mm.)] was obtained by pyrolyzing calcium phenylacetate.[12] 4,4'-Dichlorobenzil [m.p. 195–196° (from *n*-butanol)] was prepared from 4-chlorobenzaldehyde.[13,14,15]

1,3-Bis-(4'-chlorophenyl)-2-propanone.—This compound was synthesized according to Kenner and Morton.[16] Since experimental details are lacking, they are given here.

4-Chlorophenylacetic acid (171 g., 1.0 mole) was dissolved in 500 ml. of hot water containing sodium carbonate (53 g., 0.5 mole). After making the solution just acid to litmus with acetic acid, a solution of lead acetate trihydrate (190 g., 0.5 mole) in 200 ml. of water was added. The lead salt precipitated at once. After cooling, it was filtered with suction and dried at 90–100°.

The salt was transferred to a 2-l. distillation flask and heated in a silicone oil-bath to 280–290°. After 15 minutes at this temperature, the pressure was reduced to 5 to 10 mm. and the product was collected until a red oil began to distil. Recrystallization of the distillate from 95% ethanol gave 65 g. (0.23 mole, 46%) of colorless ketone, m.p. 90–92° (reported: 93°,[16] 98–99°[17]). The semicarbazone melted 116–118° (reported[18] 118°).

Tetracyclones.—The procedure employed was that for tetracyclone reported by Dilthey and Quint[4] and modified by Johnson and Grummitt.[18] The quantities of starting materials varied from 0.05 to 0.12 mole. When 4,4'-dichlorobenzil was used, about 20% of thiophene-free benzene was added to the solvent to aid its solution. A typical procedure is given here.

A solution of 25 g. (0.119 mole) of benzil and 33.2 g. (0.119 mole) of 1,3-bis-(4'-chlorophenyl)-2-propanone in 300 ml. of 95% ethanol (purified by refluxing with and distilling from potassium hydroxide) was brought just to the boiling point. A solution of 3.6 g. of potassium hydroxide in 20 ml. of ethanol was added through the condenser. Spontaneous boiling ensued and was allowed to subside after which the mixture was refluxed for 15 minutes longer. The cooled solution was filtered to give 47.3 g. (0.104 mole, 88%) of deep purple crystals, m.p. 238–239°. Recrystallization of 5 g. by dissolving it in 250 ml. of benzene, adding 150 ml. of absolute ethanol and allowing to cool gave 4.8 g. (96%) of crystals, m.p. 239–240°.

(12) H. Apitzsch, *Ber.*, **37**, 1428 (1904); see also A. Popow, *ibid.*, **6**, 560 (1873).

(13) R. E. Lutz and R. S. Murphy, THIS JOURNAL, **71**, 478 (1949).

(14) A. Hantzsch and W. Glower, *Ber.*, **40**, 1519 (1907).

(15) We are indebted to the Heyden Chemical Company, Garfield, N. J., for generous samples of 4-chlorobenzyl chloride and 4-chlorobenzaldehyde.

(16) J. Kenner and F. Morton, *J. Chem. Soc.*, 679 (1934).

(17) H. E. Zaugg, R. T. Rapala and M. T. Leffler, THIS JOURNAL, **70**, 3224 (1948).

(18) J. R. Johnson and O. Grummitt, *Org. Syntheses*, **23**, 92 (1943).

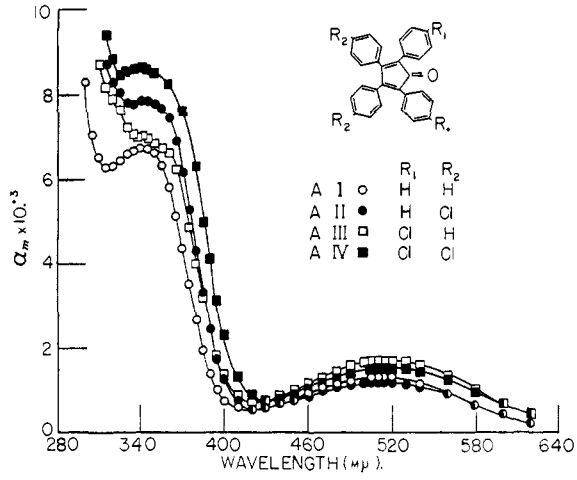


Fig. 1.

Tetraphenylphthalic Anhydrides.[9]—The tetracyclone (6.6 mmoles.) and chloromaleic anhydride[19] (b.p. 88° (14 mm.)) (1.0 g., 7.6 mmoles.) were refluxed in 15 ml. of bromobenzene (b.p. 156.2–157.0°) for 8 hr. (B-II), 10 hr. (B-III) and 6 hr. (B-IV). The solution was cooled in an ice–salt-bath, filtered, washed with cold bromobenzene and recrystallized from chlorobenzene (b.p. 132–134°). The crystals were freed from solvent by grinding and drying at reduced pressure at 156°.

Summary

2,5-Diphenyl-3,4-bis-(4'-chlorophenyl)-cyclopentadienone, 3,4-diphenyl-2,5-bis-(4'-chlorophenyl)-cyclopentadienone and tetrakis-(4-chlorophenyl)-cyclopentadienone have been synthesized. Reaction with chloromaleic anhydride converted these compounds to 3,6-diphenyl-4,5-bis-(4'-chlorophenyl)-phthalic anhydride, 4,5-diphenyl-3,6-bis-(4'-chlorophenyl)-phthalic anhydride, and tetrakis-(4-chlorophenyl)-phthalic anhydride, respectively. The absorption spectra of tetracyclone and of the three chlorotetracyclones have been presented.

(19) Kindly supplied by the General Chemical Division, Allied Chemical and Dye Corporation, New York 6, N. Y.

BROOKLYN, N. Y. RECEIVED JULY 13, 1950

[CONTRIBUTION FROM THE RESEARCH DIVISION, BRISTOL LABORATORIES, INC.]

Terpene Derivatives. Basic Ethers[1]

BY WILLIAM B. WHEATLEY, WILLIAM E. FITZGIBBON, LEE C. CHENEY AND S. B. BINKLEY[2]

Despite the tremendous amount of research that has been carried out in the field of terpene chemistry there have been few publications on basic ethers of the terpene alcohols. A patent issued to Rothenberger[3] describes the reaction of terpene haloalkyl ethers with various amines to give terpene basic ethers. In another patent, which covers the reaction of terpenes and alcohols to give ethers,[4] the use of aminoalcohols is indicated. Except for these patents, the literature appears to be devoid of references to such compounds.

The lack of investigation of terpene basic ethers is even more surprising in view of the long use of some terpene alcohols as medicinal agents; *e.g.*, menthol.[5] These considerations, together with the availability of several useful intermediates, led to the preparation of a series of terpene basic ethers.

Isobornyl β-chloroethyl ether served as the starting material for the preparation of a number of basic ethers, being caused to react with both primary and secondary amines. It reacted readily in all cases tried, with the exception of diisopropylamine. However, isobornyl β-iodoethyl ether, prepared from the chloro compound by means of

(1) Presented before the Division of Medicinal Chemistry of the American Chemical Society, Chicago, September 3–8, 1950.

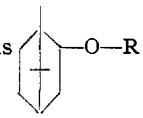
(2) Department of Biochemistry, University of Illinois College of Medicine, Chicago, Ill.

(3) Rothenberger, U. S. Patent 2,316,625 (*C. A.*, **37**, 5806 (1943)).

(4) Borglin, U. S. Patent 2,321,978 (*C. A.*, **37**, 6674 (1943)).

(5) A patent issued to Kropp in 1930 (U. S. Patent 1,733,462 (*C. A.*, **24**, 469 (1930)) claims basic oxime ethers as pharmaceutical compounds suitable for subcutaneous injection. Included in the examples is the O-β-diethylaminoethyl ether of camphor oxime.

TABLE I

ISOBORNYL ETHERS  —O—R

R	Method of prepn.	Yield, %	B.p., °C.	Mm.	$n^{25}D$	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
$-CH_2-CH_2-N(CH_3)_2$	A	89	91–92	0.5	1.4643	$C_{14}H_{27}ON$	74.6	74.8	12.1	12.2
$-CH_2-CH_2-N(C_2H_5)_2$	B	42	85–87	1.3	1.4658	$C_{16}H_{31}ON$	75.8	75.4	12.3	12.4
$-CH_2-CH_2-NC_5H_{10}$[a]	B	57	121–123	1.3	1.4839	$C_{17}H_{31}ON$	76.9	77.5	11.8	12.2
$-CH_2-CH_2-NC_4H_8O$[b]	B	60	104–106	0.4	1.4833	$C_{16}H_{27}O_2N$	71.9	72.2	10.9	11.0
$-CH_2-CH_2-N(i\text{-}C_3H_7)_2$	C	68	106–110	0.6	1.4657	$C_{18}H_{35}ON$	76.8	76.7	12.5	12.5
$-CH_2-CH_2-N(CH_2-CH_2OH)_2$	B	64	170–175	0.7	1.4907	$C_{16}H_{31}O_3N$	67.3	67.3	11.0	11.0
$-CH_2-C(CH_3)_2-N(CH_3)_2$	E	88	98–103	1.0	1.4690	$C_{16}H_{31}ON$	75.8	75.5	12.3	12.2
$-CH_2-CH_2-CH_2-N(CH_3)_2$	D	74	85–97	1.0	1.4648	$C_{15}H_{29}ON$				
$-CH_2-CH_2-NHCH_3$	B	50	121–129	14	1.4696	$C_{13}H_{25}ON$	73.9	73.5	11.9	12.0
$-CH_2-CH_2-NHCH(CH_3)_2$	B	32	70–71	1.0	1.4650	$C_{15}H_{29}ON$	75.3	73.4	12.2	10.9

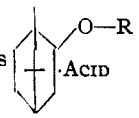
[a] NC_5H_{10} = 1-piperidyl. [b] NC_4H_8O = 4-morpholinyl.

TABLE II

TERPENE β-DIMETHYLAMINOETHYL ETHERS. R—O—CH_2—CH_2—$N(CH_3)_2$

R	Method of prepn.	Yield, %	B.p., °C.	Mm.	$n^{25}D$	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
Bornyl	D	65	75–81	2.0	1.4650	$C_{14}H_{27}ON$	74.6	74.6	12.1	12.2
2-Isobornyl-4-methylphenyl	D	83	165–168	1.0	1.5230	$C_{21}H_{33}ON$	80.0	80.8	10.5	10.7
Fenchyl	D	73	120–125	12	1.4604	$C_{14}H_{27}ON$	74.6	75.6	12.1	12.5
Nopyl	D	39	97–102	0.6	1.4730	$C_{15}H_{27}ON$	75.9	75.7	11.5	11.2
Hydronopyl	D	50	99–104	0.6	1.4699	$C_{15}H_{29}ON$	75.3	75.0	12.2	12.1
Menthyl	D	69	134–140	24	1.4531	$C_{14}H_{29}ON$	74.0	75.2	12.9	13.2
Menthylphenyl	D	81	156–157	1.0	1.5136	$C_{20}H_{33}ON$	79.2	79.5	11.0	11.1
α-Terpinyl	D	59	84–89	2.0		$C_{14}H_{27}ON$				
Geranyl	F	80	101–103	1.0		$C_{14}H_{27}ON$				
Tetrahydrogeranyl	G	86	92–97	1.0	1.4352	$C_{14}H_{31}ON$				

TABLE III

ISOBORNYL ETHER SALTS  —O—R ·ACID

R	M.p., °C.	Recrystn. solvent	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
$-CH_2-CH_2-N(CH_3)_2$	161.0–162.0	Me_2CO–MeOH	$C_{14}H_{27}ON\cdot C_6H_8O_7$[c]	57.5	57.7	8.4	8.4
	267–269 dec.[d]	*i*-PrOH	$C_{14}H_{27}ON\cdot CH_3I$[a]	49.0	49.3	8.2	8.3
$-CH_2-CH_2-N(C_2H_5)_2$	136.5–138.0	Me_2CO	$C_{16}H_{31}ON\cdot C_6H_8O_7$	59.3	58.7	8.8	8.7
$-CH_2-CH_2-NC_5H_{10}$[e]	251.0–252.5[d]	*i*-PrOH–Et_2O	$C_{17}H_{31}ON\cdot HCl$	67.6	67.7	10.7	10.6
$-CH_2-CH_2-NC_4H_8O$[f]	205.5–207.0	*i*-PrOH–Et_2O	$C_{16}H_{29}O_2N\cdot HCl$	63.2	63.2	10.1	10.0
$-CH_2-CH_2-N(i\text{-}C_3H_7)_2$	179.5–181.5	*i*-PrOH–EtOAc	$C_{18}H_{35}ON\cdot HCl$	68.0	68.1	11.4	11.6
$-CH_2-CH_2-N(CH_2CH_2OH)_2$	136.0–139.5	*i*-PrOH–Et_2O	$(C_{16}H_{31}O_3N)_2\cdot H_2SO_4$	57.5	57.6	9.6	9.7
$-CH_2-C(CH_3)_2-N(CH_3)_2$	131.5–133.5	MeOH–Et_2O	$C_{16}H_{31}ON\cdot C_6H_8O_7$	59.3	59.5	8.8	9.0
$-CH_2-CH_2-CH_2-N(CH_3)_2$	126.0–128.5	*i*-PrOH–SSB[b]	$C_{15}H_{29}ON\cdot C_6H_8O_7$	58.4	57.8	8.6	8.5
$-CH_2-CH_2-NHCH(CH_3)_2$	209.0–213.0	EtOAc	$C_{15}H_{29}ON\cdot HCl$	65.3	65.1	11.0	10.8

[a] Methiodide. [b] Skellysolve B (petroleum ether, b. p. 60–71°). [c] $C_6H_8O_7$ = citric acid. [d] Uncorrected. [e] —NC_5H_{10} = 1-piperidyl. [f] —NC_4H_8O = 4-morpholinyl.

sodium iodide, did react with diisopropylamine. Other basic ethers were prepared from the sodium derivative of the terpene alcohol and a dialkylaminoalkyl chloride. Isoborneol reacted incompletely with sodium hydride even on being refluxed overnight in toluene, so powdered sodium was used to convert the secondary and tertiary alcohols to the sodium derivatives. With one primary alcohol, geraniol, the method of Cusic,[6] wherein the alcohol, dialkylaminoalkyl chloride hydrochloride and flake caustic are heated together on the steam-bath, gave the basic ether in good yield. The other primary alcohols and phenols were easily converted to the sodium derivatives by means of sodium hydride. Hydrogenation of two unsaturated basic ethers over Adams catalyst gave the saturated compounds without difficulty. An interesting property of these terpene basic ethers is their ability to form beautifully crystalline non-hygroscopic dihydrogen citrates, whereas the hydrochlorides are frequently oily or hygroscopic.

In Table I are summarized the basic ethers of isoborneol which were prepared: the salts of these

(6) Cusic, U. S. Patent 2,461,038 (*C. A.*, **43**, 6671 (1949)).

TABLE IV

TERPENE β-DIMETHYLAMINOETHYL ETHER SALTS, R—O—CH_2—CH_2—$N(CH_3)_2$· ACID

R	M.p., °C.	Recrystn. solvent	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
Bornyl	166.5–168.0	MeOH	$C_{14}H_{27}ON \cdot C_6H_8O_7$	57.5	57.8	8.5	8.4
2-Isobornyl-4-methylphenyl	232.0–235.0[b]	MeOH–Me_2CO	$C_{21}H_{33}ON \cdot HCl$	71.7	70.2	9.7	9.5
Fenchyl	160.0–161.0	H_2O–*i*-PrOH	$C_{14}H_{27}ON \cdot C_6H_8O_7$	57.5	57.4	8.5	8.5
Nopyl	126.0–129.0	Me_2CO	$C_{15}H_{27}ON \cdot C_6H_8O_7$	58.7	58.5	8.2	8.2
Hydronopyl	135.0–137.0	Me_2CO	$C_{15}H_{29}ON \cdot C_6H_8O_7$	58.5	59.0	8.6	9.0
Menthyl	131.0–133.0	*i*-PrOH–Et_2O	$C_{14}H_{29}ON \cdot C_6H_8O_7$	57.3	57.3	8.9	8.9
Menthylphenyl	92.0–94.0	*i*-PrOH–SSB[a]	$C_{20}H_{33}ON \cdot C_6H_8O_7$	63.0	62.8	8.3	8.4
α-Terpinyl	123.0–124.0	*i*-PrOH	$C_{14}H_{27}ON \cdot C_6H_8O_7$	57.5	57.4	8.5	8.5
Dihydro-α-terpinyl	131.0–132.5	*i*-PrOH–SSB[a]	$C_{14}H_{29}ON \cdot C_6H_8O_7$	57.3	57.3	8.9	9.0
Geranyl	105.5–108.0	*i*-PrOH–SSB[a]	$C_{14}H_{27}ON \cdot C_6H_8O_7$	57.5	58.0	8.5	9.0
Tetrahydrogeranyl	108.0–109.0	EtOH–EtOAc	$C_{14}H_{31}ON \cdot C_6H_8O_7$	57.0	57.2	9.3	9.5

[a] Skellysolve B (petroleum ether, b. p. 60–71°). [b] Uncorrected.

ethers are to be found in Table III. Using β-dimethylaminoethyl chloride, a number of other terpene alcohols were converted into basic ethers. These ethers and salts thereof are found in Tables II and IV, respectively.

Pharmacology.—Pharmacological evaluation of these basic ethers indicates that they possess only slight activity as antihistaminic or antispasmodic agents.

Experimental[7]

The following terpenes or terpene derivatives were used as obtained from the indicated commercial sources without further purification: isoborneol, geraniol and menthol (Matheson, Paragon Division); borneol (Fritzche Bros.); nopol (Glidden Co.); α-terpineol, menthylphenol, isobornyl β-chloroethyl ether and isobornyl β-amino-β-methylpropyl ether (Hercules Powder Co.).[8]

Hydronopol.—Hydrogenation of nopol over Raney nickel at 1000–1500 lb. pressure and 180–250° afforded hydronopol in 67% yield; b.p. 134° at 7 mm.[9]

Fenchyl Alcohol.—Reduction of fenchone (Eastman Kodak Co., technical grade) with lithium aluminum hydride[10] gave fenchyl alcohol in 95% yield; b.p. 92–96° at 20 mm.

2-Isobornyl-4-methylphenol.—Camphene (Eastman Kodak Co., practical grade) and *p*-cresol were condensed in the presence of boron trifluoride etherate and the resulting isobornyl 4-methylphenyl ether rearranged to give 2-isobornyl-4-methylphenol.[11]

Preparation of Basic Ethers (Tables I and II). Method A.—Dimethylamine was passed into a solution of 325 g. (1.5 moles) of isobornyl β-chloroethyl ether in 830 ml. of toluene until the gain in weight amounted to 180 g. (4.0 moles). This mixture was heated in a high pressure bomb at 130–160° for 20 hours. The dimethylamine hydrochloride (112 g., 92%) was removed by filtration. The filtrate was extracted with a total of one liter of 10% hydrochloric acid in three portions. Basification of the acid extracts with potassium hydroxide liberated the amine, which was extracted into benzene. The benzene extracts were shaken with saturated sodium chloride solution and filtered through anhydrous potassium carbonate. Distillation gave 301 g. (89% yield) of isobornyl β-dimethylaminoethyl ether, b.p. 91–92° at 0.5 mm.

Method B.—With less volatile amines, the following general procedure was used. A solution of one mole of isobornyl β-chloroethyl ether and 2.2 moles of the amine in toluene was stirred and refluxed for eight to sixteen hours. Overnight reflux was often used because of convenience; a shorter reaction time might well have been as satisfactory. The reaction mixture was worked up as described above in method A.

In the experiment in which diethylamine was used, the reaction mixture was heated on the steam-bath for 26 hours in a sealed bottle. Refluxing was continued for 72 hours in the case of diethanolamine because of the limited solubility of the amine in toluene. A 25% aqueous solution of methylamine was used for the preparation of isobornyl β-methylaminoethyl ether.

Method C.—Since isobornyl β-chloroethyl ether failed to react with diisopropylamine even at 200°, the chloride was converted to the iodide by the action of sodium iodide in acetone.[12] The isobornyl β-iodoethyl ether reacted smoothly with diisopropylamine at 200°.

Method D.—Sodium isobornoxide was prepared by refluxing overnight a toluene solution of isoborneol with powdered sodium. The dialkylaminoalkyl chloride was liberated from its hydrochloride by the action of a strong potassium hydroxide solution and extracted into toluene. This toluene solution was shaken with anhydrous potassium carbonate for three to four hours, filtered, and added dropwise to the sodium isobornoxide solution. After refluxing overnight, the reaction mixture was cooled. Methanol was added to destroy any unreacted sodium, then water until all sodium chloride had dissolved. The product was isolated as described in method A. The majority of the ethers in Table II were prepared from β-dimethylaminoethyl chloride and the terpene alcohol in a similar manner except that sodium was replaced by sodium hydride in the preparation of the ethers of nopol, hydronopol, menthylphenol and 2-isobornyl-4-methylphenol.

Method E.—Isobornyl β-amino-β-methylpropyl ether was methylated by means of formaldehyde and formic acid.[13]

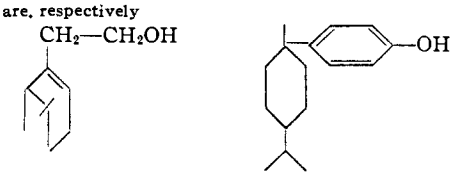
Method F.—Fifty grams (0.325 mole) of geraniol, 50 g. (0.35 mole) of β-dimethylaminoethyl chloride hydrochloride and 49 g. (1.21 moles) of flake sodium hydroxide were heated together on the steam-bath for 6.5 hours.[6] Water was added to dissolve the solid material; from this point the work-up was the same as described in method A.

Method G.—Hydrogenation of 30.9 g. (0.137 mole) of geranyl β-dimethylaminoethyl ether in 100 ml. of absolute ethyl alcohol and 50 ml. of glacial acetic acid over Adams platinum oxide catalyst was accomplished in six hours at room temperature and at three atmospheres pressure. The catalyst was removed by filtration, the filtrate diluted with a liter of water, then rendered basic with sodium hydroxide. The product was isolated by extraction with ether and subsequent distillation.

α-Terpinyl β-dimethylaminoethyl ether dihydrogen citrate (52.1 g., 0.125 mole) was dissolved in 100 ml. of 95% ethyl alcohol and 50 ml. of water and hydrogenated under

(7) All melting points are corrected unless otherwise noted.

(8) The formulas given by the manufacturers for nopol and menthylphenol are, respectively



(9) Bain, THIS JOURNAL, **68**, 638 (1946).

(10) Nystrom and Brown, *ibid.*, **69**, 1197 (1947).

(11) Kitchen, *ibid.*, **70**, 3608 (1948).

(12) Finkelstein, *Ber.*, **43**, 1531 (1910).

(13) Clarke, Gillespie and Weisshaus, THIS JOURNAL, **55**, 4571 (1933).

the same conditions. Absorption of hydrogen ceased after 2.5 hours of shaking. Dilution of the filtered solution with one liter of ether precipitated the product.

Preparation of Salts of the Basic Ethers. Hydrochlorides.—The basic ether was dissolved in cold ether and the solution saturated with dry hydrogen chloride.

Dihydrogen Citrates.—An ether solution of the basic ether was added to a solution of a 10% excess of anhydrous citric acid (Pfizer) in methanol or acetone.

Sulfate.—In one case (*cf.* Table III) a sulfate was prepared by adding the calculated amount of concentrated sulfuric acid to an acetone solution of the basic ether.

Quaternary Salt.—The methiodide of isobornyl β-dimethylaminoethyl ether was prepared by adding 2.1 ml. (0.033 mole) of methyl iodide to a solution of 6.7 g. (0.03 mole) of the basic ether in 30 ml. of isopropyl alcohol. The solution became noticeably warm, and on cooling deposited crystals of the quaternary iodide (8.1 g., 74% yield).

Acknowledgment.—The authors are indebted to Mr. Richard M. Downing for the microanalyses reported herein. Samples of a number of intermediates were kindly supplied by the Hercules Powder Company and Glidden Company.

Summary

A series of terpene basic ethers is reported. Preliminary pharmacological data indicate a low order of antihistaminic and antispasmodic activity.

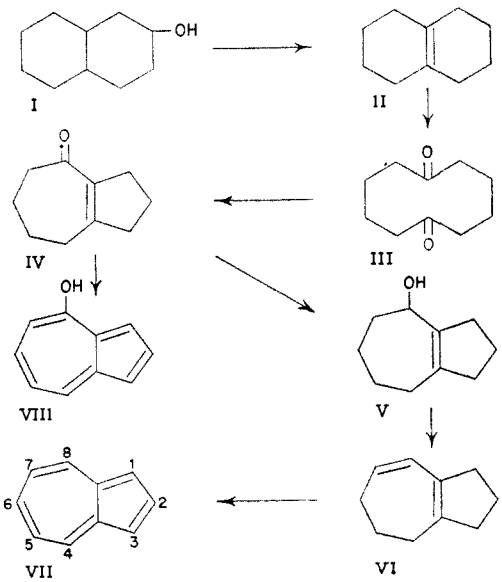
SYRACUSE 1. N. Y. RECEIVED MAY 3. 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING. UNIVERSITY OF WASHINGTON]

Azulene. I. An Improved Synthesis[1a,b]

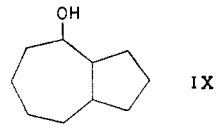
BY A. G. ANDERSON, JR., AND JERRY A. NELSON[1c]

A study of the chemistry of azulene (VII) in progress in this Laboratory required a synthetic method enabling continuous preparation of the pure material as a routine procedure. Consideration and some preliminary investigation of the methods reported in the literature[2] indicated that, while none was satisfactory for our needs, two of the syntheses appeared to be adaptable providing certain major difficulties could be overcome.



The synthesis of Plattner and St. Pfau[2a] from (9,10)-octalin (II) *via* 1,6-cyclodecanedione (III) and 4-keto-1,2,3,4,5,6,7,8-octahydroazulene (IV) was considered unsatisfactory in two respects. First, the route to II from decahydronaphthalene involved lengthy ozonization to decahydro-9-naphthol and dehydration of this decalol with zinc chloride to give mixed octahydronaphthalenes, from which the (9,10)-isomer was isolated in 14% overall yield. The direct dehydration of decahydro-2-naphthol with phosphorus pentoxide and phosphoric acid by Linstead[3] as later modified by Campbell and Harris[4] to give II in excellent yield seems to have been overlooked in connection with the preparation of azulene. We have found this procedure ideal for the preparation of the desired octalin in large quantities.

The second difficulty was the low yield (14%) of crude blue oil realized from the catalytic dehydrogenation of 4-hydroxydecahydroazulene (IX) and the lengthy purification of the crude product which gave only 1% (from the bicyclic alcohol) of crystalline azulene. As the formation of water in the dehydrogenation seemed undesirable, the preparation of a suitable oxygen-free intermediate was investigated. Reduction of IV with lithium aluminum hydride gave what is probably 4-hydroxy-1,2,3,4,5,6,7,8-octahydroazulene (V). This unsaturated alcohol was unstable, eliminating water spontaneously on standing, and could not be isolated in pure form. It was dehydrated directly by azeotropic removal of water from a refluxing benzene solution to give 1,2,3,4,5,6-hexahydroazulene (VI) in 97% yield from the ketone. The diene was dehydrogenated smoothly in the vapor phase under a nitrogen atmosphere at 320–340° over a 30% palladium-on-charcoal catalyst[5] suspended on asbestos in an electrically heated apparatus similar to that described by Nunn and Rapson[2g] to give azulene, with unreacted diene as the only major contaminant. Subsequent experimentation showed that better



IX

(1) (a) Presented before the Division of Organic Chemistry at the 118th Meeting of the A.C.S., Chicago, Ill., September, 1950. (b) From the Ph.D. dissertation of Jerry A. Nelson. (c) Shell Oil Fellow, 1949–1950.

(2) (a) Pl. A. Plattner and A. St. Pfau, *Helv. Chim. Acta*, **19**, 858 (1936); **20**, 224 (1937); (b) **22**, 202 (1938); (c) H. Arnold, *Ber.*, **76**, 777 (1943); (d) Pl. A. Plattner, A. Furst and K. Jirasek, *Helv. Chim. Acta*, **29**, 730, 740 (1946); Pl. A. Plattner and G. Büchi, *ibid.*, **29**, 1608 (1946); (e) Pl. A. Plattner and A. Studer, *ibid.*, **29**, 1432 (1936); (f) Pl. A. Plattner, A. Furst and A. Studer, *ibid.*, **30**, 1091 (1947); (g) J. R. Nunn and W. S. Rapson, *J. Chem. Soc.*, 825 (1949).

(3) R. P. Linstead, A. B. Wang, J. H. Williams and K. D. Errington, *J. Chem. Soc.*, 1136 (1937).

(4) W. P. Campbell and G. C. Harris, THIS JOURNAL, **63**, 2721 (1941).

(5) R. P. Linstead and S. L. S. Thomas, *J. Chem. Soc.*, 1130 (1940).