

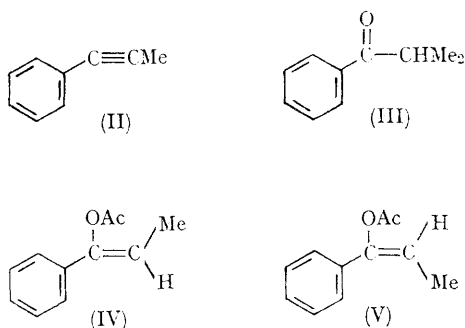
Reaction of Lead Tetra-acetate with Phenylacetylene

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RECENTLY the reactions of lead tetra-acetate with olefins and alcohols have been extensively investigated.¹ However, the reactions with acetylenic compounds have been largely neglected.² We report the result of our investigation of the reaction of lead tetra-acetate with phenylacetylene (I).

The reaction was carried out by refluxing a mixture of phenylacetylene, lead tetra-acetate,



and glacial acetic acid for 1 hr. The major product was methylphenylacetylene (II), and (III), (IV), and (V) were minor products. There was also a considerable amount of the unchanged phenylacetylene.

The products were isolated by gas chromatography and identified by their infrared and n.m.r. spectra. The n.m.r. spectrum of (II) exhibited absorptions at τ 2.50 (singlet, 5H) and 8.0 (singlet, 3H). It was identified³ as methylphenylacetylene. The n.m.r. spectrum of (III) showed complex peaks at τ 2.01 (multiplet, 2H, aromatic hydrogen), 2.45 (multiplet, 3H, aromatic hydrogen), 4.48 (multiplet, 1H, tertiary hydrogen), and 8.84 (doublet, 6H, methyl group). The infrared

spectrum showed carbonyl absorption at 1680 cm^{-1} . It was identified as isopropyl phenyl ketone by comparison with an authentic sample, and by reduction to the corresponding alcohol, which was found to be identical with 2-methyl-1-phenylpropanol. Compounds (IV) and (V) were identified on the basis of spectral data and reduction products. The infrared spectrum of (IV) showed peaks at 1740 and 1220 cm^{-1} , indicating the presence of an acetoxy-group. Similarly, (V) also showed peaks at 1750 and 1210 cm^{-1} . On treatment with lithium aluminium hydride (IV) and (V) gave a single product, 1-phenylpropanol. The n.m.r. spectrum of (IV) showed absorptions at τ 2.47 (singlet, 5H, phenyl hydrogens), 4.58 (quartet, 1H, olefinic hydrogen), 7.96 (singlet, 3H, CH_3CO group), and 8.24 (doublet, 3H, methyl group on a double bond). A very similar spectrum was obtained for (V); it showed peaks at τ 2.25 (singlet, 5H), 3.90 (quartet, 1H), 7.80 (singlet, 3H) and 9.0 (doublet, 3H). A deshielding effect of the acetoxy-group on the vinyl hydrogen in the *cis*-isomer would be expected to shift the vinyl resonance downfield,⁴ and on this basis the isomer with the vinyl hydrogen at 3.90 [compound (V)] was assigned the *cis*-configuration.⁵

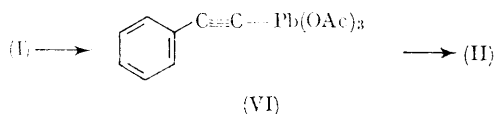
When lead tetra-acetate (88 g.) and phenylacetylene (10 g.) (a 2:1 molar ratio) in glacial acetic acid (150 ml.) was refluxed for 1 hr., a total of 7.03 g. (58%) of distilled product was obtained. The yields were (I), 11%; (II), 24%; (III), 4%; (IV), 14%; and (V), 5%. A change in the ratio of lead tetra-acetate and phenylacetylene changed only the distribution of products. A surprising effect was noted when acetic anhydride was added to the reaction mixture in small quantities. As the mixture warmed and the lead tetra-acetate dissolved, the solution began to boil vigorously and refluxed for several minutes without any

additional application of heat. In a subsequent run the reaction was terminated immediately after the mixture had ceased to reflux, and gas chromatography revealed that the products had already been formed.

When the reaction was carried out in refluxing pyridine for 1 hr., the product, obtained in 59% yield, contained 50% of (I) and 9% of (II).

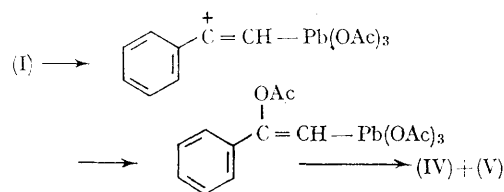
These results appear to be the first case where an acetylenic hydrogen is replaced by a methyl group by lead tetra-acetate. The formation of compound (IV) and (V) can be considered as the result of addition of methyl acetate to the acetylenic bond. The only other reported example of such addition seems to be in the reaction of styrene with lead tetra-acetate to yield 1-phenylpropanol.⁶

The mechanism for the formation of (II) is not quite clear. Since (II) was obtained when the reaction was carried out in pyridine, we are inclined to reject a free-radical mechanism. We propose that the lead ester (VI) may be a plausible intermediate which decomposes to yield (II).

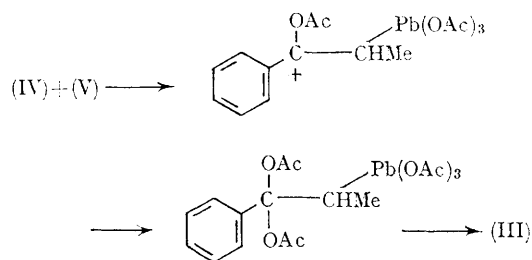


Since methylphenylacetylene was stable in refluxing acetic acid either with or without lead tetra-acetate, it cannot be an intermediate for (IV)

or (V). It is tempting to propose the following mechanism for the formation of (IV) and (V).



Compound (III) could have formed from (IV) and (V) as shown below. In support of this suggestion, it was noted that the yield of (III) increased as the reaction time was extended and as the molar ratio of lead tetra-acetate to phenylacetylene was increased.



(Received, June 7th, 1966; Com. 387.)

¹ For a review of the subject, see R. Criegee, in "Oxidation in Organic Chemistry", ed. K. B. Wiberg, Academic Press, New York, 1965.

² J. Jadot and M. Neuray, *Bull. Soc. roy. Sci. Liège*, 1962, **30**, 247.

³ Identification was made by comparison of its infrared and n.m.r. spectrum with the spectrum of an authentic sample, and by retention time on gas-chromatographic columns.

⁴ H. O. House and V. Kramar, *J. Org. Chem.*, 1963, **28**, 3362.

⁵ The *cis*-isomer is defined as the one with the methyl and phenyl group on the same side.

⁶ Ref. 1, p. 348.