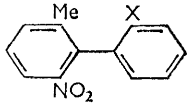
479. *Synthetical Experiments in the* o-*Terphenyl Series. Part III.*[1] *The* o-*Biphenylyl Radical as an Arylating Agent*

By K. C. Chan and R. L. Huang

In our study on the synthesis of *o*-substituted *o*-terphenyls, we have investigated the use of the *o*-biphenylyl radical as an arylating agent for aromatic systems, including benzene, *p*-xylene, and naphthalene.

de Tar and Howard[2] arylated benzene with the 2′-methyl-6′-nitro-2-biphenylyl radical liberated from (*a*) the diazonium salt from the amine (I) and (*b*) the peroxide of the acid (II), and obtained the *o*-terphenyl (III) in 13 and 5% yields, respectively.

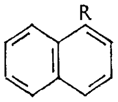


(I) X = NH_2
(II) X = CO_2H
(III) X = Ph

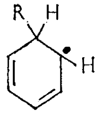
R·N:N·Me_2
(IV)
R = *o*-Ph·C_6H_4

Among the methods available for generation of the *o*-biphenylyl radical, that of Elks and Hey,[3] through action of acetic acid on aryl-triazens, appears most promising because (*a*) it gives relatively good yields and (*b*) it enables the reaction to be carried out in a homogeneous system. The triazen (IV) required in this study was prepared, in one step, from *o*-aminobiphenyl.

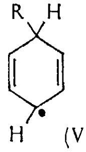
When liberated in the absence of any aromatic solvent, the *o*-biphenylyl radical appears mainly to abstract a hydrogen atom to give biphenyl, which was formed in over 80% yield, and dimerised to *oo*′-quaterphenyl only to a very small extent. Inasmuch as the radical $\cdot CH_2\cdot CO_2H$, derived from acetic acid by abstraction of an α-hydrogen atom, is known to give succinic acid,[4] and no trace of this acid could be found, it is assumed that the source from which the *o*-biphenylyl radical abstracted a hydrogen atom is the *N*-Me group from the triazen, rather than the *C*-Me group in acetic acid.



(V)

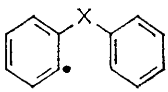


(VI)



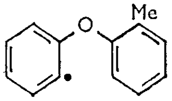
(VII)

(R = o − Ph·C_6H_4)



(VIII)

(X = O, CO, or $CH_2\cdot CH_2$)



(IX)

In the presence of benzene, *p*-xylene, or naphthalene, attack by the radical appears to be directed mainly at the aromatic hydrocarbon, as indicated by the greatly reduced yield of biphenyl. However, only in the case of naphthalene was a modest yield of the terphenyl (V), or the β-isomer, obtained; with benzene and xylene, no product other than polymer resulted. The terphenyl (V) has practically identical m. p. and elemental composition as *oo*′-quaterphenyl and its non-identity with the latter was established by mixed m. p. and by a comparison of the ultraviolet and infrared absorption of the two hydrocarbons.

Homolytic arylation of benzene (and other aromatic systems) proceeds initially[5] by addition of the attacking entity to form a radical which in our case could be represented by (VI). This could then behave in one of three ways: (*a*) suffer abstraction of a hydrogen atom by the radical R· to yield *o*-terphenyl; (*b*) disproportionate with a like radical; and

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[1] Part II, R. L. Huang and K. H. Lee, *J.*, 1959, 923.

[2] DeLos F. de Tar and J. C. Howard, *J. Amer. Chem. Soc.*, 1955, **77**, 4393.

[3] J. Elks and D. H. Hey, *J.*, 1943, 441.

[4] M. S. Kharasch and M. T. Gladstone, *J. Amer. Chem. Soc.*, 1943, **65**, 15.

[5] R. J. Convery and C. C. Price, *J. Amer. Chem. Soc.*, 1958, **80**, 4101; DeLos F. de Tar and R. A. J. Long, *ibid.*, p. 4742; S. Chang, D. H. Hey, and G. H. Williams, *J.*, 1959, 1871.

(*c*) polymerise through resonance hybrids such as (VII). The radicals produce by the addition of the *o*-biphenylyl radical to the aromatic systems studied appear to react mainly by the third route. As a synthetical approach to the *o*-terphenyl structure therefore, this reaction appears limited.

In binuclear systems such as the biphenylyl radical, the possibility exists for intramolecular arylation, in this case to give biphenylene. With the radical (VIII), for example, cyclisation with formation of a new five- or six-membered ring is well known. The failure of free *o*-biphenylyl to cyclise forming the four-membered ring in biphenylene however, is understandable. It was thought of interest therefore to study the behaviour of the radical (IX), when this is generated from the corresponding triazen, to see whether it cyclises, or whether it abstracts a hydrogen atom from either the *N*-Me group in the triazen or from *C*-Me in the tolyl group. The main product was found to be phenyl *o*-tolyl ether (32% yield), accompanied by small quantities of a hydrocarbon, probably 2,2′-diphenoxybibenzyl, and polymer. No cyclisation product was found.

EXPERIMENTAL.

1-(o-*Biphenylyl*)-3,3-*dimethyltriazen*.—A cooled mixture of aqueous dimethylamine (26%, 22 g.) and aqueous sodium carbonate (16 g.) was added with stirring to a cooled solution of the diazonium chloride prepared from *o*-aminobiphenyl (51) g.) in dilute hydrochloric acid. Stirring was continued for 0·5 hr. and the separated triazen was extracted with ether. After removal of the solvent from the dried extract, the product was fractionated to give 1-(*o*-biphenylyl)-3,3-dimethyltriazen (45·6 g.), b. p. 128—130°/0·5 mm., n_D^{30} 1·6443, as a viscous yellow oil (Found: C, 74·8; H, 6·6; N, 18·7. $C_{14}H_{15}N_3$ requires C, 74·7; H, 6·7; N, 18·7%). It was stable in air, and was unchanged after standing for over 24 months at room temperature (28°).

Decomposition of the triazen. The triazen (5·0 g.) was heated with glacial acetic acid (25 c.c.) on the steam-bath for 6 hr. The organic matter was taken up in benzene, then extracted with aqueous sodium carbonate, washed with water, and dried ($MgSO_4$). After removal of solvent the remaining oil (4·4 g.) was steam-distilled to give biphenyl (2·65 g.), m. p. and mixed m. p. 68—70°. The residue (1·25 g.) was chromatographed on alumina using cyclohexane and light petroleum as eluants, thirty-five 100 c.c. fractions being collected. Fractions 1—7 gave traces of biphenyl (0·09 g.), m. p. and mixed m. p. 69—70°, fractions 8—10 gave *oo*-quaterphenyl (19 mg.), m. p. and mixed m. p. 116—117° (lit.,[6] m. p. 118·5°), after two recrystallisations from acetone–methanol, and the later fractions gave an intractable gum. The aqueous sodium carbonate extract gave no trace of succinic acid.

Decomposition of the triazen in benzene. The product from the triazen (5·0 g.) in benzene (15 c.c.) and glacial acetic acid (15 c.c.) was steam-distilled to give an oil (1·12 g.) which was extracted into ether. After removal of ether, biphenyl (0·95 g.) was collected at b. p. 99—102°/0·5 mm., m. p. and mixed m. p. 67—69·5°. Attempts to isolate crystalline compounds from the dark brown non-volatile residue (2·8 g.) by chromatographic absorption were unsuccessful.

Decomposition of the triazen in p-*xylene.* The product from the triazen (5·0 g.) in *p*-xylene (11·8 g.) and glacial acetic acid (15 c.c.), after removal of *p*-xylene (10·6 g.) by distillation, was chromatographed on alumina with light petroleum followed by benzene as eluants to give (i) *p*-xylene (1·1 g.), (ii) biphenyl, m. p. and mixed m. p. 68—69° (0·3 g.), and (iii) polymer (3·9 g.).

Decomposition of the triazen in naphthalene. A mixture of the triazen (5·0 g.), naphthalene (14·0 g.), and glacial acetic acid (15 c.c.) was heated on the steam-bath for 6 hr. On working up as described above, a dark brown oil (17·2 g.) was obtained. Steam-distillation of this gave a mixture of biphenyl and naphthalene (14·9 g.). The residue (2·2 g.) was chromatographed on alumina and eluted with light petroleum followed by benzene to give *o*-(α-naphthyl)- or *o*-(β-naphthyl)-biphenyl (0·23 g.), needles (from acetone–methanol), m. p. 115—117°, mixed m. p. with an authentic sample of *oo*′-quaterphenyl, 85—103° (Found: C, 94·7; H, 6·0. $C_{24}H_{18}$ requires C, 94·3; H, 5·8%), $\lambda_{max.}$ 223 (ε 6·22 × 10^4) in *n*-hexane, $\nu_{max.}$ (in CCl_4) 3070s, 1945vw, 1925vw, 1810vw, 1600m, 1500m, 1480s, 1440m, 1430m, 1395m, 1080w, 1050w, 1025m, 1010m, 970m, 950w, 920w, 865w, 700s cm.$^{-1}$, and (ii) a polymer (1·8 g.).

The above infrared absorption spectrum is different from that of *oo*′-quaterphenyl.

2-*Amino*-2′-*methyldiphenyl Ether*.—2-Methyl-2′-nitrodiphenyl ether was prepared in 43%

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[6] J. Dale, *Acta Chem. Scand.*, 1957, **11**, 640.

yield, as described by Fox and Turner,[7a] and had b. p. 158—160°/1·5 mm. (Cook [7b] reports b. p. 194—196°/14 mm., and Mole [7c] m. p. 39—40°). Reduction of this ether (30 g.) with iron dust and acetic acid gave, after fractionation, the desired ether, b. p. 126—128°/0·3 mm. (13 g.), ν_{NH_2} 3350 cm.$^{-1}$. It was very unstable, even under nitrogen.

1-[2-(o-*Methylphenoxy)phenyl*]-3,3-*dimethyltriazen.*—As described for the preparation of 1-(*o*-biphenylyl)-3,3-dimethyltriazen, the above amine (13 g.) gave the desired triazen (11·5 g.), b. p. 138—142°/0·2 mm., n_D^{24} 1·6191 (Found: C, 70·5; H, 6·6; N, 16·4. $C_{15}H_{17}N_3O$ requires C, 70·6; H, 6·7; N, 16·5%).

Decomposition of the triazen. The above triazen (12·8 g.) and glacial acetic acid (20 c.c.) was heated on the steam-bath for 6 hr. and the product was chromatographed on alumina with light petroleum–benzene (80 : 20 v/v) followed by benzene as eluants, sixty-five 50 c.c. fractions being collected. Fractions 7—10 gave 2-methyldiphenyl ether (2·9 g.), b. p. 82—85°/0·3 mm. This was oxidised by potassium permanganate to give the corresponding acid which was identical in m. p. and infrared absorption with that derived from an authentic specimen of *o*-phenoxybenzaldehyde (m. p. and mixed m. p. 113—114°). Fractions 11—16 gave a viscous oil (0·52 g.), probably 2,2′-diphenoxybibenzyl, b. p. 188—191°/0·15 mm. (Found: C, 85·4, 85·5; H, 6·0, 6·1. $C_{26}H_{22}O_2$ requires C, 85·2; H, 6·1%). It could not be induced to crystallise from organic solvents. The later fractions gave an intractable brown gum.

We thank Professor D. H. Hey, F.R.S., for supplying us with a specimen of *oo*′-quaterphenyl and its infrared spectrum.

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[7] (*a*) D. L. Fox and E. E. Turner, *J.*, 1930, 1115; (*b*) A. N. Cook, *J. Amer. Chem. Soc.*, 1901, **23**, 806; (*c*) E. E. Turner and J. D. C. Mole, *J.*, 1939, 1720.