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PHOTOCHEMISTRY OF *o*-DIALKENYLBENZENES: *o*-(2-METHYLPROPENYL)STYRENE

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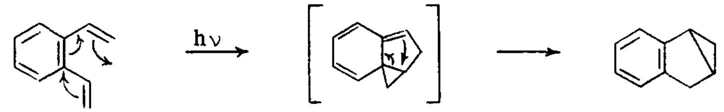
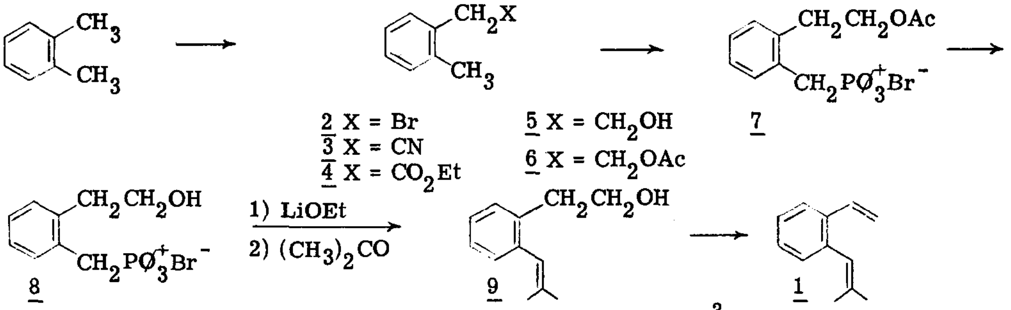
The photochemistry of *o*-divinylbenzene (eq. 1) has been shown to be closely related to that of 1,3,5-hexatrienes.[1,2] Further studies on the closely related *o*-(2-methylpropenyl)styrene (1), prepared as outlined below, reveal some new features of these reactions.

(1) 



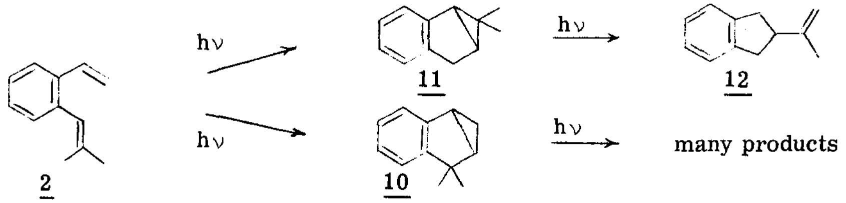
2 X = Br
3 X = CN
4 X = CO_2Et

5 X = CH_2OH
6 X = CH_2OAc

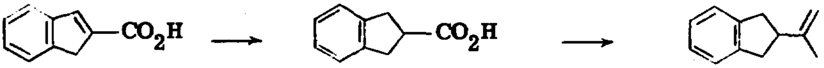
o-Tolylacetonitrile (3), prepared by treating the bromide 2[3] with potassium cyanide in refluxing aqueous ethanol, was converted to the ester 4 in refluxing ethanol, water, and sulfuric acid in an overall 62% yield from *o*-xylene. Reduction and acetylation of 4 gave the acetate 6 in 92% yield. The acetate was treated with N-bromosuccinimide in benzene, and the phosphonium salt 7 precipitated from the solution upon addition of triphenylphosphine and heating. Hydrolysis of 7 in aqueous hydrobromic acid gave the alcohol 8 in an overall 46% yield from 6. The Wittig reaction gave, in 60% yield, the alcohol 9, which was dehydrated to 1 in 54% yield on potassium hydroxide at 185° *in vacuo*. IR 3030, 1660, 1630, 1600, 990 cm^{-1}; NMR (CCl_4) doublets at τ 8.9 (J = 1.5 Hz, 3H) and 9.1 (J = 1.5 Hz, 3H), doublet of doublets at 3.8 (J = 18, 11 Hz, 1H), 5.2 (J = 18, 1.5 Hz, 1H), and 5.6 (J = 11, 1.5 Hz, 1H), multiplet at 4.4 (1H), broad multiplet at 3.2-3.8 (4H); UV (95% ethanol) λ_{max} 226 (ε 19,000), 255 (12,000); calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92; found: C, 90.87; H, 9.01.

Irradiation of a 0.3% ethereal solution of 1 under nitrogen for 30 hours using a 450W high pressure mercury arc lamp through a Vycor filter gave two major components, observed in approximately equal amounts upon glc analysis on a 50' x 3/8" 20% Carbowax 20M column at 180° and 80 psi (retention times: 46 and 54 min; retention time of 1: 45 min). The more volatile component was assigned structure 10 on the basis of its elemental analysis (calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92; found: C, 90.92; H, 9.03.) and its spectra: IR 3062, 3030, 1384, 1361 cm^{-1}; NMR (CCl_4) multiplet at τ 2.6-3.0 (4H), doublets of doublets of doublets at 7.6 (J = 3.2, 6.2, 7.9 Hz, 1H) and 8.3 (J = 4.4, 6.2, 7.9 Hz, 1H), doublets of triplets at 9.0 (J = 4.4, 7.9 Hz, 1H) and 9.8 (J = 3.2, 4.4 Hz, 1H), singlets at 8.55 and 8.60 (3H each); UV (absolute ethanol) λ_{max} 213 (ε 5,300), 223 (4,400), 257 (540), 263 (750), 269 (830); MS *m/e* 115, 128, 143, 158 (parent). The less volatile component was assigned structure 11 on the basis of its elemental analysis (calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92; found: C, 91.12; H, 9.07) and its spectra: IR 3030, 1376 cm^{-1}; NMR (CCl_4) multiplet at τ 2.7-3.0 (4H), doublets of doublets at 6.85 (J = 6.6, 17.2 Hz, 1H) and 7.7 (J = 1.6, 6.6 Hz, 1H), broadened doublet of triplets at 7.2 (J = 17.2, ~1.5 Hz, 1H), doublet of triplets at 8.4 (J = 1.8, 6.6 Hz, 1H), singlets at 8.75 and 9.3 (3H each); UV (absolute ethanol) λ_{max} 225 (ε 5,800), 260 (710), 267 (1,100), 273 (1,280), 280 (1,230); MS *m/e* 115, 143, 128, 158 (parent).

(2)



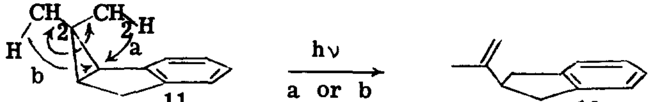
When a solution of 1 was irradiated for eight days, a new major component (retention time; 45 min at 205° and 90 psi) was found. It was shown to be identical with 12, the synthesis of which is outlined below. 2-Carboxyindene (13)[4] was esterified, hydrogenated and saponified to give 2-carboxyindane (14) in 70% yield. The acid 14 was treated with methyllithium in refluxing benzene, and the resulting ketone was subjected to the Wittig reaction to give, in an overall yield of 62% from 14, the hydrocarbon 12, NMR (CCl_4) singlet at τ 3.0 (4H), multiplets at 5.3 (2H), and 7.2 (5H), triplet at 8.3 (J = 1 Hz, 3H); UV (95% ethanol) λ_{max} 255 (ε 760), 260 (970), 267 (1,280), 274 (1,280); MS *m/e* 116, 129, 143, 158 (parent); calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92; found: C, 91.03; H, 8.92.


13 14 12

A solution of 20 mg each of 10 and 11 in 180 ml of anhydrous ether was irradiated using the above source. The ratio of 10 to 11, as measured by glc, remained approximately the same after 14, 24, 35, and 47 min of irradiation (when 10 and 11 were mostly consumed). When a solution of 10 was irradiated for one hour, there were 19 peaks observable in the gas chromatogram of the photolysis mixture. When a solution of 11 was irradiated for five hours, only 12 could be found in the mixture.

These results, summarized in eq. 2, indicate that, in contrast to the behavior of 1,3,5-hexatrienes, terminal alkyl substituents do not greatly influence the direction of photocyclization of divinylbenzenes, and that benzobicyclo[3.1.0]hexenes themselves undergo further photolytic reactions. The formation of 12 from 11 can be explained as a homo-(1,3) sigmatropic shift (eq. 3), which would be suprafacial, if concerted, and photochemically allowed.[5] Alternatively, a stepwise homolysis of the conjugated cyclopropane ring, giving a *tertiary* and *benzylic* biradical intermediate, followed by a sterically undemanding intramolecular hydrogen atom transfer (eq. 4), could account for this isomerization.[6] This

(3)



11 12

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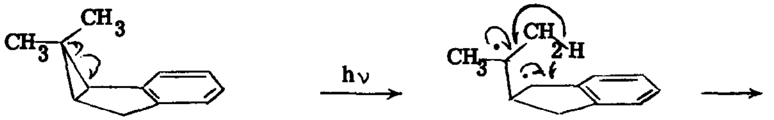

11 12

mechanism correctly predicts which bond in the cyclopropane ring should be broken in going to the indane ring system.

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