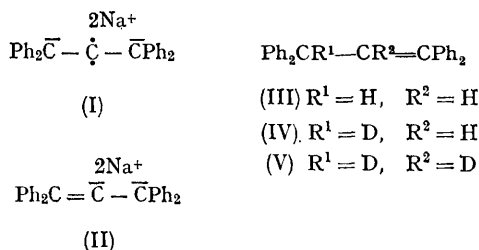


# The Reaction of Tetraphenylallene with the Alkali Metals

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It has been reported<sup>1</sup> that treatment of tetraphenylallene with sodium yielded a red, crystalline disodium salt, formulated as the diradical (I). The alternative dianion (II) was rejected on the basis of chemical reactivity. Reported here are the nature of this sodium salt, the elucidation of an unusual rearrangement reaction, and the establishment of a strong and unusual metal-ion effect.



Reaction of tetraphenylallene<sup>1,2</sup> with sodium in ether at 25° yielded 1,1,3,3-tetraphenylpropene (III)<sup>1,2</sup> (90%). When the reaction run at 25° was quenched with deuterium oxide, the product was 3-deuterio-1,1,3,3-tetraphenylpropene (IV) [n.m.r. (CDCl<sub>3</sub>): τ 3.1 (twenty-proton aromatic multiplet) and 3.5 (one-proton vinyl singlet)]. Reaction at -78° yielded a mixture of monodeuterated (IV) (90%) and the dideuterated tetraphenylpropene (V) (10%)<sup>3</sup> (mass spectrometry). In contrast, the product from reactions at -30, 0, and 25° was shown to contain less than 1% of the dideuterated species (V). The tetraphenylallene dianion is thus considerably more reactive than was originally supposed.

Remarkably, reaction with lithium followed by quenching with water in the presence of oxygen yielded tetraphenylpropene (III) (3%) and a rearrangement product, 5,7-diphenyl-5H-dibenzo[*a,c*]cycloheptatriene (VI) (12%).<sup>4</sup> Conclusive proof of structure rests on the following synthesis.

Ozonolysis of 9-methyl-10-phenylphenanthrene<sup>5</sup> yielded 2-acetyl-2'-benzoylbiphenyl (10%) which was closed with sodium methoxide to 7-phenyl-dibenzo[*a,c*]cycloheptatrien-5-one (67%). Further reaction with phenylmagnesium bromide yielded 5,7-diphenyldibenzo[*a,c*]cycloheptatrien-5-ol<sup>6</sup> (67%), which on reduction with zinc dust and concentrated hydrochloric acid in acetic acid yielded the desired 5,7-diphenyldibenzo[*a,c*]cycloheptatriene (VI) (86%).

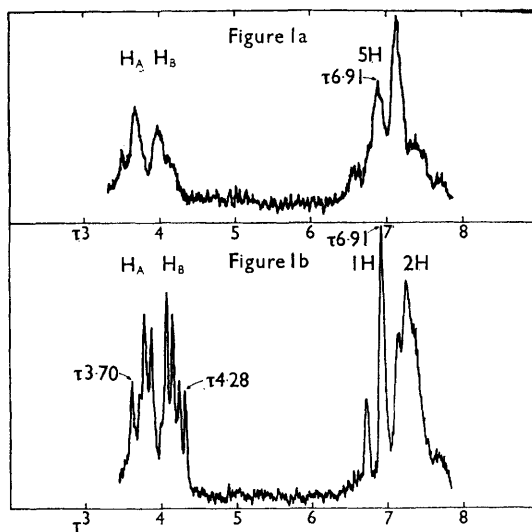


FIGURE 1. N.m.r. spectra of compounds (VII) (Figure 1a) and (VIII) (Figure 1b). Present in both spectra, but not shown, are a fourteen-proton aromatic multiplet at τ 2.75 and a one-proton vinyl singlet at τ 3.15. The latter is assigned to the lone vinyl hydrogen on the seven-membered ring.

When the lithium reaction was quenched with the exclusion of oxygen, the labile hydrocarbon (VII) was isolated (40%). Oxidation of (VII) to

<sup>1</sup> W. Schlenk and E. Bergmann, *Annalen*, 1928, **463**, 228.

<sup>2</sup> D. Vorlander and C. Siebert, *Ber.*, 1906, **39**, 1024.

<sup>3</sup> The 1:1 atoms of deuterium in the tetraphenylpropene from reaction at -78° are bound to the three carbon atoms of the propene chain. Bromination yielded 2-bromo-3-deuterio-1,1,3,3-tetraphenylpropene which showed 1.0 atoms of deuterium in its mass spectrum. Dehydrobromination yielded tetraphenylallene whose deuterium content exceeded that of an authentic sample by less than 1%.

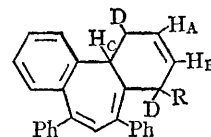
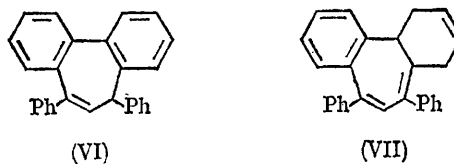
<sup>4</sup> A small amount (0.3%) of (VI) was also isolated from the reaction of sodium with tetraphenylallene at 0°.

<sup>5</sup> C. K. Bradsher and R. Rosher, *J. Amer. Chem. Soc.*, 1939, **61**, 1524.

<sup>6</sup> Satisfactory analytical and spectral data have been obtained for the intermediates.

the dibenzocycloheptatriene (VI) (55%) by refluxing for 72 hours with an excess of 2,2-diphenyl-1-picrylhydrazyl in benzene<sup>8</sup> established the skeleton of the molecule. Catalytic hydrogenation of (VII) (Pd/C) yielded a 1,2,3,4,6,7-hexahydro-derivative (65%). The placement of the double bonds in (VII) is supported by n.m.r. spectroscopy (Figure). The spectrum of the dideuterated product (VIII)<sup>9</sup> clearly shows that the vinyl hydrogens form an AB quartet ( $J_{AB} = 10.0$  c./sec.,  $\delta_{AB} = 0.45$  p.p.m.) each component of which is split by one neighbouring hydrogen ( $J_{AX} = 5.9$  c./sec.,  $J_{BY} = 4.8$  c./sec.). The low field aliphatic doublet ( $J = 12.5$  c./sec.) at  $\tau$  6.8 is tentatively assigned to the angular benzylic hydrogen ( $H_C$  in formula VIII). Further deuterium substitution as in (IX)<sup>9</sup> caused proton B to become an apparent doublet (superposed quartet and doublet), thus substitution occurred at the position adjacent to vinyl proton B; protons A and C remained unchanged. Double-resonance irradiation of (VII) at  $\tau$  7.18 caused both vinyl hydrogens to become resolved into an AB quartet ( $J = 10$  c./sec.). Irradiation of (VIII) at  $\tau$  7.13 caused proton A to

become a doublet (B remained a quartet), while irradiation at  $\tau$  7.30 caused proton B to become a doublet (A remained a quartet). Proton C at  $\tau$  6.8 is not coupled to the vinyl hydrogen atoms.



(VIII) R = H

(IX) R = 0.5H, 0.5D

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<sup>7</sup> Potassium (*cf.* A. K. Hoffman and A. Zweig, *J. Amer. Chem. Soc.*, 1962, **84**, 3278) and sodium-potassium alloy yielded the same rearrangement products, (VI) and (VII), isolated from the lithium reactions. In addition, 1,1,3,3-tetraphenylpropane was isolated (15%) from the sodium-potassium alloy reaction.

<sup>8</sup> E. A. Braude, A. G. Brook, and R. P. Linstead, *J. Chem. Soc.*, 1954, 3574.

<sup>9</sup> Compound (VIII) was isolated (45%) when the lithium reaction was quenched with  $D_2O$ . Compound (IX) (equal intensity peaks in the mass spectrum at  $m/e$  348 and 349, indicating an equimolar mixture of dideuterated and trideuterated compounds) was isolated (65%) when the dideuterated compound (VIII) was treated with excess of butyl-lithium followed by deuterium oxide.