

Anal. Calcd. for $C_{12}H_{10}$: C, 93.46; H, 6.54. Found¹⁸: C, 93.65; H, 6.48.

The mass spectrum of the compound (major peaks at $m/e = 154, 153, 152, 128, 76, 63, 51, 39, 28$) indicated a molecular weight of 154. The infrared spectrum (CS_2 solution) contained bands at 655(s), 690(s), 747(s), 789(s), 1330(m), 1612(w), 2990(w), 3028(w) and 3070(w) cm^{-1} , as well as several weak bands in the 850–1250 cm^{-1} region. The ultraviolet spectrum is summarized in Table I, and the n.m.r. spectrum is shown in Fig. 1. The hydrocarbon is assigned the structure, benzobicyclo[2.2.2]octatriene.

Pyrolysis of Benzobicyclo[2.2.2]octatriene.—The hydrocarbon (1.5 mg.) was sealed under vacuum in a Pyrex tube and heated at 310° for 1.5 hr. Upon cooling to room temperature the liquid product crystallized to a solid mass of naphthalene, m.p. and mixed m.p. 78–79°, identity confirmed by the ultraviolet spectrum.

Decomposition of Benzenediazonium-2-carboxylate in the Presence of Naphthalene.—Sufficient anhydrous ether was added

(18) Spang Microanalytical Laboratory, Ann Arbor, Mich.

to 10 g. of naphthalene to dissolve it at the reflux temperature. In this solution 0.35 g. (2.4 mmoles) of the diazonium carboxylate I was stirred for 63 hr. at reflux. The ether was removed under reduced pressure and the product was chromatographed on 350 g. of ordinary alumina, using petroleum ether (30–60°)–benzene mixtures as eluent. After the elution of naphthalene there was obtained, in the 2:1 petroleum ether–benzene eluates, a series of colorless crystalline fractions. Combination of this material and sublimation at 98° (0.6 mm.) provided 0.034 g. (7%) of dibenzobicyclo[2.2.2]octatriene, m.p. 119.5–120.5° (reported 118.5–119°, 119–120°²⁰) identical by mixed m.p. and infrared spectrum with an authentic sample.²⁰

Acknowledgment.—We are grateful to Dr. A. A. Bothner-By for advice and assistance in calculating the n.m.r. spectrum.

(19) S. J. Cristol and N. L. Hause, *J. Am. Chem. Soc.*, **74**, 2193 (1952).

(20) W. R. Vaughan and A. C. Schoenthaler, *ibid.*, **80**, 1956 (1958). We are grateful to Dr. Vaughan for a comparison sample of this compound.

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY, EAST LANSING, MICH.]

Dicarbonium Ions of the Triarylmethyl Type. Ions from *o*-, *m*- and *p*-Xylylene Glycols¹

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Tetraphenyl-*p*-xylylene glycol and tetraphenylphthalan have *i*-factors in sulfuric acid of 7 and 5, respectively, indicating that each ionizes to the corresponding dicarbonium ion in that solvent. From the spectra of tetraphenyl-*o*-, *m*- and *p*-xylylene glycols in varying concentrations of aqueous sulfuric acid, values of pK_{R^+} (glycol to monocarbonium ion) for the latter two and $pK_{R^{++}}$ (mono- to dicarbonium ion) for all three were determined. Values of pK_{R^+} for the *m*- and *p*-glycols were -7.9 and -8.1; $pK_{R^{++}}$ for the *o*-, *m*- and *p*-isomers were -16.4, -9.9 and -10.5, respectively. The monocation from the *o*-glycol is undoubtedly in the colorless, cyclic oxonium ion form; this accounts in great measure for the 10⁶ difference in difficulty of formation of the *o*-*vis-à-vis* the *m*- and *p*-dicarbonium ions. The electronic spectra of the three dicarbonium ions are compared. Hydrolysis or methanolysis of the *m*- or *p*-dications gave the glycols or their dimethyl ethers. Hydrolysis of the *o*-dication gave tetraphenylphthalan as expected, but methanolysis gave 9-methoxy-9,10,10-triphenyl-9,10-dihydroanthracene *via* rapid intramolecular alkylation. Tetra-*p*-anisyl-*p*-xylylene glycol is completely ionized to dicarbonium ion in about 0.2–0.4% sulfuric acid–acetic acid.

Introduction

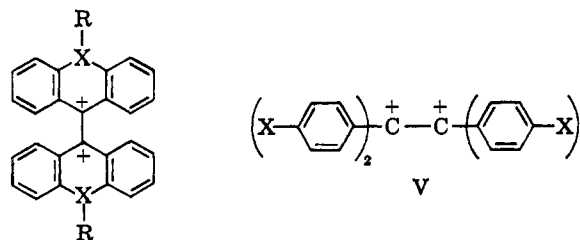
Evidence for several structurally different types of stable multicharged carbonium ions now exists. The ionization of certain benzotrihalides proceeds with the loss of two halide ions from a single carbon, giving ions of type I.^{2–4} The cyclobutene dication II,^{2a,5} which



may be considered as the homolog of the cyclopropenium cation,⁶ was produced by loss of two halide ions from adjacent carbon atoms.

Multicharged carbonium ions with more classical structures have also been described, but in most examples one has the option of representing the ion with charges on carbon or on some more electronegative element, usually nitrogen, oxygen or sulfur. Bis-xanthylum (III)^{7–11} and acridinium (IV)¹² salts and

certain of their non-benzo analogs^{13,14} are known, although their chemistry has been investigated only briefly. Substituted tetraarylethylene dications (V, X = OCH₃,^{15–18} N(CH₃)₂^{15,16,19}) are known but the



III, X = O or S, R = electron pair
IV, X = N, R = alkyl

parent dication (V, X = H) has not yet been prepared.²⁰ Finally, one must mention the many triaryl-

(1) We are indebted to the National Science Foundation, Grant 14289 (T. S.), and the Petroleum Research Fund of the American Chemical Society, Grant 488C (R. R. R.), for financial support.

(2) (a) H. Hart and R. W. Fish, *J. Am. Chem. Soc.*, **82**, 5419 (1960); (b) **83**, 4460 (1961).

(3) H. Hart and J. S. Fleming, *Tetrahedron Letters*, 983 (1962).

(4) Similar ions may be produced by addition of two protons to arylacetylenes, but the evidence is not yet as firm as with I, where crystalline salts have been isolated²; see M. E. Peach and T. C. Waddington, *J. Chem. Soc.*, 600 (1962).

(5) H. H. Freedman and A. M. Frantz, Jr., *J. Am. Chem. Soc.*, **84**, 4165 (1962).

(6) See R. Breslow, H. Höver and H. W. Chang, *ibid.*, **84**, 3168 (1962), and earlier references cited there.

(7) A. Werner, *Chem. Ber.*, **34**, 3300 (1901).

(8) A. Werner *Ann.*, **322**, 296 (1902).

(9) A. Schönberg and S. Nickel, *Chem. Ber.*, **67**, 1795 (1934).

(10) A. Schönberg and W. Asker, *J. Chem. Soc.*, 272 (1942).

(11) R. Wizinger and Y. Al-Atter, *Helv. Chim. Acta*, **30**, 189 (1947).

(12) R. M. Acheson, "Acridines," Interscience Publishers, Inc., New York, N. Y., 1956, pp. 280–285.

(13) F. Arndt, P. Nachtweg and E. Scholz, *Chem. Ber.*, **57**, 1903 (1924).

(14) F. Arndt and C. Lorenz, *ibid.*, **63**, 3121 (1930).

(15) R. Wizinger and J. Fontaine, *ibid.*, **60B**, 1377 (1927).

(16) R. E. Buckles and N. A. Meinhardt, *J. Am. Chem. Soc.*, **74**, 1171 (1952).

(17) R. E. Buckles and W. D. Womer, *ibid.*, **80**, 5055 (1958).

(18) R. E. Buckles, R. E. Erickson, J. D. Snyder and W. B. Person, *ibid.*, **82**, 2444 (1960).

(19) D. H. Anderson, R. M. Elofson, H. S. Gutowsky, S. Levine and R. B. Sandin, *ibid.*, **83**, 3157 (1961).

(20) Tetraphenylethylene dichloride, with silver tetrafluoroborate in liquid sulfur dioxide, gave purple solutions from which the predominant product (about 47%) was 9,10-diphenylphenanthrene: H. Hart and H. Tanida, unpublished results.

carbinols which, in strong acid, not only lose the hydroxyl group but are protonated on basic substituents.²¹

In the present paper we report on three dicarbonium ions obtained from tetraphenylxylylene glycols. Study of such ions seemed warranted in order to answer questions such as: (a) how difficult is it to introduce a second positive charge on carbon (*i.e.*, what are the pK_R 's for the first and second ionization of the glycols); (b) how do the mono- and dicarbonium ions compare spectroscopically; (c) how does orientation (*o,m,p*) at the central ring affect the pK_R 's and spectra; (d) what is the charge distribution, calculated and observed; (e) do these dicarbonium ions show unusual chemical reactivity, and can they be synthetically useful? In this paper cryoscopic and spectroscopic evidence is presented for the existence of these dications, and their pK_R 's and certain of their reactions are discussed. In subsequent papers, the charge distribution as studied *via* the n.m.r. spectra of suitably deuterated dicarbonium ions, and the affect of many structural variations on pK_R 's, spectra, electron transfer and other reactions will be discussed.²²

Results

Cryoscopic Measurements.—The results of cryoscopic measurements on sulfuric acid solutions of tetraphenyl-*p*-xylylene glycol ($pX(OH)_2$)²⁹ and tetraphenylphthalan (TPP) are given in Table I. The

TABLE I

CRYOSCOPIC MEASUREMENTS ON SOLUTIONS OF
TETRAPHENYL-*p*-XYLYLENE GLYCOL [$pX(OH)_2$] AND
TETRAPHENYLPHTHALAN (TPP) IN SULFURIC ACID

Compound	Sample, g.	H ₂ SO ₄ , g.	T, °C.	T, °C.	<i>i</i> ^c
$pX(OH)_2$	1.5257	97.10	9.941	1.728	7.67
				1.717 ^d	7.62
	1.7174	80.00	9.929	2.333	7.55
	1.7204	85.12	9.889	2.143	7.39
				2.093 ^e	7.22
TPP	0.460	107.4	8.969	0.308	4.99
	.490	107.4	8.637	.332	5.05
	.450	107.4	8.301	.326	5.39
	.950	106.8	8.637	.640	4.99
	.940	106.7	8.301	.658	5.05
	1.41	106.3	8.301	.966	5.18

^a Initial freezing point before adding the sample. ^b The temperature lowering. ^c Calculated from $i = \Delta T/6.12m_s$, where m_s is the molality of the solute. ^d Same sample as above, after 4 hours. ^e Same sample as above, after 13 hours.

(21) See, for example, A-M. Anthony-Barbier and P. Rumpf, *Bull. soc. chim. France*, 1474 (1959), for an analysis of the equilibria between neutral molecule, two monocations, two dications and one trication when malachite green is dissolved in aqueous acid of varying strength.

(22) It should be pointed out that these dicarbonium ions are probably not new, but unequivocal evidence for their existence has not been presented, nor have they been studied quantitatively. Thiele and Balhorn²³ stated that the dimethyl ether of tetraphenyl-*p*-xylylene glycol gave orange solutions in concentrated sulfuric acid, and that the corresponding dibromide was thermochemical (yellow in hot toluene or ethylene bromide). The dichloride gave orange-yellow solutions in sulfuric acid.²⁴ Weitz and Schmidt²⁵ obtained yellow solutions, presumably of the dicarbonium ion, when the dichloride was treated in benzene with silver perchlorate. There are no reports on ionization of the *m*-glycol or its derivatives. Schlenk and Brauns²⁶ described solutions of tetraphenyl-*o*-xylylene glycol or tetraphenylphthalan in sulfuric acid as orange-red. No mention is made in any of these papers of recovery of the glycols on hydrolysis. Finally, Sloan and Vaughan,²⁷ during a study of diradicals of the triarylmethyl type, gave the spectra²⁸ of carbonium ions from a number of dihalides in acidic solvents.

(23) J. Thiele and H. Balhorn, *Chem. Ber.*, **37**, 1463 (1904).

(24) F. Ullman and C. Schlaepfer, *ibid.*, **37**, 2001 (1904).

(25) E. Weitz and F. Schmidt, *ibid.*, **75B**, 1921 (1942).

(26) W. Schlenk and M. Brauns, *ibid.*, **48**, 716 (1915).

(27) G. J. Sloan and W. R. Vaughan, *J. Org. Chem.*, **22**, 750 (1957).

(28) G. J. Sloan, Appendix of Ph.D. Thesis, University of Michigan, Ann Arbor, Mich., 1954. We are indebted to Professor Vaughan for calling this work to our attention.

(29) The following symbols will be used to conserve space. X stands for the tetraphenylxylylene group, and will be preceded by *o*, *m* or *p* depend-

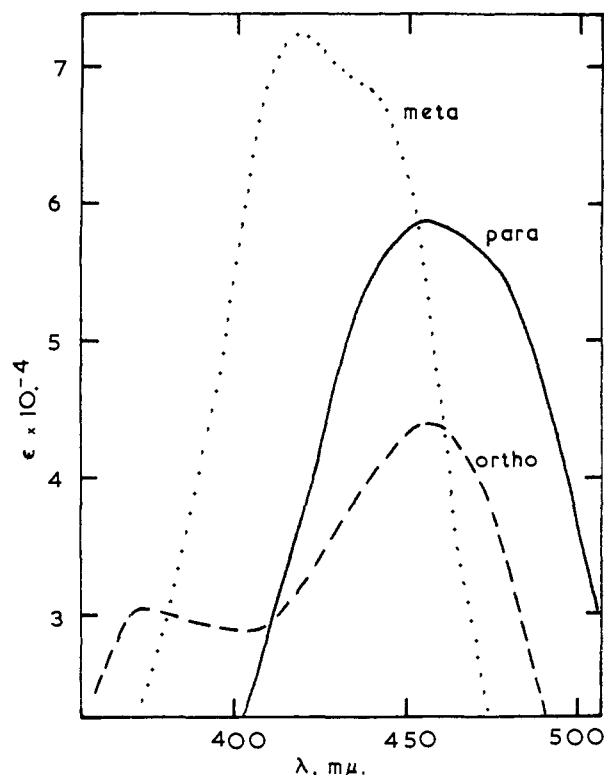
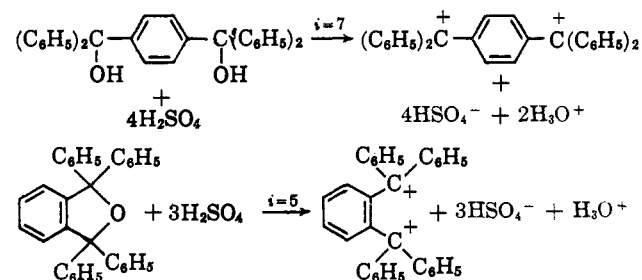


Fig. 1.—Absorption spectra of dicarbonium ions from the three tetraphenylxylylene glycols in sulfuric acid.

resulting *i*-factors³⁰ of 7 and 5, respectively, are in accord with expectation for ionization to dicarbonium ions.³¹



Freezing point measurements were not made on the *m*-glycol, primarily because it was difficult to obtain pure, in large quantity.

Spectra and pK_R Determination.—The spectrum of $pX(OH)_2$ is virtually unchanged between 68 and 100% sulfuric acid; since in the latter solvent, cryoscopic measurements are consistent with ionization to the dicarbonium ion pX^{++} , it is clear that the visible spectrum in this range of acid strength is due to that species. Similarly, the spectra of $oX(OH)_2$ and TPP, identical between 89–100% sulfuric acid, must be due to oX^{++} , since cryoscopy of TPP in 100% acid was consistent with ionization to the dicarbonium ion. The *m*-glycol, $mX(OH)_2$, has a constant spectrum between 69 and 100% sulfuric acid, and it is reasonable to assign it to the ion mX^{++} . The spectra of the three ions are shown in Fig. 1 and described in Table II.

ing on the orientation at the central ring. No prefix is used when referring to the entire group of glycols or ions. An appropriate superscript following X will indicate mono- or dicarbonium ion and, in the case of the neutral molecule or monocarbonium ion, the group(s) at the remaining ionization site(s) will follow in brackets (usually OH or OCH₃). Thus tetraphenyl-*o*-xylylene dication will be oX^{++} , and the monocarbonium ion from tetraphenyl-*m*-xylylene glycol will be $mX^+(OH)$.

(30) R. J. Gillespie, *Rev. Pure Appl. Chem.*, **9**, 1 (1959).

(31) The values for $pX(OH)_2$ are a bit high, but the error is large for large values of *i*; the results, when taken with the spectroscopic data, clearly establish the ionization as shown in the equation.

TABLE II
SPECTRA OF DICARBONIUM IONS FROM TETRAARYLXYLYLENE
GLYCOLS IN SULFURIC ACID

Ion	λ_{\max} , m μ	ϵ	% acid below which no color is apparent	% acid above which the spectrum is constant
pX^{++}	455	59,000	50	68
mX^{++}	440	70,000	50	69
	419	73,000		
oX^{++}	455	44,000	78	89
	373	30,500		
TA pX^{++a}	530	92,000	<i>d</i>	40
	455	50,000		
DP pX^{++b}	461	48,000	<i>d</i>	<i>d</i>
DP mX^{++c}	447	35,000	<i>d</i>	<i>d</i>

^a Tetra-*p*-anisyl-*p*-xylylene glycol dication. ^b α, α' -Diphenyl-*p*-xylylene glycol dication. ^c α, α' -Diphenyl-*m*-xylylene glycol dication. ^d Not determined.

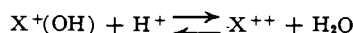
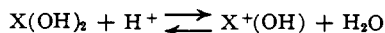
The ionization of carbinols to carbonium ions is best described quantitatively in terms of pK_{R^+} defined as

$$pK_{R^+} = \log \frac{a_{R^+} a_{H_2O}}{a_{ROH} a_{H^+}}$$

$$= \log \frac{C_{R^+}}{C_{ROH}} + \log \left(\frac{a_{H_2O}}{a_{H^+}} \times \frac{f_{R^+}}{f_{ROH}} \right)$$

$$= \log (C_{R^+}/C_{ROH}) + H_{R^+} \quad (1)$$

where H_{R^+} is defined operationally as shown,^{32,33} and has been evaluated^{33a,34} for aqueous sulfuric acid relative to pure water. With glycols, ionization may be stepwise. pK_{R^+} as defined in eq. 1 describes the



first step precisely. One may define $pK_{R^{++}}$ as

$$pK_{R^{++}} = \log \frac{C_{R^{++}}}{C_{R^+}} + \log \left(\frac{a_{H_2O}}{a_{H^+}} \times \frac{f_{R^{++}}}{f_{R^+}} \right)$$

the second term of which would be equal to H_{R^+} provided that

$$\left(\frac{f_{R^{++}}}{f_{R^+}} \times \frac{f_{ROH}}{f_{R^+}} \right) = 1$$

This assumption is reasonable when one considers the structures of the species involved and, in the absence of values for an $H_{R^{++}}$ function, we will define $pK_{R^{++}}$ as in eq. 2.³⁵

$$pK_{R^{++}} = \log (C_{R^{++}}/C_{R^+}) + H_{R^+} \quad (2)$$

Determination of pK_{R^+} or $pK_{R^{++}}$ depends on a method for evaluating the ratios C_{R^+}/C_{ROH} and $C_{R^{++}}/C_{R^+}$, respectively. The former is ordinarily a simple matter for carbinols since R^+ and ROH usually have quite different spectra. But as will be noted from Fig. 1 and Table II, the dicarbonium ions of concern here absorb in the same region as one would anticipate for the monocarbonium ions (the latter should be similar to the triphenylmethyl cation, which has maxima

(32) A. M. Lowen, M. A. Murray and G. Williams, *J. Chem. Soc.*, 3318 (1950).

(33) (a) N. C. Deno, J. J. Jaruzelski and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3044 (1955); (b) N. C. Deno, P. T. Groves and G. Saines, *ibid.*, **81**, 5790 (1959); (c) N. C. Deno, H. E. Berkheimer, W. L. Evans and H. J. Patterson, *ibid.*, **81**, 2344 (1959). See also V. Gold and B. W. V. Hawes, *J. Chem. Soc.*, 2102 (1951), and F. H. Westheimer and M. S. Kharasch, *J. Am. Chem. Soc.*, **68**, 1871 (1946).

(34) R. D. Bushick, Ph.D. Thesis, University of Pittsburgh, 1961. We thank Professor E. M. Arnett for making a copy of the thesis available to us. These values were used in the present work, because of the careful temperature control and extended range over which measurements were made.

(35) A similar problem arises when one deals with triarylcabinols containing easily protonated substituents,³⁶ but the need for a separate acidity function does not appear urgent.³⁷

(36) M. A. Murray and G. Williams, *J. Chem. Soc.*, 3322 (1950).

at 431 and 408 m μ). This makes difficult the evaluation of the extinction coefficient ϵ_{R^+} , a quantity necessary for evaluating both pK_{R^+} .

Nevertheless, it was possible to obtain rather good estimates of the pK_{R^+} 's for *m*- and *p*-X(OH)₂ in the following way. Spectra of solutions of the glycols in aqueous sulfuric acid were determined and the absorbance *A* at a given wave length was plotted against H_{R^+} (see Table III and Fig. 2). Such curves revealed two breaks, presumably corresponding to the first and second ionizations; from the differential plots of the data, the values of pK_{R^+} and $pK_{R^{++}}$ (the values of H_{R^+} at the breaks) were well defined, and are given in Table IV.

TABLE III

ABSORBANCE OF TETRAPHENYL-*m*- AND -*p*-XYLYLENE GLYCOLS
IN AQUEOUS SULFURIC ACID

Wt. % H ₂ SO ₄	$-H_{R^+}^a$	$A_m^{b,c}$	$A_p^{c,d}$	Wt. % H ₂ SO ₄	$-H_{R^+}^a$	$A_m^{b,c}$	$A_p^{c,d}$
50.0	6.47	0.07		60.0	8.61	0.89	0.97
51.0	6.62	.08		61.0	8.90	0.95	1.01
52.0	6.83	.09		62.0	9.17	1.03	1.13
53.0	7.02	.12	0.07	63.0	9.45	1.11	1.18
54.0	7.23	.16	.08	64.0	9.76	1.22	1.20
55.0	7.46	.23	.12	65.0	10.06	1.37	1.20
56.0	7.67	.34	.18	66.0	10.37	1.49	1.27
57.0	7.90	.56	.31	67.0	10.70	1.56	1.41
58.0	8.09	.72	.52	68.0	11.00	1.62	1.50
59.0	8.37	.80	.83	69.0	11.33	1.63	1.50

^a See footnote 34. ^b $\lambda = 419$ m μ ; 2.10×10^{-5} M glycol. ^c 1-Cm. cell width. ^d $\lambda = 455$ m μ ; 2.80×10^{-5} M glycol.

TABLE IV

IONIZATION CONSTANTS IN AQUEOUS SULFURIC ACID

Compound	$pK_{R^+}^a$	$pK_{R^{++}}^b$
$pX(OH)_2$	-8.1	-10.5
$mX(OH)_2$	-7.9	-9.9
$oX(OH)_2$...	-16.6
TA $pX(OH)_2$	-3.1 (est.)	-3.7 (est.)

^a Defined in eq. 1. ^b Defined in eq. 2.

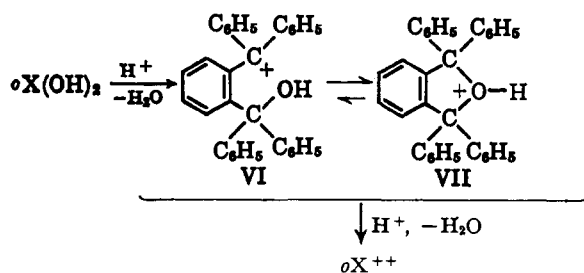
One can independently check the results for self-consistency; if the first break does in fact represent pK_{R^+} , one can calculate, from the value of *A* at this point, a figure for the extinction coefficient ϵ_{R^+} of the monocarbonium ion (assuming no dication present). With this, and $\epsilon_{R^{++}}$ determined from completely ionized glycol, *A* (and thus $pK_{R^{++}}$) can be calculated (i.e., the value of H_{R^+} when $C_{R^+} = C_{R^{++}}$). The value of $pK_{R^{++}}$ obtained this way agrees well with that taken from the second break in the *A vs. H_{R⁺}* curve.³⁷

A plot of *A vs. H_{R⁺}* for the *o*-glycol showed only a single break (see Fig. 2 and Table V), which is ascribed to conversion of monocation to dication; the value of $pK_{R^{++}}$ is given in Table IV. The product of the first ionization, $oX^+(OH)$, is most certainly present predominantly as the cyclic, colorless oxonium ion VII.

Tetra-*p*-anisyl-*p*-xylylene glycol (TA $pX(OH)_2$) in aqueous sulfuric acid was examined and the results are

(37) A sample calculation, using data at 419 m μ with $mX(OH)_2$, illustrates the method. pK_{R^+} is -7.85, from the differential plot; at this value of H_{R^+} , the observed absorbance *A* was 0.50. Since C_{R^+} at this point is 1.05×10^{-5} M (half the initial glycol concentration), $\epsilon_{R^+} = 47,600$. Since $\epsilon_{R^{++}} = 73,000$ (see Table II), one calculates that when $C_{R^{++}} = C_{R^+}$ (assuming no un-ionized glycol remains), *A* should be 1.26. The value of H_{R^+} when *A* = 1.26 is -9.84, in close agreement with the value -9.90 taken from the differential plot of *A vs. H_{R⁺}*. Furthermore, the calculated value of ϵ_{R^+} is reasonable.

Alternatively, one can readily show that (*A' - A*), the difference in the molar absorbances at the first and second breaks, should be $\epsilon_{R^+} \times C_0/2$, where *C*₀ is the initial glycol concentration. For the *m*-glycol at 419 m μ , (*A' - A*)_{calcd.} is 0.83; the observed difference, using the differential plot, is 0.79.



given in Table VI. The spectrum showed two maxima which shifted from 500 and 425 $m\mu$ in dilute (25%) acid (cf. λ_{\max} 500 $m\mu$ for di-*p*-anisylphenylcarbinol^{33a}) to 530 and 455 $m\mu$ in 40% acid. Above this the spectrum was constant until in concentrated (100%) acid there was a slight hypsochromic shift to 525 and 445 $m\mu$, possibly due to protonation on methoxyl. pK_{R++} is estimated (Table IV) at -3.7 ± 0.2 on the basis that (a) λ_{\max} of the long wave length band at this value of H_{R+} is about halfway (515 $m\mu$) between its value at low (monocation) and high (dication) acidities; and (b) calculations of the extinction coefficient of the monocation ϵ_{R+} , assuming $C_{R+} = C_{R++}$, $C_{ROH} =$

TABLE V

ABSORBANCE OF TETRAPHENYL-*o*-XYLYLENE GLYCOL IN AQUEOUS SULFURIC ACID
 $\lambda = 455 m\mu$, initial glycol concentration $6.20 \times 10^{-5} M$, 1-cm. cell width

Wt. % H_2SO_4	$-H_{R++}$	A	Wt. % H_2SO_4	$-H_{R++}$	A
78.0	14.60	0.10	86.0	17.21	1.58
80.0	15.28	.22	87.0	17.50	1.61
81.0	15.60	.30	88.0	17.82	1.63
82.0	15.94	.47	89.0	18.10	1.66
83.0	16.24	.68	92.0	18.99	1.67
84.0	16.58	1.00	97.0	20.40	1.67
85.0	16.87	1.31			

0, show a maximum value at 500 $m\mu$ for 33% acid ($\epsilon_{R+} 74,000$). Actually, calculations between 33 and 35% acid give reasonable values for the position of the maximum and for its extinction coefficient; pK_{R++} cannot lie below 32 or above 36% acid. Even in 33% acid there may be a bit of un-ionized glycol, for the extinction coefficient of di- and tri-*p*-anisylcarbinols is about 100,000.^{33a} The value of pK_{R+} for $TApX(OH)_2$ is probably about -3.1 and cannot lie below -2.8 ; the proximity of the two pK_R 's mitigates against their precise determination.

TABLE VI

ABSORBANCE OF TETRA-*p*-ANISYL-*p*-XYLYLENE GLYCOL IN AQUEOUS SULFURIC ACID

Wt. % H_2SO_4	$-H_{R+}$	λ_{\max}	ϵ	λ_{\max}	ϵ
26.0	2.17	425	5,000	500	10,000
28.0	2.49	427	12,500	502	26,000
29.0	2.64	430	14,200	504	28,900
30.0	2.78	450	18,300	505	38,000
31.0	2.94	450	26,200	505	50,500
32.0	3.10	450	38,000	510	69,100
33.0	3.26	455	42,300	515	75,000
35.0	3.60	455	47,600	526	85,600
40.0	4.50	455	49,800	530	92,150
60.0	8.61	455	51,800	530	96,000
100.0	..	445	52,500	525	88,500

The spectra of the diarylcarbinols α, α' -diphenyl-*p*-xylylene glycol (VIII) and the corresponding *m*-isomer IX were determined in 98% sulfonic acid, where they presumably form the dicarbonium ions. Each spectrum had a single, nearly symmetrical band, with λ_{\max} and ϵ given in Table II. The spectra in 98%

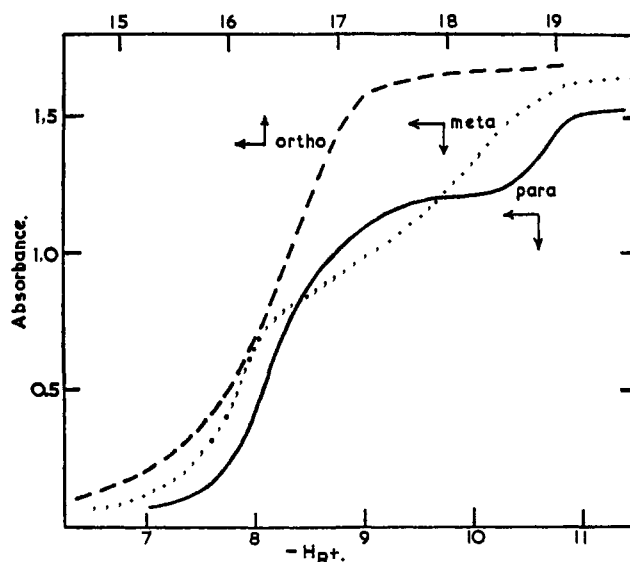
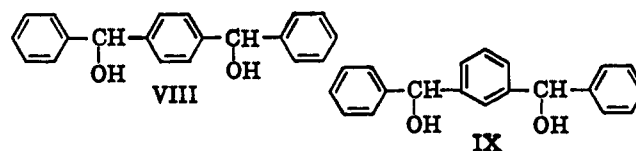
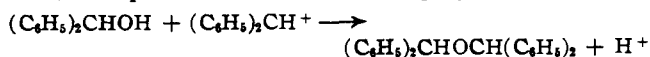


Fig. 2.—Absorbance vs. $-H_{R+}$ for tetraphenyl-*o*- (455 $m\mu$), -*m*- (419 $m\mu$) and -*p*- (455 $m\mu$) xylylene glycols.

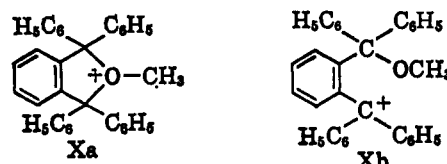
acid were stable for long periods, but it was not possible to obtain accurate pK_R values, because the colors faded rapidly in solutions whose H_{R+} was in the region of the pK_R . This is true also for benzhydrol itself



although its pK_{R+} has been estimated,^{33a} and is presumably due to reaction between carbonium ion and un-ionized carbinol to produce ethers.³⁸ In the present case, the products seemed to be polymeric.



Products.—Solvolysis of sulfuric acid solutions of mX^{++} , pX^{++} and $TApX^{++}$ gave the expected products; hydrolysis gave recovered glycol in excellent yield, and methanolysis gave the corresponding dimethyl ethers. Hydrolysis of oX^{++} gave TPP rather than $oX(OH)_2$ as expected, by loss of a proton from the first hydrolysis product VII. Methanolysis of oX^{++} seemed worth investigating, for if the initial product were the monocation Xa (analogous to VII),



one might anticipate either displacement on the methyl group, leading to TPP and dimethyl ether, or possibly reaction in form Xb with a second mole of methanol to produce the dimethoxy compound. In fact, when a sulfuric acid solution of oX^{++} was added to ice-cold absolute methanol, a white precipitate formed immediately; it proved to be 9-methoxy-9,10,10-triphenyl-9,10-dihydroanthracene (XI, $R = CH_3$),³⁹ presumably arising by an intramolecular alkylation from Xb. The process is not reversible, since XI ($R = CH_3$) gave the expected monocarbonium ion in

(38) H. M. Smith and C. M. Welch, *J. Am. Chem. Soc.*, **72**, 4748 (1950); H. M. Smith and R. G. Thompson, *ibid.*, **77**, 1778 (1955).

(39) A. Haller and A. Guyot, *Bull. soc. chim. France*, [3] **31**, 979 (1904).

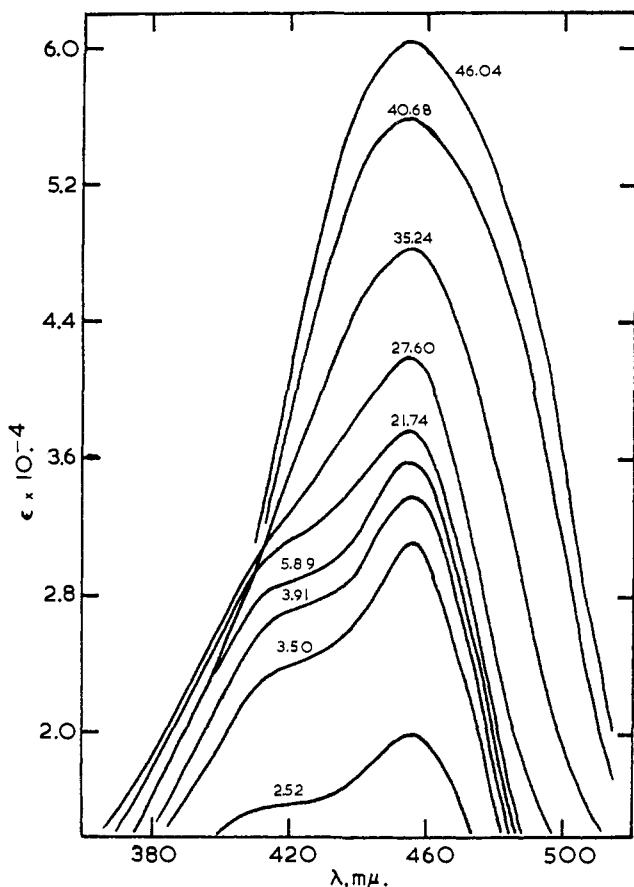
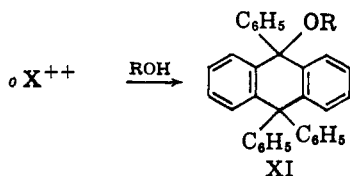


Fig. 3.—Spectra of tetraphenyl-*p*-xylylene glycol in sulfuric acid-acetic acid mixtures (figures above each curve are wt. per cent sulfuric acid).

concentrated sulfuric acid, hydrolysis of such solutions giving the known⁴⁰ carbinol (XI, R = H). If the order of addition was reversed, and methanol was added to a sulfuric acid solution of *o*X⁺⁺, the product was TPP, formed by reaction of *o*X⁺⁺ with water produced by the methanol-sulfuric acid reaction.⁴¹



Spectra in Sulfuric-Acetic Acid.—Sulfuric-acetic acid mixtures are appreciably more acidic than aqueous sulfuric acid, when measured by the H_0 function.⁴² It was of interest to examine, for comparison with aqueous solutions, the ionization of the glycols in this solvent mixture. The spectra of *p*X(OH)₂ in varying concentrations of sulfuric-acetic acid are shown in Fig. 3. Above 46% sulfuric acid, the spectrum is essentially constant with a single absorption maximum at 455 m μ , ϵ 59,900, as in aqueous acid (cf. Table II). In very low acid concentrations a marked shoulder is apparent at 425–430 m μ ; there is very little change in the spectrum between 6–20% acid, above which the shoulder disappears and the absorption at 455 m μ ultimately reaches nearly twice its value in 20% acid. Appreciable ionization of *p*X(OH)₂ occurs even in 2.5% sulfuric-acetic acid.⁴³

(40) E. Barnett, J. W. Cook and I. G. Nixon, *J. Chem. Soc.*, 504 (1927).

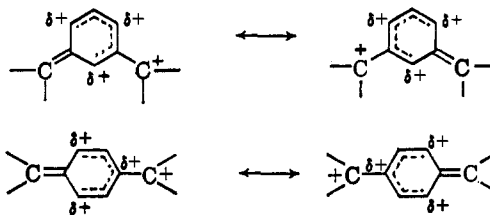
(41) R. J. Gillespie and J. A. Leisten, *Quart. Rev.*, **8**, 40 (1954).

(42) N. F. Hall and W. F. Spengeman, *J. Am. Chem. Soc.*, **62**, 2487 (1940).

Tetra-*p*-anisyl-*p*-xylylene glycol is yellow even in acetic acid, with maxima at 500 and 430 m μ (see Table VII). Very small amounts (0.02%) of sulfuric acid cause a strong increase in absorption and a spectral shift, which is virtually complete to 530 and 456 m μ in 0.2% sulfuric-acetic acid; this is the spectrum of the dicarbonium ion TApX⁺⁺ (see Table II) and is unaltered with increasing acid strength, until very strong acid causes a small hypsochromic shift (methoxyl protonation?).

Discussion

The *pK*'s.—It is clear from the cryoscopic and spectral results that the three tetraphenylxylylene glycols do in fact ionize readily to doubly charged carbonium ions in sulfuric acid solutions. The difference between *pK*_{R+} and *pK*_{R++} is only about 2, and for the anisyl glycol, less than 1, showing that charge build-up is not serious as long as the charge can be dispersed over many atoms and accommodated by a polar solvent. The *pK*_{R+}'s for *m*- and *p*X^{+(OH)} (Table IV) are slightly lower than for the triphenylmethyl cation (about -7) but are much closer to it than to that of the diphenylmethyl cation (about -14), showing that the central ring is, as expected, included in charge distribution in the monocations. Values slightly lower than for the triphenylmethyl cation probably reflect the small electron-withdrawing effect of the -C(OH)(C₆H₅)₂ group as a *m*- or *p*-substituent. It is perhaps surprising that orientation (*m* or *p*) at the central ring makes relatively little difference in the *pK*'s since, in terms of valence-bond structures, resonance contributors to *m*X⁺⁺ would reinforce the positive charge on three atoms in the central ring, whereas in *p*X⁺⁺ all six carbon atoms are involved. Indeed the



para dication requires slightly higher acidities for its formation; in valence-bond terms, this may be due to greater repulsion between the positive charges (+ and $\delta+$; see contributing structures).⁴⁴

TABLE VII

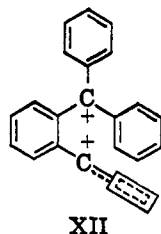
ABSORBANCE OF TETRA-*p*-ANISYL-*p*-XYLYLENE GLYCOL IN SULFURIC-ACETIC ACIDS

Wt. % H ₂ SO ₄	λ_{max} , m μ	ϵ	λ_{max}	ϵ
0.0	430	4,160	500	11,950
.019	450	40,600	510	71,800
.193	456	45,000	530	88,300
.756	458	53,000	530	101,500
1.50	459	53,000	530	101,300
6.01	457	53,000	530	101,500
9.33	457	53,000	530	101,300

The greater than 10⁶ increase in the difficulty with which the *ortho* dication *o*X⁺⁺ is formed compared with its *meta* and *para* analogs may be the result of several factors, not of equal importance. The dication itself may be less stable than its central ring isomers for two reasons. Steric effects must limit the geometries available to *o*X⁺⁺, but this probably does not seriously

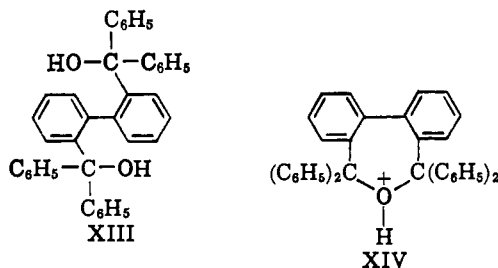
(43) The H_R of sulfuric-80% aqueous acetic acid has been determined (W. N. White and C. A. Stout, *J. Org. Chem.*, **27**, 2915 (1962)), but H_R for sulfuric-glacial acetic acid is not yet known. Detailed discussion of these spectra is deferred until those data become available.

(44) Discussion of an m.o. treatment of these ions is reserved for a later paper.



restrict the spreading of charge, for structures approaching XII are possible; indeed the appearance of two bands in the visible spectrum of oX^{++} (Fig. 1) as contrasted with one for mX^{++} and pX^{++} may be associated with these geometric limitations. Secondly, it is known that the charge density in the triphenylmethyl cation is greatest at the aliphatic carbon atom,⁴⁵ and one might expect that the proximity of these two carbon atoms in oX^{++} should be a destabilizing influence.

We believe that both of these effects are probably minor relative to a third. One cannot use pK_R 's to compare relative stabilities of cations unless the species (carbinols) from which they are formed have identical energies; *i.e.*, $pK_{R^{++}}$ is not a measure of the energy of R^{++} , but only of the energy difference between R^+ and R^{++} . Since $oX^+(OH)$ is much more stable than either m - or $pX^+(OH)$ because of oxygen participation (VII), it is much more difficult to form the dication from it, but the three dications may have comparable energies. This is illustrated in the qualitative energy diagram (Fig. 4), which also includes supporting evidence derived from a study of XIII.⁴⁶ The dication from XIII should have few of the restrictions of



geometry, or close positioning of charged atoms associated with oX^{++} , yet the $pK_{R^{++}}$ for XIII is about -15 ⁴⁶; once again the monocation has the cyclic structure XIV, this time probably slightly less stable than VII because of the seven-membered ring. Thus the geometric restrictions and charge repulsions in oX^{++} cannot be responsible for more than 1.6 pK unit, probably less, in the approximately 6- pK unit difference between oX^{++} and pX^{++} .

The first ionization constant of $TApX(OH)_2$ is appreciably lower ($pK_{R^+} = -3.1$) than that of dianisylphenylcarbinol (-1.24 ^{33a}); we do not know why these values are not closer. But formation of the dication $TApX^{++}$ is easily completed ($pK_{R^{++}} = -3.7$); indeed, more easily than the formation of the dianisylmethyl monocation ($pK_{R^+} = -5.71$ ^{33a}).

Products.—For the most part the products of reaction of the dicarbonium ions described in this paper with mononucleophiles were as anticipated, except for the reaction of oX^{++} with methanol which surprisingly gave 9-methoxy-9,10,10-triphenyl-9,10-dihydroanthracene (XI). This reaction may proceed *via* intramolecular alkylation in the monocation Xb; it cannot involve the dication oX^{++} , which indeed is stable with respect to the monocation XV as shown by

(45) A. Streitwieser, Jr., "Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 361.

(46) H. Hart and T. Sulzberg, unpublished results.

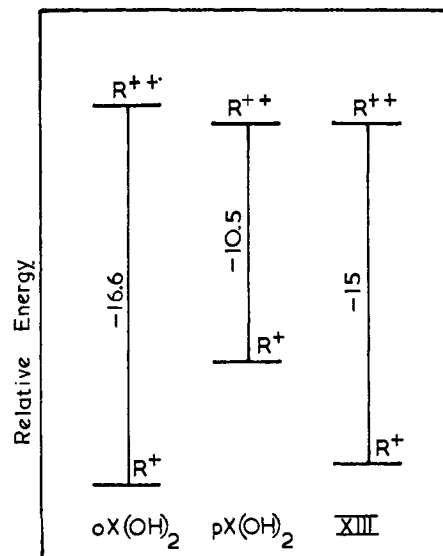
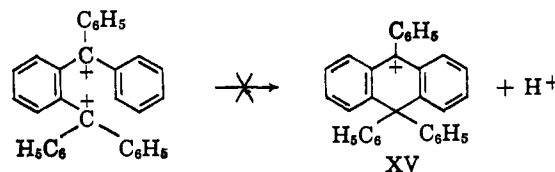


Fig. 4.—Relative energy diagram for the three mono- and dicarbonium ions from tetraphenyl-*o*- and *p*-xylylene glycols and from XIII; the numbers are values of $pK_{R^{++}}$ as defined in eq. 2.

the recovery of TPP on hydrolysis of its sulfuric acid solutions, and by the cryoscopic experiments on TPP (which would have given a value $i = 4$ rather than 5, had the ion produced been XV instead of oX^{++}).



One might have expected the dication to react directly with two moles of methanol to produce the dimethyl ether $oX(OCH_3)_2$. The dimethyl ether has in fact been prepared.⁴⁷ After several unsuccessful routes ($oX(OH)_2$ gave only a monopotassium salt when refluxed with potassium in dioxane; the monoether $oX(OH)(OCH_3)$ prepared from this salt and methyl iodide only gave TPP when treated with methanolic hydrogen chloride) $oX(OH)_2$ was converted by phenylisopropylpotassium to its dipotassium salt $oX(OK)_2$ which, with methyl iodide, gave $oX(OCH_3)_2$. The ether is reportedly unstable (no analysis given), its melting point falling rapidly in laboratory (acid?) air. Surprising in the light of the present result is the report that the product of this decomposition is TPP rather than XI, for one would expect both reactions to proceed *via* the same monocation Xb. The different results may have been due to the presence of moisture as well as acid in the earlier⁴⁷ experiments. Clearly the reaction course seems delicately balanced on as yet undefined factors.⁴⁸

A discussion of the electronic spectra and charge densities in dicarbonium ions⁴⁹ of the triarylmethyl type is deferred to a later paper.

Experimental⁵⁰

Preparation of the Glycols.—Tetraphenyl-*p*-xylylene glycol, m.p. 169–170° from benzene-petroleum ether, was prepared from dimethyl terephthalate and phenylmagnesium bromide.²⁸ Tetra-

(47) G. Wittig and M. Leo, *Chem. Ber.*, **64**, 2395 (1931).

(48) It is interesting that $oX(OCH_3)_2$ could be converted by sodium-potassium alloy in absolute dioxane to a dipotassium salt $oX(OK)_2$ which gave the expected *o*-(bis-benzhydryl)-benzene with alcohol, but which with tetramethylethylene bromide gave 9,9,10,10-triphenyl-9,10-dihydroanthracene.

(49) The electronic distribution of radical cations prepared from these indications is also being investigated.

(50) Melting points are uncorrected. Analyses are by Spang Micro-analytical Laboratory, P. O. Box 1111, Ann Arbor, Mich.

phenyl-*m*-xylylene glycol was prepared by hydrolysis of a 98% sulfuric acid solution of the corresponding dichloride which in turn was obtained by treatment of the crude glycol from dimethyl isophthalate and phenylmagnesium bromide with acetic acid-acetyl chloride-hydrogen chloride.⁵¹ The glycol, after recrystallization from 90–120° ligroin, melted sharply at 87°; evacuation overnight in a drying pistol gave solvent-free glycol, m.p. 112–113°.⁵² Tetraphenyl-*o*-xylylene glycol, m.p. 203–204°, was obtained from dimethyl phthalate and phenyllithium.⁴⁷ Tetraphenylphthalan, m.p. 174–176° from acetic acid, was obtained by refluxing the *o*-glycol with glacial acetic acid containing a little water.⁴⁷ Tetra-*p*-anisyl-*p*-xylylene glycol, m.p. 167–168° from acetone, was obtained from dimethyl terephthalate and *p*-methoxyphenylmagnesium bromide.⁴⁷ α,α' -Diphenyl-*p*-xylylene glycol, m.p. 173° from ethanol, was obtained from terephthalaldehyde and phenylmagnesium bromide.⁵³ The *m*-isomer was obtained by reduction of *m*-dibenzoylbenzene with lithium aluminum hydride in ether-benzene; recrystallized from toluene-ligroin (90–120°), m.p. 153–155°.⁵⁴

Hydrolysis and Methanolysis Experiments.—The deep red solution of 1.5 g. of tetraphenyl-*p*-xylylene glycol in 15 ml. of 100% sulfuric acid was poured onto 100 g. of ice. The white precipitate, taken up in ether, was washed with water, 5% sodium bicarbonate, dried, and the solvent removed (air stream), yielding 1.38 g. (92%) of recovered glycol, m.p. and m.m.p. 169–170°.

A solution of 2.0 g. of tetraphenyl-*p*-xylylene glycol in 50 ml. of methanol containing 2 drops of concentrated sulfuric acid was refluxed for 2 hours (white crystals began to deposit almost immediately). The crystals were filtered and recrystallized from benzene-petroleum ether (60–90°), yielding 1.8 g. (87%) of the dimethyl ether, m.p. 185°.²³

The red solution of 0.1 g. (0.21 mmole) of tetraphenyl-*m*-xylylene dichloride in 5 ml. of 98% sulfuric acid was added to 50 ml. of ice-cold methanol. The resulting colorless solution was treated with 50 ml. of 5% sodium carbonate, and the resulting white solid was filtered and recrystallized from aqueous methanol, yielding 0.08 g. (82%) of the corresponding dimethyl ether, m.p. 103°.⁵³

The orange-red solution of 1.19 g. (2.7 mmoles) of tetraphenyl-*o*-xylylene glycol in 10 ml. of 98% sulfuric acid was poured onto 50 ml. of ice-water. The white solid was taken up in benzene, washed with 5% sodium carbonate, then water, dried (calcium chloride) and the solvent removed *in vacuo*, to give 0.960 g. (84%) of tetraphenylphthalan, m.p. and m.m.p. 173–174° from benzene.

A solution of 1.00 g. (2.25 mmoles) of tetraphenyl-*o*-xylylene glycol in 10 ml. of 98% sulfuric acid was added to 75 ml. of ice-cold absolute methanol. The white solid was washed with 5% sodium carbonate, water, and dried giving 0.885 g. (89%) of

9-methoxy-9,10,10-triphenyl-9,10-dihydroanthracene, m.p. 220.5–221° after recrystallization from benzene-ligroin (90–120°).³⁹ A completely analogous procedure using ethanol in place of methanol gave an 84% yield of 9-ethoxy-9,10,10-triphenyl-9,10-dihydroanthracene, m.p. 254–255°³⁹ from toluene-ligroin (90–120°). The structure of the 9-methoxy compound is clear not only from its m.p., analysis, formation of the analogous 9-ethoxy compound whose m.p. is also known, but also by the following experiment. The 9-methoxy-9,10,10-triphenyl-9,10-dihydroanthracene (1.00 g., 2.3 mmoles) was dissolved in 10 ml. of 98% sulfuric acid, and the resulting red solution poured onto 50 ml. of ice-water. The resulting white solid, washed with sodium carbonate, water, and dried, gave 0.80 g. (83%) of the known 9,10,10-triphenyl-9,10-dihydro-9-anthrol, m.p. 204–204.5° from ligroin (90–120°).⁴⁰

To a magnetically stirred orange-red solution of 0.150 g. (0.34 mmole) of tetraphenyl-*o*-xylylene glycol in 50 ml. of 98% sulfuric acid there was added dropwise 50 ml. of absolute methanol. The color lightened slowly with the formation of a white solid. When addition was complete, the solid was filtered, washed with water, sodium carbonate, water, and dried at 100°. The product, m.p. and m.m.p. with tetraphenylphthalan 175–176°, weighed 0.120 g. (80%).

The cherry-red solution of 2.0 g. of tetra-*p*-anisyl-*p*-xylylene glycol in 15 g. of 100% sulfuric acid was poured onto 100 g. of ice. The white solid was taken up in ether, washed with water, sodium carbonate, water, and dried over magnesium sulfate. Evaporation of the ether gave 1.79 g. (90%) of recovered (m.p. and m.m.p.) glycol.

Cryoscopic Procedure.—The apparatus has been described.^{2a} The initial freezing point of sulfuric acid was checked at 2-hour intervals to see that it remained constant $\pm 0.005^\circ$ before solute was added. The solute was added as solid, using a special addition funnel which delivered the solid as powder, close to the sulfuric acid surface. The weight of sample was determined by difference weighings on the delivery funnel. In order to eliminate errors such as freezing too rapidly or too slowly (with Dry Ice initiation of nucleation) or improper stirring, the solute-acid mixture was melted and refrozen 4 or 5 times; the mean freezing point depression was used.

Spectra.—Stock solutions of aqueous sulfuric acid of varying strengths were analyzed by titration with sodium hydroxide to phenolphthalein end-point. Sulfuric-acetic acid solutions were prepared according to Hall and Spengeman.⁴² Solutions for pK_R studies were prepared by dissolving a known weight of carbinol in 25 ml. of glacial acetic acid⁵⁴ and diluting 0.100 \pm 0.001 ml. of this solution to 10 ml. with sulfuric acid of appropriate strength. The small sample was delivered from a La Pine 0.50-ml. microburet.

Spectra were recorded on a Cary 11 spectrophotometer, using 1-cm. glass-stoppered quartz cells; earlier experiments were done on a Beckman DK-2 instrument.

(54) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1955, p. 281.

(51) W. Schlenk and M. Brauns, *Chem. Ber.*, **48**, 661 (1915).

(52) R. Deluchat, *Compt. rend.*, **190**, 438 (1930).

(53) O. Stark and O. Garben, *Chem. Ber.*, **46**, 2252 (1913).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, THE OHIO STATE UNIVERSITY, COLUMBUS, O.]

The Stereochemistry of Liquid-Phase Nitration of (+)-3-Methylheptane, *cis*- and *trans*-Decalins and *cis*- and *trans*-Hydrindanes

BY HAROLD SHECHTER AND DEVIN K. BRAIN¹

RECEIVED DECEMBER 11, 1962

Liquid-phase nitration of (+)-3-methylheptane yields racemic 3-methyl-3-nitroheptane; the stereochemistry of the nitro compound was confirmed upon its conversion to optically inactive 3-amino-3-methylheptane and *N*-phenyl-*N'*-3-(3-methylheptyl)-thiourea. Reactions of *cis*- and *trans*-decalins, respectively, with aqueous nitric acid give *trans*-9-nitrodecalin as the principal tertiary nitration product (>77–86.5%); the composition and stereochemistry of the 9-nitrodecalin were determined upon its conversion to *trans*-9-aminodecalin and to *trans*-*N*-9-decalylacetamide. *trans*-9,10-Dinitrodecalin is also formed in nitration of *cis*- or *trans*-decalins. Nitrations of *cis*- and *trans*-hydrindanes yield 8-nitrohydrindanes of near-identical stereochemistry and composition. The stereochemistries of liquid-phase nitrations are interpreted in terms of hydrocarbon radical intermediates.

Saturated hydrocarbons react with nitric acid or nitrogen dioxide in the liquid phase to give nitro compounds along with nitrates, carbonyl derivatives and various oxidation and polynitration products. Liquid-phase nitrations of alkanes, cycloalkanes and arylalkanes have been extensively investigated.² In general,

(1) Abstracted in part from the Ph.D. dissertation of D. K. Brain, The Ohio State University, Columbus, Ohio, 1954.

(2) A. V. Topchiev, "Nitration of Hydrocarbons and Other Organic Compounds," Pergamon Press, New York, N. Y., 1959, pp. 144–215.

the ease of nitration of saturated carbon-hydrogen bonds is tertiary > secondary > primary.³ Alkyl and cycloalkylbenzenes nitrate preferentially at benzyl positions rather than at other carbon-hydrogen bonds of the substituent or the aromatic nucleus.³ Nitric

(3) (a) The principal products of nitration of 2,7-dimethyloctane,^{3b} ethylbenzene^{3c} and cyclohexylbenzene^{3d} are 2,7-dimethyl-2-nitrooctane, 1-nitro-1-phenylethane and 1-nitro-1-phenylcyclohexane, respectively; (b) M. I. Kononov, *Ber.*, **28**, 1855 (1895); (c) M. I. Kononov, *J. Russ. Phys. Chem. Soc.*, **31**, 255 (1899); (d) N. Kursanoff, *ibid.*, **38**, 1295 (1906).