A Successful Route to Isobenzofulvene and Some of its Derivatives

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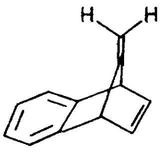
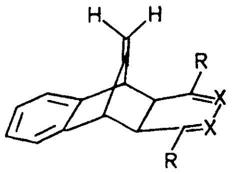
Summary The 1,6-elimination of hydrogen bromide from 2-bromomethylindene has been used to generate isobenzofulvene for the first time, under conditions which allow its trapping in adduct form.

Our *s*-tetrazine pathway to a variety of isobenzo-systems, including 8,8-disubstituted isobenzofulvenes, is now a well established procedure.[1,2] Basic to our studies on peri-selectivity,[3] we required the parent isobenzofulvene. However, application of the aforementioned route to the synthesis of this compound, *via* 1,4-dihydro-9-methylene-1,4-methanonaphthalene (**1**)† was unsuccessful. Thus (**1**) reacted with 3,6-di(2-pyridyl)-*s*-tetrazine to form (**2**), δ (CDCl$_3$, 60 MHz) 3·82 (s), 3·96 (s, CH), and 4·48 (s, exocyclic CH$_2$). However, (**2**) rearranged to the unsymmetrical isomer (**3**) (*inter alia* five ^{1}H n.m.r. singlets at δ 2·80, 4·14, 4·34, 4·62, and 4·98) rather than the expected fragmentation to isobenzofulvene. Another approach, as used by Tanida[2] for the generation of 8,8-dimethylisobenzofulvene, was also unsuccessful since the intermediate diene (**4**) preferentially reacted with trapping agents such as *N*-methylmaleimide to form 1 : 1 adducts, *e.g.*, (**5**).

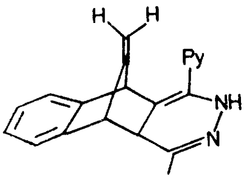
The following elimination route was developed and has led to the generation of isobenzofulvene for the first time.



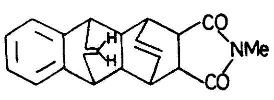
(1)



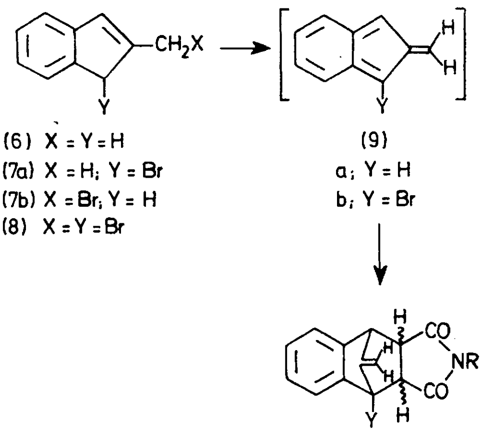
(2) R = Py; X = N
(4) R = H; X = CH



(3)



(5)



(6) X = Y = H
(7a) X = H; Y = Br
(7b) X = Br; Y = H
(8) X = Y = Br

(9)
a; Y = H
b; Y = Br

(10)
a; Y = H
b; Y = Br

Reaction of 2-methylindene (**6**) with *N*-bromosuccinimide (NBS) yields a mixture of the unstable monobromo-derivatives (**7a**), δ 2·05 (s, Me), 5·05 (s, allylic H) 6·31 (s br, vinylic H) and 7·0—7·4 (m, ArH), and (**7b**), δ 3·39 (s, PhCH_2), 4·25 (s, >CHBr) 6·64 (s, vinylic H), and 7·0—7·4 (m, ArH), with the former isomer predominating.‡ Treatment of (**7**) with LiBr and Li$_2$CO$_3$ in dimethylformamide under reflux, in the presence of trapping agents, led to the formation of 1 : 1 adducts (**10a**) in moderate yield. *N*-Methyl maleimide yielded the *endo*-adduct, m.p. 166 °C, *m/e* 239·0944, δ 2·28 (s, *N*-Me), 3·45 (m), 4·01 (m, CH), 4·62 (s, vinylic CH$_2$), and 7·09 (m, ArH), while *N*-ethyl maleimide gave a mixture of both the *exo*- and *endo*-adducts. Similarly (**8**) yielded 1-bromobenzofulvene (**9b**) as the *endo*-adduct (**10b**) with *N*-methyl maleimide in excellent yield, m.p. 203 °C, *m/e* 317·0048, δ 2·32 (s, *N*-Me), 3·55 (2H, m, 2 × CH), 4·13 (1H, m, CH), 4·82 and 4·96 (2 × s, exocyclic vinylic CH$_2$), and 7·12—7·28 (m, ArH).

(*Received*, 23*rd February* 1976; *Com.* 187.)

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† This compound was prepared from the addition of benzyne to fulvene in CH$_2$Cl$_2$. It is a clear liquid, δ (CDCl$_3$, 60 MHz) 4·14 (s, exocyclic CH$_2$), 4·20 (dd, bridgehead CH), and 6·9—7·4 (m, aromatic and vinylic H).

‡ Ratio solvent dependent; 4 : 1 in benzene, 2 : 1 in CCl$_4$.

[1] R. N. Warrener, *J. Amer. Chem. Soc.*, 1971, **93**, 2346; G. M. Priestly and R. N. Warrener, *Tetrahedron Letters*, 1972, 4295; P. L. Watson and R. N. Warrener, *Austral. J. Chem.*, 1973, **26**, 1725.
[2] H. Tanida, T. Irie, and K. Tori, *Bull. Chem. Soc. Japan*, 1972, **45**, 1999.
[3] M. N. Paddon-Row, *Austral. J. Chem.*, 1974, **27**, 299.