seven by the addition of 32.0 g. of two percent aqueous ammonium hydroxide. The ether layer was separated and dried over sodium sulfate. After removal of the ether by distillation, 18.2 g. of liquid remained. Fractionation produced 1.1 g. of product, b.p. 105–108° (1 mm) n_D^{25} 1.4383, d_4^{25} 0.9027, 3.0 g. of material, b.p. 143° (1 mm), n_D^{25} 1.4433, d_4^{25} 0.9283 and 1.8 g., b.p. 166–168° (1 mm), n_D^{25} 1.4458, d_4^{25} 0.9355.

Anal. Calcd. for trimer, Mol. wt., 396; M.R. 113; for tetramer, Mol. wt., 538; M.R., 151. Found: first fraction, Mol. wt., 368; M.R., 115.2. Second fraction, mol. wt., 503 (average); M.R., 150.9. Third fraction, Mol. wt., 517; M.R., 150.4.

The second fraction is probably a mixture of the first and third.

Tris(trimethylsilylmethyl)bromosilane. Tris(trimethylsilylmethylsilane (18 g., 0.06 mole), in 300 cc. of carbon tetrachloride was placed in a 500 cc. three-necked flask fitted with stirrer, reflux condenser, and dropping funnel. Bromine (13 g., 0.08 mole) in 100 cc. of carbon tetrachloride was added dropwise over a 2-hr. period. After approximately one half of the bromine had been added the reaction slowed up markedly. The flask was then illuminated with a 200 watt bulb, then allowed to stand for 50 hr. at room temperature with continued illumination. It was then heated to reflux and a stream of nitrogen passed through it for 1 hr. After cooling, a 5% aqueous solution of ammonium hydroxide (60 cc.) was then added and this mixture stirred for 30 min. The aqueous layer was then removed (*p*H approximately 10 by Alkacid test paper). Fractionation produced tris(trimethylsilylmethyl)bromosilane, 4.3 g., b.p. 110° (1.8 mm), n_D^{25} 1.4725, 20% yield.

Anal. Calcd. for $C_{12}H_{33}BrSi_4$: Br, 21.7. Found: Br, 22.1.

Tris(trimethylsilylmethyl)silanol. Tris(trimethylsilylmethyl)bromosilane (10 g., 0.03 mole) in 30 cc. of acetone was treated with 6.6 g. of 10% aqueous ammonium hydroxide (0.046 mole). The mixture was stirred for 2 hr. at room temperature, and the layers separated. The aqueous layer was slightly basic. The organic layer was dried over sodium sulfate and the acetone evaporated. There remained 9 g. of liquid which was fractionated yielding 3.7 g. of tris(trimethylsilylmethylsilyl)silanol, b.p. 112–113° (5.0 mm.), n_D^{25} 1.4540, d_4^{25} 0.8594, yield 40%.

Anal. Calcd. for $C_{12}H_{34}OSi_4$: C, 47.06, H, 11.11; Si, 36.68; Mol. wt., 306; M.R. 97. Found: C, 47.87; H, 10.93; Si, 35.8, 36.6, 36.5; mol. wt., 295; M.R., 96.

BUFFALO, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

Stable Organic Biradicals

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The preparations of seventeen glycols, two of the corresponding glycol ethers and eleven of the corresponding chlorides are described. While only somewhat more than half of these substances constitute new compounds, the present procedures are superior to previously reported methods of synthesis and are of general applicability to all compounds of this type, bis-triarylmethanol where the alcohol centers are separated by at least one aromatic ring. Ten of the chlorides were converted by treatment with "molecular" silver to potential biradicals of the bis-triarylmethyl type. Of these, seven had been previously prepared and declared to be non-radical in character. One of them, the Tschitschibabin hydrocarbon (XXIX A), however, has more recently been shown to possess radical character by its paramagnetic resonance (ESR) spectrum. All ten potential radicals were examined by the ESR technique, and all but one, the Thiele hydrocarbon (XVII), were shown to absorb micro waves of the resonant frequency. The results make it clear that if no interaction between the two "odd" electrons of a biradical (*e.g.*, quinoidation) can be envisioned in terms of Kekule structures, the substance will be a biradical. If interaction is possible, the detectability of radical character will depend upon the energy difference between the state involving interaction and the state in which the electrons are unpaired.

The problem posed by the possible interconversion of singlet (quinoid) and triplet (biradical) states in certain types of organic molecules is an intriguing one, and the type of compound potentially capable of such interconversion is very nearly as old as the stable free radical itself.[2] However, from the period 1904–1907 when the first attempts to prepare the quinoid forms (see below) were published until the late 1920's, no interest seems to have attached to the problem. As will become apparent in the sequel (see Discussion) early attempts to provide criteria for judging the radical character of biradicals were not altogether satisfactory. Of the ten potential biradicals selected for the present study seven had been examined before and considerable confusion is apparent in the literature as to the problem of quinoid-biradical interconvertibility and the nature of biradicals with "insulated" radical centers. It is the purpose of this paper and the previously published theoretical treatment of the paramagnetic resonance study[3] to provide an answer to the question posed by earlier work: When can one expect interaction between the "odd" electrons of a biradical? The present paper does not treat the theoretical findings in detail but is chiefly concerned with improved methods for the preparations of certain organic biradicals and the intermediates necessary for their syntheses, and with the general conclusions based upon the ESR data.

The species of biradical selected for study are of the bis-triarylmethyl type where the radical centers are separated by various groups which serve

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[1] (1) Abstracted from a portion of the Ph.D. Dissertation of Gilbert J. Sloan, University of Michigan, 1954.

[2] (2) M. Gomberg, *J. Am. Chem. Soc.*, **22**, 757 (1900); *Ber.*, **33**, 3150 (1900).

[3] (3) H. S. Jarrett, G. J. Sloan, and W. R. Vaughan, *J. Chem. Phys.*, **25**, 697 (1956).

either to insulate the radical electrons or to permit their interaction through quinoidation. The general mode of synthesis is presented in Chart I.

CHART I[a]

SYNTHESIS OF BIRADICALS

$$\underset{\text{I}}{\text{H—Y—H}} \longrightarrow \underset{\text{II}}{\text{Ac—Y—Ac}} \longrightarrow \underset{\text{III}}{\text{HO}_2\text{C—Y—CO}_2\text{H}}$$

$$\longrightarrow \underset{\text{IV}}{\text{CH}_3\text{O}_2\text{C—Y—CO}_2\text{CH}_3}$$

$$\text{III} \longrightarrow \underset{\text{V}}{\text{ClCO—Y—COCl}} \longrightarrow \underset{\text{VI}}{\text{H}_2\text{NCO—Y—CONH}_2}$$

$$\longrightarrow \underset{\text{VII}}{\text{N}\equiv\text{C—Y—C}\equiv\text{N}}$$

$$\text{IV or VII} + \text{ArMgX} \longrightarrow \text{glycol (VIII–XVII)}$$

$$\text{glycol} \longrightarrow \text{dichloride (XVIII–XXIV)}$$

$$\longrightarrow \text{biradical (XXVII–XXXII)}$$

[a] The figure Y represents the bracketed structures appearing in the three series of compounds represented in Table I. For compounds I through IV see Table II (Experimental); for compounds VI, see Table III; and for compounds VII see Table IV.

The structures of the glycols, dichlorides, and biradicals are presented in Table I.

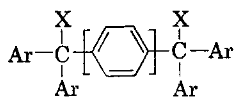
many of the compounds described have been prepared previously, the published methods were not generally applicable to all members of the series, and the yields obtained were poor.

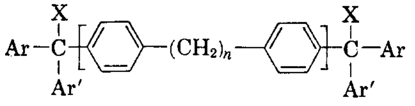
The nitriles (VIIA through VIIE) are the most flexible intermediates, since they provide for the introduction of identical or different aromatic substituents; but the best previously reported syntheses of them involved six steps, with overall yields of the order of 3%.[4,5] In this work, the nitriles were conveniently prepared by treatment of the corresponding amides with phosphorus pentachloride, or more directly, by the pyrolysis of the zinc salts of the acids in the presence of lead thiocyanate. In no case was the overall yield below 25%.

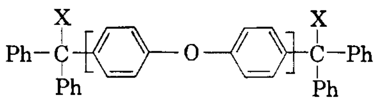
The latter reaction, which seems not to have been used for many years, was developed by Reid,[6] who applied it with excellent results to the preparation of many low-molecular weight nitriles. Its successful application to non-volatile, bifunctional acids indicates that it has considerable generality. It is interesting to note that the origin of the nitrile carbon is not certain. *A priori*, the most probable course of the reaction would involve decarboxylation of the salt, followed by attack of the resulting radical on

TABLE I

STRUCTURE OF GLYCOLS, CHLORIDES, AND RADICALS


Series 1


Series 2


Series 3

	Series	Glycols (X = OH) Substituents	n	Chlorides (X = Cl)	Glycol Ethers	Radicals (X = electron)
VIII[a,b]	1	Ar = phenyl		XVIII	XXV (X = OC_2H_5)	XXVII[c,d]
IXA[e]	2	Ar = Ar′ = phenyl	0	XIXA[e]		XXIXA[f,g]
B[b,h]	2	Ar = Ar′ = phenyl	1	B[h]		B[g]
C[h]	2	Ar = Ar′ = phenyl	2	C[h]		C[g]
D[i]	2	Ar = Ar′ = phenyl	3	D		D
E[j]	2	Ar = Ar′ = phenyl	4	E[j]		E[g]
X[k]	1	Ar = *p*-xenyl		XX[k]		XXVIII[g]
XIA[l]	2	Ar = Ar′ = *p*-xenyl	0	XXI[l]		XXX
B	2	Ar = Ar′ = *p*-xenyl	1			
C	2	Ar = Ar′ = *p*-xenyl	2			
D	2	Ar = Ar′ = *p*-xenyl	4			
XII[i]	1	Ar = *p*-tolyl		XXII		
XIII	2	Ar = Ar′ = *p*-tolyl	0			
XIV	1	Ar = *p*-anisyl			XXVI (X = OCH_3)	
XV	2	Ar = Ar′ = *p*-anisyl	0			
XVI	2	Ar = phenyl, Ar′ = 1-naphthyl	0	XXIII		XXXI
XVII[m,n]	3			XXIV[m]		XXXII[g]

[a] Reference 10. [b] Not previously analyzed. [c] Thiele hydrocarbon. [d] Non-radical. [e] Reference 11. [f] Tschitschibabin hydrocarbon; cf. ref. 18. [g] Previously reported non-radical; cf. ref. 19. [h] Reference 17. [i] Converted directly to chlorde. [j] Reference 18. [k] Reference 36. [l] Reference 16. [m] Reference 39. [n] Not isolated, but converted directly to XXIV (see Experimental).

SYNTHESES

The synthetic methods presented here constitute a general approach to a fairly large group of biradicals of considerable theoretical interst. Although

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(4) J. N. Ashley, *et al.*, *J. Chem. Soc.*, 108 (1942).

(5) D. J. Cram and H. Steinberg, *J. Am. Chem. Soc.*, **73**, 5691 (1951).

(6) E. E. Reid, *Am. Chem. J.*, **43**, 162 (1910).

the lead thiocyanate or on the decomposition products of the latter, somewhat as follows:

$$(RCO_2)_2Zn \longrightarrow 2R\cdot + Zn + 2CO_2$$

$$2R\cdot + Pb(SCN)_2 \longrightarrow Pb + 2RSCN$$

$$2RSCN + Pb + Zn \longrightarrow 2RCN + PbS + ZnS$$

If this is in fact the case, then the use of C^{14}-labeled acids should give inactive nitriles, and conversely, C^{14}-labeled thiocyanate should give active nitriles.[7] This latter reaction might prove useful in the "exchange" of C^{14} or C^{12} in biologically important acids.

The esterification of 4,4′-dicarboxybiphenyl presents an interesting problem. The acid cannot be esterified by the Fischer method, nor by treatment with diazomethane, probably because of its extremely low solubility in ordinary solvents. Prolonged refluxing with *n*-butanol and a strong acid, with removal of the water produced in the reaction, provides the butyl ester, but in rather poor yield. However, by treatment with phosphorous pentachloride, the acid can be converted to the acid chloride, which in turn affords the methyl ester in good yield on treatment with methanol.

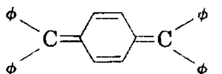
The reactions of the esters and ketones with Grignard reagents are, in general, straightforward. The resulting glycols, however, frequently are difficult to purify. Some of them form difficultly crystallizable oils which can be purified only by chromatography or conversion to the corresponding crystalline dichloride. The glycols VIII (Table I, series 1), and IXA (Table II, series 2) form solvates with many ordinary crystallizing solvents. The benzene solvate of VIII is remarkably stable; even extensive drying in high vacuum does not remove the benzene. It is interesting to note that the solvate is formed directly in the hydrolysis of the Grignard complex, presumably by reaction with the benzene liberated by hydrolysis of excess phenylmagnesium bromide. The absence of strongly polar functions from both moieties of the molecular compounds suggests that the source of their stability is geometrical, rather than electrical. Assuming that this is the case, it is still not clear whether the retention of the solvent molecules is due to the geometry of the glycol molecule, or that of the glycol crystal. Many cases of the latter type are known,[8] and some information might be gained by a careful study of the stoichiometry of the complexes, since the number of molecules of solvent retained per molecule of solvated species is frequently non-integral in complexes of the "clathrate" or crystalline type.

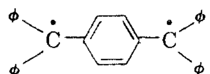
The dichlorides in this series of compounds become colored at elevated temperatures, even in ordinary organic solvents. That the colored thermochromic forms are ionic is strongly suggested by a qualitative similarity of the spectra obtained in hot acetic acid to those obtained in concentrated sulfuric acid. This effect would not be thought to render purification of the chlorides difficult, but it may be that the extensive decomposition which takes place during recrystallization involves the ion as a reactive intermediate. Such decomposition may be minimized by quickly dissolving the chloride in an excess of a low-boiling solvent, then quickly adding just enough of a second solvent, in which the chloride is insoluble, to cause rapid precipitation. Alternatively, the poor solvent can be allowed to distill isothermally into the solution in good solvent, resulting in slow precipitation at room temperature.

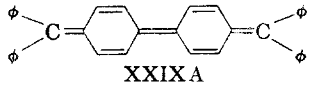
It should be noted that many of the Grignard reactions, especially those with *p*-xenylmagnesium bromide, were carried out in tetrahydrofuran, rather than in ether. The former solvent is excellent for this reaction, since it is readily purified (see p. 461), is much less hygroscopic than ether, and causes the formation of *p*-xenylmagnesium bromide to go nearly to completion in less than one-half hour. The biradicals were prepared *in vacuo* by reaction of the dichlorides with "molecular" silver[9] in benzene solution, and the extent of dehalogenation was checked in a number of cases and found to be 84–99% complete in two hours. Measurements of paramagnetic resonance absorption were made at intervals from a few minutes' treatment with silver to essentially complete dehalogenation, with positive results being observed in all but one case.

DISCUSSION

In 1904 Thiele prepared tetraphenylquinonedimethane, XXVIIa, in the course of an attempt to prepare the unsubstituted quinonedimethane. This substance is colored and very reactive; it can be considered to be an electromer of the biradical XXVIIr, but shows no reactivity toward oxygen.[10] A related hydrocarbon (XXIXA) prepared by Tschitschibabin,[11] however, is a violet solid, whose solutions absorb oxygen rapidly. It, then, is a substance with an even number of electrons, capable of formulation as a quinone, but giving every chemical evidence of free radical nature. At the time of Tschitschibabin's work, little could be said in favor of either structure on theoretical grounds, and experimental criteria for a decision were lacking.


XXVIIa


XXVIIr


XXIXA

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(7) A preliminary attempt to establish the fate of the C^{14} of $(RC^{14}O_2)_2Zn$ in this reaction has given some indication that the radioactivity does not appear in the nitrile. Work on the reaction mechanism is continuing.

(8) W. Schlenk, Jr., *Fortschr. chem. Forsch.*, 2, 92 (1951).

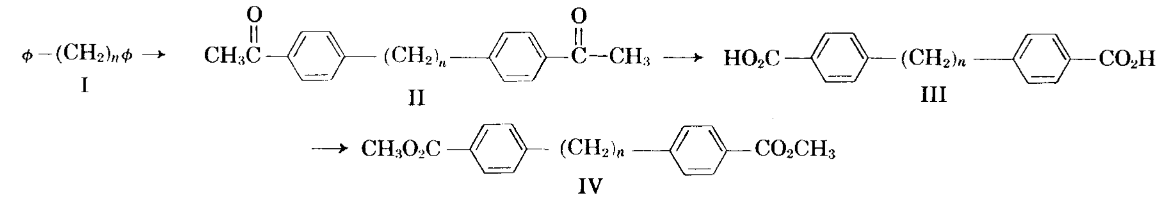
(9) M. Gomberg and L. H. Cone, *Ber.*, **39**, 3274 (1906).

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

(11) A. E. Tschitschibabin, *Ber.*, **40**, 1810 (1907).

TABLE II

PREPARATION OF α,ω-BIS(4-ACETOPHENYL)-, α,ω-BIS(4-CARBOXYPHENYL)-, AND α,ω-BIS(4-CARBOMETHOXYPHENYL)-ALKANES



n	Cpd.	Yield, %	M.P., °C.	Crystn. Solvent	Cryst. Form[a]	Cpd.	Yield, %	M.P., °C.	Cpd.	Yield %	Proc.	M.P., °C.	Crystn. Solvent	Cryst. Form[a]
0	IIA[b]	66	192–193	Dioxane	pl	IIIA[c]	90		IVA[d]	85	A	215–217	Chloroform	pl
1	IIB[e]	63	93.5–94.5	Dioxane	pl	IIIB[f]	92	329–332	IVB[g]	74	B	81–82	Methanol	nd
2	IIC[e]	41	167–168	Dioxane	pl	IIIC[h]	95		IVC[i]	74	B,C	117–118	Methanol	lv
3	IID[j]	79	84–86	Methanol	nd	IIID[k]	95	300–304	IVD[l]	86	B	90–92	Methanol	nd
4	IIE[m]	56	110–112	Methanol	nd	IIIE[n]	94	327–332	IVE[o]	82	C	91.5–93.0	Methanol	nd

[a] pl = plates, nd = needles, lv = leaves. [b] S. L. Silver and A. Lowry, *J. Am. Chem. Soc.*, **56,** 2429 (1934), report a yield of 43% and m.p. 191°. [c] O. Doebner, *Ber.*, **9,** 271 (1876). [d] M. Weiler, *Ber.*, **32,** 1063 (1899) reports m.p. 212–213° (uncor.) for IVA prepared in essentially the same way. Tschitschibabin, *Ber.*, **40,** 1810 (1907) reports m.p. 224° for IVA prepared in a different way. [e] R. E. Lutz, *et al.*, *J. Org. Chem.*, **12,** 617 (1948) report m.p.'s 92.5–93.0° and 167–168°, respectively. [f] P. Mitter, *Ber.*, **45,** 1207 (1912) reports a m.p. of 334–336° for IIIB prepared by a different method. [g] P. Mitter, *Ber.*, **45,** 1207 (1912) reports the same melting point. [h] C. Fischer and R. Wolffenstein, *Ber.*, **37,** 3215 (1904) report that IIIC does not melt at 320°. [i] C. Fischer and R. Wolffenstein, *Ber.*, **37,** 3215 (1904) report m.p. 119°. [j] D. J. Cram and H. Steinberg, *J. Am. Chem. Soc.*, **73,** 5691 (1951) report a yield of 77% and m.p. 83–85°. [k] D. J. Cram and H. Steinberg, *J. Am. Chem. Soc.*, **73,** 5691 (1951) report m.p. 304–307°. [l] D. J. Cram and H. Steinberg, *J. Am. Chem. Soc.*, **73,** 5691 (1951) report a 77% yield, m.p. 85–88°, using essentially the same procedure. [m] An analytical sample was recrystallized three times from ethanol; m.p. 110–112°. Calcd. for $C_{20}H_{22}O_2$: C, 81.59; H, 7.53. Found: C, 81.52; H, 7.52. [n] An analytical sample was recrystallized from glacial acetic acid, m.p. 327–332°. Further recrystallization did not change the melting point, but the acid did not analyze satisfactorily for carbon. This difficulty appears to be a general one with these compounds.[c,f,h,k] Calcd. for $C_{18}H_{18}O_4$: C, 72.57; H, 6.08. Found: C, 73.08; H, 6.09. [o] An analytical sample was recrystallized twice from methanol, m.p. 92.0–92.5°. Calcd. for $C_{20}H_{22}O_4$: C, 73.60; H, 6.80. Found: C, 73.94; H, 707.

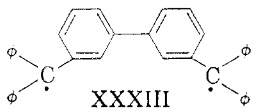
Of the techniques subsequently used to establish the free radical nature of the triarylmethyls, two, the determination of molecular weight and the study of deviations from Beer's law, are inapplicable to the Tschitschibabin hydrocarbon because the number of molecules present in a solution of this substance is the same regardless of whether the quinone or the biradical structure is correct. A determination of the magnetic susceptibility of the compound offered a solution to the problem, since the radical form would be expected to be paramagnetic, and the quinone form diamagnetic. An application of this method indicated that the quinone structure is correct.[12]

Aside from the reactivity of XXIXA toward oxygen, Bent and Gould have shown that it adds sodium more readily than does triphenylmethyl.[13] Now all radicals with essentially free electrons should have much the same electron affinity,[14] and one may therefore consider any observed difference in apparent electron affinity (*e.g.* sodium addition) to be due to a difference in degree of radicalness. Thus XXIXA is better formulated as the biradical XXIXAr.

XXIX AR

This formulation is supported by still another diagnostic for free radicals: it promotes the conversion of *para* to *ortho* hydrogen at a rate corresponding to 10% biradical, while XXVII is inactive.[15] Thus the physical and chemical evidence are in harmony for XXIXA.

Insulated compound such as the Schlenk[16] hydrocarbon XXXIII and the biphenyls XXIXB and XXIXC (Table I), first prepared by Wittig and Leo[17] exhibit free radical chemistry, and the Schlenk hydrocarbon actually is paramagnetic (magnetic susceptibility method, see below). However, surprisingly XXIXE (Table I) exhibits no free radical character,[18] and XXIXC appears to be diamagnetic.[19] Thus the chemical and physical evidence can be contradictory.



XXXIII

Because the peroxides obtained from freshly prepared solutions of the radicals contain less than the expected amounts of oxygen, and since the colors of the solution are lasting, Wittig and Leo have attributed failure to observe radical properties in certain such compounds to disproportionation simultaneous with dehalogenation.[18] However, more recent work has shown that certain triarylmethyl solutions appear to retain their original colors (actually the absorption spectra do change, but not visually) while their paramagnetisms are falling to zero as a consequence of demonstrable disproportionation,[20,21] thus weakening the Wittig and Leo argument.

In an attempt to obtain an insulated biradical similar to those which appear to disproportionate but which is incapable of such degradation XXXII (Table 1) was prepared.[22] That it unhappily proved to be wholly diamagnetic (magnetic susceptibility method) was attributed to dimerization (or polymerization).

Two features of previous investigations of the type just cited seemed to us sufficiently questionable to justify a reexamination of the entire biradical problem. First, in view of the relatively slow disproportionation of alkyl substituted triarylmethyls and the steric problems posed by biradical dimerizations, it seemed highly unlikely that bis-triarylmethyls would disproportionate or dimerize so quickly as to prevent detection of paramagnetism. Second, serious doubt had recently been cast upon the validity of the magnetic susceptibility method for obtaining paramagnetic data on free radicals. In brief the suggestion that the over-all diamagnetism of a radical is much greater than the value calculated from Pascal constants or obtained from measurements on the hydrocarbons or halides[23,24] provides grounds for doubting any data relating to the paramagnetic properties of biradicals, since the diamagnetism must be subtracted from a measured susceptibility to give the paramagnetism.

The possibility of detecting paramagnetic species by the resonance absorption of microwaves[25] offered a new approach which is independent of assumptions regarding diamagnetism. The successful application of this technique to solutions of XXIXA, which in agreement with chemical (and as it happens magnetic) properties previously determined were shown to contain paramagnetic species at ordinary temperatures[26] encouraged us to undertake similar examination of the potential biradicals listed in the last column of Table I. It will be noted

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[12] E. Müller and I. Müller-Rodloff, *Ann.*, **517**, 134 (1935).

[13] H. E. Bent and R. E. Gould, *J. Am. Chem. Soc.*, **57**, 1217 (1935).

[14] G. W. Wheland, *J. Chem. Phys.*, **2**, 474 (1934).

[15] G. M. Schwab and N. Agliardi, *Ber.*, **73**, 85 (1940).

[16] W. Schlenk and M. Brauns, *Ber.*, **48**, 716 (1915).

[17] G. Wittig and M. Leo, *Ber.*, **61**, 854 (1928).

[18] G. Wittig and M. Leo, *Ber.*, **62**, 1405 (1929).

[19] E. Müller, *Angew. Chem.*, **51**, 662 (1938).

[20] P. W. Selwood and R. F. Preckel, *J. Am. Chem. Soc.*, **65**, 895 (1943).

[21] C. S. Marvel, M. B. Mueller, C. M. Himel, and J. F. Kaplan, *J. Am. Chem. Soc.*, **61**, 2771 (1939).

[22] E. Müller and W. Bunge, *Ber.*, **69**, 2164 (1936).

[23] P. W. Selwood and R. M. Dobres, *J. Am. Chem. Soc.*, **72**, 3860 (1950).

[24] G. W. Wheland, *Advanced Organic Chemistry*, pp. 695–696, John Wiley and Sons, Inc., New York, 1949.

[25] For a recent review see J. E. Wertz, *Chem. Revs.*, **55**, 829 (1955).

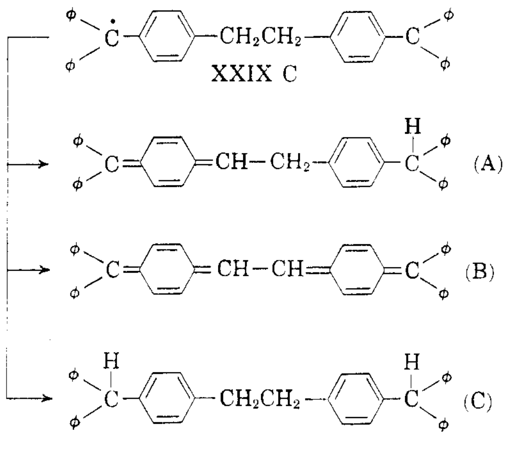
[26] C. A. Hutchinson, Jr., A. Kowalksy, R. C. Pastor, and G. W. Wheland, *J. Chem. Phys.*, **20**, 1485 (1952).

that only three are new compounds (XXIXD, XXX, and XXXI), and that for XXVII, XVIII, XXX, and XXXI the same type of possibility for escape to diamagnetism through quinoidation exists as for XXIXA, which has been included for comparison, owing to the independent data available.[26] That XXIXA proves to be other than completely diamagnetic appears to constitute another situation such as is encountered in porphyrindine,[27] in which a diamagnetic ground state is in equilibrium with a paramagnetic excited state. That this situation is typical will appear in the sequel.

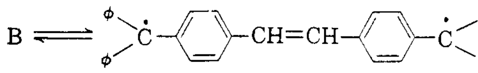
Consideration of Table V leads to some rather striking conclusions. First, it is evident that in all the cases in which no interaction between the two odd electrons of a potential biradical can be envisioned on the basis of classical organic chemistry, the substances are indeed paramagnetic. Even in the case of the Tschitschibabin hydrocarbon (XXIXA), where interaction can occur, paramagnetism is detectable. Whether the spins of the two odd electrons of the paramagnetic species are essentially independent (in which case the molecule would be a doubled doublet) or whether they are constrained to be parallel (in which case the molecule would be a triplet) is not conclusively established in this work. *A priori*, the fact that the biphenyl nucleus is non-coplanar[3,28] might lead one to suspect that the two halves of the molecule are uncoupled, and that the former situation obtains. However, it has been demonstrated that even appreciable twisting about the 1,1′-bond of biphenyl does not completely uncouple the halves of the molecule.[28] Concordant with this, convincing arguments can be adduced to support the contention that the two odd electrons couple through the distorted biphenyl nucleus to yield a triplet excited state lying only slightly higher than the diamagnetic ground state.[3]

The failure of the Thiele hydrocarbon (XXVII) to show similar properties is probably due to the increased separation of the singlet and triplet states.[28]

All of the molecules for which no interacting forms can be written show paramagnetic resonance. It should be noted, however, that even in the absence of light and oxygen, the paramagnetic species slowly disappear; there is little doubt that this must be attributed to some form of disproportionation. Although no attempt was made in this study to isolate degradation products, there is precedent for this conclusion. In a study of 1,2-bis[4′-(diphenylmethyl)phenyl]ethane (XXIXC), Müller reports the isolation of three degradation products, and gives a scheme whereby one of these might be formed by intramolecular and the others by intermolecular disproportionation:[19]



Of especial significance is the fact that compound B, although found to be diamagnetic, is reported to be deep purple and sensitive to oxygen. This is in accord with a second unexpected situation, seen in Table V. The degradation to colored, diamagnetic substances *which retain oxygen-sensitivity* is a fairly general occurrence in free radicals. The excitation of B to a triplet state presents an attractive explanation for the oxygen sensitivity of degraded solutions of XXIXC. But molecular orbital calculations[29] indicate that, even at room temperature, B should be in equilibrium with a detectable amount of the excited paramagnetic form:



If this were the case, the degraded solution would continue to show paramagnetism. That it does not is an indication that the disproportionation is essentially intramolecular. The retention of reactivity toward oxygen might then be explained as a result of a photo-excitation of A to a transient paramagnetic state. This hypothesis could be tested by exposing a sample of the degraded material to oxygen in the dark.

In the case of the diphenylmethane derivative XXIXB, both inter- and intramolecular disproportionation might lead to the same product. If this were so, it is difficult to see why the degraded solutions should differ in color from those of XXIXC. Further, it is not at all apparent why the diphenylpropane and diphenylbutane derivatives should behave so differently from the diphenylmethane and diphenylethane derivatives. It is of course possible that in the two former cases, the biradical form is in equilibrium with a monomeric diamagnetic ring compound, while in the two latter cases, the radical carbons do not approach within bonding distance of each other, and that this difference results in a different disproportionation mechanism. Work on the chemical properties of these compounds is continuing.

It is of extreme interest and importance to note

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(27) E. Müller, *Fortschr. chem. Forsch.*, **1**, 325 (1949).

(28) H. Suzuki, *Bull. Chem. Soc. Japan*, **27**, 597 (1954).

(29) Private communication from Dr. H. S. Jarrett.

that in view of the demonstrated non-coplanarity of triphenylmethyl,[30] the systems under discussion here cannot be coplanar. They are, nevertheless, strongly (but not maximally) resonance stabilized. A similar situation has been shown to exist in triarylcarbonium ions by the elegant cryoscopic and spectroscopic work of Newman and Deno.[31] These authors demonstrated conclusively that even in cases where coplanarity is made impossible by large *ortho* substituents, resonance stabilization exists. Evidence is advanced to support the contention that the reduction of resonance which accompanies the distortion from planarity is accomplished by removal of one or two of the rings from resonance, rather than by an overall diminution of resonance throughout the system. The nonequivalence of the rings implied in this idea has not yet been adequately demonstrated.

EXPERIMENTAL

Melting points are uncorrected. Microanalyses by Goji Kodama, University of Michigan.

1. α,ω-Bis(4-acetophenyl)alkanes (II). A solution of 0.05 mole of the α,ω-diphenylalkane and 157 g. (2.0 moles, 142 ml.) of acetyl chloride in 100 ml. of carbon disulfide was added dropwise during 1 hr. to a vigorously stirred suspension of 267 g. (2.0 moles) of anhydrous aluminum chloride in 200 ml. of carbon disulfide. The reaction mixture was cooled in an ice-salt bath during the addition, after which it was refluxed, with continued stirring, for 2 additional hr. The condenser was then set down for distillation and the carbon disulfide removed. The mixture remaining in the flask was poured while still warm into a well-stirred mixture of ice and concentrated hydrochloric acid. The resulting solid was filtered off, washed well with water, and crystallized with a Norit treatment.

2. α,ω-Bis(4-carboxyphenyl)alkanes (III). To a solution of the appropriate diaceto compound (0.05 mole) in 500 ml. of methanol was added 500 ml. of 1*N* potassium hypochlorite. The resulting mixture was stirred for 2 to 3 hr. at 65–75°. The excess hypochlorite was destroyed by the addition of acetone and any undissolved solid was filtered off. The filtrate was cooled to room temperature and made acid to Congo Red by the careful addition of concentrated hydrochloric acid; the white precipitate was collected in a basket centrifuge and washed several times with warm water. The solid acid was air-dried, then dried thoroughly at 110°.

3. α,ω-Bis(4-carbomethoxyphenyl)alkanes (IV). *Procedure A.* A mixture of 48.4 g. (0.2 mole) of 4,4′-dicarboxybiphenyl, IIIA, 110 g. (0.53 mole) of phosphorus pentachloride, and 200 ml. of toluene was refluxed for 1 hr. The toluene was distilled on a steam bath at reduced pressure, leaving a brown crystalline residue, which was cooled in an ice bath. The reaction flask was again fitted with a reflux condenser, the top of which carried a dropping funnel with a pressure equalizing side-arm, containing 250 ml. of absolute methanol. The methanol was added during 0.5 hr., after which the mixture was refluxed for 2 hr., cooled and alkalized with 10% sodium carbonate solution. The solid which separated was collected, washed with water, dried, and recrystallized from chloroform, giving 46 g. (85% yield) of silvery white plates, m.p. 215–217°; reported 224°,[11] 214°.[32]

Procedure B. A mixture of 0.1 mole of the appropriate diacid, 300 ml. of absolute methanol, and 5 ml. of concentrated sulfuric acid was refluxed overnight. Most of the methanol was then distilled, the residue was poured into water and the mixture alkalized with 10% sodium carbonate solution. The resulting mixture was extracted with ether; the ether solution was washed with water, dried, and the ether distilled on a steam bath. The residue was then crystallized from methanol.

Procedure C. The diacid was treated with a 50% excess of diazomethane in ether. The mixture was allowed to stand for 0.5 hr. with occasional swirling; the excess diazomethane was then destroyed by glacial acetic acid. After removal of any insoluble material by filtration, the ether was evaporated under an air-jet, and the residue crystallized from methanol.

4. α,ω-Bis(4-chloroformylphenyl)alkanes (V). *1,3-Bis(chloroformylphenyl)propane* (VA). Compound IIID (5.68 g., 0.02 mole), was ground in a mortar with 12 g. of phosphorus pentachloride until reaction set in. The mixture was allowed to stand for 0.5 hr., then ground with ice, and the resulting solid was collected and dried in a vacuum desiccator, giving 7.09 g. of crude product. This was recrystallized from benzene and petroleum ether (b.p. 60–75°),[33] giving 4.45 g. (71% yield) of white needles, m.p. 75–76°. An analytical sample was recrystallized twice from benzene and petroleum ether, m.p. 76.0–76.5°.

Anal. Calcd. for $C_{17}H_{14}Cl_2O_2$: C, 63.57; H, 4.39; Cl, 22.08. Found: C, 63.66; H, 4.77; Cl, 22.10.

1,4-Bis(4-chloroformylphenyl)butane (VB). Compound IIIE (5.96 g., 0.02 mole) was treated with 12 g. of phosphorus pentachloride as in the preparation of VA above. The crude product was recrystallized from benzene and petroleum ether, giving 3.40 g. (51% yield) of white needles, m.p. 91–93°. An analytical sample was recrystallized twice from benzene and petroleum ether, m.p. 93.0–93.5°.

Anal. Calcd. for $C_{18}H_{16}Cl_2O_2$: C, 64.49; H, 4.81; Cl, 21.15. Found: C, 64.58; H, 4.93; Cl, 21.19.

These acid chlorides, as well as that of 1,2-bis(4-carboxyphenyl)ethane (IIIC) were also prepared by refluxing the acids for several hours with thionyl chloride in the presence of a trace of pyridine. The products were not purified for analysis, but were converted to the amides after removal of the excess thionyl chloride by distillation.

5. α,ω-Bis(4-carbamylphenyl)alkanes (VI). The crude acid chloride, prepared as in Section 4, was triturated with concentrated ammonium hydroxide and the mixture was allowed to stand for 1 hr. The granular solid was then collected, washed well with water, and dried. For conversion to the dinitrile, the diamide was used without further purification. For analysis, the diamide was recrystallized from glacial acetic acid. Although repeated recrystallization did not change the melting point, the amides did not analyze satisfactorily for carbon (see Table III).

6. α,ω-Bis(4-cyanophenyl)alkanes (VII). *Procedure D.* To a mixture of equal parts (by weight) of the appropriate diamide and phosphorus pentachloride was added approximately 5 parts of xylene. The mixture was refluxed for 1 hr.; the xylene was then evaporated in an air jet, and the mixture alkalized with 10% sodium carbonate solution. The solid which separated was collected, washed with water, and dried. The crude product was then sublimed and recrystallized once.

Procedure E. The diacid (0.010 mole) was neutralized with 0.5*N* potassium hydroxide solution; the resulting solution was heated to about 80° and added to a solution of 1.5 g. (0.011 mole) of zinc chloride in 10 ml. of hot water. The zinc salt was filtered off, washed several times with warm water, air dried, then dried overnight at 110°. The dry zinc salt was then ground thoroughly with 4.05 g. (0.0125 mole) of lead thiocyanate in a glass mortar. The resulting mixture was heated strongly in a sublimation

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(30) H. S. Jarrett and G. J. Sloan, *J. Chem. Phys.*, 22, 783 (1954).

(31) M. S. Newman and N. C. Deno, *J. Am. Chem. Soc.*, **73**, 3644 (1951).

(32) F. Ullmann, *Ann.*, **332**, 38 (1904).

(33) Whenever petroleum ether is referred to in the remainder of this paper, it is of this boiling range.

TABLE III

α,ω-BIS(4-CARBAMYLPHENYL)ALKANES

Starting Material	Product	Yield, %[a]	Analyses Calcd. C	H	N	Found C	H	N
IIIC[b]	VIA	99	71.62	6.01	10.44	73.44	6.18	10.41
VA	VIB	95	72.31	6.43	9.92	73.43	6.07	10.02
VB	VIC	97	72.94	6.80	9.45	73.91	6.80	9.51

[a] The yields reported here are of crude product, based on the diacid. [b] Converted to the diacid chloride by thionyl chloride.

apparatus with a Bunsen burner until it became black, and for about 10 min. longer. The sublimate was collected, and the residue was extracted with several 20 ml. portions of hot absolute ethanol or acetonitrile. The combined extracts were treated with Norit, evaporated to a suitable volume, and cooled; the crystals which separated were collected and combined with the sublimate. The total yield was lowered if an attempt was made to sublime all of the product from the reaction mixture.

TABLE IV

α,ω-BIS(4-CYANOPHENYL)ALKANES

Starting Material	Product	Proc.	M.P., °C.	Crystn. Solvent	Cryst. Form	Yield, %
IIIA	VIIA[a]	E	232–234	Acetonitrile	Needles	59
IIIB	VIIB[b]	E	165–167	Methanol	Needles	43
IIIC	VIIC[c]	E	196–200	Ethanol	Prisms	79
VIA	VIIC[c]	D	196–200	Ethanol	Prisms	79
VIB	VIID[d]	D	94–95	Ethanol	Prisms	60
VIC	VIIE[e]	D	132–133	Ethanol	Plates	55

[a] This compound, was also prepared according to directions of T. S. Work, *J. Chem. Soc.*, 1315 (1940), with essentially the same results. [b] This compound was also prepared according to the directions of M. Schöpff, *Ber.*, **27**, 2321 (1894), with essentially the same results. [c] P. Kattwinkel and R. Wolffenstein, *Ber.*, **34**, 2423 (1901) report m.p. 198°. [d] J. N. Ashley, *et al.*, *J. Chem. Soc.*, 103 (1942) report the same melting point for VIID prepared by another method. [e] An analytical sample was recrystallized 5 times from ethanol, m.p. 133.5–134.0°. Calcd. for $C_{18}H_{16}N_2$: C, 83.04; H, 6.20; N, 10.77. Found: C, 82.99; H, 6.14; N, 10.60.

7. *α,ω-Bis[4-(diarylhydroxymethyl)phenyl]alkanes* (VIII–XIV). *Procedure F.* Phenylmagnesium bromide in twofold excess was prepared from equivalent amounts of bromobenzene and magnesium in absolute ether, in a nitrogen atmosphere. The solution was then transferred through glass wool, under nitrogen pressure, to a flask containing the carbonyl compound. The resulting solution was refluxed in a nitrogen atmosphere for a period specified in the procedures for the individual compounds, then poured onto a mixture of ice and 10% sulfuric acid. The layers were separated; the ethereal solution was washed with 10% sulfuric acid, 10% sodium carbonate solution, and water.

Procedure G. A solution of *p*-xenylmagnesium bromide was prepared from 9.32 g. (0.04 mole) of 4-bromobiphenyl and 0.97 g. (0.04 atom) of magnesium in 40 ml. of tetrahydrofuran in a nitrogen atmosphere. The solution was then transferred through glass wool, under nitrogen pressure, to a flask containing 0.005 mole of diester. The resulting solution was refluxed in a nitrogen atmosphere for a period specified in the procedures for the individual compounds; most of the solvent was removed by distillation, and the residue was hydrolyzed with ice and 10% sulfuric acid. About 50 ml. of ether was added to the mixture, the organic layer was separated, filtered,[34] and washed with 10% sodium carbonate solution, and water.

α,α,α′,α′-Tetraphenyl-α,α′-dihydroxy-p-xylene (VIII). Dimethyl terephthalate (0.10 mole) was treated with 0.6 mole of phenylmagnesium bromide according to Procedure F. The reflux time was 2 hr., with stirring. The ethereal solution was dried over anhydrous sodium sulfate, stripped on a steam bath, and the residue fractionally crystallized from benzene and petroleum ether, giving 17.94 g. (42.3% yield, based on 15.8 g. of dimethyl terephthalate) of white crystalline powder, m.p. 170–171°. An analytical sample was recrystallized from benzene and petroleum ether, m.p. 170–171° dec., after sintering above 169°. The sample was placed in an Abderhalden drying pistol at room temperature and a pressure of 0.05 mm. for 4 hr., before analysis.

Anal.[35] Calcd. for $C_{38}H_{32}O_2$: C, 87.66; H, 6.20. Found: C, 87.22; H, 6.46.

4,4-Bis(diphenylhydroxymethyl)biphenyl (IXA). To 13.5 g. (0.05 mole) of IVA was added phenylmagnesium bromide, according to Procedure F; the solution was refluxed for 4 hr. After hydrolysis, 100 ml. of benzene was added, and the organic layer was separated and filtered, giving 1.00 g. (after recrystallization from chloroform) of white solid, m.p., and mixture m.p. with IVA, 215–217°. The filtrate was washed and evaporated on a steam bath, leaving a yellow oil which solidified to an oily solid weighing 15.45 g. (70% yield). A small sample was recrystallized three times from benzene and petroleum ether, m.p. 177–178° dec., after sintering at 160–165°. Losses in crystallization were large: the crude glycol was therefore converted to the chloride without further purification.

Bis[4-(diphenylhydroxymethyl)phenyl]methane (IXB). Compound IVB (25.2 g., 0.10 mole) was treated according to Procedure F, with a reflux time of 4 hr. The ethereal solution was dried over sodium sulfate, and evaporated on a steam bath. The residue was an oil weighing 21.2 g. (80% yield) which was converted to the chloride without further purification. An attempt at purification of the chloride by chromatography of a benzene solution on alumina resulted in hydrolysis, and gave only glycol in the eluate, m.p. 92–94° dec., after sintering above 86°. The melting point did not change on crystallization from benzene-petroleum ether.

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(34) The insoluble material was quaterphenyl, in amounts varying from a few mg. to 1 g., m.p. and mixture m.p. with authentic material, 318–320°.

(35) For a discussion of this analysis see p. 752.

Anal. Calcd. for $C_{39}H_{32}O_2$: C, 87.94; H, 6.06. Found: C, 88.21; H, 6.35.

1,2-Bis[4'-(diphenylhydroxymethyl)phenyl]ethane (IXC). Compound IVC (9 g., 0.023 mole) was treated according to Procedure F, with a reflux time of 12 hr. The ethereal solution was evaporated on a steam bath, leaving a yellow oil which was crystallized from benzene and petroleum ether to give 9.6 g. (76% yield) of nearly white powder, m.p. 174–176° dec., after sintering above 170°. A second recrystallization gave 8.5 g. (67.5% yield) of white powder, m.p. 179–180° dec., after sintering above 174°. Wittig and Leo[19] report m.p. 176–178°, after sintering.

1,3-Bis[4'-(diphenylhydroxymethyl)phenyl]propane (IXD). Compound IVD (9.6 g., 0.0308 mole) was treated according to Procedure F. The product was an oil weighing 13.1 g. (77% yield) which was converted to the chloride without further purification.

1,4-Bis[4'-(diphenylhydroxymethyl)phenyl]butane (IXE). Compound IVE (4.18 g., 0.01 mole) was treated according to Procedure F with a reflux time of 4 hr. The ethereal solution was evaporated on a steam bath leaving an oil which was crystallized from benzene and petroleum ether to give 5.19 g. (90% yield) of light yellow powder, m.p. 120–130° dec., after sintering above 70°. A second recrystallization gave 4.45 g. (77.5% yield) of white powder, m.p. 128–130° dec., after sintering above 80°. Wittig and Leo[18] report m.p. 145–150°.

α,α,α',α'-Tetra-p-xenyl-α,α'-dihydroxy-p-xylene (X). Dimethyl terephthalate (0.97 g., 0.004 mole) was treated according to Procedure G. The ethereal solution was steam-distilled until the distillate was clear. On cooling, the residue solidified to a yellow solid, which on recrystallization from chloroform gave 2.36 g. (62.2% yield) of nearly white powder, m.p. 278–280° dec. An analytical sample was recrystallized 3 times from chloroform; white powder, m.p. 284–286° dec., after sintering above 282°. Wittig and Kröhne[36] report 289–291°.

4,4-Bis(di-p-xenylhydroxymethyl)biphenyl (XIA). Compound IVA (1.35 g., 0.005 mole) was treated according to Procedure G, with a reflux time of 6 hr., but the mixture was hydrolyzed before the removal of the tetrahydrofuran, which was then evaporated on a steam bath. The mixture was then cooled, and the solid which formed was collected, triturated with water in a glass mortar, filtered, and dried. The crude product was dissolved in about 100 ml. of boiling xylene, which was then distilled down to about 50 ml. and cooled, giving 3.4 g. of white powder, m.p. about 260° dec., after sintering above 220°. A second recrystallization from xylene gave 2.9 g. (70.5% yield), m.p. 283–288° dec., after sintering above 278°. Schlenk[16] reports the melting point as somewhat above 260°.

Bis[4-(di-p-xenylhydroxymethyl)phenyl]methane (XIB). Compound IVB was treated according to Procedure G, with a reflux time of 12 hr. The ethereal solution was allowed to stand at room temperature until it had evaporated to a volume of about 25 ml., and the solid which separated was collected; 3.61 g. of nearly white powder, m.p. 145–150° dec., after sintering above 90°. Recrystallization from ethyl acetate and petroleum ether gave 3.5 g. (86% yield), m.p. 97–100°.

Anal. Calcd. for $C_{63}H_{48}O_2$: C, 90.40; H, 5.78. Found: C, 90.11; H, 5.89.

1,2-Bis[4'-(di-p-xenylhydroxymethyl)phenyl]ethane (XIC). Compound IVC was treated according to Procedure G, with a reflux time of 6 hr. The ethereal solution was filtered, and the solid was washed with fresh ether, giving 3.56 g. of white powder, m.p. 256–260° dec. The filtrate was steam distilled until the distillate was clear, and the residue was recrystallized from chloroform, giving 0.36 g. of white powder, m.p. 256–260° dec. The two products were combined and recrystallized from chloroform, giving 2.30 g. (63% yield) of white powder, m.p. 258–260° dec., after sintering above 250°. An analytical sample was recrystallized from chloroform, m.p. 272.0–272.5° dec.

Anal. Calcd. for $C_{64}H_{50}O_2$: C, 90.32; H, 5.92. Found: C, 89.50, 91,00; H, 5.71, 6.10.

1,4-Bis[4'-(di-p-xenylhydroxymethyl)phenyl]butane (XID). Compound IVE was treated according to Procedure G, with a reflux time of 12 hr. The ethereal solution was evaporated on a steam bath, leaving a yellow oil which crystallized on cooling. It was recrystallized from ethyl acetate and petroleum ether, giving 1.28 g. (29% yield) of white powder, m.p. 232–234°, after sintering above 210°. An analytical sample was crystallized three times from chloroform, m.p. 241.5–242.0° dec.

Anal. Calcd. for $C_{66}H_{54}O_2$: C, 90.17; H, 6.19. Found: C, 90.31; H, 6.07.

α,α,α',α'-Tetra-p-tolyl-α,α'-dihydroxy-p-xylene (XII). A Grignard solution was prepared from 12.8 g. (0.075 mole, 9.25 ml.) of *p*-bromotoluene and 1.83 g. (0.075 atom) of magnesium in 50 ml. of tetrahydrofuran in a nitrogen atmosphere. To this was added a solution of 2.43 g. (0.0125 mole) of dimethyl terephthalate in 30 ml. of warm tetrahydrofuran, with stirring. The solution, which became deep red, was stirred under reflux for 8 hr., in a nitrogen atmosphere, during which time a light precipitate separated. The reaction mixture was hydrolyzed with ice and 10% sulfuric acid, and 100 ml. of ether was added. The ether layer was separated, washed, and dried; on distilling most of the ether and cooling, a white solid separated; this was collected, giving 0.62 g. of white needles, m.p. and mixed m.p. with authentic 4,4'-bitolyl, 121–122°. The filtrate from the initially precipitated bitolyl was evaporated on the steam bath leaving a yellow oil which became hard on cooling, but did not crystallize. The oil was converted directly to the chloride.

4,4'-Bis(di-p-tolylhydroxymethyl)biphenyl (XIII). A Grignard solution was prepared from 6.84 g. (4.92 ml., 0.04 mole) of *p*-bromotoluene and 0.97 g. (0.04 atom) of magnesium in 50 ml. of anhydrous ether, in a nitrogen atmosphere. To this was added 1.35 g. (0.005 mole) of IVA. The mixture was refluxed for 4 hr. with stirring, then 100 ml. of dry benzene was added and stirring under reflux was continued for 4 hr. longer in a nitrogen atmosphere. The reaction mixture was then hydrolyzed and worked up as in the preparation of XII above. The residue was crystallized from benzene and petroleum ether, giving 1.9 g. of light yellow powder, m.p. 110–114°. A sample (0.9 g.) of this material was chromatographed on a small alumina column, giving 0.53 g. of lustrous white powder, m.p. 204–205°, after sintering above 198°. An analytical sample from the eluate was recrystallized twice from benzene and petroleum ether, m.p. 204–205°.

Anal. Calcd. for $C_{42}H_{38}O_2$: C, 87.77; H, 6.66. Found: C, 87.68; H, 6.65.

α,α,α',α'-Tetra-p-anisyl-α,α'-dihydroxy-p-xylene (XIV). A Grignard solution was prepared from 56.1 g. (0.3 mole, 37.6 ml.) of *p*-bromoanisole and 7.29 g. (0.3 atom) of magnesium in 150 ml. of anhydrous ether. To this were added 100 ml. of benzene and 9.7 g. (0.05 mole) of dimethyl terephthalate, and the resulting mixture was refluxed for 8 hr., after which it was hydrolyzed with a saturated solution of ammonium chloride. The organic layer was separated, washed with water, and steam-distilled until the distillate was clear. The residue was recrystallized from benzene, giving 10.0 g. of light orange powder, m.p. 98–120°. This was recrystallized from acetone, giving 9.54 g. of light orange powder, m.p. 157–160°, sintering above 150°, which was taken up in 250 ml. of benzene and chromatographically adsorbed in 100 g. of alumina. Elution with 150 ml. of

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(36) G. Wittig and H. Kröhne, *Ann.*, 529, 142 (1937).

benzene gave about 0.1 g. of a white solid, m.p. 270–274.[37] The alumina was then eluted with 2 l. of benzene containing 10 ml. of absolute ethanol. The solvent was evaporated from the eluate, and the residue was recrystallized from acetone to give 7.3 g. (26% yield) of cream-colored powder, m.p. 164–167°, after sintering above 158°. An analytical sample was recrystallized four times from acetone; short white needles, m.p. 170–171°. *Anal.* Calcd. for $C_{44}H_{34}O_6$: C, 76.85; H, 6.09. Found: C, 76.80; H, 6.07.

4,4'-Bis(di-p-anisylhydroxymethyl)biphenyl (XV). A solution of *p*-anisylmagnesium bromide was prepared from 7.5 g. (0.04 mole, 5.0 ml.) of *p*-bromoanisole and 0.97 g. (0.04 atom) of magnesium in 40 ml. of tetrahydrofuran, and transferred through glass wool, under nitrogen pressure, to a flask containing a suspension of 1.35 g. (0.005 mole) of IVA in 10 ml. of tetrahydrofuran. The resulting purple solution was refluxed for 6 hr., during which time the purple color disappeared, giving a clear amber solution. Most of the tetrahydrofuran was removed by distillation; the residue was hydrolyzed with ice and 10% sulfuric acid, and 100 ml. of ether was added. The mixture was worked up as in the preparation of XIV above. The residue was taken up in ether from which, on slow evaporation, a pale yellow solid separated; 0.75 g. (23% yield), m.p. 204–208° dec., after sintering above 190°. An analytical sample was recrystallized from acetone, then taken up in benzene and passed through a small column of alumina; from the eluate a white microcrystalline powder was isolated, m.p. 215.5–216.0° dec. The melting point was unchanged by further recrystallization. *Anal.* Calcd. for $C_{50}H_{36}O_6$: C, 78.98; H, 6.00. Found: C, 78.54; H, 5.74.

4,4'-Bis(phenyl-1-naphthylhydroxymethyl)biphenyl (XVI). A Grignard solution was prepared from 18.6 g. (0.09 mole, 12.6 ml.) of 1-bromonaphthalene and 2.19 g. (0.09 atom) of magnesium in 100 ml. of anhydrous ether. To this was added 10.86 g. (0.03 mole) of 4,4'-dibenzoylbiphenyl, m.p. 218.0–219.5°,[38] in several portions, followed by 100 ml. of dry benzene. After 3.5 hr. of refluxing, the mixture was hydrolyzed and the organic layer washed with 10% sulfuric acid, 10% sodium carbonate solution, and water. After distillation of most of the solvent, the residue was steam-distilled until no further organic material came over. The water was decanted from the residue, which was then taken up in 500 ml. of chloroform. The solution was filtered, evaporated to 75 ml., and cooled, giving 4.08 g. of nearly white powder, m.p. 242–246° dec. A second crop, consisting of 9.56 g. of brown solid, m.p. 170–180°, was collected; this was recrystallized twice from chlorobenzene, giving 6.05 g. of white powder, m.p. 260–262° dec. An analytical sample was recrystallized from chlorobenzene, m.p. 260–262° dec.

Anal. Calcd. for $C_{45}H_{34}O_2$: C, 89.29; H, 5.54. Found: C, 89.56; H, 5.89.

8. α,ω-Bis[4-(diarylchloromethyl)phenyl]alkanes (XVIII–XXIV). *Procedure H.* The glycol was dissolved in the minimum amount of anhydrous ether or benzene, and after addition of a few ml. of acetyl chloride, dry hydrogen chloride was passed in through a diffuser tube. The precipitation of the chloride almost always began within a few minutes after the first introduction of the gas, but was not complete until several hours had elapsed. The mixture was therefore allowed to stand overnight at about 5° before collection of the chloride, which was recrystallized from benzene by addition of just enough of a saturated solution of hydrogen chloride in acetic acid to cause the start of precipitation from the hot solution.

A second method of crystallization was used for the preparation of samples for analysis and dehalogenation to the radical A centrifuge tube containing a nearly saturated solution of the chloride was placed in a jar containing petroleum ether. The closed jar was allowed to stand at room temperature until a volume of petroleum ether equal to the original volume of benzene had distilled into the centrifuge tube. The tube was removed, and the white, crystalline precipitate collected.

Procedure I. The glycol was treated with 10 ml. of thionyl chloride and 5 ml. of dry benzene per gram of glycol; the resulting solution was refluxed overnight, and evaporated on a steam bath. To the residue was added enough benzene to redissolve it, and the solution was again evaporated. The residue was then recrystallized.

α,α,α',α'-Tetraphenyl-α,α'-dichloro-p-xylene (XVIII). A solution of 2.6 g. (0.005 mole) of VIII and 5 ml. of acetyl chloride in 50 ml. of benzene was treated according to Procedure H, giving 2.30 g. (96% yield) of white powder, m.p. 256–258° dec., after sintering above 254°. An analytical sample was recrystallized three times from benzene and acetic acid saturated with hydrogen chloride; white powder, m.p. 262–264° dec., after sintering above 258°.

Anal. Calcd. for $C_{32}H_{24}Cl_2$: C, 80.16; H, 5.06. Found: C 80.27; H 5.36.

4 4'-Bis(diphenylchloromethyl)biphenyl (XIXA). The crude glycol (IXA) prepared from 0.04 mole of 4,4'-dibenzoylbiphenyl was dissolved in about 150 ml. of ether and 10 ml. of acetyl chloride and treated according to Procedure H, giving 14.4 g. (65% yield) of nearly white powder, m.p. 212–216° dec., after sintering above 202°. An analytical sample was recrystallized from benzene and acetic acid saturated with hydrogen chloride; nearly white powder, m.p. 223–225° dec., after sintering above 218°. Tschitschibabin[11] reports the melting point as 219°, "to a turbid liquid which becomes clear at 223°."

Bis[4-(diphenylchloromethyl)phenyl]methane (XIXB). The crude glycol (IXB) prepared from 0.05 mole of IVB was dissolved in 200 ml. of ether and 10 ml. of acetyl chloride and treated according to Procedure H, giving 15.85 g. (56% yield) of light yellow powder, m.p. 163–164° dec., after sintering above 160°. Fractional crystallization from benzene and acetic acid saturated with hydrogen chloride gave 13.42 g. (47% yield) of nearly white powder, m.p. 182–184° dec., after sintering above 174°. Wittig and Leo[17] report the melting point (no recrystallization) as 157–160°.

1,2-Bis[4-(diphenylchloromethyl)phenyl]ethane (XIXC). A solution of 1.5 g. (0.00274 mole) of IXC in 25 ml. of boiling glacial acetic acid was saturated with hydrogen chloride as the solution cooled. The mixture was allowed to stand overnight, giving 1.30 g. (81%) of pale yellow powder, m.p. 186–190°. Recrystallization from benzene and acetic acid saturated with hydrogen chloride gave 1.20 g. of nearly white powder, m.p. 192–194° dec. Wittig and Leo[17] report m.p. 184–186° dec.

1,3-Bis[4-(diphenylchloromethyl)phenyl]propane (XIXD). The crude glycol (IXD) prepared from 0.0308 mole of IVD was dissolved in about 200 ml. of ether and 10 ml. of acetyl chloride and treated according to Procedure H, giving 10.78 g. (59% yield) of pale yellow powder, m.p. 154–156° dec., after sintering above 150°. An analytical sample was recrystallized three times from benzene and acetic acid saturated with hydrogen chloride; nearly white powder, m.p. 154–156° dec., after sintering above 150°.

Anal. Calcd. for $C_{41}H_{34}Cl_2$: C, 82.40; H, 5.73. Found: C, 81.63; H, 5.66.

1,4-Bis[4'-(diphenylchloromethyl)phenyl]butane (XIXE). A

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[37] The high-melting white solid obtained from the first (benzene) eluate was recrystallized twice from benzene, giving white leaflets, m.p. 276–278°. Unlike the glycols of this series, this compound gave no coloration with concentrated sulfuric acid. *Anal.* Found: C, 81.68; H, 6.15. This is consistent with the empirical formula $C_{36}H_{34}O_4$, whose calculated percentage composition is: C, 81.48; H, 6.46; the most probable structure then, is the reduction product of the glycol, α,α,α',α'-tetra-*p*-anisyl-*p*-xylene.

[38] W. Schlenk and M. Brauns, ref. 16, reported m.p. 216° and a yield of 60% in the Friedel-Crafts reaction of benzoyl chloride on biphenyl. Their yield could be achieved only by doubling the amounts of benzoyl chloride and aluminum chloride, and increasing reaction time to 12 hr.

solution of 4.45 g. (0.00775 mole) of IXE in about 50 ml. of ether and 3 ml. of acetyl chloride was treated according to Procedure H, giving 4.07 g. (86% yield) of pale yellow powder, m.p. 165–166° dec., after sintering above 161°. Wittig and Leo[18] report m.p. 159–161°.

α,α,α′,α′-Tetra-p-xenyl-α,α′-dichloro-p-xylene (XX). To a solution of 1.26 g. (0.00169 mole) of X in 75 ml. of boiling benzene was added 5 ml. of acetyl chloride. Dry hydrogen chloride was passed into the solution for 0.5 hr. as it cooled. The hot solution became bright purple immediately on contact with the gas. The color became lighter on cooling, and a white precipitate formed: 0.95 g. (72% yield), m.p. 281–284° dec.; the sample started to discolor above 260° and to sinter above 270°. Wittig and Kröhne[36] report 265–266° dec., with no carbon and hydrogen analysis. An analytical sample was recrystallized from xylene; white platelets, with no change in melting behavior. *Anal.* Calcd. for $C_{56}H_{40}Cl_2$: C, 85.81; H, 5.14. Found: C, 85.72; H, 5.07.

4,4′-Bis(di-p-xenylchloromethyl)biphenyl (XXI). The glycol IXA (0.5 g., 0.000607 mole), was treated according to Procedure I, giving 0.33 g. (63% yield) of pale purple powder, m.p. 278–280° dec., after sintering above 272°. The filtrate from this material was colorless, and on standing several hours gave a second crop, 0.05 g. of white powder, m.p. 254–256° dec., after sintering above 252°. Schlenk[16] reports the m.p. as "about 271°."

α,α,α′,α′-Tetra-p-tolyl-α,α′-dichloro-p-xylene (XXII). The crude glycol (XII) from 2.43 g. of dimethyl terephthalate was dissolved in 50 ml. of benzene and 5 ml. of acetyl chloride, and treated according to Procedure H, giving a green solution from which 2.83 g. of nearly white needles separated. The filtrate was distilled down to about 20 ml. and resaturated with hydrogen chloride, giving a second crop; 0.31 g., nearly white needles, m.p. above 300°. Yield: 47%, based on dimethyl terephthalate. *Anal.* Calcd. for $C_{36}H_{32}Cl_2$: C, 80.74; H, 6.02. Found: C, 80.37; H, 6.11.

4,4′-Bis(phenyl-1-naphthylchloromethyl)biphenyl (XXIII). A suspension of 0.6 g. (0.0097 mole) of the glycol XVI in 25 ml. of chloroform was treated with 5 ml. of acetyl chloride; dry hydrogen chloride was then passed in for 3 hr., giving a clear deep blue solution. This was evaporated on a steam bath, leaving 0.5 g. of pale blue solid, m.p. 187–192°, after sintering above 175°. The solid was dissolved in 15 ml. of benzene and, after evaporation to 5 ml., 3 ml. of acetic acid saturated with hydrogen chloride was added to the hot benzene solution. From the resulting hot, purple-blue solution a white solid separated. On cooling, the color disappeared completely from the supernatant solution. The solid was filtered off: 0.36 g. (46%), m.p. 256–258° dec.

Anal. Calcd. for $C_{58}H_{44}Cl_2$: C, 85.80; H, 5.46; Cl, 8.73. Found: C, 85.41; H, 5.26; Cl, 8.70.

4,4′-Bis(diphenylchloromethyl)diphenyl ether (XXIV). A Grignard solution from 8.4 g. (0.08 mole, 5.5 ml.) of bromobenzene and 1.75 g. (0.08 atom) of magnesium, in 50 ml. of tetrahydrofuran, was added to a suspension of 7.56 g. (0.02 mole) of 4,4′-dibenzoyldiphenyl ether[39] in 25 ml. of tetrahydrofuran. The mixture was refluxed for 2 hr. and hydrolyzed with ice and 10% sulfuric acid. Ether was added and the organic layer was separated, washed with water, 10% sodium bicarbonate, and water. It was then dried over magnesium sulfate and concentrated on the steam bath to 9.65 g. (95%) of viscous, pale yellow oil (XVII), which was taken up in about 25 ml. of anhydrous ether. The resulting solution was saturated with anhydrous hydrogen chloride after addition of a few ml. of acetyl chloride. The white precipitate which formed was filtered off and washed twice with cold ether. The product became pale yellow on drying; yield 9.3 g. (82% based on ketone), m.p. 169–171° dec., after sintering above 162°. Recrystallization from benzene and acetic acid saturated with hydrogen chloride afforded 4.8 g. (42%) of pale yellow powder, m.p. 173–175° dec., after sintering above 172°. Dilthey[39] reports 165° after "decomposition" at 120°, and a yield of "about 75%."

9. α,ω-Bis[4-(diarylmethyl)phenyl]alkanes (XXVII–XXXII). The free radical solutions were prepared in the vacuum system shown in Figure 1(Top). Figure 1(Bottom) shows in detail the reaction vessel proper. Before each run, the reaction vessel and the flask A were cleaned thoroughly with a mixture of nitric and sulfuric acids. They were then rinsed several times with distilled water, dilute ammonia, and again with distilled water. dried in a vacuum oven at 150°, and cooled in a desiccator.

From a weighing funnel, 2 × 10^{-5} mole of the appropriate dihalide was poured into the reaction vessel; then 4 × 10^{-4} atom of "molecular" silver[9] was added. The constriction E was freed of solid particles by means of a pipe cleaner and the vessel was sealed onto the vacuum manifold. After the manifold had been swept out with nitrogen, 2 ml. of specially purified benzene was placed in flask A and frozen in liquid nitrogen. The entire apparatus was evacuated to less than 10^{-5} mm., stopcock B was closed, and the benzene distilled into the U-trap C. The system was then reevacuated and, with stopcock B again closed, the benzene was allowed to melt. Dry nitrogen (containing less than 25 ppm. of oxygen) was then admitted slowly through a bypass to a pressure slightly above atmospheric. The process of freezing and evacuation was repeated and the benzene was distilled into the reaction vessel D. Stopcock B was then opened, and the reaction vessel was sealed off the line at the constriction E.

The benzene was allowed to melt, and the vessel was shaken in the dark for a few minutes, then inverted, allowing the solution to filter into the thin-walled tip. After a measurement of the resonance absorption, the solution was returned to the compartment containing the silver, for continued shaking. After completion of the dehalogenation (see Section 10) the filtered solutions were stored in the dark, and removed only for the duration of the measurements. Some observations on the free radicals are summarized in Table V.

10. Determination of extent of dehalogenation. Accurately weighed samples of about 10^{-3} mole of each of several of the dihalides were converted to the corresponding radicals by means of a tenfold excess of "molecular" silver in 10 ml.

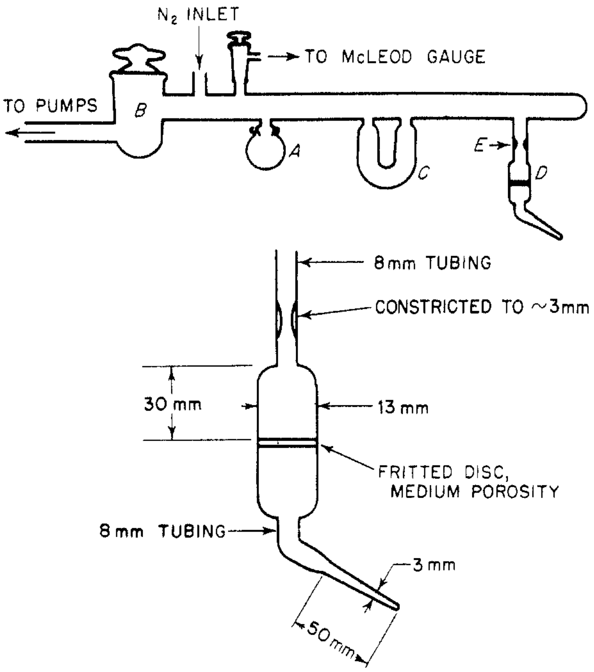

FIG. 1. PREPARATION OF FREE RADICAL SOLUTIONS. (TOP) VACUUM LINE ASSEMBLY. (BOTTOM) REACTION CELL

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[39] W. Dilthey, E. Bach, H. Grütering, and E. Hausdörfer, *J. Prakt. Chem.*, [2], **117**, 337 (1927).

TABLE V

OBSERVATIONS ON FREE RADICAL SOLUTIONS

Starting Material	Product	Initial Color	Color of Degraded Solution	Color after Exposure to Air	Paramagnetic Resonance Absorption Intensity[a]
XVIII	XXVII	Orange	Orange	Orange	–
XIXA	XXIXA	Deep purple	Deep purple	Colorless	+
XIXB	XXIXB	Bright red	Pale yellow	Colorless	++
XIXC	XXIXC	Wine red[b]	Pale blue	Colorless	++
XIXD	XXIXD	Yellow	Pale yellow	Pale yellow	++
XIXE	XXIXE	Yellow	Pale yellow	Pale yellow	++
XX	XXVIII	Brick red	Brick red	Brick red	+[c]
XXI	XXX	Royal blue	Royal blue	Colorless	+
XXIII	XXXI	Deep purple	Deep purple	Colorless	+
XXIV	XXXII	Yellow	Pale yellow	Pale yellow	++
ϕ_3CCl[d]	ϕ_3C.	Yellow	Colorless	Colorless	+

[a] *Cf.* ref. 3. [b] Green in thin layers. [c] Weak resonance, possibly due to partial dehalogenation to monoradical. [d] *Cf.* ref. 30.

of benzene. The preparations were carried out in the same manner as for the resonance experiments, in vessels 100 mm. long by 25 mm. in diameter. The end of the vessel containing the silver was scratched with a file, and a rubber tube through which pure nitrogen was flowing was slipped over the scratched tube. The tip of the tube was then broken off, whereupon the nitrogen pressure caused the radical solution to pass through the fritted disc. The thin-walled tip of the other end of the reaction vessel was the broken, and the radical solution forced out by the nitrogen stream. The silver was then washed with several 10 ml. portions of 6N ammonia. The aqueous ammoniacal washings were made slightly acid with dilute nitric acid, and 5 ml. of 0.1N silver nitrate was added. The silver chloride suspension was digested, cooled, and filtered. The weights of the samples used, durations of the dehalogenations, weights of silver chloride recovered, and percentages of the organic chlorine to which these weights correspond are assembled in Table VI.

TABLE VI

EXTENT OF DEHALOGENATION

Compound	Sample, Wt.	Shaking, Hr.	Silver Chloride, Wt.	Chlorine Recovered, %
XIXA	0.5593 g.	2	0.2669 g.	92.5
XIXC	0.5810	1.5	0.2546	89.2
XIXE	0.6221	2	0.2887	99.0
XXIV	0.5714	2	0.2416	84.0

11. Miscellaneous. 4,4'-Dicarbo-n-butoxybiphenyl (XXXIV). A mixture of 9.66 g. (0.04 mole) of IIIA, 200 ml. of n-butyl alcohol, and 10 ml. of methanesulfonic acid was refluxed for 2 days in a flask equipped with a Barrett moisture test receiver. The mixture was stripped on a steam bath at aspirator pressure; the residue was then taken up in ether, the solution was washed with 10% sodium carbonate and with water, and dried over calcium chloride. The ether was distilled off, and the residue was distilled at 1 mm. in a sausage flask, giving a pale yellow oil. This was crystallized from acetone by cooling the solution in dry ice and filtering quickly, giving 6.2 g. (44% yield) of pale yellow plates, m.p. 42.5–43.0°. An analytical sample was recrystallized five times from acetone; white plates, m.p. 47.7–48.0°. *Anal.* Calcd. for $C_{22}H_{26}O_4$: C, 74.55; H, 7.40. Found: C, 74.34; H, 7.30.

α,α,α',α'-Tetraphenyl-α,α'-diethoxy-p-xylene (XXV). To 1.94 g. (0.01 mole) of dimethyl terephthalate was added 35 ml. of 1.3N phenylmagnesium bromide solution. The mixture was allowed to stand for several hours, with occasional swirling, then hydrolyzed with ice and 10% sulfuric acid. The layers were separated; the ethereal solution was washed with 10% sulfuric acid, 10% sodium carbonate, and water. The resulting solution was dried over sodium sulfate and evaporated on a steam bath. The residue was taken up in 95% ethanol, and the solution treated with Norit. A solid separated from the filtrate; this did not dissolve on prolonged refluxing with as much as 200 ml. of ethanol. The mixture was then cooled, and the solid recrystallized five times from ethyl acetate; white powder, m.p. 208–209°.

Anal. Calcd. for $C_{36}H_{34}O_2$: C, 86.71; H, 6.87. Found: C, 86.20; H, 7.11.

α,α,α',α'-Tetra-p-anisyl-α,α'-dimethoxy-p-xylene (XXVI). Dry hydrogen chloride was passed into a water-white solution of 0.45 g. (0.000853 mole) of XIV in 15 ml. of dry benzene. The solution became pink on first contact with the gas, then darkened until it was deep maroon. From it, a lustrous green solid separated. The solid was collected; on standing in air it became gray, but the green color returned in an atmosphere of hydrogen chloride. The green solid was then dissolved in 50 ml. of warm methanol, giving a clear red solution. On addition of one ml. of pyridine, the red color was instantly discharged, and a white precipitate formed. The mixture was refluxed for 0.5 hr., cooled, and filtered, giving 0.37 g. (70% yield), m.p. 175–176° dec. An analytical sample was recrystallized twice from benzene and petroleum ether; light orange powder, m.p. 175–176° dec.

Anal. Calcd. for $C_{38}H_{38}O_6$: C, 77.27; H, 6.48. Found: C, 77.02; H, 6.42.

Purification of tetrahydrofuran. Commercial tetrahydrofuran was distilled from sodium and mineral oil. Storage of this product over sodium always resulted in formation of dense, colored precipitates, and did not prevent formation of peroxides. A dry, peroxide-free product is obtained by distillation from phenylmagnesium bromide. It is convenient to prepare about 0.1 mole of the latter in 100 ml. of tetrahydrofuran, in a flask equipped with a take-off head, and then fill the flask with freshly distilled tetrahydrofuran.

Purification of benzene. Two liters of reagent grade benzene was stirred vigorously with 200 ml. of reagent grade concentrated sulfuric acid for 24 hr. The process was repeated until the acid no longer became yellow (4 times). The benzene was then stirred for 24 hr. with 200 ml. of 1% potassium permanganate solution, washed with water, 5% sodium bicarbonate, and water. It was dried over calcium chloride, distilled from sodium, and stored over sodium ribbon.

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