Photolysis and Flash Thermolysis of some 1,3-Dihydrobenzo[*c*]thiophen 2,2-Dioxides

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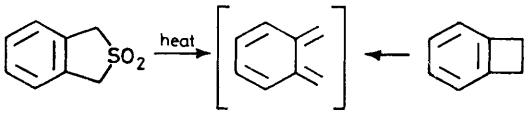
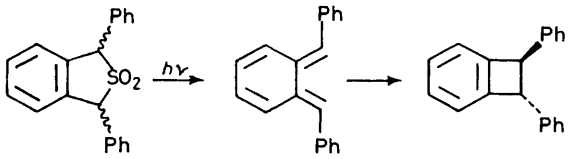
The thermolysis and photolysis of the title compounds (7) have been studied. Benzocyclobutenes (8) are the major products at lower temperatures whereas alkenes (9), derived from a [1,5] hydride shift, predominate at higher temperatures and on photolysis.

THERMOLYSIS of 1,3-dihydrobenzo[*c*]thiophen 2,2-dioxide (1) has been shown [1,2] to proceed *via* the disrotatory loss of sulphur dioxide to give the *o*-quinodimethane (5,6-dimethylenecyclohexa-1,3-diene) (2) which, by careful choice of conditions, undergoes conrotatory ring-closure to give benzocyclobutene (3).

Compound (1) is reported [3] to be photochemically stable; other workers,[4] however, have shown that if the dioxide (1) is irradiated during thermolysis the yield of



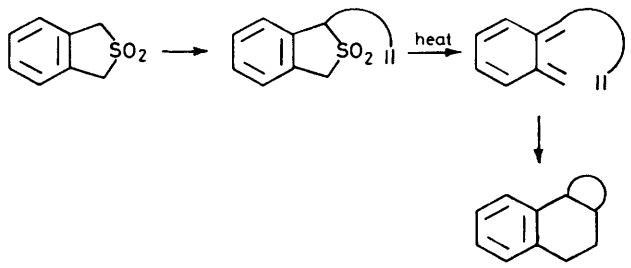
(1) (2) (3)



(4) (5)

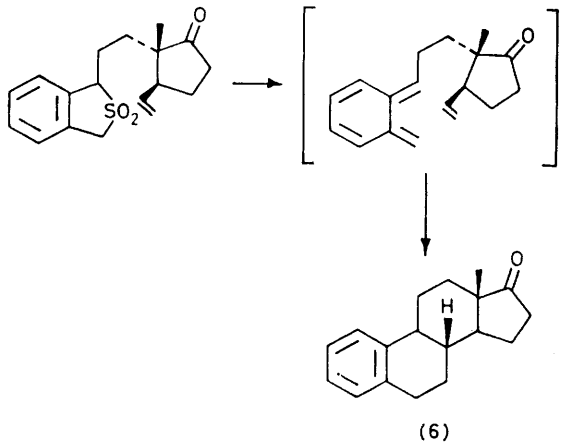
benzocyclobutene is substantially increased. 1,3-Diphenyl-1,3-dihydrobenzo[*c*]thiophen 2,2-dioxide (4) does extrude sulphur dioxide on photolysis [3] to give the benzocyclobutene (5). Benzocyclobutenes are important synthetically since *o*-quinodimethanes may be generated thermally and be trapped intramolecularly by dienes to form polycyclic materials.[5]

The sulphone (1) is an ideal starting material for synthetic schemes based on this principle since it may be alkylated and SO_2 extruded to give the required *o*-quinodimethane directly (Scheme 1). Recently,



SCHEME 1

Oppolzer *et al.*[6] have shown that compound (1) may be readily alkylated and that thermolysis in an inert solvent produces an *o*-quinodimethane, which may be trapped by a dienophile in the alkyl chain giving a tricyclic system. Nicolaou *et al.*[7] have devised a stereoselective synthesis of estra-1,3,5(10)-trien-17-one (6) in



(6)

SCHEME 2

which the key step is the alkylation of the sulphone (1), followed by intramolecular trapping of the *o*-quinodimethane (Scheme 2).

SCHEME 3

A complication of these synthetic schemes is the possibility that the generated *o*-quinodimethane may react *via* a second pathway involving a [1,5] hydride shift of the *Z*-form, as shown in Scheme 3. In some instances this can be the major reaction.[8] We have examined methods of controlling the ratio of the products of these two reaction paths and the results of flash-vacuum thermolysis and photolysis are reported here.

RESULTS AND DISCUSSION

Phase-transfer catalysis has been used extensively for the preparation of many sulphides.[9] We have found that 1,3-dihydrobenzo[*c*]thiophen can be prepared, simply and efficiently, from a dichloromethane solution

of αα'-dibromo-*o*-xylene and aqueous sodium sulphide using triethylhexadecylammonium chloride as the phase-transfer catalyst. This is much more convenient and simpler than the reported processes.[10] Oxidation to the sulphone (1) was accomplished using acetic acid and hydrogen peroxide, as described by Oliver and Ongley.[10]

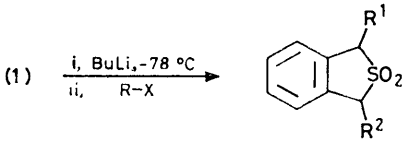
Treatment of 1,3-dihydrobenzo[*c*]thiophen 2,2-dioxide in ether with n-butyl-lithium at −78 °C followed by addition of an alkyl halide gave compounds (7), as shown in Table 1. Flash-vacuum thermolysis of (7a) at 600 °C

TABLE 1

Preparation of the substituted 1,3-dihydrobenzo[*c*]thiophen 2,2-dioxides (7) using Bu^nLi at −78 °C

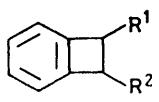
Alkyl halide	Product	M.p. (°C)	Yield
MeI	(7a)	95—97	83
2 MeI	(7b)	68—71	64
$PhCH_2Br$	(7c)	105—107	52
$H_2C{=}CHCH_2Br$	(7d)	53—55	74

did not produce any methylbenzocyclobutene (8a), but gave only the *o*-methylstyrene (9a).[11] At 450 °C, however, methylbenzocyclobutene (8a) was produced. A similar pattern occurred with the other compounds (7);



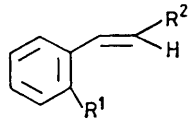
(7)

a; R^1 = Me, R^2 = H
b; R^1 = R^2 = Me
c; R^1 = CH_2Ph, R^2 = H
d; R^1 = $CH_2CH{=}CH_2$, R^2 = H



(8)

a; R^1 = Me, R^2 = H
b; R^1 = R^2 = Me
c; R^1 = CH_2Ph, R^2 = H
d; R^1 = $CH_2CH{=}CH_2$, R^2 = H



(9)

a; R^1 = Me, R^2 = H
b; R^1 = Et, R^2 = H
c; R^1 = Me, R^2 = Ph
d; R^1 = Me, R^2 = $CH{=}CH_2$

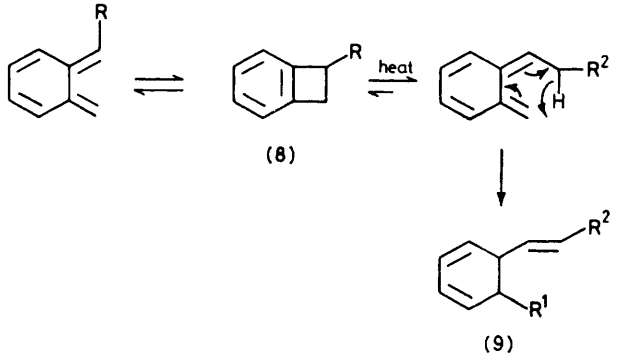
o-alkylstyrenes were the major products at higher temperatures and benzocyclobutenes at lower temperatures (see Table 2).

TABLE 2

Thermolysis of the substituted 1,3-dihydrobenzo[*c*]thiophen 2,2-dioxides (7)

(7)	*T* (°C)	Yield of (8) (%)	Yield of (9) (%)	Recovered (7) (%)
a	600		77	
a	450	38		55
b	540	33	55	
b	450	35		60
c	700		68	
c	600		57	16
c	450			83
d	450	20	60	
d	380	55		35

These results suggest that at lower temperatures sulphur dioxide is extruded to yield (*E*)-*o*-quinodimethane, which ring-closes to give the benzocyclobutenes (8). At the higher temperatures the (*Z*)-*o*-quinodimethane predominates, which then undergoes a [1,5]-hydride shift to give compounds (9), as shown in Scheme 4. We have not been able to obtain compound (8c)

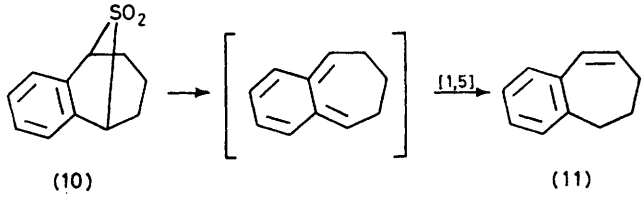


SCHEME 4

from the sulphone (7c) under any thermolysis conditions. Presumably, when R = aryl, (8) is much less stable than (9), or extrusion of SO_2 results in the formation of *o*-quinodimethane in the *Z*-geometry.

Only compounds (7c) and (7d) are photochemically labile. No trace of any benzocyclobutenes was found on sensitised (benzophenone) or unsensitised photochemical decomposition; only the corresponding *trans*-alkenes were formed.

It seems clear from our experiments that for benzocyclobutene formation and, presumably, intramolecular (4 + 2) reactions, the sulphone (7) must be decomposed at as low a temperature as possible. At higher temperatures the competing [1,5] hydride shifts become the major reaction pathway. Other factors, such as strain, may dictate which product is formed, as shown in the following example. Treatment of the sulphone (1) with two mol equiv. of n-butyl-lithium followed by 1 mol equiv. of 1,3-dibromopropane gave the dioxide (10). Flash-vacuum thermolysis of (10) at 550 °C gave the benzocycloheptene (11), in quantitative yield (Scheme 5).



SCHEME 5

This process is more efficient than the previous synthesis of the heptene (11).[12]

EXPERIMENTAL

M.p.s were determined using a Kofler heating stage. I.r. spectra were recorded on a Perkin-Elmer 257 instrument. N.m.r. spectra were recorded at 90 MHz on a Varian E.M.

390 instrument. Mass spectra were recorded at 20 eV on on a V.G. Micromass 16B instrument. G.l.c. analyses were performed on a Pye 104 flame ionisation chromatograph filled with a 3% OV 17 column.

1,3-Dihydrobenzo[c]*thiophen*.—αα'-Dibromo-*o*-xylene (13.2 g, 50 mmol) dissolved in dichloromethane (100 cm^3) was added to a solution of hydrated sodium sulphide (30 g) in water (100 cm^3), containing triethylhexadecylammonium chloride (5 cm^3 of a 50% aqueous solution). The mixture was stirred in the dark at room temperature for 18 h. The organic layer was separated and washed several times with water; drying and removal of solvent gave the product as a pale yellow solid (6.1 g, 89%), m.p. 20—22 °C (lit.,[10] 22.5—23.5 °C); δ($CDCl_3$) 7.14 (4 H, s) and 4.26 (4 H, s). 1,3-Dihydrobenzo[*c*]thiophen 2,2-dioxide (1) was prepared as previously described,[10] m.p. 150—152 °C (lit.,[10] 150—151 °C).

General Procedure for the Alkylation of 1,3-Dihydrobenzo[c]*thiophen 2,2-Dioxide* (1).—n-Butyl-lithium (1 mol equiv.) was added to a stirred solution of the dioxide (1) in dry ether under a nitrogen atmosphere and at −78 °C. The solution was allowed to warm to room temperature and was stirred for 1 h; it was then cooled to −78 °C and the alkyl halide (1 mol equiv.) was added slowly. The mixture was again allowed to warm to room temperature and was stirred for 2 h. Dilute hydrochloric acid was added with stirring. The ether layer was separated and the aqueous layer extracted with dichloromethane. The organic fractions were combined, dried, and the solvent removed to give the crude product. Pure products could be obtained by recrystallisation from dichloromethane–light petroleum or by column chromatography on M.F.C. silica, with light–petroleum ether (60 : 40) as eluant.

(*a*) Methyl iodide (1 mol equiv.) gave 1-methyl-1,3-dihydrobenzo[*c*]thiophen 2,2-dioxide [6] (7a) (83%); δ($CDCl_3$) 6.57 (4 H, m), 4.31 (3 H, m), and 1.66 (3 H, d, *J* 1 Hz); *m/e* 182 (M^+), 118, 103, and 76; $\nu_{max.}$ (Nujol) 1 320 and 1 125 cm^{-1}.

(*b*) Methyl iodide (2 mol equiv.) gave *1,3-dimethyl-1,3-dihydrobenzo*[c]*thiophen 2,2-dioxide* (7b) (64%), m.p. 68—71 °C (EtOH); δ($CDCl_3$) 6.92 (4 H, m), 4.07 (2 H, m), 1.67 (3 H, d, *J* 1 Hz), and 1.40 (3 H, d, *J* 1 Hz); *m/e* 196 (M^+), 132, 118, and 117; $\nu_{max.}$ (Nujol) 1 325 and 1 125 cm^{-1} (Found: C, 61.2; H, 5.95; S, 16.4. Calc. for $C_{10}H_{12}O_2S$: C, 61.15; H, 6.2; S, 16.35%).

(*c*) Benzyl bromide gave *1-benzyl-1,3-dihydrobenzo*[c]*thiophen 2,2-dioxide* (7c) (52%), m.p. 105—107 °C (dichloromethane–light petroleum); δ($CDCl_3$) 7.18 (9 H, m), 4.37 (1 H, m), 4.10 (2 H, s), and 3.20 (2 H, m); *m/e* 258 (M^+), 194, and 91; $\nu_{max.}$ (Nujol) 1 325 and 1 130 cm^{-1} (Found: C, 69.45; H, 5.45; S, 12.25. Calc. for $C_{15}H_{14}O_2S$: C, 69.7; H, 5.5; S, 12.4%).

(*d*) Prop-2-enyl bromide gave *1-propen-2-yl-1,3-dihydrobenzo*[c]*thiophen 2,2-dioxide* (7d) (74%), m.p. 53—55 °C (dichloromethane–light petroleum); δ($CDCl_3$) 7.40 (4 H, s), 6.00 (1 H, m), 5.27 (2 H, m), 4.53 (3 H, m), and 2.83 (2 H, m); *m/e* 208 (M^+), 144, and 103; $\nu_{max.}$ 1 330 and 1 125 cm^{-1} (Found: C, 63.2; H, 5.8; S, 15.3. Calc. for $C_{11}H_{12}O_2S$: C, 63.45, H, 5.8; S, 15.4%).

(*e*) The dioxide (1), n-butyl-lithium (2 mol equiv.), and 1,3-dibromopropane (1 mol equiv.) gave *1,3-dihydro-1,3-propanobenzo*[c]*thiophen 2,2-dioxide* (10) (51%), m.p. 185—186 °C (dichloromethane–light petroleum); δ($CDCl_3$) 7.33 (4 H, s), 4.07 (2 H, d, *J* 5 Hz), 2.57 (2 H, d × t, *J* 4.5 and 10 Hz), 1.97 (2 H, m), 1.50 (1 H, m), and 0.87 (1 H, m); *m/e* 208 (M^+), 144, 129, 116, and 103; $\nu_{max.}$ 1 330 and 1 130 cm^{-1} (Found C, 63.25; H, 5.8; S, 15.15. Calc. for $C_{11}H_{12}S_2O$: C, 63.45; H, 5.8; S, 15.4%).

General Thermolysis Procedure.—Typically the sulphone (*ca.* 120 mg) was vaporised through the furnace (10 cm) at various temperatures (Table 2) under reduced pressure (0.01 mmHg). The product was collected on a cold finger (filled with acetone–solid CO_2) and washed with deuteriochloroform into an n.m.r. tube. The nature and ratio of the products were analysed by comparison (n.m.r. and g.l.c.) with authentic materials.

(*a*) Thermolysis of the dioxide (7a). Column chromatography on alumina (elution with light petroleum) of the 450 °C thermolysis product gave 1,2-dihydro-1-methylbenzocyclobutene (8a) [13] (38%) as a colourless oil; δ($CDCl_3$) 7.01 (4 H, m), 3.36 (3 H, m) and 1.18 (3 H, d, *J* 4 Hz).

(*b*) Thermolysis of the dioxide (7b). Column chromatography of the 450 °C thermolysis product on alumina (elution with light petroleum) gave 1,2-dihydro-1,2-dimethylbenzocyclobutene (8b) [14] (35%); δ($CDCl_3$) 7.01 (4 H, m), 3.37 (2 H, m), and 2.16 (6 H, d, *J* 3 Hz).

(*c*) Thermolysis of the dioxide (7c). The only products obtained from these reactions were the *cis*- and *trans*-2-methylstilbene (9c) [15] which could be separated by column chromatograph (alumina).

(*d*) Thermolysis of the dioxide (7d). Chromatography on alumina (elution with light petroleum) of the 380 °C thermolysis product gave 1,2-dihydro-1-(prop-2-enyl)benzocyclobutene (8d) (55%); δ($CDCl_3$) 7.08 (4 H, m), 5.90 (1 H, m), 5.10 (2 H, m), 3.53 (2 H, m), 2.73 (1 H, d × d, *J* 21 and 13 Hz), and 2.40 (2 H, m); *m/e* 144 (M^+).

(*e*) Thermolysis of the dioxide (10). The product from the 550 °C thermolysis run was pure 6,7-dihydro-5*H*-benzocycloheptene (11) [12] in quantitative yield.

General Procedure for Photolysis.—The compound (250 mg), dissolved in methanol, was photolysed in a quartz tube at 254 nm using a Rayonette photochemical reactor.

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