Photochemical 1,3-Addition of Methanol to t-Butylbenzene

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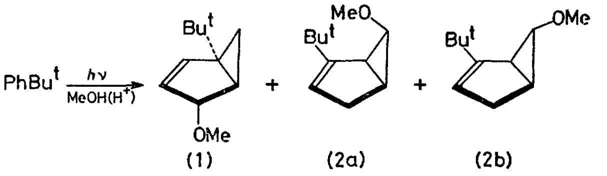
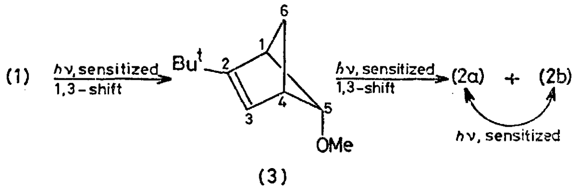
Summary Irradiation of t-butylbenzene in methanol containing a trace of hydrochloric acid gives 4-methoxy-1-t-butyl- (**1**) and 6-methoxy-2-t-butyl-bicyclo[3.1.0]-hex-2-ene (**2a, b**); the 4-methoxy-adduct is formed by addition of methanol to t-butylbenzvalene and the 6-methoxy-adducts may be formed by a sensitized vinylcyclopropane rearrangement, *via* a bicyclo[2.1.1]-hexene intermediate, of the 4-methoxy-adduct.

Irradiation of benzene or alkylbenzenes in protic solvents is known to yield bicyclo[3.1.0]hexene derivatives.[1–3] Wilzbach and his co-workers have reported that the 4-substituted adducts are formed by solvation of benzvalene while the 6-substituted adducts are formed by benzene-sensitized vinylcyclopropane rearrangements of the 4-substituted adducts, in which rupture of the 1,5-bond occurs exclusively, yielding planar cyclohexenylene di-radicals.[2] While investigating the photochemical behaviour of various monosubstituted benzenes in protic solvents, it was found that irradiation of t-butylbenzene in methanol containing a trace of hydrochloric acid gave the *exo*-4-methoxy-(**1**) and *exo*- and *endo*-6-methoxy-bicyclohexenes (**2a**) and (**2b**). We now report that (**1**) is the primary photo-adduct and that (**2a** and **b**) are formed by the sensitized rearrangement of (**1**); the conversion of (**1**) into (**2**) may proceed *via* a bicyclo[2.1.1]hexene intermediate formed by 1,3-migration of the C-6 bridge (a vinyl-cyclopropane–cyclopentene-type of rearrangement[4]) in (**1**).

Irradiation of a solution of t-butylbenzene (69 mM) in methanol containing hydrochloric acid (*ca.* 1 mM) in a quartz tube with an unfiltered 30 W low-pressure mercury lamp at room temperature for 22·5 h gave the photo-adducts (**1**) and (**2**) (94%, based on consumed t-butylbenzene), which consisted of (**1**) (43%), (**2a**) (37%), and (**2b**) (20%). The photo-adducts were analysed by g.l.c.–mass spectrometry and each isomer was identified by i.r. and n.m.r. spectra.[†] Periodic g.l.c. analysis during the irradiation of t-butylbenzene under similar conditions indicated that the ratio of (**2a** + **2b**) : (**1**) increased with irradiation time; the ratios were 0·68 : 1, 0·99 : 1, and 1·33 : 1 after irradiation for 5, 7, and 22·5 h, respectively. Irradiation of (**1**) alone in t-butylbenzene at room temperature gave the isomeric adducts (**2a**) and (**2b**). In addition, the ratios of (**2b**) to (**2a**) increased to limiting values (*ca.* 0·6 : 1) with irradiation time, indicating that (**2a**) and (**2b**) undergo photochemical epimerization.





(**3**)

These facts, together with results for related reactions,[2] suggest that (**1**) is formed by addition of methanol across a cyclopropyl bond of a t-butylbenzvalene intermediate and that (**2a**) and (**2b**) are formed by a photo-sensitized rearrangement of (**1**). In this case, the rearrangement cannot

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[†] N.m.r. data (100 MHz, CCl_4) for the photoadducts are as follows: (**1**), δ −0·14 (1H, t, *J* 4·2 Hz), 0·75 (1H, m), 0·92 (9H, s), 1·67 (1H, m), 3·24 (3H, s), 3·98 (1H, br. s), 5·34 (1H, dd, *J* 5·6 and 1·8 Hz), and 6·10 (1H, dd, *J* 5·6 and 1·0 Hz); (**2a**), δ 1·03 (9H, s), 1·40—1·95 (3H, m), 2·39 (2H, m), 3·04 (3H, s), and 5·05 (1H, t, *J* 2·5 Hz); (**2b**), δ 0·98 (9H, s), 1·40—1·95 (3H, m), 2·39 (2H, m), 3·24 (3H, s), and 5·31 (1H, t, *J* 2·5 Hz). The olefinic resonances in the n.m.r. spectra of (**2a**) and (**2b**) were assigned from their position and their triplet nature, indicating that (**2**) was a mixture of 2-t-butylbicyclohexene isomers. If (**2**) were a mixture of 3-t-butylbicyclohexene isomers, the olefinic protons would appear as multiplets at lower fields. For examples on n.m.r. spectra of bicyclo[3.1.0] hexenes, see refs. 1 and 5, and also R. H. Chung, G. J. Lin, J. M. Nicholson, A. Tseng, O. Tucker, and J. W. Wheeler, *J. Amer. Chem. Soc.*, 1972, **94**, 2183; P. K. Freeman, M. F. Grostic, and F. A. Raymond, *J. Org. Chem.*, 1965, **30**, 771. We thank a referee for his comments on the n.m.r. data.

be explained by the intermediacy of a cyclohexenylene diradical,[2] as suggested by Wilzbach and his co-workers, *via* rupture of the 1,5-bond in (**1**). If the rearrangement proceeded this way 6-methoxy-3-t-butylbicyclohexene isomers would have been formed instead of (**2**). Thus, the observed formation of (**2**) may be explained by a pathway *via* the favourable intermediate (**3**) formed by 1,3-migration of the C-6 bridge in (**1**). This intermediate then rapidly undergoes 1,3-migration[5] of the C-5 bridge to give (**2**).‡ Attempts to isolate (**3**) have so far been unsuccessful.

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‡ On the basis of heats of formations of allylic radicals, we would have expected the C(1)–C(5) bond to break rather than the C(4)–C(5) bond. For heats of formation of allylic radicals see D. M. Golden and S. W. Benson, *Chem. Rev.*, 1969, **69**, 125; M. Kobayashi, 'Chemistry of Free Radicals,' eds. H. Sakurai and K. Tokumaru, Nankodo, Tokyo, 1967, p. 4.

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