60 Mc. Conditions for the spectrum of I were described earlier.[2] For the spectrum of V the solvent was deuterium oxide and the internal standard was acetonitrile. It was not possible to attain as good resolution in deuterium oxide as in the case of the disultone. The errors in the derived constants are therefore likely to be higher.

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[10] G. Manecke, *Chem. Ber.*, **85**, 160 (1952).

Monochloro Products from Camphene. Identification of Camphenol as 6-Hydroxycamphene[1,2]

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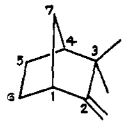
Received March 30, 1964

Camphenol, a crystalline alcohol, was prepared from camphene (**1**) by Tishchenko.[3] The structure of camphenol is the subject of this paper. Tishchenko obtained from reaction of camphene (**1**) and chlorine in carbon tetrachloride solution a monochloride fraction that he concluded must consist of **2** (*cis* and *trans*), **3**, and **4**. This monochloride mixture was treated with potassium acetate under conditions that caused only partial reaction, yielding a chloride fraction, thought to contain recovered **2** and **3**, and an acetate fraction. Saponification of the acetate fraction gave camphenol. Structure **6** was assigned to camphenol on the basis of oxidation and rearrangement reactions, and it was assumed that its acetate and chloride precursors had the related structures **5** and **4**.



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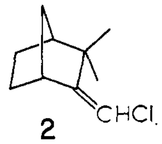

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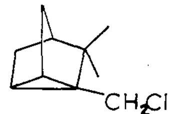

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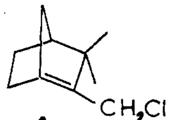

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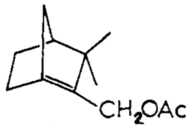

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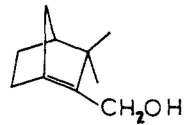

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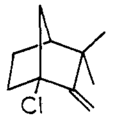

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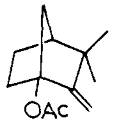

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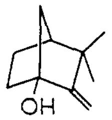

9

Chiurdoglu, Goldenberg, and Geeraerts reported later that camphenol had structure **9**.[4] They concluded on the basis of infrared spectra that the monochloride fraction consisted of **2**, **3**, and **7**, and that, on treatment of this fraction with potassium acetate, **7** reacted to form **8**, which on saponification gave **9**. More recent publications by Tishchenko[5] and by Chiur-

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[1] This work was supported in part by a grant from the Central Fund for Research of the Pennsylvania State University. Grateful acknowledgement is hereby made of this support. We are also pleased to acknowledge the assistance of the National Science Foundation in providing funds to aid in the purchase of the Varian A-60 n.m.r. spectrometer which was used in this research.

[2] Much of this work is contained in the senior theses of T. J. G. (June, 1962) and D. L. D. (June, 1963), The Pennsylvania State University.

[3] D. Tishchenko, *J. Gen. Chem. USSR*, **23**, 1051 (1953).

[4] G. Chiurdoglu, Ch. Goldenberg, and J. Geeraerts, *Bull. soc. chim. Belges*, **66**, 200 (1957).

[5] D. V. Tishchenko, *J. Gen. Chem. USSR*, **27**, 2943 (1957).

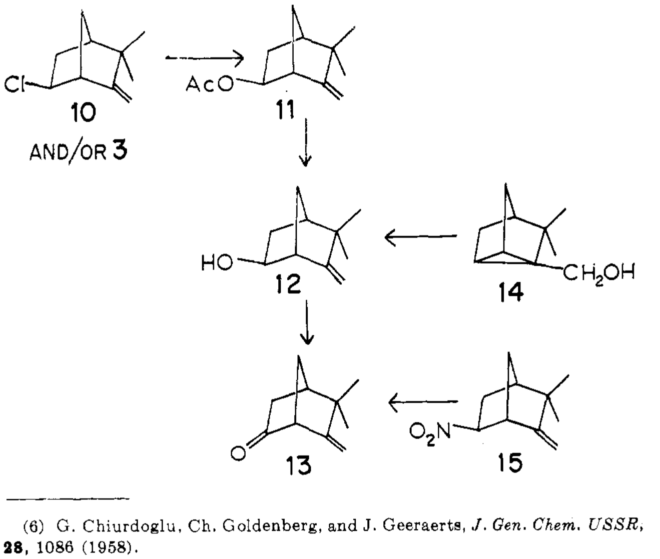
doglu, Goldenberg, and Geeraerts[6] emphasized the discrepancies between their original publications, but did not include further experimental information.

Our study was prompted by the belief that neither **4** nor **7** seemed reasonable structures for the precursor of camphenol. Structure **4** violates Bredt's rule.[7] Structure **7** has a bridgehead chlorine that would be expected to undergo nucleophilic substitution only with extreme difficulty,[8] yet formation of the acetate precursor of camphenol occurs readily. The double bond should not aid in stabilizing a bridgehead carbonium ion since a p-orbital at the bridgehead carbon would be constrained to a position nearly perpendicular to the plane of the π-orbital of the double bond.

We repeated the sequence of reactions described by Tishchenko and isolated a crystalline alcohol that was presumably camphenol. This alcohol was shown to be secondary, and therefore neither **6** nor **9**, by its oxidation to a ketone with chromic anhydride–pyridine, a reagent not expected to cause skeletal rearrangement. Conversion of the ketone to camphene by a Wolff–Kishner reduction indicated that it was 5-, 6-, or 7-ketocamphene, and that camphenol must be a 5-, 6-, or 7-hydroxycamphene.[9]

The most probable structure for camphenol is **12**. The corresponding acetate, **11**, is a reasonable product to expect from reaction of potassium acetate with **3** or with **10**, reactive monochlorides that could be present in the monochloride fraction. It is assumed that the hydroxyl group of camphenol is *exo*, as shown in **12**, because formation of the corresponding *exo* acetate (**11**) from **3** or **10** is more reasonable mechanistically than formation of the *endo* isomer.[10]

Prior to Tishchenko's work, Lipp had assigned structure **12** to an alcohol synthesized by treating **14** with phosphorous tribromide, reacting the bromide with potassium acetate, and saponifying the acetate.[11] As properties reported for this alcohol agree closely with those observed in this work, the camphenol of Tishchenko is probably also the alcohol prepared earlier by Lipp. The properties of our ketone are consistent with those reported[12,13] for a ketone prepared from 6-nitrocamphene (**15**), to which structure **13** has been assigned.[14]



Spectral evidence is in accord with our structural assignments. The n.m.r. spectrum (p.p.m.) of camphenol exhibited sharp peaks at 4.83 and 4.60 (=CH_2), a complex peak centered at 3.71 (H–C–O), a peak at 2.84 (H–O), and a peak at 2.56 (bridgehead H). The ketone spectrum showed sharp peaks at 5.06 and 4.82 (=CH_2) and a peak at 3.03 p.p.m. (bridgehead H). The acetate also showed peaks at 4.94 and 4.68 p.p.m. (=CH_2). The infrared spectrum of camphenol exhibited absorptions characteristic[15] of an exocyclic methylene group at 885, 1655, and 3075 cm.$^{-1}$, and the spectra of the acetate and ketone showed similar absorptions.

We are now investigating the components of the monochloride mixture formed from camphene. However, the identification of camphenol as 6-hydroxycamphene has removed the need for assuming a violation of Bredt's rule or an exception to the inertness of bridgehead halides.

Experimental

Spectra are of carbon tetrachloride solutions. N.m.r. spectra were taken at 60 Mc.; chemical shifts are relative to tetramethylsilane. Distillations were done with a platinum, spinning-band column. An 8 ft. × 0.25 in. column packed with 20% silicone oil 550 (Dow Corning) on 30–60-mesh Chromosorb P (Johns-Manville) was used for g.l.p.c. separations. Melting points were taken between cover glasses on a block.

Camphenol (12).—The reaction of camphene and chlorine was carried out essentially as described.[3] The monochloride fraction was obtained in 25% yield, b.p. 60–75° (3 mm.), lit.[3] b.p. 60–61° (2 mm.). This fraction was treated with potassium acetate in acetic acid as described.[3] A fraction collected at 50–60° (1 mm.) consisted principally of monochlorides; the acetate product was collected at 60–61° (0.75 mm.), lit. 73–74° (1 mm.),[3] 107–110° (15 mm.),[11] and 60–64° (0.6 mm.).[4] The infrared spectrum of the acetate fraction showed a strong band (carbonyl) at 1740 cm.$^{-1}$. The acetate fraction was saponified in methanolic potassium hydroxide. The crude product was cooled to Dry Ice temperature in a pentane solution, and the liquid was decanted from the precipitate. On warming, an oil remained which solidified after removal of the remaining pentane. Camphenol was isolated in yields of greater than 50% by this procedure without resorting to distillation. Material obtained in this manner had a wide melting point range but after sublimation had m.p. 58–59°, lit. m.p. 59.5–60°[3] and 59.5–60.5°[11]; infrared and n.m.r. spectra of the crude and sublimed materials were virtually identical. The infrared spectrum showed absorption (hydroxyl) at 3625 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.72; H, 10.70.

A hydrogen phthalate ester was prepared with phthalic anhydride in pyridine and recrystallized from heptane: m.p. 140–141.5°, lit.[3] m.p. 142–143°.

Anal. Calcd. for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 72.29; H, 7.00.

A *p*-nitrobenzoate ester was prepared with *p*-nitrobenzoyl chloride in pyridine and recrystallized from heptane: m.p. 128.5–130°, lit.[11] m.p. 132–133°.

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(6) G. Chiurdoglu, Ch. Goldenberg, and J. Geeraerts, *J. Gen. Chem. USSR*, **28**, 1086 (1958).

(7) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 10.

(8) D. E. Applequist and J. D. Roberts, *Chem. Rev.*, **54**, 1065 (1954); U. Schöllkopf, *Angew. Chem.*, **72**, 147 (1960).

(9) 7-Ketocamphene and the epimeric 7-hydroxycamphenes have been prepared in optically active form [E. E. van Tamelen and C. I. Judd, *J. Am. Chem. Soc.*, **80**, 6305 (1958)], but spectra of these compounds are not available.

(10) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(11) P. Lipp, *Ber.*, **80**, 165 (1947).

(12) Y. Asahina and T. Tukamoto, *ibid.*, **70**, 584 (1937).

(13) S. Nametkin and A. Zabrodin, *ibid.*, **59**, 368 (1926); S. S. Nametkin and A. S. Zabrodina, *Bull. acad. sci. URSS, Classe sci. math., Sér. chim.*, 1015 (1937); *Chem. Abstr.*, **32**, 2920 (1938).

(14) Reduction of this ketone (ref. 12) with sodium in ethanol furnished an alcohol that may be the *endo* isomer of camphenol.

(15) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., Methuen and Co., Ltd., London, 1962, Chapter 3.

Anal. Calcd. for $C_{17}H_{19}NO_2$: C, 67.76; H, 6.36; N, 4.65. Found: C, 67.94; H, 6.34; N, 4.84.

Oxidation of Camphenol to Ketone 13.—A solution of 0.35 g. of camphenol in 10 ml. of pyridine was added to 1.0 g. of chromic anhydride in 10 ml. of pyridine, and the mixture was stirred for 22 hr. Water was added, and the mixture was extracted with ether. The ether solution was washed with dilute hydrochloric acid, with water, and with dilute sodium bicarbonate solution, and was dried over sodium sulfate. Most of the solvent was removed through a small distillation column, and the remaining solution subjected to g.l.p.c. One large peak was observed in addition to the ether peak and a very small peak that had the retention time exhibited by camphenol. Collection of the material from the large peak furnished a solid, m.p. 65–70°, lit.[12,13] m.p. 77–78°. The infrared spectrum showed strong absorption (carbonyl) at 1750 cm.$^{-1}$. Without further purification, this material was converted to a semicarbazone derivative which was recrystallized from ethanol–water: m.p. 201–203°; lit. 205 m.p. dec.[13] 213.5.[12]

Anal. Calcd. for $C_{11}H_{17}N_3O$: C, 63.74; H, 8.27. Found: C, 63.94; H, 8.35.

Wolff-Kishner Reduction of Ketone 13.[16]—Sodium (1.2 g.) was added to 20 ml. of diethylene glycol and then 0.29 g. of the ketone (prepared as described above but not purified by g.l.p.c.) and 2 ml. of hydrazine hydrate were added. The solution was refluxed for 18 hr. Then 2 ml. more of hydrazine hydrate was added, and refluxing was continued for an additional 18 hr. Benzene was used to extract the solution and to rinse out the apparatus. Portions of this benzene solution were subjected to g.l.p.c. The retention time of the only significant peak (except for benzene) was the same as that exhibited by camphene, and collected material gave an infrared spectrum identical with that of camphene. The yield of camphene in this reduction was about 20%.

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[16] A similar reduction of this ketone has been reported (ref. 12).

Nitrene Chemistry. An Analysis of the Products from the Pyrolysis of 2-Butylazidobenzene

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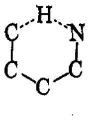
Received April 6, 1964

Previously we reported[1] that pyrolysis of 2-butylazidobenzene (I) led to the formation of a nitrene intermediate which cyclized to give only 2-ethylindoline (II) and no 2-methyl-1,2,3,4-tetrahydroquinoline (III). We concluded that when given a choice an aryl nitrene will ring close to a five-membered ring. Only in a reaction such as the pyrolysis of 2-azido-2′,4′,6′-trimethylbiphenyl,[2] where five- and six-membered ring closure must involve quite different types of mechanisms, do we find six-membered ring formation. These observations agree with a mechanism put forward by Barton[3] in which it was assumed that nitrenes, like the presumed intermediates in the Hofman–Freytog–Loeffer reaction, the photochemically induced cyclization of ketones, and the photolysis of nitrites and hypochlorites, require a six-membered transition state.



However, photolysis of acid azides leads to acyl nitrenes which are reported[4] to form both γ- and δ-lactams. These results, as well as our finding that (*S*)(+)-1-azido-2-(2-methylbutyl)benzene on pyrolysis definitely forms a small amount of 2,3-dimethyl-1,2,3,4-tetrahydroquinoline[5] caused us to experience some doubt about the completeness of our earlier work.[1]

Accordingly we have reinvestigated the pyrolysis of I both in the vapor phase[1] and in solution.[6] The products obtained were analyzed by gas phase chromatography (g.p.c.) and shown to consist of five components. The g.p.c. trace of the total distillable pyrolysate indicated the presence of at least four compounds (A, B, C, and D; see Table I) while the trace of the hydrogenated distilled pyrolysate showed only three compounds present (A, B, and D). Furthermore, after hydrogenation the relative proportions of the various components changed markedly: A increased, B and D decreased, and C vanished completely.

We interpret the g.p.c. findings as follows. Pyrolysis of I leads to five products: II, III, IV, and at least two isomers of V. G.p.c. (before hydrogenation) component A corresponds to amine IV, B partially to indoline II, C is one isomer of V, and D is III. If we assume that one of the isomers of V is eluted from the column together with II (component B), then we can account for the fact that the relative proportion of B decreased after hydrogenation. Furthermore, it seems reasonable to assume that V consisted merely of a mixture of side-chain unsaturated derivatives of IV. This assumption is consistent with the fact that the infrared spectrum of component C shows NH_2 absorption,[7] and further, that on hydrogenation the relative proportion of component A, compound IV, markedly increased while C vanished.

Scheme I shows the distribution of products from both the solution and vapor phase reactions. The total yield, and relative proportions of compound II and III are essentially the same from both reactions, however, large differences are found in the proportions of IV and V. It appears that the aryl nitrene is prone to abstract hydrogen atoms and form a primary amine. When the nitrene is generated in the vapor phase, practically all of the hydrogen abstraction occurs intramolecularly; when generated in solution, however, a large portion of hydrogen is abstracted intermolecularly. From a synthetic point of view, the vapor phase reaction is by far the more desirable procedure.

The identity of the g.p.c. components was established as follows. Component A was shown to be 2-butylaniline (IV) by a comparison of its infrared spectrum with that of an authentic sample. Component B was assumed to be 2-ethylindoline (II) because its infrared spectrum exhibited secondary amine[7] absorption, its ultraviolet spectrum in ethanol had a maximum at 290 mμ (indoline absorbs at 290.5 mμ while tetrahydroquinoline absorbs at 300 mμ[8]), and its elemental analysis and n.m.r. spectrum were consistent with that expected for structure II. Component D was assigned the struc-

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[1] G. Smolinsky, *J. Org. Chem.*, **26**, 4108 (1961).

[2] G. Smolinsky, *J. Am. Chem. Soc.*, **82**, 4717 (1960).

[3] D. H. R. Barton and L. R. Morgan, Jr., *J. Chem. Soc.*, 626 (1962).

[4] J. W. ApSimon and O. E. Edwards, *Can. J. Chem.*, **40**, 896 (1962); W. L. Meyer and A. S. Levinson, *J. Org. Chem.*, **28**, 2859 (1963).

[5] G. Smolinsky and B. I. Feuer, *J. Am. Chem. Soc.*, in press.

[6] G. Smolinsky, *ibid.*, **83**, 2489 (1961).

[7] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 214.

[8] T. Masamune, *J. Am. Chem. Soc.*, **79**, 4418 (1957).