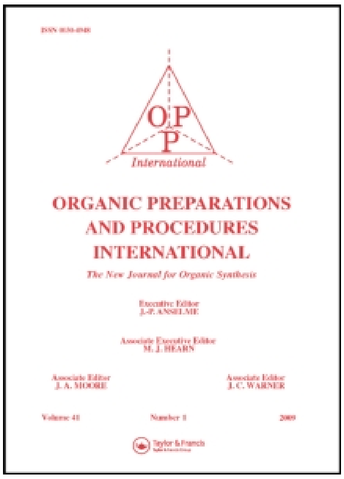

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THE NITRATION OF DIPHENYLCYCLOPROPENONE

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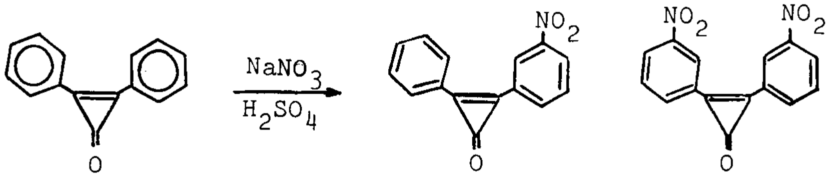
Two methods have been employed for the preparation of arylphenylcyclopropenones. One entails the reaction of the appropriate acetylene with phenyl (bromodichloromethyl)mercury[1] and the other reaction of phenylketene dimethylacetal with an arylidene chloride in the presence of potassium _t_-butoxide.[2] Since the latter reaction failed with nitrobenzylidene chlorides, it occurred to us that direct nitration of the readily available diphenylcyclopropenone[3] might provide an alternative route.

Nitration was effected by addition of a molar equivalent of sodium nitrate to a solution of diphenylcyclopropenone in sulphuric acid. As diphenylcyclopropenone is completely protonated in this medium, it was anticipated that the mononitro product would be _meta_-orientated. This was confirmed by photochemical decarbonylation[4] to 3-nitrodiphenylacetylene, an authentic sample of which was prepared from _m_-iodonitrobenzene and cuprous phenylacetylide.[5]



Similarly the use of two molar equivalents of sodium nitrate gave a dinitrodiphenylcyclopropenone, which is presumably the 3,3'-isomer.

Experimental

3-Nitrodiphenylcyclopropenone. To a solution of 2 g. (.01 mole) diphenylcyclopropenone in 30 ml. of conc. sulphuric acid was added 0.8 g. (.01 mole) of sodium nitrate. The solution was allowed to stand at r.t. for 1 hr., then heated for a further hour on the steam-bath and poured onto ice. The sticky precipitate was washed with water. Crystallization from ethyl acetate gave 1.2 g. (49%) of 3-nitrodiphenylcyclopropenone, m.p. 171-172°.

Anal. Calcd. for $C_{15}H_9NO_3$: N, 5.58. Found: N, 5.60.

3,3'-Dinitrodiphenylcyclopropenone. An identical procedure to the above was employed except that 1.6 g. of sodium nitrate was added. The 3,3'-dinitrodiphenylcyclopropenone (1 g., 35%) had m.p. 179° dec. (from ethyl acetate).

Anal. Calcd, for $C_{15}H_8N_2O_5$: N, 9.46. Found: N, 9.47.

3-Nitrodiphenylacetylene. (a) This compound, m.p. 70-71° (from 40-60° petroleum ether) was prepared from m-iodonitrobenzene and cuprous phenylacetylide.[5]

Anal. Calcd. for $C_{14}H_9NO_2$: N, 6.28. Found: N, 6.17.

(b) A solution of 3-nitrodiphenylcyclopropenone (0.5 g.) in ethyl acetate (200 ml.) in a pyrex flask under a nitrogen atmosphere was irradiated with ultraviolet light, or sunlight, until the characteristic infrared bands of the cyclopropenone at 1850 and 1630 cm.$^{-1}$ had disappeared. The solution was evaporated and the residue recrystallized from 40-60° petroleum ether, yielding 3-nitrodiphenylacetylene identical with the above sample.

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