same manner as was III. Dimethylaniline (2.54 g., 0.02 mole) in 30 ml. of acetic acid was added. When the solution had come to room temperature, the product was filtered off, dried, and recrystallized three times from toluene. Only a few hundred milligrams of yellow-brown product melting at 196–197.5° remained.

Anal. Calcd. for $C_{34}H_{31}N_9O_3$: C, 66.5; H, 5.1; N, 20.5. Found: C, 65.2; H, 6.3; N, 19.3.

p-(2-Methoxy-4-nitrophenylazo)-*N*,*N*-dimethylaniline (XII).—2-Methoxy-4-nitroaniline (3.3 g., 0.02 mole) was diazotized in a standard way and allowed to couple with 2.4 g. (0.02 mole) of dimethylaniline to give a nearly quantitative crude yield. Recrystallization from ethanol gave violet crystals, m.p. 173.5–175°.

Anal. Calcd. for $C_{15}H_{16}N_4O_3$: C, 60.0; H, 5.4; N, 18.7; O. 16.0. Found: C, 59.7; H, 6.0; N, 18.4; O, 15.7.

p-(*o*-Phenoxyphenylazo)-*N*,*N*-dimethylaniline (XIV) was prepared in the usual way.

Anal. Calcd. for $C_{20}H_{19}N_3O$: C, 75.7; H, 6.0; N, 13.2; O, 5.0. Found: C, 75.5; H, 5.9; N, 13.2; O, 5.0.

The Tetraphenylphenols

PETER YATES[1] AND JOHN E. HYRE

Department of Chemistry, Harvard University, Cambridge, Massachusetts

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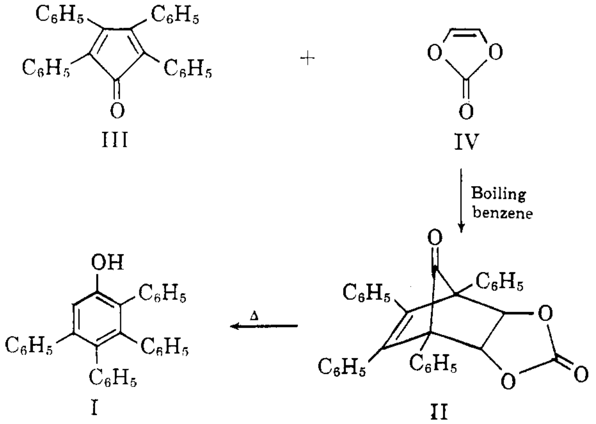
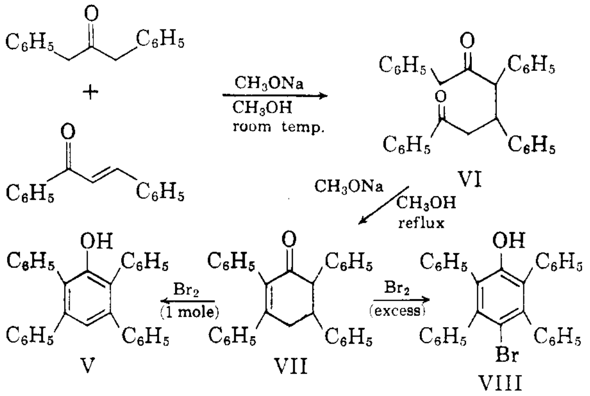
In connection with another investigation we have had occasion to synthesize the three tetraphenylphenols.

2,3,4,5-Tetraphenylphenol (I) was prepared by the following route:



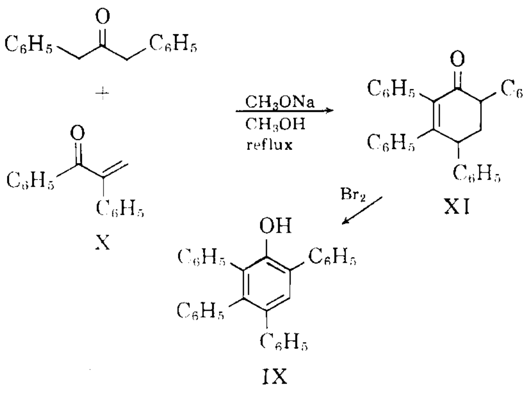
A Diels–Alder adduct II, of undetermined stereochemistry, was obtained when tetracyclone (III) and vinylene carbonate (IV)[2] were heated together in boiling benzene. The adduct has bands in its infrared spectrum at 5.50 and 5.59 μ; these can be assigned to the stretching vibrations of the carbonate[3] and ketonic[4] carbonyl groups, respectively. When II was heated at its melting point, gas evolution occurred and it was converted to a compound, $C_{30}H_{22}O$, which in its infrared spectrum shows no carbonyl band but a sharp hydroxyl band at 2.81 μ. On the basis of its genesis and spectrum this compound is assigned structure I. It was also obtained together with the adduct II when the Diels–Alder reaction was carried out in refluxing xylene.

2,3,5,6-Tetraphenylphenol (V) was prepared by the following route:



Michael addition of dibenzyl ketone to benzalacetophenone gave the δ-diketone VI (infrared bands at 5.84 and 5.93 μ) when carried out with methanolic sodium methoxide at room temperature. The same reagent at reflux effected the aldolization and dehydration of VI to give the cyclohexenone VII. This shows in its infrared spectrum a band at 6.00 μ and in its ultraviolet spectrum a maximum at 295 mμ (log ε 3.86) in accord with expectation.[5] Oxidation of VII with one molar equivalent of bromine gave 2,3,5 6-tetraphenylphenol (V) (infrared band at 2.83 μ). When excess of bromine was used for the oxidation, a brominated product, $C_{30}H_{21}OBr$, was obtained which is considered to have structure VIII on the basis of its ultraviolet spectrum (*vide infra*).

The remaining tetraphenylphenol, IX, was prepared by the following route, analogous to that used for the synthesis of V, although in this case the intermediates were not characterized (X → XI → IX).



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[1] Present address: Department of Chemistry, University of Toronto.

[2] M. S. Newman and R. W. Addor, *J. Am. Chem. Soc.*, **77**, 3789 (1955).

[3] *Cf.* C. L. Angell, *Trans. Faraday Soc.*, **52**, 1178 (1956).

[4] *Cf.* C. F. H. Allen, T. Davis, D. W. Stewart, and J. A. VanAllan, *J. Org. Chem.*, **20**, 306 (1955).

Michael addition of dibenzyl ketone to methylenedeoxybenzoin (X)[6] gave a viscous oil from which no crystalline product was obtained directly. The infrared spectrum of the oil—bands at 6.01 and 6.29 μ—showed that it was rich in the cyclohexenone XI; the spectrum was similar to, but not identical with, that of the cyclohexenone VII.[7] Treatment of the oil with bromine in carbon tetrachloride gave crystalline 2,3,4,6-tetraphenylphenol (IX) (infrared band at 2.81 μ).[8]

The melting points and ultraviolet spectra of the tetraphenylphenols are listed in Table I. It may be noted that the isomer assigned the structure of the highest symmetry (V) has the highest melting point. Detailed discussion of the ultraviolet spectra is not possible because of the complexity of the absorbing systems and the unavailability of closely related model compounds. However, it may be pointed out that the K-band of V, which has no phenyl group in the *para* relationship to the hydroxyl group, occurs at a somewhat shorter wave length and is of appreciably weaker intensity than the K-bands of I and IX, each of which has a phenyl group in the *para* position on the phenolic ring. This may be compared with the case of the phenylphenols,[9] where the K-bands of the *ortho* and *meta* isomers occur at lower wave length and are of weaker intensity than the K-band of the *para* isomer. The large hypochromic effect observed on bromination of V suggests strongly that the bromine attacks the phenolic ring to give VIII, the intensity of whose K-band is reduced relative to that of the K-band of V largely because of increased steric hindrance to coplanarity of the peripheral phenyl groups and the phenolic ring. Attack of bromine at the *para* position of one of the peripheral rings would not be expected to give rise to a large hypochromic effect, while preferential attack at the *ortho* position of a peripheral ring appears unlikely.

TABLE I

	M.p., °C.	λ_{max},[a] mμ	log ε
2,3,4,5-Tetraphenylphenol (I)	183–184	243 300	40,200 5,900
2,3,5,6-Tetraphenylphenol (V)	277–278	239 304	31,600 4,850
2,3,4,6-Tetraphenylphenol (IX)	244–245	247 308	43,200 7,200
4-Bromo-2,3,5,6-tetraphenylphenol (VIII)		249	19,800

[a] In cyclohexane.

Experimental[10]

5,6-Dihydroxy-1,2,3,4-tetraphenylbicyclo[2.2.1]hept-2-en-7-one Carbonate (II).—Tetracyclone (2.00 g.) and vinylene carbonate[2] (1.00 g.) were heated together in refluxing benzene (20 ml.) for 24 hr. The solvent was removed under reduced pressure and the residue was crystallized from benzene–petroleum ether to give the adduct II (1.5 g., 60%), m.p. 208–209° dec., $\lambda_{max}^{CHCl_3}$ 5.50, 5.59 μ.

Anal. Calcd. for $C_{32}H_{22}O_4$: C, 81.68; H, 4.71. Found: C, 81.66; H, 4.81.

When the Diels–Alder reaction was carried out on the same scale in boiling xylene, the product was found to be a mixture of II and the phenol I by infrared spectral comparison.

2,3,4,5-Tetraphenylphenol (I).—The adduct II (0.50 g.) was heated at 215° for 5 min., after which time gas evolution had ceased. The residue was recrystallized from benzene–petroleum ether to give the phenol I (0.40 g., 95%) as plates, m.p. 183–184°, $\lambda_{max}^{CHCl_3}$ 2.81 μ.

Anal. Calcd. for $C_{30}H_{22}O$: C, 90.42; H, 5.57. Found: C, 89.83, 90.70; H, 5.60, 6.01.

1,3,4,6-Tetraphenyl-1,5-hexanedione (VI).—Benzalacetophenone (5.00 g.) and dibenzyl ketone (5.00 g.) were dissolved in methanol (50 ml.) and saturated methanolic sodium methoxide (1 ml.) was added to the solution. After 5 min. a crystalline deposit began to appear after 1 hr. the mixture was cooled in an ice bath and the product filtered. This was recrystallized from methanol to give VI as cubes (7.56 g., 75%), m.p. 195–196°, $\lambda_{max}^{CHCl_3}$ 5.84, 5.93 μ.

Anal. Calcd. for $C_{30}H_{26}O_2$: C, 86.09; H, 6.26. Found: C, 86.13; H, 6.35.

2,3,5,6-Tetraphenyl-2-cyclohexenone (VII).—A suspension of VI (5.05 g.) in methanol (50 ml.) was treated with saturated methanolic sodium methoxide (5 ml.), and the mixture was boiled under reflux in a nitrogen atmosphere for 24 hr. The tan solid which separated when the reaction mixture was cooled was filtered and recrystallized from benzene–petroleum ether to give the cyclohexenone VII (3.70 g., 75%), m.p. 159–160°, $\lambda_{max}^{CHCl_3}$ 6.00, 6.27 μ, λ_{max}^{EtOH} 295 mμ (log ε 3.86).

Anal. Calcd. for $C_{30}H_{24}O$: C, 89.89; H, 6.04. Found: C, 89.89; H, 5.78.

2,3,5,6-Tetraphenylphenol (V).—A solution of VII (1.08 g., 0.0027 mole) in acetic acid (20 ml.) was treated with bromine (0.43 g., 0.0027 mole). After all of the bromine had been consumed, water was added to the reaction mixture, and the precipitated product was filtered and recrystallized from benzene–petroleum ether to give the phenol V as needles (0.85 g., 80%), m.p. 272–273°, $\lambda_{max}^{CHCl_3}$ 2.83 μ.

Anal. Calcd. for $C_{30}H_{22}O$: C, 90.42; H, 5.57. Found: C, 90.54; H, 5.77.

4-Bromo-2,3,5,6-tetraphenylphenol (VIII).—A solution of VII (1.03 g.) in acetic acid (20 ml.) was treated with successive small portions of bromine until the color of the latter persisted when the reaction mixture was heated on the steam bath. Water was added to the reaction mixture and the precipitated product was filtered and recrystallized from benzene–petroleum ether to give VIII as rhombs (0.75 g., 60%), m.p. 329–330° ($\lambda_{max}^{CHCl_3}$ 2.81 μ.

Anal. Calcd. for $C_{30}H_{21}OBr$: C, 75.47; H, 4.43; Br, 16.74. Found: C, 75.95; H, 4.39; Br, 16.42.

2,3,4,6-Tetraphenylphenol (IX).—A solution of methylenedeoxybenzoin[6] (5.01 g.) and dibenzyl ketone (5.01 g.) in methanol (40 ml.) was treated with saturated methanolic sodium methoxide (12 ml.). The mixture was boiled under

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[5] *Cf.* 2,3,4,5-tetraphenyl-2-cyclopentenone, λ_{max} 295 mμ (log ε 4.13): E. D. Bergmann, *Bull. soc. chim. France*, 703 (1952).

[6] H. Fiesselmann and J. Ribka, *Chem. Ber.*, **89**, 27 (1956).

[7] Reaction of dibenzyl ketone with methylenedeoxybenzoin in the presence of methanolic sodium methoxide in the cold also gave an oil from which no crystalline product was obtained; the infrared spectrum of this product, with bands at 5.83 and 5.94 μ, resembled that of the diketone VI.

[8] Professor D. G. Farnum, Cornell University, has informed us that he has prepared the tetraphenylphenol IX by an alternative route and has established the identity of his product with that obtained by us. He has also corroborated the structural assignment V by oxidation of this compound to a quinone. We are grateful to him for his kindness in informing us of these results. *Cf.*, also, D. G. Farnum and M. Burr, *J. Am. Chem. Soc.*, **82**, 2651 (1960).

[9] A. Burawoy and J. T. Chamberlain, *J. Chem. Soc.*, 2310 (1952); V. Prelog, O. Metzler, and O. Jeger, *Helv. Chim. Acta*, **30**, 675 (1947).

[10] Melting points are uncorrected.

reflux for 3 hr., then cooled and poured into water (100 ml.). The resulting mixture was extracted with three 50-ml. portions of dichloromethane and the combined extracts were washed with water, dilute hydrochloric acid, water, and saturated brine, and dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure left the crude product as a viscous, brown oil (8 g.), $\lambda_{max}^{CHCl_3}$ 6.01, 6.29 μ. A solution of 0.8 g. of this oil in carbon tetrachloride (30 ml.) was treated with a solution of bromine (1.5 g.) in carbon tetrachloride (10 ml.) and the mixture was boiled under reflux for 1 hr. It was then cooled and treated with aqueous sodium bisulfite to discharge the excess of bromine. The organic layer was separated and washed with water, aqueous sodium bicarbonate, water, and saturated brine. It was dried over anhydrous sodium sulfate and stripped of solvent under reduced pressure. The residue was crystallized from benzene–petroleum ether to give the phenol IX, m.p. 244–245°, $\lambda_{max}^{CHCl_3}$ 2.81 μ.

Anal. Calcd. for $C_{30}H_{22}O$: C, 90.42; H, 5.57. Found: C, 90.47; H, 5.61.

Isocyanide Bond Refraction

RICHARD G. GILLIS

Defence Standards Laboratories, Department of Supply, Maribyrnong, Victoria, Australia

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Extensive tabulations of bond refractions have been made by Vogel[1] and by Gillis.[2] The isocyanide bond refraction, which has not previously been determined, is now reported for comparison with that of the cyanide bond. The new value is based on the properties of four alkyl isocyanides shown in Table I.

TABLE I

PROPERTIES OF ALKYL ISOCYANIDES

R	B.P.	d^{20}_4	n^{20}_D	R^a_D	$(N\equiv C)^a$	$(Mn^{20}_D)^a$
Me	59–60	0.7497	1.3466	11.68	5.10	29.16
Et	78–79	0.7478	1.3658	16.49	5.27	28.51
n-Pr	99–100	0.7665	1.3832	21.04	5.17	28.27
n-Bu	129–130	0.7818	1.3976	25.64	5.12	28.26
				Mean	5.17	28.55

[a] The symbolism is Vogel's.[1]

$(N\equiv C)$ determined from each of these alkyl isocyanides is greater than $(C\equiv N)$ determined from the corresponding alkyl cyanide,[1] and the difference of the means is significant at the 0.01 level. (The bond refraction coefficients 28.55 for isocyanides and 29.91 for cyanides[1] are also significantly different.) This result is in contrast with the low bond refractions normally associated with systems containing dative bonds.[2–4] It is probably owing to the effect of the lone pairs of electrons on the nitrogen and carbon atoms, because the bond refraction as determined is a measure of the polarizability of the six electrons in the bond plus that of the lone pair in each case. Linnett[5] has suggested that these pairs are in some way connected with the lower value for the $N\equiv C$ force constant in methyl isocyanide as compared with that of $C\equiv N$ in methyl cyanide.

Methyl isocyanide has a lower boiling point and smaller dipole moment[6] than methyl cyanide. These facts are compatible with the terminal lone pair in isocyanide being less strongly bound than in cyanides. Further evidence is being sought from retention data on various donor and acceptor stationary phases in gas chromatography.

Experimental

The isocyanides were prepared from the corresponding iodide and silver cyanide by the method of Jackson and McCusick.[7] It was advantageous to dilute the reaction mixture with a little ethylene glycol which made the pasty complex easier to stir. The products were fractioned in a column packed with helices, and physical properties were determined[2,3] on fractions shown to be homogeneous by gas chromatography.

Acknowledgment.—This paper is published by the permission of the Chief Scientist, Australian Defence Scientific Service, Department of Supply, Melbourne, Victoria, Australia.

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[2] R. G. Gillis, *Rev. Pure and Appl. Chem.*, **10**, 21 (1960).

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[5] J. W. Linnett, *J. Chem. Phys.*, **8**, 91 (1940).

[6] S. N. Ghosh, R. Trambarulo, and W. Gordy, *ibid.*, **21**, 308 (1953).

[7] H. L. Jackson and B. C. McCusick, *Org. Syn.*, **35**, 62 (1955).

Chlorination of Phenyl Ether

HAROLD WEINGARTEN AND R. M. SCHISLA

Research and Engineering Division, Monsanto Chemical Company, St. Louis, Missouri

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Previous studies of phenyl ether (I) chlorination are very sparse in the chemical literature, possibly due to the difficulty in separating the liquid or low melting products. Vapor phase chromatography has allowed us to examine this system in a much more precise way. We were particularly anxious to check some previously reported results[1] which we considered anomalous. They are (a) monochlorination of I in acetic acid yields no detectable amounts of 2-chlorophenyl ether (II), and (b) chlorination of 4-chlorophenyl ether (III) yields a significant amount of 3,4-dichlorophenyl ether (IV). Although the first seemed not too improbable, the second would require some revision of our concept of electrophilic substitution.

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[1] R. Q. Brewster and G. Stevenson, *J. Am. Chem. Soc.*, **62**, 3144 (1940).