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Novel C–C Reductive Cleavage of Terphenyls with Alkali Metal–Hexamethylphosphoric Triamide

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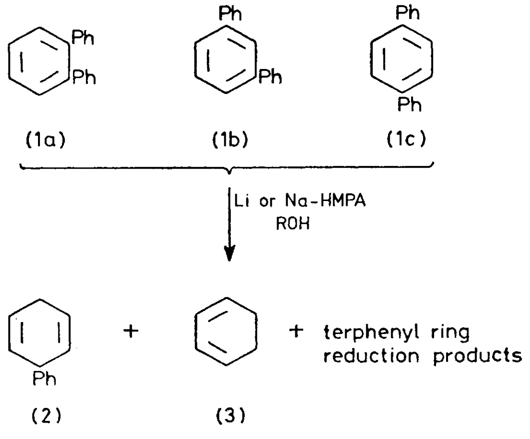
Summary *o*-, *m*-, and *p*-terphenyls (**1a**—**c**) as well as biphenyl undergo, during alkali metal–hexamethylphosphoric triamide reduction, C–C reductive cleavage, the terphenyls giving 3-phenylcyclohexa-1,4-diene (**2**) and cyclohexa-1,3-diene (**3**) and biphenyl giving cyclohexa-1,3-diene (**3**).

DURING g.l.c. analysis of the reaction mixture obtained after reduction of *p*-terphenyl (**1c**) with alkali metal–hexamethylphosphoric triamide (HMPA), a peak appeared on the chromatogram prior to that corresponding to the totally hydrogenated product. The possibility of any impurities being present in (**1c**) (Koch-Light) was eliminated as (**1c**) was found to be homogeneous. Similar reduction of *o*- and *m*-terphenyls (**1a** and **b**), free of impurities, also led to g.l.c. peaks with the same retention times as those of (**1c**). Therefore we considered the possibility of a reductive cleavage of a C–C bond during the reduction which would explain the presence in the reaction mixture of biphenyl (or its partially reduced derivatives) as well as benzene (or its hydro-derivatives). Comparison of the retention times excluded the possibility of the unknown compound being biphenyl. Consequently we re-investigated[1] the reduction of biphenyl with alkali metals in HMPA as well as in liquid ammonia. Careful examination of the g.l.c. chromatograms and comparison of the retention times of the pure unknown compound with the products obtained from the reduction of biphenyl, together with u.v., i.r., and n.m.r. spectral data proved that the unknown compound was 3-phenylcyclohexa-1,4-diene (**2**).



This result led us to examine much more carefully the composition of the crude reaction mixture obtained after the reduction of biphenyl and the terphenyls to see if benzene or its hydro-derivatives were present. Careful g.l.c. analysis showed that in the reaction mixtures of all the reduced hydrocarbons, the same product having a very short retention time was present. Comparison of these chromatograms, taken under different conditions, with those of benzene and its hydro-derivatives proved that this product was cyclohexa-1,3-diene (**3**).

The reductions of the terphenyls were carried out under various conditions; different metals (Li or Na), different proton donors, and various HMPA–tetrahydrofuran ratios were used. Products obtained from reductive C–C bond cleavage were detected in each case; the total yield of these products in the crude reaction mixtures was $\leqslant 25\%$. Precise quantitative data and their variation with reaction conditions will be given elsewhere.

We also investigated this C–C reductive cleavage with other aromatic hydrocarbons. Thus, we checked carefully the reaction mixtures after the reduction of some secondary or tertiary alkyl-benzene derivatives, *e.g.*, cumene, t-butylbenzene, or *p*-t-butyltoluene, but in all cases we found ring reduction products only.

It seems that this reductive cleavage of a C–C bond occurs specifically in C_{Ar}–C_{Ar} systems such as biphenyl and terphenyls. This can be concluded from the fact that the C_{Ar}–C_{Ar} bond between phenyl and naphthyl groups in 1-phenylnaphthalene was not cleaved at all. Here we found only ring reduction products in the reaction mixture.

This reductive cleavage of a C–C bond in biphenyl-type systems has not been observed before during reduction with alkali metals in liquid ammonia or in amines.

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[1] P. J. Grisdale, T. H. Regan, J. C. Doty, J. Figueras, and J. L. R. Williams, *J. Org. Chem.*, 1968, **33**, 1116; W. Kotlarek, *Tetrahedron Letters*, 1974, 3861.