Acid-catalysed Cleavage of a 1,3-Photoadduct of Benzene and *cis*-3,4-Dichlorocyclobutene: *X*-Ray Structure of 3,4-Dichlorotricyclo[4,3,1,$0^{2,5}$]dec-8-en-10-yl *p*-Nitrobenzoate

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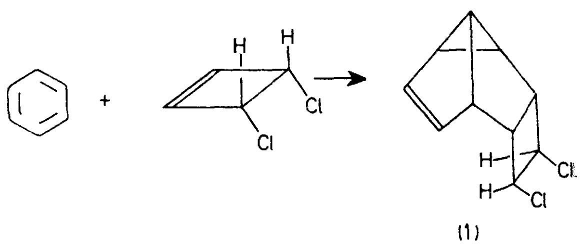
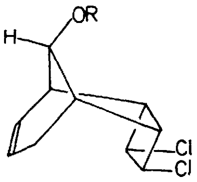
Summary The structure of the alcohol, obtained from acid treatment of the photoadduct (**1**) of benzene and *cis*-3,4-dichlorobutene, was established as (**2**) by a single crystal *X*-ray structure analysis of its *p*-nitrobenzoate racemate (**3**).

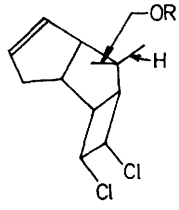


(1)



(2) R = H

(3) R = CO C_6H_4-*p*-NO_2



(4)

1,3-PHOTOCHEMICAL addition of benzene to olefins results in the formation of dihydrosemibullvalene derivatives.[1,2] In order to explore the synthetic utility of this addition solvolysis of these photoadducts was investigated.[2,3]

Irradiation[4] of benzene and *cis*-3,4-dichlorocyclobutene at 254 nm gave the adduct (**1**), m.p. 77—78° in 36% isolated yield. On treatment with HCl in aqueous dioxan it was converted into an alcohol, m.p. 118—119°; M^+ 220, 218; ν_{max} (Nujol) 3·0 μm. The ^{1}H n.m.r. spectrum ($CDCl_3$; 220 MHz), δ 1·88 (1H, exchangeable in D_2O), 2·13—2·68 (4H), 3·34 (m, 2H), 4·22br (1H), 4·47 br (2H), and 5·79 (m, 2H), suggested the cleavage of the cyclopropane ring in (**1**). As the physical data did not permit differentiation between the plausible structures (**2**) and (**4**), the *p*-nitrobenzoate (**3**) of the product, m.p. 162—163°, was subjected to an *X*-ray structure determination.

The *p*-nitrobenzoate (**3**) crystallized in space group $P\bar{1}$ with $a = 7{\cdot}150(5)$, $b = 6{\cdot}728(5)$, $c = 18{\cdot}175(13)$ Å, $\alpha = 106{\cdot}25(6)°$, $\beta = 89{\cdot}27(5)$, $\gamma = 101{\cdot}15(6)°$ and $Z = 2$. Intensity data were collected from a single crystal mounted on an Enraf Nonius CAD-4 automatic diffractometer, and 1688 independent reflections were measured with Cu-K_α radiation. The structure was solved by the Σ_2 procedure, implemented with the computer program by Long[5] and has been refined to a current value of *R* 9·3%. The crystal structure of the molecule shows that (**2**) is the correct structure with *endo* attachment of the cyclobutane ring and *anti* orientation of the hydroxy-group.†‡

The solvolysis reaction is thus established as a useful synthetic entry to bicyclo[3,2,1] derivatives functionalized at the C-10 position.

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† Probable mechanisms for the cleavage of (**1**) and other evidence in favour of the structure (**2**) are discussed elsewhere, G. Subrahmanyam and R. Srinivasan, submitted for publication.

‡ The structure of the acid-catalysed cleavage products of the benzene–cyclopentene photoadducts was revised to the bicyclo-[3,2,1] derivative based on this study and other data.

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