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The Reaction of Methylphenylacetylene with Palladium Chloride

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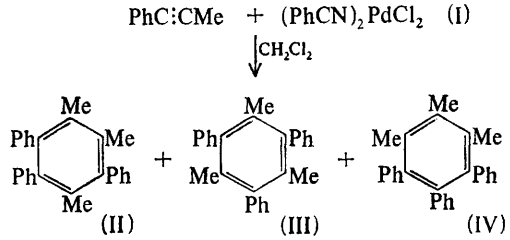
SOME years ago, during a re-investigation of the reaction of diphenylacetylene with palladium chloride originally discovered by Malatesta *et al.*,[1] one of us reported[2] that in non-hydroxylic solvents diphenylacetylene was catalytically trimerised to hexaphenylbenzene by dichlorobis(benzonitrile)-palladium (I). Similar results were obtained for *pp'*-disubstituted diphenylacetylenes[3] and in all cases the catalyst was deactivated by the formation of a tetraphenylcyclobutadienepalladium chloride complex: this was shown not to be an intermediate in the trimerisation reaction. Attempts to extend these reactions to monosubstituted acetylenes, *e.g.* phenylacetylene, have not been very fruitful. Although products were very readily formed, they tended to be uncharacterisable and labile polymeric complexes; in addition, small quantities of tetramers and a trimer of phenylacetylene were sometimes isolated.[4]

The reaction of (I) with methylphenylacetylene was more successful; in methylene chloride at 40° a mixture of organic trimers was obtained, together with a small amount of an amorphous brown solid, shown to contain most of the palladium. At least 63 moles of the acetylene could be trimerised per mole of (I). The trimers were separated by fractional crystallisation. By a combination of this method and quantitative ^{1}H n.m.r. analysis the mixture was shown to contain 58% of 1,2,4-trimethyl-3,5,6-triphenylbenzene (II) [m.p. 223°; *M*, 348 (mass-spectrometric); λ_{max} 2820 Å ($CHCl_3$); ^{1}H n.m.r. in CH_2Cl_2, singlets due to the methyl groups at τ 7·23 and 8·00 (intensity ratio 1 : 2)], 39% of 1,3,5-trimethyl-2,4,6-triphenylbenzene, (III) [m.p. 320°; *M*, 348 (mass-spectrometric); λ_{max} 2820 Å ($CHCl_3$); ^{1}H n.m.r. in CH_2Cl_2, one singlet due to the methyl groups at τ 8·38] and 3% of 1,2,3-trimethyl-4,5,6-triphenylbenzene (IV) [m.p. 155°; *M*, 348 (mass-spectrometric), 354 (osometric); λ_{max} 2820 Å ($CHCl_3$); ^{1}H n.m.r. in CH_2Cl_2, singlets due to the methyl groups at τ 7·67 and 7·94 (intensity ratio 1 : 2)].



(II) (III) (IV)

The isomers (II) and (III) are known compounds which have previously been reported to arise (though in a 30 : 1 ratio) from the trimerisation of methylphenylacetylene with $Hg[Co(CO)_4]_2$.[5,6] The isomer (IV), however, has never been reported and is a very novel product from such a reaction since its formation must involve, formally at least, cleavage of a C⋮C bond. The structure shown is assigned to (IV) largely on the basis of the evidence cited above, and the similarity of its u.v. and i.r. spectra to those of (II) and (III). It is thermally stable and was not isomerised on heating at 160° for one hour.

In benzene at 25° methylphenylacetylene and (I) reacted to give the same mixture of isomeric trimers (II), (III), and (IV) obtained above (29%) and a yellow complex (V) (61%). Analysis and molecular weight determinations showed (V) to have the composition $[(PhC_2Me)_3PdCl_2]_2$.† In chloroform or methylene chloride solution, (V) disproportionated rapidly to give $PdCl_2$ and a mixture of the trimers (II) and (III); none of the isomer (IV) was detected. On reaction of (V) with two moles of triphenylphosphine (II), (III), and dichlorobis(triphenylphosphine)palladium were obtained quantitatively.

But-2-yne undergoes somewhat similar reactions which will be described shortly.

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† The molecular formula is represented thus for convenience; no structural implications are to be drawn from this.

[1] L. Malatesta, G. Santarella, L. M. Vallarino, and F. Zingales, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1959, **27**, 230; *Angew. Chem.*, 1960, **72**, 34.

[2] A. T. Blomquist and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1962, **84**, 2329.

[3] P. M. Maitlis, D. Pollock, M. L. Games, and W. J. Pryde, *Canad. J. Chem.*, 1965, **43**, 470; also P. M. Maitlis and D. F. Pollock, unpublished results.

[4] P. M. Maitlis and J. Bloodworth, unpublished results.

[5] W. Hübel and C. Hoogzand, *Chem. Ber.*, 1960, **93**, 103.

[6] The formation of isomer (II), though in unspecified yields, from reaction of methylphenylacetylene with $PdCl_4^{2-}$–HCl–MeOH has also been briefly mentioned by F. Zingales, *Ann. Chim. (Italy)*, 1962, **52**, 1174.