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AROMATIC BROMINATION OF DIPHENYLCYCLOPROPENONE BY N-BROMOSUCCINIMIDE

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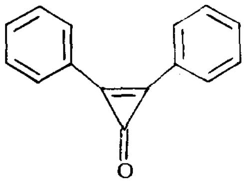
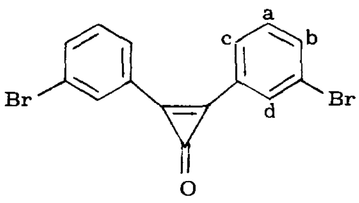
In the young chemistry of the "aromatic" [3]annulenones, a leading role has been played by diphenylcyclopropenone (I).[1-2] Amongst the reactions of (I), attention has focused on the cyclopropenone moiety, whilst the attack on the phenyl rings, leaving the three-membered ring intact, has, surprisingly, hardly been studied.[3] We wish to report the synthesis of bis(*m*-bromophenyl)cyclopropenone (II) by direct bromination of (I), applying the heterolytic variant of the Wohl-Ziegler reaction.[4] Indeed, in this electrophilic aromatic substitution, the structure of the cyclopropenone moiety was retained. *Meta*-substituted derivatives of (I) could not be obtained by the general method of Tobey and West, *viz.*, the electrophilic substitution of aromatic compounds by trichlorocyclopropenium salts, which gave predominantly *para*-substituted diarylcyclopropenones.[5]

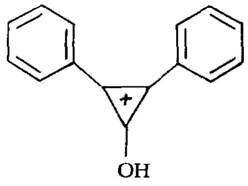
Treatment of a solution of (I) (0.025 mole) in 80% aqueous sulfuric acid (v/v, 250 ml) with N-bromosuccinimide (0.05 mole) at 25°C and heating to 60°C gave colourless crystals of (II), mp 187° (cyclohexane) in 35% yield.[6] $\lambda_{\text{max}}^{\text{Cyclohexane}}$ nm (lg ε) 222 (4.48), 286 (4.32), 296 (4.31), 305 (4.32), 320 (4.06), and 368 (3.08). The ir absorptions at 1835 and 1630 cm^{-1} (nujol) indicated



(I)



(II)



(III)

the presence of the unaltered cyclopropenone system.[7] The *meta*-substitution pattern in both of the phenyl groups of (II) were established unequivocally by the ir and the nmr spectra. The out-of-plane C - H bending vibrations at 790 and 690 cm^{-1}, and the absence of any other significant bands in the 900-600 cm^{-1} region were characteristic of a *meta*-disubstituted benzene. The isomeric bis(*p*-bromophenyl)cyclopropenone[6] (from trichlorocyclopropenium tetrachloroaluminate and bromobenzene, mp 240°) absorbed in this region at 840 and 818 cm^{-1}. The nmr spectrum of (II) (100 MHz, $CDCl_3$) was analyzed according to the method of Zanger for the determination of aromatic substitution patterns.[8] It was a virtually first-order spectrum of a *meta*-disubstituted benzene derivative, exhibiting the following four equally integrated proton bands (in ppm, downfield from Me_4Si): a di-*ortho* (broad) triplet at 7.46 (J_o 7.5 Hz, a), an *ortho*/di-*meta* doublet of triplets at 7.73 (J_o 7.5 Hz, J_m 1.8 Hz, b), an *ortho*/di-*meta* doublet of triplets at 7.86 (J_o 7.5 Hz, J_m 1.8 Hz, c) and a di-*meta* (narrow) triplet at 8.05 ppm (J_m 1.8 Hz, d). The respective calculated[9] chemical shifts were 7.38, 7.73, 7.87, and 8.12 ppm. These data could not accommodate any aromatic substitution patterns other than those of (II).

The *meta*-bromination of the phenyl rings in (I) was most probably due to the fact that the substrate was the hydroxycyclopropenium ion (III). This "aromatic" cation served also as a "protective form" of the cyclopropenone ring of (I) during the bromination.

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9. The shielding parameters of cyclopropenone (σ_o −0.63, σ_m −0.24, and σ_p −0.24 ppm) were estimated from the nmr spectrum of (I).