Cyclooctatetraenoquinones. II. The synthesis and transformations of compounds related to dibenzo[*a*,*e*]cyclooctene-5,6,11(12*H*)-trione

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Received September 11, 1969

Bromination of 11-acetoxydibenzo[a,e]cycloocten-5(6H)-one (6) gave the 6-bromo derivative (8), which on further bromination gave a hydrogen bromide adduct (12 or 13) of 6,6,12-tribromodibenzo-[a,e]cyclooctene-5,11(6H,12H)-dione (14). Treatment of this adduct with aqueous-ethanolic ammonia followed by sublimation gave 11-oxoindeno[1,2-c]isocoumarin (4), not dibenzo[a,e]cyclooctene-5,6,11(12H)-trione (3) as earlier suggested. The conversion of 12 or 13 to 4 has been shown to involve the formation of 3-bromo-2-(a-carboethoxyhenyl)indone (17), which gave 4 and ethyl bromide on being heated at 180°. Oxidation of dibenzo[a,e]cyclooctene-5,11(6H,12H)-dione with selenium dioxide gave a bimolecular product 25 considered to be derived by loss of carbon monoxide from the dimer of dibenzo[b,f]pentalene-5,10-dione (27), a selenium-containing product, 28, and the hydrate 29 of 3.

Canadian Journal of Chemistry, 48, 796 (1970)

1,2-Cyclooctatetraenoquinone (1) and its 1,4isomer (2) are of interest because of their possible aromaticity (1). The first reference in the chemical literature to a potential cyclooctatetraenoquinone derivative appeared in 1940 when the preparation of a compound provisionally assigned structure **3** was reported (2). This would be converted by enolization to a hydroxydibenzo derivative of **1**. We report here on a reinvestigation of the structure of the supposed trione **3**, which has led to the assignment to it of the revised structure (**4**),¹ and on experiments directed towards the synthesis of compound **3**.



The product earlier considered to be **3** was obtained (2) by a series of reactions starting from dibenzo [a,e] cyclooctene-5,11(6H,12H)-dione²(5).



This dione was originally prepared from diphenylsuccinonitrile, but is obtained more conveniently from 5,6,11,12-tetrahydrodibenzo [a,e]cyclooctene (1). Treatment of 5 with acetic anhydride and potassium acetate gave the enol acetate 6 as previously described (2). This product showed bands in its infrared (i.r.) spectrum at 5.66 (enol ester C=O stretch), 5.96 (conjugated ketone C=O stretch), and 7.33 μ (medium; acetate C-H bend) in good accord with the structural assignment 6. Its proton magnetic resonance (p.m.r.) spectrum in deuteriochloroform showed signals at δ 2.17 (3H) and 6.82 (1H), assignable to the acetyl methyl and vinyl protons, respectively, and multiplets at δ 7.0–7.6 (7H) and 8.1–8.3 (1H), assignable to the aromatic protons; in addition there were two 1-proton multiplets at δ 3.9–4.3 and 4.3-4.9, which must be assigned to the methylene protons at C-6 if structure 6 is correct. This pattern could be accounted for in terms of this structure if at the temperature of the probe (27°) the two tub conformations 7a and b were undergoing interconversion at a rate slow on the p.m.r. time scale. That this is indeed the case was shown by recording the p.m.r. spectrum in carbon disulfide at 27 and 0°. At the former temperature the spectrum resembled that in deuteriochloro-

¹Preliminary accounts of this work have appeared previously (3, 4); Wawzonek and Stowell (5) have also made this structural revision.

²See footnotes 4 and 6 in reference 1.



form, but at the latter temperature the methylene protons gave rise to a simple AB system with δ 3.80 and 4.63 and $J_{gem} = 12.5$ Hz. Thus when the temperature is lowered the 8-membered ring becomes conformationally "frozen" and the individual signals for H_a and H_b in 7a or b can be observed (6). In dimethyl sulfoxide at 27°, the protons in question give rise to an envelope at δ 4.0–4.6, but at 40° this becomes a broad singlet at δ 4.30 (half-height width = 5.5 Hz); clearly the interconversion of 7a and b at the higher temperature has become rapid on the p.m.r. time scale.

Treatment of **6** with bromine in acetic acid gave the compound that was previously considered to be **8**; this structure was preferred to **9** because of the apparent unreactivity of the bromo compound when treated with potassium acetate in boiling acetic acid (2). While its i.r. spectrum $[\lambda_{max} 5.64,$ 5.90, and 7.31 μ (m)] did not provide an unambiguous basis for choice between structures **8** and **9**, the p.m.r. spectrum of the bromo compound in deuteriochloroform [δ 2.23 (s, 3H), 7.00 (s, 2H), 7.2–7.6 (m, 6H), 7.7–8.0 (m, 1H), and 8.3–8.5 (m, 1H)] definitively excluded structure **8** since it showed no signal corresponding to the C-6 methylene protons. However, the latter spectrum



could only be reconciled with structure 9 by assuming that the signals of the protons at C-6 and C-12 were accidentally superimposed. That this was indeed the case was revealed by spectra taken in trifluoroacetic acid or dimethyl sulfoxide, which showed two 1-proton singlets in place of the 2-proton signal; the apparent singlet could also be resolved in deuteriochloroform at 100

MHz, when the separation of the component signals was ca. 1 Hz.

Also in accord with the assignment of structure 9 was the observation that brief treatment of the bromo compound with zinc in boiling acetic acid returned 6 in virtually quantitative yield. With respect to the reactivity of the bromo compound with potassium acetate (*vide supra*), we have found that reaction in boiling acetonitrile or acetic acid, although slow, does occur with the formation of a compound whose i.r. spectrum included a carbonyl-stretching band at 5.80μ ; this product was not obtained pure. Some analogy for the bromination of 6 to give 8



appeared to be provided by the claim that treatment of the diacetate 10 with bromine gave the bromo compound 11. However, in our hands the product from this reaction was the bromo ketone 9, which by coincidence has a closely similar carbon and hydrogen (but not bromine) content to that of 11.

Further bromination of 9 in chloroform gave a polybromo product that was not purified or characterized in the earlier work, but was treated with boiling aqueous-ethanolic ammonia followed by sublimation to give the compound considered to be 3 (2). In the present case the polybromo compound was purified and assigned the formula $C_{16}H_{10}Br_4O_2$. Its i.r. spectrum (Nujol) showed a weak hydroxyl-stretching band at 2.95 μ , but no band in the carbonyl-stretching region. Its p.m.r. spectrum showed a 1-proton singlet at δ 4.71, assignable to a hydroxyl proton since it was absent after brief treatment with D_2O_1 , and a 1-proton singlet at δ 5.66, together with 6- and 2-proton multiplets in the aromatic proton region. The polybromo compound is therefore assigned either structure 12 or 13. These structures are very closely related for both are hydrogen bromide adducts of the tribromo dione 14. The lability that would be expected of a compound of this type was displayed in several ways. The polybromo compound melted with gas evolution; on attempted purification by thin-layer



chromatography (t.l.c.) it decomposed to give at least 5 products, all showing carbonyl absorption in their i.r. spectra; although its i.r. spectrum in Nujol or ethanol-free chloroform lacked carbonyl absorption, a band at $5.80 \,\mu$ immediately developed in the spectrum of a solution in chloroform containing ethanol. The formation of **12** or 13 from 9 can be interpreted as occurring via attack of bromine on the enol acetate function to give the dibromo dione 15 (cf. the conversion of 10 to 9), followed by bromination at a position adjacent to a carbonyl group to give the tribromo dione 14; alternatively, bromination at the position adjacent to the carbonyl group of 9 may precede attack at the enol acetate function. The bromination next to the carbonyl group provides the hydrogen bromide that converts 14 to 12 or 13 by transannular addition.

When the polybromo compound was treated briefly with boiling aqueous-ethanolic ammonia and the resulting crude product was sublimed at ca. 200°, the compound previously assigned structure 3 was obtained as orange needles, m.p. 254-255° [lit. (2) m.p. 254-256°]. Its i.r. spectrum $[\lambda_{max} (CCl_4) 5.69, 5.80 (m), 5.84, and 6.13 \mu]$ and p.m.r. spectrum [δ (CDCl₃) 7.3–7.9 (m, 6H) and 8.2-8.5 (m, 2H)] clearly showed that it could not be 3. Indeed the latter spectrum indicated that its formula was $C_{16}H_8O_3$ rather than $C_{16}H_{10}O_3$, and this was confirmed by the observation of a molecular ion peak with m/e 248 in its mass spectrum. The spectral data and mechanistic considerations suggested that it was 11-oxoindeno-[1,2-c] isocoumarin (4). This was proved by direct comparison with an authentic sample of 4 pre-



pared by the method of Pailer *et al.* (7) by condensation of phthalide and phthaldehydic acid to give 2-(*o*-carboxyphenyl)-indan-1,3-dione (16) followed by dehydration, eq. [1].

The next goal was the elucidation of the course of this interesting transformation. Thin-layer chromatography established that the indenoisocoumarin 4 was not present in the crude product formed on treatment of the polybromo compound with aqueous-ethanolic ammonia, and thus 4 must be formed during the sublimation. This crude product was similarly shown to contain neither the acid 16 nor its ethyl ester. Column chromatography of the crude product on silica readily effected the separation of an intensely yellow oil, which was the least polar component of the crude product and represented ca. 25% of its weight. This gave 4 in high yield on being heated at 180° (20 mm). High resolution mass spectrometry established the composition of the yellow compound as $C_{18}H_{13}BrO_3$; its p.m.r. spectrum showed signals at δ (CCl₄) 1.12 (t, J = 7.0 Hz, 3H) and 4.14 (q, J = 7.0 Hz, 2H) indicating the presence of a $-CO_2CH_2CH_3$ grouping, and multiplets at δ 7.0–7.7 (7H) and 7.9–8.16 (1H) attributable to aromatic protons. These data and the fact that the yellow compound is the precursor of 4 led to the assignment to it of structure 17. Its i.r. spectrum $[\lambda_{max} (CCl_4) 5.84 \mu]$ and ultraviolet (u.v.) spectrum $[\lambda_{max} (C_6H_{14}) 235 (\log \mu)]$ ε 4.6), 242 (log ε 4.6), 252 (infl., log ε 4.4), 328 (log ε 2.8), and 392 mµ (log ε 3.2)] were in full accord with this structural assignment (8) Its conversion to 4 may be envisaged as occurring via the intermediacy of either 18 or 19 (see Scheme 1). Loss of bromide ion to give 20 or 21 followed by nucleophilic attack of bromide ion on the ethyl group would then give 4 and ethyl bromide. Alternatively, in the case of 18, a concerted 4center reaction could lead to the direct elimination of ethyl bromide; in the case of 19, however, the analogous 6-center concerted elimination is sterically inhibited. It seems reasonable to postulate that such polar reactions could occur in the reaction melt. Analogous formation of lactones by elimination of alkyl bromides has been observed previously (9). In the case at hand the formation of ethyl bromide in the conversion of 17 to 4 was established by trapping it in dichloromethane and identifying it by p.m.r. and mass spectrometry.

The formation of 17 by the action of aqueous-

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ethanolic ammonia on the polybromo compound 12 or 13 can be interpreted as involving initial reversion to the tribromo dione 14 by loss of the elements of hydrogen bromide in the basic medium, followed by ethanolysis to give 22 (see Scheme 2). Cyclization of this to either 23 or 24 followed by elimination of hydrogen bromide would then give 17.

Having shown that the compound hitherto considered to be the trione 3 was in fact 4, we investigated an alternative route for the synthesis of 3, viz., the oxidation of the dione 5 with selenium dioxide. The reaction was carried out in boiling aqueous dioxane, conditions under which cyclooctane-1,2-dione is formed from cyclooctanone in 65% yield (10). The progress of the reaction was followed by vapor-phase chromatography (v.p.c.), and the mixture was worked up after $3\frac{1}{2}$ days when little starting material remained. Three products were obtained: red, yellow, and colorless. The red compound was indicated to have the formula $C_{31}H_{16}O_3$ by mass spectrometry, and its p.m.r. spectrum [δ (CDCl₃) 7.1-8.3 (m, 13H) and 8.3-8.8 (m, 3H)] suggested that all of its protons were aromatic and that 3 of them were in the ortho relationship to carbonyl groups. On this basis it was concluded that the red product was compound 25, which had been obtained previously by Brand and Stephan (11) from the dione 26 by oxidation with selenium





dioxide. This conclusion was confirmed by direct comparison with a sample of 25 prepared from 26, which was itself obtained from α,β -diphenylsuccinic acid (12). The conversion of 5 to 25 can be considered as involving initial oxidation to 26, followed by further oxidation to 27 and Diels-Alder dimerization (13) of this intermediate with subsequent loss of carbon monoxide (see Scheme 3) as proposed previously (11). Compound 25 was obtained in 4% yield from 5.

The yellow compound formed on treatment of **5** with selenium dioxide was shown by mass spectrometry and elemental analysis to have the formula $C_{16}H_{10}O_2Se$. Its i.r. spectrum showed a band at 5.92 μ , and its p.m.r. spectrum showed signals at δ (CDCl₃) 4.50 (s, 2H), 7.24–7.52 (m, 6H), and 7.84–8.15 (m, 2H). On this basis it is assigned structure **28**. It was obtained in 20% yield.

 δ 3.35 and 3.78 (J = 16 Hz, 2H) and aromatic proton signals at 6.9-8.05 (m, 8H). These spectra suggested structure 29, and high resolution mass spectrometry established that the formula of the product corresponded to this structure, although the elemental analytical data could only be reconciled with it by the assumption that it was a hydrate $C_{16}H_{12}O_4 \cdot 1/4 H_2O^3$ Acetylation with acetic anhydride and sulfuric acid gave a diacetate, whose i.r. $[\lambda_{max}\,(CCl_4)\,5.65$ and $5.84\,\mu]$ and p.m.r. spectra [\delta (CDCl₃) 2.13 (s, 3H), 2.25 (s, 3H), 3.17 and 3.87 (AB system, J = 16 Hz, 2H), 6.9–7.65 (m, 7H), and 7.85–8.1 (m, 1H)] were in good accord with its formulation as 30. The spectra of the diol and its diacetate could conceivably also be interpretable in terms of structures without bridging of the 8-membered ring, such as 31 and 32, if they are assumed to be conformationally frozen at room temperature, as in the case of **6** at 0° (vide supra). However, the





The major product (70%) was a colorless solid shown by its i.r. spectrum $[\lambda_{max} (CHCl_3) 2.95 (ms)]$ and 5.90 µ] to be a hydroxy ketone. Its p.m.r. spectrum (CF₃CO₂H) showed an AB system at

³The tendency of compounds of this type to exist as hydrates is high (14).

positions of the methylene proton signals in the p.m.r. spectra of the 2 compounds and the occurrence in the p.m.r. spectrum of the acetate of only a 1-proton signal attributable to a proton in the *ortho* relationship to a carbonyl group favor structures **29** and **30**. The former finds analogy in compound **33** which is obtained by hydration of the corresponding dione (15).

Compound 29 is a hydrate of the desired trione 3 (as is 31), and attempts were made to dehydrate it. Like 33 it was unaffected by treatment with p-toluenesulfonic acid in boiling benzene with distillation of the solvent to remove any water formed as its azeotrope with benzene. A solution of the compound and dicyclohexylcarbodiimide showed no change after standing for several months. The compound melted at 198-199° without decomposition and sublimed unchanged at ca. 150° (10^{-2} mm), behavior that again paralleled the properties of 33 (15). However, on being heated at 300° (20 mm) the melt evolved gas, and a new product sublimed. The i.r. spectrum of the crude product showed that it was again a hydroxy ketone $[\lambda_{max}]$ $(CHCl_3)$ 2.9 (wm) and 5.86 μ]; its p.m.r. spectrum showed a broad 1-proton signal at δ 2.9 that can be assigned to a hydroxyl proton since its position was concentration-dependent, a 1-proton singlet at δ 4.25, and an 8-proton aromatic multiplet at δ 7.2–8.2. These data suggest the assignment to this product, which was not further characterized, of structure 34, whose formation can be rationalized as involving an intramolecular aldol condensation of the elusive trione 3, eq. [2].



Experimental

Melting points were determined in capillary tubes with a Thomas-Hoover "Uni-Melt" apparatus and are uncorrected.

Infrared spectra were recorded in carbon tetrachloride solutions, unless otherwise stated, and were calibrated with the 3.51, 6.24, and 9.72 μ bands of polystyrene film. Proton magnetic resonance spectra were recorded in deuteriochloroform solutions, unless otherwise stated. The band positions are reported in parts per million

downfield from tetramethylsilane as internal reference (δ scale).

Analytical t.1.c. was carried out with thin layers of silica gel (Merck) on microscope slides. Preparative t.1.c. was carried out with 1.0 mm thick layers of silica gel (Merck) on 20×20 cm square glass plates. Unless otherwise stated, thin-layer chromatograms were developed with dichloromethane, analytical chromatograms were developed with ble with iodine vapor, and preparative chromatograms by the quenching of a u.v. phosphor added to the silica gel.

Solutions in organic solvents were dried over anhydrous magnesium sulfate and stripped of solvent with a rotary evaporator in conjunction with a water aspirator. The term "aqueous workup" used here means that the solution in question was poured into about 3 times its volume of water and extracted 3 times with dichloromethane, and the dichloromethane solution was washed 3 times with water, dried, and stripped of solvent.

11-Acetoxydibenzo[a,e]cycloocten-5(6H)-one (6)

Compound 6 was prepared by treating dibenzo[*a*,*e*]cyclooctene-5,11-(6*H*,12*H*)-dione (5) (1) with acetic anhydride and potassium acetate, as described by Wawzonek (2). Several recrystallizations from 95% ethanol gave colorless rhomboidal platelets, m.p. 137–138° [1it. (2) m.p. 138–139°]; λ_{max} 5.66, 5.96, 7.33 (ms), and 8.35 µ; δ 2.17 (s, 3H), 3.9–4.3 (m, 1H), 4.3–4.9 (m, 1H), 6.82 (s, 1H), 7.0–7.6 (m, 7H), and 8.1–8.3 (m, 1H). At 27° in carbon disulfide, the nuclear magnetic resonance (n.m.r.) spectrum was similar to that in deuteriochloroform, but at 0°, the two 1-proton envelopes in the δ 3.9–4.9 region became an AB signal system, δ 3.80 and 4.63, J = 12.5 Hz. In dimethyl sulfoxide at 27°, the protons in question gave rise to an envelope at δ 4.0–4.6; at 40° this had become a broad singlet at δ 4.30 (half-height width = 5.5 Hz).

11-Acetoxy-6-bromodibenzo[a,e]cycloocten-5(6H)-one(9)

Compound 9 was obtained when the enol acetate 6 was treated with bromine in acetic acid as described by Wawzonek (2). Recrystallization from benzene gave colorless prisms, m.p. 229–229.5° (without gas evolution) [lit. (2) m.p. 219–223° with gas evolution]; λ_{max} 5.64, 5.90, 7.31 (m) and 8.36 μ ; δ 2.23 (s, 3H), 7.00 (s, 2H), 7.2–7.6 (m, 6H), 7.7–8.0 (m, 1H), and 8.3–8.5 (m, 1H); δ (CF₃CO₂H) 2.47 (s, 3H), 7.02 (s, 1H), 7.20 (s, 1H), 7.3–7.75 (m, 6H), 7.75–8.05 (m, 1H), and 8.3–8.6 (m, 1H); the p.m.r. spectrum in DMSO- d_6 showed 1-proton singlets at δ 7.00 and 7.27.

Anal. Calcd. for C₁₈H₁₃BrO₃: C, 60.50; H, 3.65; Br, 22.38. Found: C, 60.59; H, 3.80; Br, 22.39.

Reduction of 9 with Zinc and Acetic Acid. Formation of 6

In a 5 ml round-bottomed flask were placed compound 9 (10.5 mg, 0.029 mmole), zinc dust (3.6 mg, 0.055 mmole), and acetic acid (2 ml). The mixture was boiled under reflux for 0.5 h, then a further 3 mg of zinc dust was added, and the mixture was boiled under reflux for another 5 min, allowed to cool, filtered, and subjected to aqueous workup. The product was the enol acetate 6 (8 mg, 100%); the i.r. spectrum of this "crude" product was identical with that of authentic 6, and t.l.c. showed only one spot, corresponding to 6. Recrystallization from

95% ethanol gave colorless platelets, m.p. $139-139.5^{\circ}$, undepressed on admixture with authentic 6.

Treatment of 9 with Potassium Acetate

A mixture of 9 (126 mg, 0.353 mmole) and potassium acetate (107 mg, 1.09 mmoles) in acetonitrile (5 ml) was boiled under reflux for 3 h; much of the potassium acetate failed to dissolve. The mixture was poured into water, and the solid that precipitated was collected by filtration. The light orange solid weighed 74 mg, after being dried over phosphorus pentoxide. Its i.r. spectrum was similar to that of the starting material, but there was an additional band at 5.80 µ (m). Recrystallization from benzenehexane gave canary-yellow prisms, m.p. 225-229.5° identified as starting material (9) by mixture m.p. and i.r. spectral comparison; the yellow color of the recovered 9 is attributed to a small amount of impurity. The material which gave rise to the 5.80 μ band presumably remained in the mother liquor from recrystallization of the recovered 9. and was not investigated.

When 9 was heated at reflux for 4 h with potassium acetate in acetic acid, aqueous workup gave a sticky orange solid, the i.r. spectrum of which was very similar to that of the solid obtained by treating 9 with potassium acetate in boiling acetonitrile (*vide supra*).

Treatment of 9 with Dimethyl Sulfoxide and Collidine

A solution of 9 (4 mg, 0.011 mmole) and collidine (2.5 mg, 0.021 mmole) in dimethyl sulfoxide (0.5 ml) was heated at 130° for 6 h. Aqueous workup gave a yellow oil (2.5 mg), the i.r. spectrum of which was similar to that of the material obtained by treating 9 with potassium acetate (*vide supra*).

Treatment of 9 with Silver Nitrate

A solution of 9 (10 mg, 0.028 mmole) and silver nitrate (6.8 mg, 0.040 mmole) in acetonitrile (4 ml) was boiled under reflux in the dark for 18 h under nitrogen. Aqueous workup gave a bright yellow smear (7 mg); λ_{max} 5.66 (m) and 5.80 μ .

When the reaction mixture was stirred in the dark at 23° for 24 h instead of being boiled under reflux for 18 h, aqueous workup gave a solid, m.p. $225-228^{\circ}$, the i.r. spectrum of which was virtually identical to that of **9** (69% recovery).

5,11-Diacetoxydibenzo[a,e]cyclooctene (10)

Compound 10 was prepared by heating the dione 5 in acetic anhydride containing a little sulfuric acid, as described by Wawzonek (2). Aqueous workup gave a yellow oil that was recrystallized from 95% ethanol to give colorless rosettes, m.p. 149–150° [lit. (2) m.p. 150–151°]; λ_{max} 5.66, 7.34 (m), and 8.31 µ; δ 2.12 (s, 6H), 6.78 (s, 2H), 7.1–7.4 (m with spike at δ 7.23, 8H).

Treatment of 10 with Bromine. Formation of 9

A solution of bromine (58 mg, 0.36 mmole) in acetic acid (0.4 ml) was added to a solution of **10** (45 mg, 0.14 mmole) in acetic acid (1.5 ml) in a Pyrex tube. The tube was sealed and left at 23° for 7 h, during which time crystals were deposited. The tube was opened and the orange supernatant solution was removed. The colorless prisms were washed with benzene, giving **9** (30 mg, 60%), m.p. 122–128.5°; its i.r. spectrum was identical with that of authentic **9**. Recrystallization from benzene gave colorless

cubes, m.p. 230–231.5°, undepressed on admixture with authentic 9, m.p. 229–229.5°; mixed t.l.c. with authentic 9 gave a single spot.

The original supernatant solution was stripped of solvent to give a colorless solid (22.5 mg), the i.r. spectrum of which indicated it to be 9, contaminated with material giving rise to a band at 5.79 (m) μ .

Treatment of 9 with Bromine. Formation of 12 or 13

Bromine (0.8 ml, 14.6 mmoles) was added to a solution of 9 (400 mg, 1.12 mmoles) in chloroform (16 ml) in a Pyrex tube. The tube was sealed and left at 23° for 48 h, during which time no change could be discerned. The tube was opened and the solution was stripped of solvent to give a yellow solid (689 mg), m.p. 172–179° with gas evolution [lit. (2) m.p. 173–178° with gas evolution]. Recrystallization from hexane–chloroform (ethanol-free) gave microprisms, m.p. 199–200° with gas evolution; λ_{max} (Nujol) 2.95 (w) μ ; δ 4.71 (s, 1H, absent after treatment with D₂O), 5.66 (s, 1H), 7.2–7.7 (m, 6H), and 7.7–8.2 (m, 2H). The i.r. spectrum in ethanol-free chloroform was similar to that in Nujol, but in chloroform containing 0.75% of ethanol included a weak band at 5.80 μ .

Anal. Calcd. for $C_{16}H_{10}Br_4O_2$: C, 34.70; H, 1.82; Br, 57.72. Found: C, 34.55; H, 1.79; Br, 58.43.

The crude tetrabromo compound was obtained from 9 in essentially quantitative yield, and recrystallization gave material in ca. 55% yield that melted sharply with gas evolution. Recrystallization gave material with m.p. varying from 199-200° to 205-206.5°; sometimes the m.p. was slightly lowered by further recrystallization. This behavior may be due to dimorphism; when the m.p. was taken with a microscope-hot-stage unit, a change in crystalline form appeared to occur at ca. 180°. When the tetrabromo compound was subjected to preparative t.l.c. decomposition occurred to give at least 5 compounds, all showing carbonyl absorption in their i.r. spectra; no tetrabromo compound was recovered. The tetrabromo compound did not dissolve appreciably in aqueous ammonia, but when it was shaken with this reagent the aqueous ammonia slowly became yellow. On adding aqueous ammonia to a suspension of the compound in 95% ethanol, the tetrabromo compound readily dissolved to give a light yellow solution which became bright yellow during about 2 min.

Treatment of the Tetrabromo Compound 12 or 13 with

Aqueous-ethanolic Ammonia Followed by Sublimation. Formation of 11-Oxoindeno[1,2-c]isocoumarin (4)

A mixture of crude tetrabromo compound **12** or **13** (736 mg), 95% ethanol (17 ml), and concentrated aqueous ammonia (5 ml) was boiled under reflux for 10 min. Aqueous workup gave a yellowish solid (337 mg); λ_{max} 3.1 (br, wm), 5.82, and 5.90 (sh, s) μ . This crude solid was sublimed at 180° (20 mm) to give **4** (84 mg, 26%), m.p. 150–200°. Recrystallization from ethyl acetate gave orange needles, m.p. 254–255° [lit. (2) m.p. 254–256°]; λ_{max} 5.69, 5.80 (m), 5.84, and 6.13 (m) μ ; δ 7.3–7.9 (m, 6H) and 8.2–8.5 (m, 2H).

Mol. Wt. Calcd. for $C_{16}H_8O_3$: 248. Found: m/e 248.

The use of recrystallized tetrabromo compound, m.p. $199-200^{\circ}$, gave 4 in 52% yield.

An authentic sample of 4 was prepared from phthalide

and phthalaldehydic acid via the acid **16** by the method of Pailer *et al.* (7); m.p. $255.5-256.5^{\circ}$ [lit. (7) m.p. 257°]. A mixture of this with the compound obtained from the tetrabromo compound had m.p. $255-256^{\circ}$; the i.r. spectra and t.l.c. behavior of the 2 samples were identical.

Treatment of the Tetrabromo Compound 12 or 13 with Aqueous-ethanolic Ammonia. Formation of 3-Bromo-2-(o-carboethoxyphenyl)indone (17)

The recrystallized tetrabromo compound 12 or 13, m.p. 199–200°, (920 mg) was treated with aqueous-ethanolic ammonia (vide supra) to give a crude solid (440 mg), which was chromatographed on silica gel (28 g, 19 × 1.8 cm). The column was eluted with benzene, and the eluate corresponding to the most mobile colored band was collected. This eluate gave 17 as an intensely yellow oil (116 mg, 26%); λ_{max} 5.84 µ; λ (C₆H₁₂) 235 (log ε 4.6), 242 (log ε 4.6), 252 (infl., log ε 4.4), 328 (log ε 2.8), and 392 mµ (log ε 3.2); δ (CCl₄) 1.12 (t, J = 7.0 Hz, 3H), 4.14 (q, J = 7.0 Hz, 2H), 7.0–7.7 (m, 7H), and 7.9–8.16 (m, 1H).

Calcd. for $C_{18}H_{13}^{79}BrO_3$: 356.0048. Found: m/e 356.0021.

The rest of the reaction mixture consisted of red, polar, solid material (eluted with 1-10% methanol in dichloromethane) with i.r. absorption at 2.9, 5.9, 6.1, and 6.3 μ ; it did not give 4 on heating, and was not investigated further.

It was shown by t.l.c. that the acid 16 was not present in the original reaction mixture; p.m.r. spectroscopy showed that the ethyl ester of 16, 2-(*o*-carboethoxyphenyl)indan-1,3-dione, (*vide infra*) was absent; t.l.c. and i.r. spectroscopy demonstrated the absence of 4.

2-(o-Carboethoxyphenyl)indan-1,3-dione

The acid 16 (750 mg, 2.82 mmoles) was added to methanol (30 ml), and the suspension was stirred while a distilled solution of diazoethane (ca. 200 mg, ca. 3.6 mmoles) in ether (150 ml) (16) was added rapidly. The mixture was stirred for a further 5 min, treated with acetic acid (0.2 ml), and stripped of solvent. The residue was crystallized from benzene-hexane to give the ester as a yellow solid (205 mg, 25%), m.p. 156–165°. Recrystallization from dichloromethane-hexane gave very pale yellow needles, m.p. 160.5–164°; λ_{max} 5.71 (wm) and 5.84 µ; δ 1.15 (t, J = 7.0 Hz, 3H), 4.03 (q, J = 7.0 Hz, 2H), 4.77 (s, 1H), and 7.2–8.2 (m, 8H).

Anal. Calcd. for $C_{18}H_{14}O_4$ (mol. wt. 294.0891): C, 73.46; H, 4.80. Found (*m/e* 294.0920): C, 73.64; H, 4.66.

Pyrolysis of 17. Formation of 4 and Ethyl Bromide

When compound 17 (11 mg) was heated at 180° (20 mm) in a Pyrex tube, a bright orange compound rapidly sublimed onto the cool, upper part of the tube. This compound (6.9 mg, 90%) was shown to be 4 by i.r. spectral comparison with an authentic sample.

Pyrolysis of 17 (70 mg) was also carried out at 180° in a closed system evacuated at the water aspirator. The gas evolved was collected directly in a p.m.r. tube containing dichloromethane cooled in liquid nitrogen, while 4 sublimed onto the cooler parts of the pyrolysis tube. The p.m.r. tube, with its contents frozen, was sealed and detached from the rest of the apparatives. The presence of ethyl bromide in the dichloromethane was shown by

p.m.r. and mass spectrometry, the spectra being compared with those of authentic solutions of ethyl bromide in dichloromethane. The p.m.r. spectrum indicated that ca. 2 mg (10%) of ethyl bromide was dissolved in the dichloromethane.

Oxidation of 5 with Selenium Dioxide. Formation of Compounds 25, 28, and 29

A mixture of **5** (1.20 g, 5.1 mmoles), selenium dioxide (B.D.H.; 0.74 g, 6.7 mmoles), dioxane (Fisher Certified; freshly refluxed and distilled over sodium; 24 ml), and water (2 ml) was boiled under reflux for 84 h, at the end of which time v.p.c. indicated that very little starting material was present. Aqueous workup gave a bright orange-red solid, which was chromatographed on a column of silica gel (119 g, 29 × 3 cm). Elution with benzene and with benzene containing 1% dichloromethane gave compound **25** (51 mg, 4%); recrystallization from dichloromethane gave red prisms, m.p. 289–289.5°; λ_{max} 5.82 µ; δ 7.1–8.3 (m, 13H) and 8.3–8.8 (m, 3H).

Mol. Wt. Calcd. for $C_{31}H_{16}O_3$: 436. Found: m/e 436.

An authentic sample of 25 was prepared by heating the dione 26 (12) with selenium dioxide in acetic acid as previously described (11). Recrystallization from acetic acid gave red prisms, m.p. $288-289^{\circ}$ [lit. (11) m.p. 284°]. A mixture of this with the red compound obtained from 5 had m.p. $287.5-289.5^{\circ}$; the i.r. spectra of the two samples were identical.

Elution with benzene containing 2% dichloromethane and with dichloromethane gave compound **28**, as yellow platelets (82 mg, 4%); recrystallization from dichloromethane-hexane gave yellow rhomboidal platelets, m.p. 235-236°; λ_{max} 5.97 µ; δ 4.50 (s, 2H), 7.24-7.52 (m, 6H), and 7.84-8.15 (m, 2H).

Anal. Calcd. for $C_{16}H_{10}O_2$ Se (mol. wt. 314): C, 61.37; H, 3.22. Found (*m*/*e* 314): C, 61.56; H, 3.30.

Elution with dichloromethane containing 2% methanol gave 29 as a white solid (954 mg, 70%); recrystallization from dichloromethane-hexane gave small, colorless prisms, m.p. 195.5-198°; λ_{max} (Nujol) 3.06 (m) and 5.94 μ ; λ_{max} (CHCl₃) 2.95 (ms) and 5.89 μ ; δ (CF₃CO₂H) 3.38 (A part of AB signal system, J = 16 Hz, 1H), 3.75 (B part of AB system, J = 16 Hz, 1H), and 6.95-8.1 (m, 8H); the solubility of 29 in deuteriochloroform was too low for the signal due to the hydroxyl protons to be discerned, but signals were seen at δ 3.17 and 3.67 (AB system, J = 16 Hz), and 6.9-7.8 (m).

Anal. Calcd. for $C_{16}H_{12}O_{4}$ ·1/4 $H_{2}O$: C, 70.44; H, 4.62. Found: C, 70.30, 70.08; H, 4.37, 4.34.

Mol. Wt. Calcd. for $C_{16}H_{12}O_4$: 268.0736. Found: m/e 268.0734.

Acetylation of 29. Formation of the Diacetate 30

Compound 29 (5 mg) was dissolved in acetic anhydride (1 ml), and concentrated sulfuric acid (1 drop) was added. The mixture was left at 23° in a stoppered flask for 24 h. Aqueous workup gave a white powder (5 mg), m.p. 197-202°; λ_{max} 5.65, 5.84, 7.34, 7.80, and 8.33 µ; δ 2.13 (s, 3H), 2.25 (s, 3H), 3.17 (A part of AB system, J = 16Hz, 1H), 3.87 (B part of AB system, J = 16 Hz, 1H), 6.9-7.65 (m, 7H), and 7.85-8.1 (m, 1H).

Attempted Dehydration of 29. Formation of 34

Compound 29 melted without decomposition, and

sublimed without decomposition at 150° (10^{-2} mm) as demonstrated by i.r. spectroscopy. When heated at 300° (20 mm) in a Pyrex tube by insertion of the lower part of the tube into a preheated electric furnace, it evolved gas and gave a product that distilled onto the cooler, upper part of the tube. The crude pyrolysate was a pale yellow oil; λ_{max} 2.9 (br, m) and 5.86 $\mu;$ δ 2.9 (br s, 1H, position concentration-dependent), 4.25 (s, 1H), and 7.2-8.1 (m, 8H). The i.r. and n.m.r. spectra of the pyrolysate resembled those of 26 (12); λ_{max} 5.86 μ ; δ 4.40 (s, 2H), and 7.3-8.1 (m, 8H). A solution of 29 (5 mg) and p-toluenesulfonic acid (1 mg) in benzene (30 ml) was boiled under reflux for 72 h under a drying tube in a flask fitted with a Soxhlet extractor containing calcium carbide. The colorless reaction solution was evaporated in a stream of dry nitrogen. The i.r. spectrum of the residue indicated that it was a mixture of 29 and *p*-toluenesulfonic acid.

Compound 29 (2 mg, 0.007 mmole) and dicyclohexylcarbodiimide (2 mg, 0.01 mmole) were dissolved in dichloromethane (0.5 ml) in a Pyrex tube; the tube was sealed, and the mixture was allowed to stand at 23°. After 2 months no change in appearance was noted; in particular, there was no sign of the very insoluble dicyclohexvlurea.

We thank the National Research Council of Canada for generous support of this work. One of us (E. G. L.) gratefully acknowledges the awards of an Alcan Jamaica Independence Overseas Scholarship, a Shell Canada Fellowship, a Special Open University of Toronto Fellowship, and an NRCC Scholarship.

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