

Benzocyclobutenes. Part 9.¹ Synthesis of Bromo-, Chloro-, and Oxo-derivatives of Benzocyclobutene and Naphtho[*b*]cyclobutene

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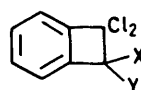
Addition of benzyne to 1,1-dichloro- and 1,1,2-trichloro-ethene gave the corresponding di- (61%) and tri- (18%) chloro derivatives of benzo-cyclobutene. Similarly 2,3-didehydronaphthalene and 1,1-dichloroethene gave 1,1-dichloronaphtho[*b*]cyclobutene. Some reactions, including reduction, chlorination, bromination, and hydrolysis of these cyclobutenes and of related compounds are described.

Although many methods are known for the preparation of benzocyclobutene and its mono- and di-one most of these methods have given low yields or have been otherwise unsuitable when there are substituents in the benzene ring.²⁻⁴ The recent report⁵ that benzyne reacts with 1,1-dichloroethene to give 1,1-dichlorobenzocyclobutene, from which benzocyclobuten-one and -dione can be made on a multigram scale in good yields, prompts us to record our independent studies^{6,7} on the addition of benzyne and 2,3-didehydronaphthalene(2,3-naphthalene) to 1,1-dichloro- and 1,1,2-trichloro-ethene, also some reactions of the cyclobutene derivatives thus obtained.

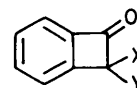
At the start of our work in 1976 it was already known that benzyne (generated by diazotisation of anthranilic acid) reacted with *cis*- and *trans*-1,2-dichloroethene to give mixtures of *cis*- and *trans*-1,2-dichlorobenzocyclobutene in total yields of 5 and 40% respectively.⁸ We began by studying the addition of benzyne (from anthranilic acid) to 1,1-dichloroethene and obtained 1,1-dichlorobenzocyclobutene (1) in 61% yield. Hydrolysis of the dichloro compound with aqueous ethanolic silver nitrate (*cf.* Hart *et al.*⁹) gave benzocyclobutenone (7) in 83% yield whereas hydrolysis with dilute sulphuric acid gave only a 40% yield. Independently, O'Leary *et al.*¹⁰ and Dürr *et al.*¹¹ reported the same reactions, the overall yields of ketone (7) from anthranilic acid being 27 and 38% respectively.

The dichloro compound (1) is a useful starting material for making other benzocyclobutene derivatives in addition to the monoketone (7) and diketone (8). Thus reduction of (1) with 4 equivalents of lithium in liquid ammonia, propan-2-ol, and ether gave benzocyclobutene (46%) and the use of 6.5 equivalents of lithium gave the diene (11) (63%). This diene had previously been made by the similar reduction of benzocyclobutene¹² and of 1-cyanobenzocyclobutene.¹² Bromination of the dichloride (1), using an excess of bromine in carbon tetrachloride in a flask heated and illuminated by a 150-W tungsten-filament light bulb placed under it, gave 1,1-dibromo-2,2-dichlorobenzocyclobutene (3) (94%). Attempts to make the corresponding monobromo compound (2) using 1 equivalent of *N*-bromosuccinimide gave a mixture of starting material and dibromide (3). However, the monobromo compound (2) (42%) was obtained by using 1 equivalent of bromine in a thermal/photochemical reaction similar to that used for the dibromide. Attempted chlorination of the dichloride (1) with *N*-chlorosuccinimide failed but chlorination with sulphuryl chloride, again using a 150-W light bulb, gave the tetrachloride (4) (64%). The latter had been prepared previously by treatment of the dione (8) with phosphorus pentachloride, also by treatment of 1,1,2,2-tetrafluorobenzocyclobutene with aluminium chloride.¹³

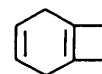
Hydrolysis of the dibromo-dichloro compound (3) proved unexpectedly difficult. When boiled with silver trifluoroacetate in aqueous acetonitrile for 4 days it gave the dione (8) (36%) and a mixture of 2,2-dichloro- and 2,2-dibromo-benzocyclo-



- (1) X = Y = H
 (2) X = Br, Y = H
 (3) X = Y = Br
 (4) X = Y = Cl
 (5) X = Cl, Y = H
 (6) X = Cl, Y = Br



- (7) X = Y = H
 (8) XY = O
 (9) X = Y = Cl
 (10) X = Cl, Y = H



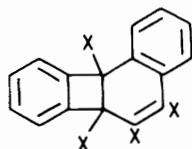
(11)

butenone (*ca.* 49 : 1) (38%). This mixture was hydrolysed again for 4 days and gave the pure dichloroketone (9) and dione (8) (29 and 32% respectively based on the dihalogenoketone mixture). Clearly the best method for making the dione (8) from dichloride (1) is by hydrolysis to the monoketone (7) followed by dibromination and then hydrolysis of the 2,2-dibromobenzocyclobutenone using the modifications⁵ made to Cava's original procedure.¹⁴

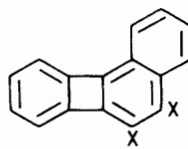
Reaction of Benzyne with Trichloroethene.—When benzenediazonium-2-carboxylate was heated in trichloroethene it gave a black oil, from which 1,1,3-trichlorobenzocyclobutene (5) (18% yield) was isolated. Generation of benzyne in 1,2-dichloroethane containing a 15-fold excess of trichloroethene gave the desired trichloride (5) in higher yield (42%) but it was contaminated with *ca.* 2% of biphenylene.

Bromination of the trichloride (5) using bromine and the light-bulb technique gave the 1-bromo-1,2,2-trichloro compound (6) (47%) after 60 h. Hydrolysis of compound (5), by boiling it with silver trifluoroacetate in aqueous acetonitrile, proceeded slowly and gave 2-chlorobenzocyclobutenone (10) (62%) after 48 h. The ¹H n.m.r. spectrum of the latter was unchanged on addition of D₂O showing that enolisation did not occur. Prolonged hydrolysis of the trichloride (5) did not yield 2-hydroxybenzocyclobutenone, perhaps because the latter was destroyed by the trifluoroacetic acid liberated during the hydrolysis. More recently this compound has been prepared by hydrolysis of 2-trimethylsilyloxybenzocyclobutenone with water alone, *i.e.* under neutral conditions.¹⁵

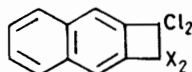
Soon after we had prepared the trichloride (5), Atkins and Fray¹⁶ suggested to us that the two products which they had obtained by the action of zinc dust on a mixture of 1,2,3,8- and 1,2,3,4-tetrachlorocyclo-octatetraene were compounds (12) and (14). We confirmed the structure of these two compounds by preparing them from the trichloride (5), treatment of which with potassium *t*-butoxide in *t*-butyl alcohol gave



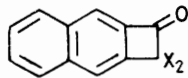
(12) X = Cl
(13) X = Br



(14) X = Cl
(15) X = Br



(16) X = H
(17) X = Br



(18) X = H
(19) X = Br
(20) X₂ = O

5,6,6a,10a-tetrachloro-6a,10a-dihydrobenzo[*a*]biphenylene (12) and a small amount of the biphenylene (14). Unlike the corresponding tetrabromo compound (13) the tetrachloro compound (12) did not lose chlorine readily under the reaction conditions. However, it was partially dechlorinated by boiling it with zinc dust in ethanol for 48 h to give the biphenylene (14) (65%) together with unchanged tetrachloride (12) (19%). The tetrabromo compound (13) had been made by addition of bromine to the biphenylene (15) which was obtained directly from 1,1,2-tribromobenzocyclobutene by reaction with potassium *t*-butoxide.¹⁷

In an attempt to add benzyne to tetrachloroethene, under conditions similar to those used with trichloroethene, the only isolable product was biphenylene (9% based on anthranilic acid). O'Leary *et al.* found that benzyne reacted with 1,1-dichloropropene to give 1,1-dichloro-2-methylbenzocyclobutene (11%) but the reaction with 1,1-dichloro-2-methylpropene did not yield a benzocyclobutene.¹⁰ As far as we are aware there have been no reports of successful (2 + 2) cyclo-additions of benzyne to tetrasubstituted alkenes and we agree with O'Leary *et al.* that this failure and the low yields with tri-substituted alkenes are mainly attributable to steric hindrance in the polysubstituted ethene π -bond.¹⁰

Reaction of 2,3-Didehydronaphthalene with Tri- and Tetrachloroethene.—Diazotisation of 3-amino-2-naphthoic acid in aqueous hydrochloric acid gave the corresponding diazonium chloride¹⁸ which, when heated in a mixture of dioxane and 1,1-dichloroethene, gave 1,1-dichlorocyclobuta[*b*]naphthalene (16) in 29% yield. Hydrolysis of the dichloro-compound gave the ketone (18), which could be reduced with sodium borohydride to the corresponding alcohol. The dichloride (16) did not react with *N*-bromosuccinimide but readily underwent photobromination to give the dibromo-dichloro-compound (17) which could be hydrolysed easily to the known naphtho[*b*]cyclobutene-1,2-dione (20).⁴ The ketone (18) reacted with *N*-bromosuccinimide to give the dibromoketone (19) and thence, by hydrolysis, the dione (20).

When 2-carboxynaphthalene-3-diazonium chloride was heated under reflux with propene oxide, dioxane, and a large excess of trichloroethene it gave 2-chloronaphthalene (55%) and none of the desired tetrachlorocyclobuta[*b*]naphthalene. In connection with our work on naphthocyclobutenes we prepared the parent hydrocarbon, naphtho[*b*]cyclobutene, in 33 and 30% yields by pyrolysis of 2-bromomethyl-3-methyl- and 2-chloromethyl-3-methyl-naphthalene respectively. While our work was in progress, Ewing and Boekelheide reported the same synthesis of the hydrocarbon (34% yield) from the

chloromethyl compound which they had made from the bromomethyl compound by halogen exchange.¹⁹ However, we were able to prepare 2-chloromethyl-3-methylnaphthalene (77%) directly from 2,3-dimethylnaphthalene by photohalogenation with sulphuryl chloride (Kulka's method²⁰).

Experimental

Unless otherwise stated the following conditions apply. I.r., ¹H n.m.r., and u.v. spectra were measured in Nujol mulls, in deuteriochloroform, and in 95% ethanol respectively. T.l.c. was carried out on plates coated with Kieselgel GF₂₅₄ (Merck) and column chromatography using silica gel M.F.C. (Hopkin and Williams Ltd.) or aluminium oxide (Brockman activity II) (B.D.H. Chemicals Ltd.). Petroleum refers to light petroleum (b.p. 60–80 °C). ¹H N.m.r. and low-resolution mass spectra were measured for all intermediates and products obtained and confirmed their structures. The expression 'heated and irradiated' means that the reaction mixture was boiled under reflux while being irradiated by a 150-W tungsten-filament light bulb placed just below the flask containing the reaction mixture.

1,1-Dichlorobenzocyclobutene (1).—Solvent-wet benzenediazonium-2-carboxylate [from anthranilic acid (13.7 g)²¹ was added to a mixture of 1,1-dichloroethene (78 ml) and 1,2-dichloroethane (500 ml). The mixture was heated, stirred, and kept at its boiling point for 15 min. It was then evaporated under reduced pressure and the residue chromatographed on a column of dry alumina,²² with light petroleum (b.p. 40–60 °C) as eluant. The eluate was distilled at 50–60 °C/0.5 Torr and gave the dichloro compound (1) (10.5 g, 61%) as a colourless oil (lit.,¹⁰ b.p. 38–40 °C/2.5 Torr (Found: C, 55.9; H, 3.6; Cl, 41.4. Calc. for C₈H₆Cl₂: C, 55.5; H, 3.5; Cl, 41.0%), δ 4.10 (s, CH₂) and 7.12–7.46 (m, 4 ArH). The recovered mixture of 1,1-dichloroethene and 1,2-dichloroethane can be re-used.

1-Bromo-2,2-dichlorobenzocyclobutene (2).—The dichloride (1) (346 mg) in CCl₄ (25 ml) was heated and irradiated. Bromine (320 mg) in CCl₄ (10 ml) was added dropwise during 15 min and refluxing was continued for 5 h. Removal of the solvent gave an oil which was chromatographed on alumina, with light petroleum (b.p. 40–60 °C) as eluant. The first fraction yielded 1,1-dichlorobenzocyclobutene (54 mg, 16%), identified by its n.m.r. spectrum. The second fraction (370 mg) was a mixture of two compounds (t.l.c.). Distillation gave the monobromo compound (2) (210 mg, 42%) as an oil, b.p. 105–106 °C/3 Torr (Found: *M*⁺, 250. C₈H₅⁷⁹Br³⁵Cl₂ requires *M*, 250), δ 5.97 (s, 1-H) and 7.2–7.6 (m, 4 ArH). It still contained a small amount of the dibromo compound (3) and a satisfactory elemental analysis could not be obtained.

1,1-Dibromo-2,2-dichlorobenzocyclobutene (3).—Bromine (5.5 g) in CCl₄ (40 ml) was added dropwise during 30 min to a boiling solution of the dichloride (1) (2.0 g) in CCl₄ (100 ml) which was heated and irradiated for 18 h. Removal of the solvent gave a yellow solid which was dissolved in light petroleum (b.p. 40–60 °C) and passed down a short column of alumina. The eluate was evaporated and the residual solid recrystallised from petroleum to give the *dibromide* (3) (3.6 g, 94%) as needles, m.p. 76–77 °C (Found: C, 28.8; H, 1.3. C₈H₄Br₂Cl₂ requires C, 29.0; H, 1.2%), δ 7.4–7.6 (m, ArH).

1,1,2,2-Tetrachlorobenzocyclobutene (4).—A mixture of the dichloride (1) (1.73 g), SO₂Cl₂ (20 ml), and CCl₄ (150 ml) was heated and irradiated. After 24 h, more SO₂Cl₂ (20 ml) was added and the mixture was heated for a further 48 h. Removal

of the solvent gave an oil which slowly solidified. This was twice recrystallised from petroleum and gave the tetrachloride (4) (1.55 g, 64%) as crystals, m.p. 65–67 °C (lit.,¹³ 78–79 °C (Found: C, 39.5; H, 1.8. Calc. for C₈H₄Cl₄: C, 39.7; H, 1.7%).

1,1,2-Trichlorobenzocyclobutene (5).—The solvent-wet benzenediazonium-2-carboxylate (from 13.7 g anthranilic acid) was washed with cold 1,1,2-trichloroethene (2 × 20 ml) and then added to a mixture of 1,1,2-trichloroethene (90 ml) and 1,2-dichloroethane (500 ml) and boiled (with stirring) until the solution became clear. Removal of the solvent gave a black oil which was purified by dry-column chromatography²² on alumina, with petroleum as eluant. The eluate was distilled and gave the trichloro compound (5) (8.7 g, 42%) as an oil, b.p. 105–107 °C/2.5 Torr. The n.m.r. spectrum showed that this material contained ca. 2% of biphenylene. A pure sample was made (18% yield) by decomposing the benzenediazonium-2-carboxylate in 1,1,2-trichloroethene alone, followed by purification as above (Found: C, 46.2; H, 2.4. C₈H₃Cl₃ requires C, 46.3; H, 2.4%), δ 5.76 (s, CHCl) and 7.23–7.54 (m, 4 ArH).

1-Bromo-1,2,2-trichlorobenzocyclobutene (6).—Bromine (15 g) in CCl₄ (100 ml) was added dropwise during 30 min to a boiling solution of the trichloro compound (5) (2.0 g) in CCl₄ (50 ml), which was heated and irradiated. After 60 h, the n.m.r. spectrum showed aromatic protons only. Removal of solvent gave a brown oil which was dissolved in petroleum and filtered through a short column of alumina. The eluate gave a solid which was recrystallised twice from petroleum and gave the bromo compound (6) (1.3 g, 47%) as crystals, m.p. 66–67 °C (Found: C, 33.4; H, 1.4. C₈H₄BrCl₃ requires C, 33.5; H, 1.4%).

Benzocyclobutenone (7).—A mixture of the dichloride (1) (8.15 g), silver nitrate (16.3 g), ethanol (80 ml), and water (20 ml) was refluxed, and stirred, for 4 h. After being filtered the solution was concentrated, diluted with water (200 ml), and extracted with ether (3 × 100 ml). The extract was dried and distilled to give benzocyclobutenone (4.6 g, 83%), b.p. 60–62 °C/1 Torr (lit.,²³ 71–72 °C/2 Torr).

Benzocyclobutene-1,2-dione (8) and 2,2-Dichlorobenzocyclobutenone (9).—A mixture of the dibromo-dichloro compound (3) (6.62 g), silver trifluoroacetate (19.0 g), water (4 ml), and CH₃CN (70 ml) was refluxed, and stirred, for 4 days while being protected from light. The mixture was filtered and the filtrate evaporated to dryness. The residue, dissolved in CH₂Cl₂, was washed successively with water (2 × 25 ml) and saturated aqueous sodium chloride (2 × 25 ml) and then dried. Removal of the solvent gave an oil which was chromatographed on a column of silica gel (in CH₂Cl₂). The first fraction gave, after sublimation, a solid (1.42 g), m.p. 50–55 °C which was shown by microanalysis to be a mixture (49:1) of 2,2-dichloro- and 2,2-dibromo-benzocyclobutenone. The second fraction gave, after sublimation at 90–105 °C/0.5 Torr, benzocyclobutene-1,2-dione (8) (0.94 g, 36%), m.p. 130–131 °C.

The above mixture of dihalogeno-ketones (0.94 g), silver trifluoroacetate (2.3 g), water (1 ml), and CH₃CN (18 ml) was refluxed as before for 4 days. The products were separated as before by chromatography. The first fraction gave 2,2-dichlorobenzocyclobutenone (9) (0.27 g, 29%), as needles (from petroleum), m.p. 52–53 °C (Found: C, 51.0; H, 2.1. C₈H₄Cl₂O requires C, 51.4; H, 2.2%). The second fraction gave the dione (8) (0.21 g, 32%).

2-Chlorobenzocyclobutenone (10).—The trichloride (5) (2.07

g), silver trifluoroacetate (6.6 g), water (2 ml), and CH₃CN (40 ml), were stirred and refluxed for 48 h while being protected from light. The mixture was worked-up as in the preceding experiment. Elution of the silica-gel column with petroleum gave starting material (0.15 g, 7%); CH₂Cl₂ then eluted material which was sublimed (40–50 °C/0.01 Torr) to give 2-chlorobenzocyclobutenone (10) (0.94 g, 62%) as crystals m.p. 65–66 °C (Found: C, 63.0; H, 3.4. C₈H₅ClO requires C, 63.0; H, 3.3%).

Reduction of 1,1-Dichlorobenzocyclobutene.—(a) *To benzocyclobutene.* Pieces of lithium (total 0.69 g, 100 mmol) were added to a stirred mixture of the dichloride (1) (4.3 g), propan-2-ol (7 ml), diethyl ether (50 ml), and liquid ammonia (ca. 100 ml) at –40 to –60 °C during 4 h. After a further 2 h all the lithium had reacted and ammonium chloride (9 g) was added cautiously. The ammonia was allowed to evaporate overnight then water (100 ml) was added. The solution was extracted with ether (4 × 50 ml) and the united extracts were washed successively with water (2 × 40 ml), 2M-hydrochloric acid (2 × 40 ml), and saturated aqueous sodium chloride (2 × 40 ml). The ethereal solution after being dried and distilled gave benzocyclobutene (1.2 g, 46%), b.p. 49–54 °C/10 Torr (lit.,¹² 79–83 °C/95 Torr).

(b) *To bicyclo[4.2.0]octa-1(6),3-diene (11).* The dichloride (1) (10 g) was reduced by lithium (2.7 g) and propan-2-ol (31 ml) in diethyl ether (100 ml) and liquid ammonia (ca. 200 ml) and the product isolated as in section (a) above. The product, compound (11) (3.9 g, 63%), was a liquid, b.p. 55–60 °C/10 Torr (lit.,¹² 78–79 °C/90 Torr) and was identified by its ¹H n.m.r. spectrum.

5,6,6a,10b-Tetrachloro-6a,10b-dihydrobenzo[a]biphenylene (12).—The trichloride (5) (1.04 g), potassium t-butoxide (2.70 g), and t-butyl alcohol (40 ml) were stirred at room temperature for 4 h. Water (75 ml) was added cautiously and the mixture cooled to 15 °C. The yellow precipitate was collected and found by t.l.c. to consist of a white product together with a small amount of an orange compound (14). The mixture, when recrystallised from petroleum, gave the dihydrobiphenylene (12) (0.38 g, 56%) as plates, m.p. 213–214 °C which was identical (i.r., n.m.r., and mass spectra) with the compound, m.p. 209–210 °C, obtained by Atkins and Fray.¹⁶

5,6-Dichlorobenzo[a]biphenylene (14).—The tetrachloro compound (12) (200 mg) and zinc dust (300 mg) in ethanol (10 ml) were stirred and refluxed for 48 h. After being filtered, the solution was evaporated and the residue chromatographed on silica gel. Elution of the orange band with light petroleum (b.p. 40–60 °C) gave 5,6-dichlorobenzo[a]biphenylene (14) (103 mg, 65%) as orange needles, m.p. 137–139 °C (Found: C, 70.5; H, 2.9. Calc. for C₁₆H₈Cl₂: C, 70.9; H, 3.0%), which was identical (i.r., u.v., n.m.r., and mass spectra) with the compound (m.p. 135–137 °C) obtained by Atkins and Fray.¹⁶

1,1-Dichloronaphtho[b]cyclobutene (16).—A mixture of 3-amino-2-naphthoic acid (10 g), concentrated hydrochloric acid (10 ml), THF (450 ml), and isopentyl nitrite (13 g) was stirred for 1.5 h. The mixture was cooled and the orange solid collected and washed with dry dioxane. The solvent-moist solid was added to a mixture of dioxane (600 ml), propene oxide (4 ml), and 1,1-dichloroethene (70 g). The mixture was heated at 100 °C, with stirring, for 3 h. Removal of the solvents under reduced pressure gave a red oil which was chromatographed on a column of dry alumina.²² Elution with CH₂Cl₂ yielded 1,1-dichloronaphthocyclobutene (16) (3.4 g, 29%) as plates, m.p. 129–130 °C (Found: C, 65.2; H, 3.7;

Cl, 31.9. $C_{12}H_8Cl_2$ requires C, 64.6; H, 3.6; Cl, 31.8%, δ 4.34 (s, CH_2) and 7.4—8.0 (m, 6 ArH).

1,1-Dibromo-2,2-dichloronaphtho[b]cyclobutene (17).—A mixture of the dichloride (16) (0.4 g) and *N*-bromosuccinimide (0.65 g) in CCl_4 (40 ml) was heated and irradiated for 48 h. The solvent was removed under reduced pressure and the residue after crystallisation from CCl_4 gave the dibromo compound (17) (0.47 g, 69%) as crystals, m.p. 145—146 °C (Found: C, 37.6; H, 1.7; Cl, 18.5. $C_{12}H_6Br_2Cl_2$ requires C, 37.8; H, 1.6; Cl, 18.6%).

Naphtho[b]cyclobutenone (18).—A mixture of the dichloride (16) (0.5 g), silver nitrate (0.76 g), ethanol (20 ml), and water (60 ml) was refluxed, with stirring, for 3 h. Removal of the solvents gave a solid which on crystallisation from CCl_4 gave naphtho[b]cyclobutenone (18) (0.32 g, 85%), m.p. 163—164 °C (Found: M^+ , 168.0562 $C_{12}H_8O$ requires M , 168.0575), v_{max} . 1 765, 1 078, 975, 960, 955, 890, and 750 cm^{-1} ; δ 4.19 (s, CH_2) and 7.5—8.0 (m, 6 ArH); λ_{max} . 243, 292sh, and 303 nm (log ϵ 4.60, 3.90, and 4.02). The ketone gave the corresponding 2,4-dinitrophenylhydrazone as orange crystals, m.p. 266—269 °C (decomp.) (from ethyl acetate) (Found: C, 62.4; H, 3.5; N, 16.1. $C_{18}H_{12}N_4O_4$ requires C, 62.1; H, 3.5; N, 16.1%).

1-Hydroxynaphtho[b]cyclobutene.—A mixture of the ketone (18) (0.25 g) and $NaBH_4$ (0.09 g) in ethanol (20 ml) was stirred at room temperature for 18 h. After removal of the solvent, dilute hydrochloric acid (15 ml) was added and the mixture warmed for 10 min. Extraction with CH_2Cl_2 gave 1-hydroxynaphtho[b]cyclobutene (0.132 g, 53%), m.p. 126—128 °C (Found: C, 84.5; H, 6.1. $C_{12}H_{10}O$ requires C, 84.7; H, 5.9%), v_{max} . 3 650, 1 200, 1 140, 1 100, 1 060, 943, 878, 830, and 740 cm^{-1} .

2,2-Dibromonaphtho[b]cyclobutenone (19).—The ketone (18) (0.3 g) and *N*-bromosuccinimide (0.7 g) in CCl_4 (30 ml) was heated and irradiated for 4 h. The mixture, after being cooled and filtered, gave a solid which, on sublimation at 100—120 °C/0.05 Torr, gave the dibromo ketone (19) (0.32 g, 55%), m.p. 162—163 °C (Found: C, 44.1; H, 1.9. $C_{12}H_6Br_2O$ requires C, 44.1; H, 1.85%), v_{max} . 1 785, 1 600, 1 120, 938, 915, 900, 820, and 765 cm^{-1} .

Naphtho[b]cyclobutene-1,2-dione (20).—(a) A mixture of the dibromoketone (19) (0.8 g) and silver trifluoroacetate (2.5 g) in CH_3CN (25 ml) and water (10 ml) was refluxed for 4 h. After being filtered the mixture was extracted with CH_2Cl_2 . The extract was washed with water, then dried and the solvent removed. The residue was sublimed at 125 °C/0.01 Torr and gave the dione (20) (0.29 g, 65%) as yellow needles, m.p. 252—255 °C (lit.,⁴ 250—255 °C) identical (i.r. spectrum) with an authentic sample.⁴

(b) The dibromo-dichloro compound (17) was similarly hydrolysed for 24 h and gave the same dione (42%).

2-Chloromethyl-3-methylnaphthalene.—A mixture of 2,3-dimethylnaphthalene (5 g), sulphuryl chloride (10 ml), and benzoyl chloride (0.125 g) in CCl_4 (50 ml) was heated and

irradiated for 6 h. The solution was concentrated to ca. half its volume, treated with charcoal, filtered, and evaporated. The residual solid was crystallised from petroleum and gave 2-chloromethyl-3-methylnaphthalene (4.7 g, 77%), m.p. 95—97 °C. A sample, purified by preparative t.l.c. on silica gel (benzene) had m.p. 97—99 °C (lit.,¹⁹ 99—101 °C), δ 2.6 (CH_3 4.73 (CH_2), and 7.2—7.8 (m, 6 ArH).

Naphtho[b]cyclobutene.—(a) 2-Bromomethyl-3-methylnaphthalene (0.5 g) was sublimed at 0.01 Torr through a quartz tube (50 × 1 cm) filled with quartz chips and heated at 850 °C. The pyrolysate was purified by preparative t.l.c. on silica gel (pentane as eluant) and gave the cyclobutene (0.108 g, 33%), m.p. 86—88 °C (lit.,¹⁹ 85—86 °C) (Found: M^+ , 154.0785. Calc. for $C_{12}H_{10}$ M , 154.0782), identical (i.r. and n.m.r. spectra) with the hydrocarbon obtained in (b) below.

(b) 2-Chloromethyl-3-methylnaphthalene (0.20 g) was sublimed through the same quartz tube as above at 780 °C during 1 h. The pyrolysate was purified by t.l.c. (petroleum) and gave the cyclobutene (0.049 g, 30%), m.p. 82—84 °C.

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