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PHOTOCHEMISTRY OF o-DIALKENYLBENZENES: o-BIS(2-METHYLPROPENYL)BENZENE

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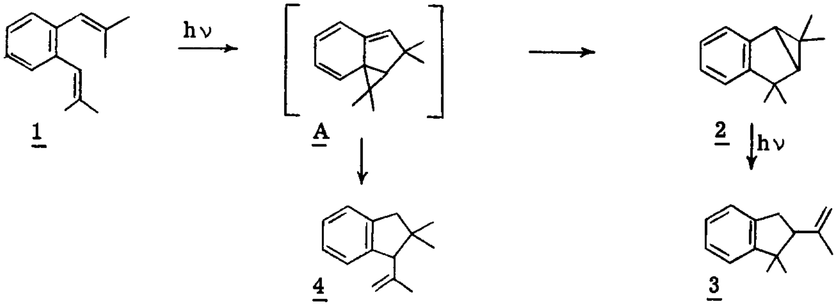
In connection with recent studies of the photochemistry of divinylbenzenes,[1,2,3] we have prepared and irradiated o-bis(2-methylpropenyl)benzene (1). The results obtained are in accord with the scheme (1) given below, involving a new mode of ring opening for the postulated nonaromatic intermediate A, as well as the photolysis of a benzobicyclo[3.1.0]-hexene.

(1)



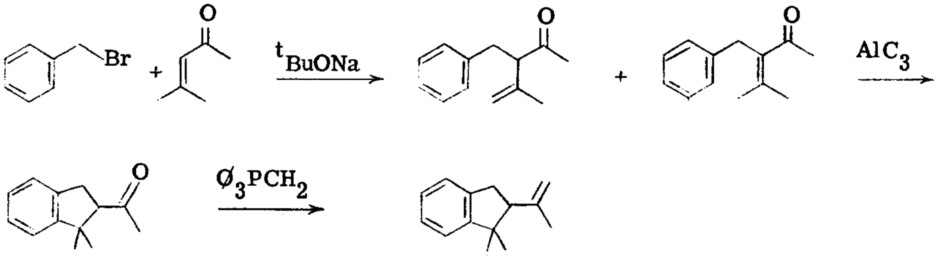
o-Bis(2-methylpropenyl)benzene (1) was prepared in 46% yield by the Wittig reaction of isopropyltriphenylphosphonium iodide[4] and methyllithium with o-phthalaldehyde. IR 1660, 1600 cm^{-1}; NMR (CCl_4) singlet at τ 2.8 (4H), broad multiplet at 3.8 (2H), doublets at 2.0 and 2.2 (J = 1.4 Hz, 6H each); UV (absolute ethanol) λ_{max} 230 (ε 15,000), 255 (9,600); calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74; found: C, 90.34; H, 9.70.

When a 0.3% ethereal solution of 1 was irradiated through a Corex filter for 23 days, glc analysis (50' x 3/8" 20% Carbowax 20M column at 210^{o} and 80 psi) showed approximately 80% 1 (r.t. = 52 min), 2% of a new component (r.t. = 89 min), and 12% of another component (r.t. = 37 min) which, upon isolation by preparative glc was assigned the structure 2 on the basis of its elemental analysis (calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74; found: C, 90.06; H, 9.92) and spectra: IR 3030, 1381, 1372, 1359 cm^{-1}; NMR (CCl_4) broad multiplet at τ 2.7-3.0 (4H), doublets at 7.55 and 8.55 (J = 8 Hz, 1H each), singlets at 8.46, 8.65, 8.72, and 9.18 (3H each); UV (absolute ethanol) λ_{max} 210 (ϵ 9,300), 214 (7,800), 246 (330), 253 (580), 260 (950), 266 (1,480), 272 (1,660); MS m/e 143, 156, 171, and 186 (parent).

When a similar solution was irradiated through a Vycor filter for 67 days, glc analysis showed 46% of 1, 3% of 2, 36% of the 89 min. r.t. component, identified as 1,1-dimethyl-2-isopropenylindane (3) (the synthesis of which is described below), and 7% of a component (r.t. = 46 min), which was isolated by glc and hydrogenated on 5% Pd/C in ethanol to give a compound which was identified as 2,2-dimethyl-1-isopropylindane (5), the synthesis of which is described below. The photoproduct is assigned structure 4: IR 3070, 1640, and 890 cm^{-1} (terminal methylene), and 1387, 1376, 1368 cm^{-1} (geminal and non-geminal methyls); NMR (CCl_4) singlets at τ 2.8 (4H), 6.6 (1H), 8.80 (3H), and 8.92 (3H), doublets at 7.2 and 7.3 (J = 16 Hz, 1H each) and multiplets at 5.1 (1H), 5.3 (1H), and 8.3 (3H); UV (absolute ethanol) λ_{max} 255 (ϵ 760), 262 (920), 267 (1,280), 274 (1,420).

The synthesis of 3 is outlined in reaction scheme (2). Benzyl bromide, mesityl oxide, and sodium t-butoxide reacted in benzene to give a mixture of alkylation products,[5] which was cyclized to 6 by heating with anhydrous aluminum chloride. Wittig reaction with methylidenetriphenylphosphorane gave 3, NMR (CCl_4) singlets at τ 2.8 (4H), 8.6, and 9.0 (3H each), broad singlets at 7.06 (1H) and 8.2 (3H), doublets at 6.93 and 7.15 (J = 5.3 Hz, 1H each), multiplet at 5.0 (2H); UV (absolute ethanol) λ_{max} 247 (ϵ 610), 253 (760), 259 (970), 264 (1,230), 271 (1,230); calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74; found: C, 90.35; H, 9.69.

(2)

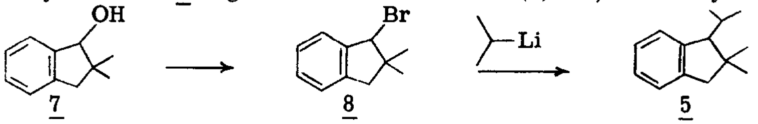


6

3

The synthesis of 5 is given in reaction scheme (3). 2,2-Dimethyl-1-indanol (7)[6] was treated with 48% aqueous hydrobromic acid to give the bromide 8 in 69% yield. The bromide 8, lithium wire, and isopropyl bromide were allowed to react in refluxing ether to give the required hydrocarbon 5, NMR (CCl_4) singlet at τ 3.0 (4H), doublets at 7.05 (J = 15.5 Hz, 1H), 7.30 (J = 9.5 Hz, 1H), 7.40 (J = 15.5 Hz, 1H), 8.78 (J = 7 Hz, 3H), 9.3 (J = 6.5 Hz, 3H), singlets at 8.68 and 8.85 (3H each), an apparent doublet of septets at 7.76 (J = 9.7, 6.8 Hz, 1H); UV (95% ethanol) λ_{max} 253 (ε 450), 263 (640), 269 (970), 276 (1,060); calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71; found: C, 89.32; H, 10.69.

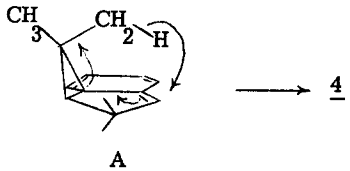
(3)



A solution of 2 was irradiated through a Vycor filter and analysed by glc after 8, 18, 28, 60, and 180 minutes. The peak corresponding to 2 had essentially disappeared after 60 minutes, but at no time was a peak corresponding to 4 observed. After 180 min, only a peak corresponding to 3 was observed. The NMR spectrum of the concentrated photolysis mixture was that of 3.

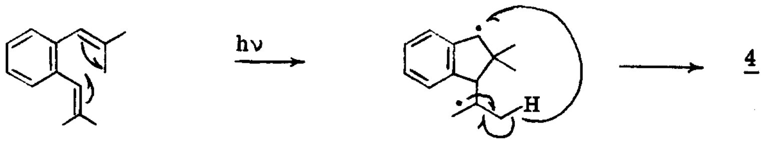
While the formation of 3 from 2 is readily rationalized as discussed in the accompanying Letter,[3] 4 must arise in some other way. An attractive mechanism invokes a hydrogen transfer reaction of the postulated intermediate A, as shown in eq. 4; space-filling models show the migrating hydrogen to be quite close (ca. 1.7 Å) to its receiving carbon. While it is tempting to regard the production of 4 as evidence for the existence of the non-aromatic intermediate A, there is another mechanism (eq. 5) which does not require A, but simply involves a biradical that could form directly from 1. In this case, however, the migrating hydrogen appears from models to be ca. 3.3 Å from its destination.[7,8]

(4)



A

(5)



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7. A preliminary account of these results has appeared in the abstracts of the 21st National Organic Chemistry Symposium of the A. C. S., June 15-19, 1969, Salt Lake City, Utah, pp. 62-70.
8. Very similar results have recently been obtained independently by L. Ulrich, H.-J. Hansen and H. Schmid. We are grateful to Professor Schmid for providing us with a preprint of his manuscript, which is to appear in *Helv. Chim. Acta*.