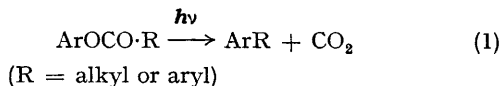


A New Synthesis of *o*-Di-*t*-butylbenzene and *t*-Butylmesitylene¹

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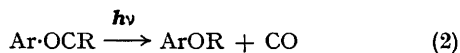
THE light-induced rearrangement of aryl esters to hydroxy-ketones (photo-Fries reaction) is accompanied by several side reactions,² one of which is a decarboxylation process (Equation 1).



We have recently documented a number of examples of this reaction and have pointed out its potential utility for the preparation of certain biaryls and alkylaromatic compounds.³ In view of numerous recent reports describing the synthesis of various hindered polyalkyl-aromatic and heteroaromatic compounds,⁴⁻⁶ we record a simple preparation of the title compounds by this new method.

Irradiation of *o*-*t*-butylphenyl pivalate⁷ (b.p. 93° at 0.7 mm.) provided a mixture of products from which a non-polar fraction was readily separated by chromatography on alumina. Vapour-phase chromatography then allowed the isolation of *o*-di-*t*-butylbenzene (1% yield)⁸ and *m*-di-*t*-butylbenzene (<1%) which were identified by direct comparison of their infrared and ultraviolet spectra as well as gas-chromatographic retention times with those of authentic samples.⁵ The presence of a trace quantity of the *para*-isomer in the photolysate was also inferred by retention-time comparisons. The latter two hydrocarbons undoubtedly arise from the *ortho*-isomer by secondary photochemical changes.^{3,9}

Along with these hydrocarbons, starting material,⁸ *o*-*t*-butylphenol (8%), and the Fries rearrangement products, 2-hydroxy-3-*t*-butylpivalophenone [14%, m.p. 69—69.5°; ν_{max} (KBr) 2400—3500, 1620 cm.⁻¹; λ_{max} (95% EtOH) 262, 343 m μ , ϵ 8200, 3440; λ_{max} (95% EtOH-NaOH) 239, 310, 349m μ , ϵ 8030, 1790, 2270] and 4-hydroxy-3-*t*-butylpivalophenone (3%, m.p. 152—153°; ν_{max} (KBr) 3280, 1650 cm.⁻¹; λ_{max} (95% EtOH) 227, 286 m μ ; ϵ 13,600, 14,300; λ_{max} (95% EtOH-NaOH) 248, 350 m μ , ϵ 7400, 28,400] were also obtained. In addition, *o*-*t*-butylphenyl *t*-butyl ether [ν_{max} (film) 1235 cm.⁻¹; λ_{max} (95% EtOH) 227, 275, 281 m μ , ϵ 7700, 1900, 1800], the product of decarbonylation, was isolated in 8% yield. The photo-decarbonylation of aryl esters has been previously described,¹⁰⁻¹² and although the formation of ethers (as in Equation 2) presumably by a radical recombination process has been implied,¹⁰ experimental evidence has heretofore been lacking.¹¹



In similar fashion, photolysis of mesityl pivalate (b.p. 85—88° at 0.6 mm.) provided the decarboxylation product in 5% yield which was identified as 2,4,6-trimethyl-*t*-butylbenzene by direct spectroscopic and gas-chromatographic comparisons with an authentic sample.⁶ An isomeric hydrocarbon which is yet to be identified, was also isolated in 4% yield.

In spite of the relatively low yields of hydrocarbons obtained the experimental simplicity of the photo-decarboxylation reaction recommends it for the preparation of compounds otherwise

obtained by more laborious routes. Attempts to prepare more highly hindered polyalkylbenzenes by this method are in progress.¹³

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¹ Previous paper: see reference 3.

² R. A. Finnegan and J. J. Mattice, *Tetrahedron*, 1965, **21**, 1015.

³ R. A. Finnegan and D. Knutson, *Chem. and Ind.*, 1965, 1837.

⁴ R. Ramasseul and A. Rassat, *Chem. Comm.*, 1965, 453; H. Wynberg and A. de Groot, *ibid.*, p. 171; H. Wynberg and U. E. Wiersum, *ibid.*, p. 1, and references therein; W. A. Gibbons and H. Fischer, *Tetrahedron Letters*, 1964, 43.

⁵ E. M. Arnett and M. E. Strem, *Chem. and Ind.*, 1961, 2008.

⁶ A. W. Burgstahler, D. J. Malfer, and M. O. Abdel-Rahman, *Tetrahedron Letters*, 1965, 1625.

⁷ All new compounds provided satisfactory microanalytical and spectroscopic data. Pentane or benzene solutions of the starting ester were irradiated with a 450 w Hanovia type 679A36 lamp mounted in a double-walled quartz immersion well.

⁸ Yield and conversion values are approximately the same since only 8% of the starting material was recovered.

⁹ A. W. Burgstahler, P.-L. Chien, and M. O. Abdel-Rahman, *J. Amer. Chem. Soc.*, 1964, **86**, 5281.

¹⁰ D. H. R. Barton, Y. L. Chow, A. Cox, and G. W. Kirby, *Tetrahedron Letters*, 1962, 1055.

¹¹ D. H. R. Barton, Y. L. Chow, A. Cox, and G. W. Kirby, *J. Chem. Soc.*, 1965, 3571.

¹² W. M. Horspool and P. L. Pauson, *J. Chem. Soc.*, 1965, 5162.

¹³ We are indebted to Professors Arnett and Burgstahler for authentic hydrocarbon specimens.