Bridged Polycyclic Compounds. LXXVIII. Reaction of Chromyl Chloride with Cyclopropanes[1]

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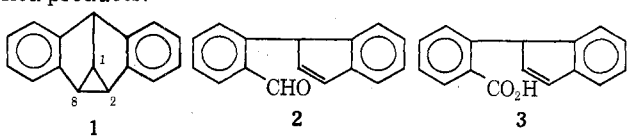
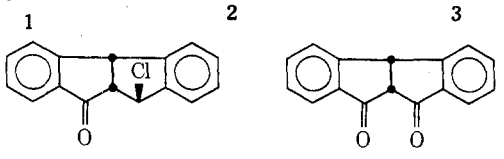
Treatment of 3,6-dibenzotricyclo[3.3.0.0^{2,8}]octadiene (1) with chromyl chloride involves reaction of the cyclopropane ring in the hydrocarbon. The nature of the products depends upon the ratio of reactants and upon the solvent. With limited amounts of chromyl chloride, in carbon tetrachloride, 2-(3-indenyl)benzaldehyde (2) is the principal product, while, in acetone, 8-chloro-3,6-dibenzo-2-bicyclo[3.3.0]octadienone (4) is the principal product. With excess chromyl chloride, in carbon tetrachloride, 2 is not isolated, but 4 and 3,6-dibenzo-2,8-bicyclo[3.3.0]octadienedione (5) are formed in modest amounts; in acetone these are major products. The unconjugated cyclopropane 6,8-dibenzotricyclo[3.2.2.0^{2,4}]nonadiene (11) is substantially less reactive toward chromyl chloride than is 1; reaction under forcing conditions leads to 9,10-anthraquinone. These results are discussed briefly.

Our interest in the stereochemistry and mechanisms of electrophilic additions to cyclopropanes[2] led us to consider whether chromyl chloride might add to cyclopropanes, a reaction which, to the best of our knowledge, has not been reported. This reagent, which is best known for the oxidation of methylarenes to arenecarboxaldehydes,[3] also reacts readily with olefins. Although reactions with terpenes had been studied by Étard[4] and by Henderson[5] with confusing results (mixtures of ketones, aldehydes, and chlorinated compounds, generally of unidentified structures, were observed), it was not until study was carried out[6] with simpler olefins that the reaction course began to become clear. Additions of chromyl chloride in carbon tetrachloride led to α-chlorohydrins of such regioselectivity that it can be assumed that chromyl chloride donates an electrophilic oxygen species and a nucleophilic chloride ion; *i.e.*, the product has the opposite orientation of that of hypochlorous acid addition. Subsequent studies by several groups,[7,8] most notably that of Freeman, have expanded our original findings[6] and have brought this complex system to a new stage of understanding and utility. Thus it is now clear[9] that carbonyl compounds result from hydride or alkide migrations from carbenium-ion intermediates.

3,6-Dibenzotricyclo[3.3.0.0^{2,8}]octadiene (1) has been a useful cyclopropane for our studies[2a] of electrophilic additions, as, in simple additions, the stereochemistry of both electrophilic and nucleophilic attack can be observed, with all additions proceeding with C-2–C-8 bond cleavage. When 1 was treated with chromyl chloride (mole/mole) in carbon tetrachloride at 0°, the reaction occurred as rapidly as the chromyl chloride was added. After 20 min, the reaction was quenched (aqueous sodium bisulfite or zinc). The product mixture was examined by nmr spectroscopy and by isolation. The principal product was shown to be 2-(3′-indenyl)benzaldehyde (2), characterized by spectral properties and by oxidation to 3, accompanied by unreacted 1 and by trace amounts of *anti*-8-chloro-3,6-dibenzo-2-bicyclo[3.3.0]octadienone (4), as well as of other unidentified products.

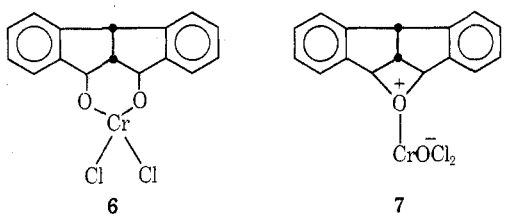


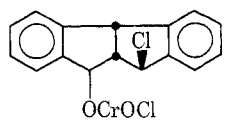


Recently, the reaction of olefins with an excess of chromyl chloride in acetone was reported to give excellent yields of α-chloro ketones.[10] Using this procedure, we obtained three products from 1; the chloro ketone 4 and the diketone 5 were formed in about 30% yield each, with perhaps 5% of 2 indicated by pmr analysis of the product mixture.

The results described above demonstrate that the cyclopropane ring in 1 is sensitive to attack by chromyl chloride. While the formation of 4 demonstrates that at least that portion of attack by nucleophile which gives 4 proceeds with inversion, the formation of 2 or of 4 gives no information regarding the stereochemistry of electrophilic attack. For this reason we decided to try the Sharpless procedure, but without an excess of chromyl chloride, in the hope that chlorohydrins could be obtained. However, when 2.0 mmol of 1 was treated with 0.70 mmol of chromyl chloride in acetone–carbon tetrachloride, no chlorohydrin was obtained, a substantial amount of 1 was recovered, and no diketone 5 was formed. The principal product was the chloro ketone 4.

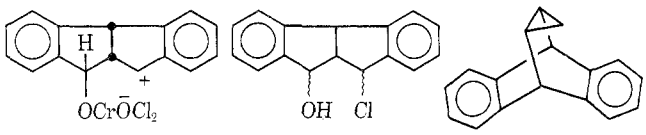
While the facts available do not permit detailed mechanistic considerations, it seems possible to assume that addition of chromyl chloride to 1 gives a 1:1 addition product similar to that with olefins,[11] *e.g.*, 6 or 7, or perhaps the equivalent ion pairs, *i.e.*, species with one or more chloride ions separated. The formation of chloro ketone 4 seems attributable to ring opening of 6 or 7 (or their equivalents) by chloride ion, giving 8, which by further oxidation–reduction is transformed to 4. The benzylic carbon atom in 4 is then oxidized by excess Cr(VI) in acetone to 5. These processes would appear to be the principal modes of reaction in acetone.





In carbon tetrachloride, however, 6 or 7 must be transformed to 9, which by bond migration and cleavage of the oxygen–chromium bond becomes the aldehyde 2. When

excess chromyl chloride is present, **2** is not found (presumably it is further oxidized by excess reagent), and a mixture of at least nine compounds results. We have not attempted the identification of these substances, except for **4** and **5**.



9 **10** **11**

The nature of the products identified in these reactions, and, in particular, the absence of chlorohydrin species **10**, do not permit us to learn anything about the stereochemistry of electrophilic attack,[12] so that our experiments only demonstrate that cyclopropane rings may react with chromyl chloride. **1** is a very reactive cyclopropane, being activated by two benzene rings, and we therefore decided to look at the unconjugated cyclopropane 6,8-dibenzotricyclo[3.2.2.$0^{2,4}$]nonadiene (**11**). It was completely inert to chromyl chloride in 5.5 hr at 0°, and, when treated at room temperature for 5 days, 61% of **11** was recovered and the only reaction product which was found was 9,10-anthraquinone (60% based upon **11** consumed). Clearly in this case the primary reaction products are oxidized more rapidly than is the cyclopropane ring.

Experimental Section

Reaction of 1 with Chromyl Chloride in Carbon Tetrachloride. A solution of 520 mg (2.5 mmol) of **1**[13] in 25 ml of carbon tetrachloride was cooled to 0°. Then 450 mg (2.4 mmol) of chromyl chloride (CrO_2Cl_2) in 3 ml of carbon tetrachloride was added dropwise with stirring and cooling. The solution was stirred at 0° for 20 min, and 40 ml of a 2.3% aqueous solution of sodium bisulfite was added followed by additional stirring for 1 hr at 0°. The solution was diluted with carbon tetrachloride, washed two times with saturated aqueous sodium chloride, and dried over magnesium sulfate and the solvent was removed *in vacuo*. Column chromatography on silica gel eluted with 25% benzene–petroleum ether (bp 60–70°) yielded 210 mg (38%) of 2-(3′-indenyl)benzaldehyde (**2**): pmr ($CDCl_3$) δ 5.86 (1 H, t, H-3), 6.62 (1 H, d, d, H-2), 6.92 (1 H, d, d, H-1), 7.1–8.0 (8 H, m, aromatics), 10.22 (1 H, s, aldehyde H), $J_{2,3}$ = 2, $J_{1,3}$ = 2, $J_{1,2}$ = 5.5 Hz; mol wt (mass spectrum) 220 (calcd, 220).

A second sample of 210 mg of **1** in carbon tetrachloride was treated as above. However, 0.10 g of zinc was added rather than sodium bisulfite to reduce any remaining oxidizing agent. The mixture was stirred for 5 min, then 40 ml of ice water was added and stirring was continued for 20 min. The rest of the work-up was identical with that described above. Pmr analysis of the crude reaction mixture showed essentially the same product composition as above. In some experiments trace amounts of the chloro ketone **4** (see below) were noted.

Reaction of 1 with Excess Chromyl Chloride in Carbon Tetrachloride. A solution of 255 mg (1.25 mmol) of **1** in 12.5 ml of carbon tetrachloride was cooled to 0°. Then 404 mg (2.6 mmol) of chromyl chloride in 8 ml of carbon tetrachloride was added dropwise with stirring and cooling. The solution was stirred at 0° for 20 min, and 250 mg of zinc powder was added. The mixture was stirred for 15 min, then 25 ml of ice water was added and stirring was continued for 30 min. The mixture was red-orange at this point and enough 2.3% aqueous sodium bisulfite was added with stirring to complete the reduction of any remaining oxidizing agent. The mixture was filtered through Celite to break up the thick emulsion and transferred to a separatory funnel. The yellow organic layer was quickly washed with dilute aqueous sodium bisulfite followed by saturated aqueous sodium chloride and dried over anhydrous sodium sulfate. Removal of the solvent *in vacuo* afforded a pink oily residue.

The residue was taken up in a small volume of carbon tetrachloride and precipitated with hexane to give 67 mg (23%) of 3,6-dibenzo-2,8-bicyclo[3.3.0]octadienedione (**5**), mp 256–258° dec (lit.[2a] mp 257–259°).

The mother liquors were concentrated and examined by tlc, which revealed eight additional products, one of which was identified as *exo*-8-chloro-3,6-dibenzo-2-bicyclo[3.3.0]octadienone (**4**) by its R_f value compared with that of an authentic sample.

The complex product mixture was examined further by pmr spectrometry, which confirmed the presence of **4** as the principal component of the mother liquor mixture (see below). **2** was not observed in the mixture, and the remaining products were not identified.

Oxidation of 2 with Jones Reagent. Treatment of **2** with Jones reagent[14] in acetone at 0° gave 2-(3′-indenyl)benzoic acid (**3**), mp 141–142° after several recrystallizations from aqueous ethanol.

Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.33; H, 5.12, mol wt, 236. Found: C, 81.21; H, 5.11, mol wt, 236 (mass spectrum).

Reaction of 3,6-Dibenzotricyclo[3.3.0.$0^{2,8}$]octadiene (1) with Chromyl Chloride in Acetone.[10] A solution of 203 mg (0.9 mmol) of **1** in 15 ml of acetone (distilled from $KMnO_4$) was cooled to −75°. Then 349 mg (2.25 mmol) of chromyl chloride in 3 ml of carbon tetrachloride was added dropwise with cooling and stirring. The solution was stirred at −75° for 90 min and then allowed to come to room temperature for 2 hr. The mixture was poured into an ice-cold solution of 360 mg (3.6 mmol) of sodium bisulfite in 11 ml of water and stirred for 30 min. The mixture was extracted two times with petroleum ether–ethyl acetate (50:50 v/v), washed with water and saturated aqueous sodium chloride, and dried over sodium sulfate. The solvent was removed *in vacuo* to give a solid residue. The residue was taken up in a minimal amount of hot benzene and treated with petroleum ether to give 68 mg (32%) of 3,6-dibenzo-2,8-bicyclo[3.3.0]octadienedione (**5**), mp 255–257°, mol wt, 234 (mass spectrum).

The mother liquors afforded 64 mg (28%) of *exo*-8-chloro-3,6-dibenzo-2-bicyclo[3.3.0]octadienone (**4**): mp 120–121° (lit.[15] mp 120–121.5°) after recrystallization from petroleum ether (bp 30–65°); pmr ($CDCl_3$) δ 3.82 (1 H, d, d, H-1), 5.15 (1 H, d, H-5), 5.8 (1, H, d, H-8), 7.2–8.0 (8 H, m, aromatics), $J_{1,5}$ = 6.5, $J_{1,8}$ = 1.3 Hz.

Reaction of 6,8-Dibenzotricyclo[3.2.2.$0^{2,4}$]nonadiene (11) with Chromyl Chloride in Carbon Tetrachloride. A solution of 273 mg (1.25 mmol) of **11**[16] in 15 ml of carbon tetrachloride was treated with 194 mg (1.25 mmol) of chromyl chloride in carbon tetrachloride at room temperature. The solution was stirred at room temperature for 5 days, poured into 20 ml of 2.3% aqueous sodium bisulfite, and stirred for 1 hr. The aqueous layer was extracted with carbon tetrachloride, the organic phases were combined, dried over magnesium sulfate, and filtered, and solvent was removed *in vacuo*. The residue obtained was placed on preparative-scale tlc plates (E. Merck, silica gel G, 20 × 20 × 0.5 cm) and eluted with benzene–methanol (98:2). Two bands were observed with uv light; the more mobile band afforded 168 mg (61%) of recovered **11**, while the other band gave 60 mg of 9,10-anthraquinone, mp 283° (lit.[17] mp 286°), mol wt (mass spectrum) 208 (calcd, 208).

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Registry No.—**1**, 2199-28-2; **2**, 50546-25-3; **3**, 50415-38-8; **4**, 50415-39-9; **5**, 29746-51-8; **11**, 30122-20-4; 9,10-anthraquinone, 84-65-1; CrO_2Cl_2, 7791-14-2.

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attack with retention. On the other hand, 9 or its epimer could be the first intermediate, leading on the one hand to 2 and on the other to 4.
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Fluorinated Bicyclics. IV.[1] Ionic and Free-Radical Bromination of 5-(Difluoromethylene)-6,6-difluoro-2-norbornene

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Ionic bromination of 5-(difluoromethylene)-6,6-difluoro-2-norbornene (1) in methylene dichloride at 25° gave 1-(bromodifluoromethyl)-3-bromo-7,7-difluorotricyclo[2.2.1.$0^{2,6}$]heptane (2) and 2,7-dibromo-5,5-difluoro-6-(difluoromethylene)norbornane in the ratio of 4:1. In contrast, free-radical bromination gave 29% 2, 22% *exo*-2-bromo-*endo*-3-bromo-5-(difluoromethylene)-6,6-difluoronorbornane, and 49% *exo-cis*-2,3-dibromo-5-(difluoromethylene)-6,6-difluoronorbornane. The nature of the ionic and free-radical intermediates is discussed. Dominant homoallylic participation from the exocyclic difluoromethylene moiety is further support for the stability of α-fluorinated electron-deficient carbon.

Previous investigations from this laboratory have demonstrated the importance of γ-fluorine polar and steric effects on additions to the norbornene double bond.[1-3] In particular, fluorine substituents at the 5,6 positions deactivate the norbornene double bond toward electrophilic addition and only free-radical addition is observed. Furthermore, 5,6-endo fluorine substituents shield the endo side of the system from attack in comparison with norbornene itself.

These studies are extended here to a more complex molecule, 5-(difluoromethylene)-6,6-difluoro-2-norbornene (1).[2] Unlike other fluorinated norbornenes, *e.g.*, 5,5,6,6-tetrafluoro- or 5,5,6-trifluoro-2-norbornene, 1 readily undergoes ionic bromination. The importance of homoallylic participation from the difluoromethylene moiety will be discussed.

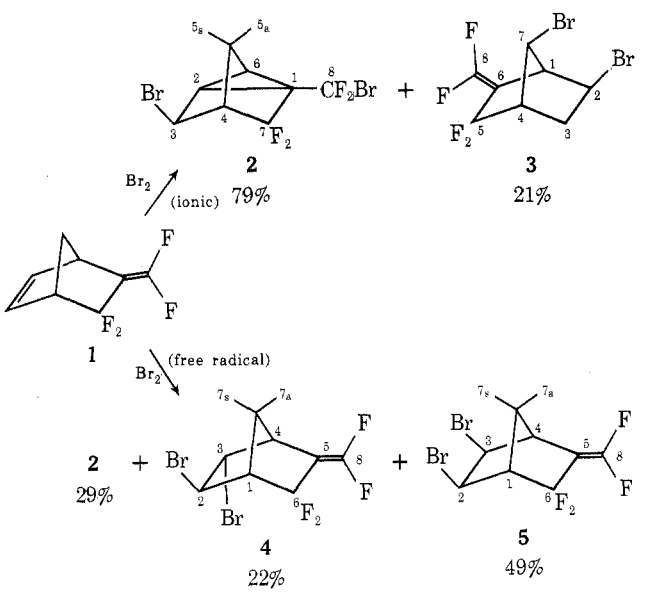
Free-radical bromination of 1 was also investigated. Studies with other methylenenorbornenes have shown that products can arise from initial radical attack at either the exocyclic[4-6] or endocyclic double bond,[7] and homoconjugate addition is often observed.[6] In this regard, the free bromination product distribution was examined and also compared with the ionic addition results.

Results

Olefin 1 rapidly consumed bromine in methylene dichloride solvent in the dark and under oxygen at 25° (ionic conditions) to afford a mixture of 79% 2 and 21% 3 by glpc.

Bromination of 1 under free-radical conditions[2] gave a mixture of 38% 2, 3.5% 3, 18% 4, and 40.5% 5 by glpc and nmr analysis (see Experimental Section). With the assumption that 3 arose only *via* an ionic pathway (*vide infra*), 17% superimposed ionic reaction was present. Correction of the observed results gave a free-radical product distribution of 29% 2, 22% 4, and 49% 5.

The reported dibromides accounted for >98% of the observed products. *No 1,2-dibromides resulting from addition across the difluoromethylene functionality were detected in either the ionic or free-radical reaction.* All dibromides were stable to the reaction and analytical conditions, and the respective product distributions are those of the kinetically controlled addition reactions.



Structural Assignments. The respective dibromide structures were established by ^1H and ^{19}F nmr and ir analyses. Appropriate double-resonance experiments at 100 and 220 MHz allowed for the assignment of long-range couplings. The chemical shift data are presented in Table I.

The dibromide 2 gave a narrow downfield resonance at δ 4.41 for a *single* proton geminal to bromine (Figure 1). The bridgehead proton H_4 appeared at δ 2.46 and the cyclopropane ring protons H_2 and H_6 gave an unresolved singlet at δ 2.21. Irradiation of H_3 revealed a 1.3-Hz coupling with proton H_{5a}. The characteristic ^{19}F AB multiplet of the geminal vinyl fluorines was absent and a narrow triplet ($J_{FF} \cong 4$ Hz) was observed at ϕ 42.0 for the fluorines adjacent to bromine. The absence of a C=CF_2 double bond stretching frequency at 1760–1777 cm^{-1}, which was observed for 1 and 3–5, and the characteristic[8] ir bands observed at 828, 833, and 867 cm^{-1} further confirmed the nortricyclene structure.

The 100-MHz spectrum of dibromide 3 is shown in Figure 2. Irradiation of the upfield protons H_{3x}, H_{3n} at δ 2.63 and 2.70 collapsed the H_2 triplet (J = 6.5 Hz) at δ 4.04 to a broad singlet. Irradiation of the allylic proton H_1 at δ