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A NEW SYNTHESIS OF SUBSTITUTED TRIPHENYLENES.
MECHANISMS OF FORMATION OF TRIPHENYLENES IN REACTIONS INVOLVING ARYNE INTERMEDIATES

H. Heaney and P. Lees
Department of Chemical Technology
Bradford Institute of Technology, Bradford, 7.

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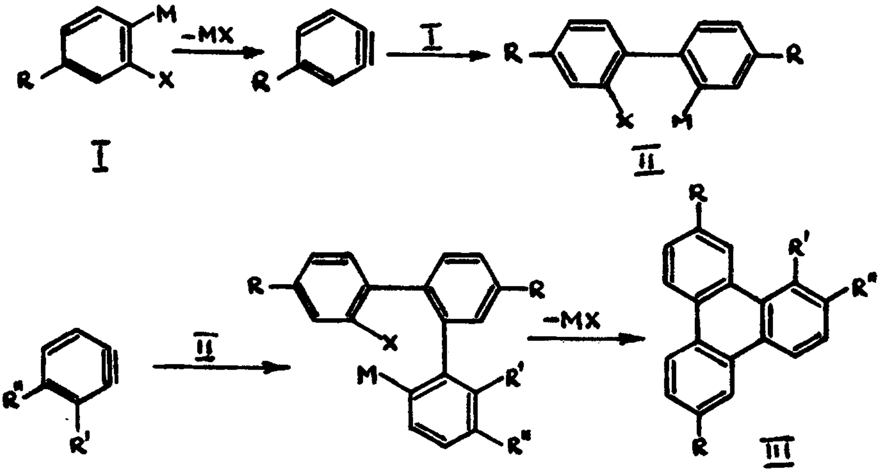
Triphenylene and substituted triphenylenes have been isolated in a number of reactions which are known to involve aryne intermediates.[1] In certain of these reactions biphenylene or substituted biphenylenes have been isolated. Dimerisation and trimerisation has been suggested as a mechanism of biphenylene and triphenylene formation respectively.[2] While it is generally agreed that dimerisation of aryne intermediates is the most likely route to biphenylenes; a concerted trimerisation, which is not favoured energetically, appears to be unlikely because of the high yields of triphenylene obtained in certain reactions involving organometallic compounds.[3,4,5,6] It should be noted, however, that triphenylene has been isolated, in low yield, along with biphenylene, after the flash photolysis of benzene-diazonium-2-carboxylate.[7] This suggests that the triphenylene could arise by a Diels-Alder type reaction between biphenylene and benzyne. A similar mechanism has been postulated to account for the formation of dodecahydrotriphenylene in reactions involving cyclohexyne.[8] We have shown that this does not constitute an important mechanism in reactions involving organometallic compounds by the fact that when benzyne was generated in the presence of biphenylene no increase in the normal yield of triphenylene was observed and the biphenylene was completely recovered.

Aryne intermediates are known to be highly reactive towards nucleophiles.[1] It has been suggested that triphenylenes are formed, in reactions involving aryne intermediates, by a stepwise series of reactions on the basis of the detection of the postulated intermediates.[4,5] We have confirmed that the normal mechanism of triphenylene formation, in reactions involving organometallic compounds, involves a stepwise series of reactions of organometallic compounds with aryne intermediates. This has been shown by the successful incorporation of a postulated intermediate (II) into the final product, the orientation of which excludes the possibility that it has been formed by a concerted trimerisation. Products, which might have arisen by such trimerisation, were not detected.



4,4'-Dimethyl-2-fluoro-2'-iodobiphenyl (b.p. 114° at 0·05 m.m. Hg, n^{20} 1·6219) prepared from 2-amino-4,4'-dimethyl-2'-fluorobiphenyl, forms a mono Grignard reagent with magnesium in tetrahydrofuran and a monolithio compound with *n*-butyl-lithium in ether in good yield. Carboxylation of the organometallic reagents give 2-carboxy-4,4'-dimethyl-2'-fluorobiphenyl, m.p. 158-160°, in only 10% yield together with 4,4'-dimethyl-2-fluorobiphenyl in 90% yield.

When benzyne was generated from o-fluorophenyl-magnesium bromide in tetrahydrofuran, triphenylene was isolated in 85% yield. When benzyne was generated by the same method in the presence of the Grignard reagent (II, R = methyl, M = MgI, X = F), 2,7-dimethyltriphenylene (III, R = methyl, R' = R'' = H) was isolated in 25% yield (m.p. and mixed m.p. 134°[*], lit.[9] m.p. 137°). When benzyne was generated from o-fluorophenyllithium in the presence of the organolithium compound (II, R = methyl, M = Li, X = F), 2,7-dimethyltriphenylene was isolated in 50% yield. 4-Methylbenzyne was generated from 4-chloro-3-iodotoluene and magnesium in tetrahydrofuran in the presence of the Grignard reagent (II, R = methyl, M = MgI, X = F), 2,6,11-trimethyltriphenylene (III, R = R'' = methyl, R' = H) was isolated in 10% yield (m.p. and mixed m.p. 136-137°[*], lit.[9] m.p. 137°). When a similar reaction was carried out using organolithium compounds 2,6,11-trimethyltriphenylene was isolated in 26% yield.

1,6,11-Trimethyltriphenylene (III, R = R' = methyl, R'' = H), m.p. 108°, and 6,11-dimethyl-2-methoxytriphenylene (III, R = methyl, R' = H, R'' = methoxyl), m.p. 133° have also been synthesised in 13% and 15% yields respectively using 3-chloro-2-iodotoluene and 4-chloro-3-iodoanisole as the dihalides from which the corresponding aryne intermediates were generated.

The reactions described establish a new method of synthesis for certain substituted triphenylenes and these reactions are being investigated further.

Satisfactory analytical results, infrared, ultraviolet (where applicable) and nuclear magnetic resonance spectra have been obtained for all compounds described.

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