# Electrophilic Substitution of Dibenz[*b*,*f*]oxepin

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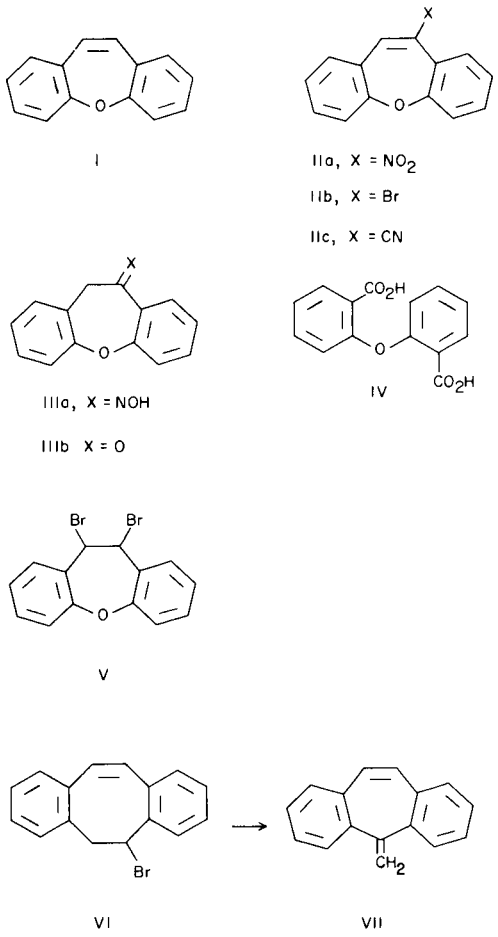
Dibenz[*b*,*f*]oxepin undergoes nitration and acid-catalyzed deuteration at the 10-position and adds bromine across the 10,11 bond. These reactions contradict predictions made by the SCFMO method. Chemical reactions and NMR spectroscopy suggest that dibenz[*b*,*f*]oxepin is only weakly aromatic.

The simplified molecular orbital treatment developed by Dewar (3), on the basis of Wheland's model for the transition state (4), has been very successful in accounting for and predicting the orientation of electrophilic aromatic substitution reactions in alternant polycyclic aromatic hydrocarbons. In particular it correctly predicts the products of nitration of phenanthrene (5), in contradiction of the earlier literature, and it gives the correct sequence of relative reactivities for several hydrocarbons (6). (For a recent review, see (7)). In view of the recent development of the self-consistent field molecular orbital method (SCFMO) (8) and its application to heterocycles, it was of interest to test its predictions by examining novel systems. Dibenz[*b*,*f*]oxepin (I) was well suited for this purpose in that the relative reactivities at the five possible sites for monosubstitution are difficult to predict from classical resonance theory. We now report an investigation of the nitration, bromination and deuteration of dibenz-[*b*,*f*]oxepin.

The nitration of dibenz[*b*,*f*]oxepin gave only one nitro compound, and isomers could not be detected by thin-layer chromatography. The NMR spectrum (see below) suggested that the nitro compound was 10-nitro-dibenz[*b*,*f*]oxepin and this was proved by chemical degradation; oxidation gave diphenyl ether-2,2′-dicarboxylic acid (IV) (9), and successive reduction and hydrolysis gave the oxime (IIIa) and ketone (IIIb).

Dibenz[*b*,*f*]oxepin readily added bromine to give the adduct V. Unlike the corresponding phenanthrene adduct, V was stable to heat but eliminated hydrogen bromide with sodium *t*-butoxide to give 10-bromodibenz[*b*,*f*]-oxepin (IIb). The structure IIb was suggested by the NMR spectrum (see below) but, in view of the known rearrangement of VI to VII (10), rigorous proof was required. This was provided by oxidation to the diacid (IV). Since 10-bromodibenz[*b*,*f*]oxepin was an oil at room temperature, it was characterized as the crystalline nitrile (IIc).

Dibenz[*b*,*f*]oxepin was deuterated by heating with deuterotrifluoroacetic acid in a sealed tube at 100°, a reaction accompanied by the formation of an orange gum. Deuterated dibenz[*b*,*f*]oxepin was readily isolated from the reaction mixture by chromatography; its NMR spectrum in deuteriochloroform solution differed from



that of the starting compound only in the intensity of the 10,11-proton resonance, which was well separated from the complex multiplet due to the 1-4 and 6-9 protons. Integrated peak areas indicated 35% deuteration at C (10). While NMR spectroscopy could detect neither dideuteration at 10,11 nor a very small amount of deuteration at 1-4 and 6.9, the results clearly show that deuteration occurs most rapidly at 10.

NMR Spectroscopy.

The NMR spectrum of dibenz[*b*,*f*]oxepin (1) in carbon disulfide solution showed a complex eight-proton multiplet in the region $\tau$ 2.62-3.07 and a sharp two-proton singlet at $\tau$ 3.39 (3.25, in deuteriochloroform (11)). In the spectrum of 10-methyldibenz[*b*,*f*]oxepin, the singlet was replaced by a one-proton quartet at $\tau$ 3.46 (J = 1.5 c/s) and a three-proton doublet at $\tau$ 7.73 (J = 1.5 c/s), so that the high field singlet in the dibenz[*b*,*f*]oxepin spectrum could be assigned to H (10,11).

In addition to an eight-proton multiplet, the NMR spectrum of the nitrodibenz[*b*,*f*]oxepin showed a one-proton singlet at $\tau$ 2.03. The movement of the singlet at $\tau$ 3.39 to $\tau$ 2.03 and the reduction in intensity by a factor of 2 showed that the $\tau$ 2.03 signal was due to H (11). It followed that nitration had occurred at C(10) and chemical degradation confirmed this deduction. Similar large shifts to low field brought about by an *ortho* nitro group have been observed in many aromatic systems, e.g., benzene (12), naphthalene (13), phenanthrene (14b), and triphenylene (15), and in nitroolefins (16).

The two-proton singlet at $\tau$ 3.39 in the dibenz[*b*,*f*]-oxepin spectrum was absent in the spectrum of the bromo- and cyanodibenzo[*b*,*f*]oxepin, suggesting that they had structures (IIb) and (IIc), respectively. Oxidative degradation established the structure of the bromide as (IIb). For both compounds the H (11) signal was in the aromatic region but for 10-bromodibenz[*b*,*f*]oxepin a sharp one-proton band at $\tau$ 2.76 was tentatively assigned to H (11). Chemical shift data for dibenz[*b*,*f*]oxepin and its derivatives are summarized in Table 1.

Discussion.

The results of the nitration, bromination and deuteration of dibenz[*b*,*f*]oxepin established that electrophilic substitution takes place predominantly at the 10-position. Calculations by Dewar and Gleicher (17) using the Pariser-Parr-Pople method gave the sequence $4 > 2 >> 3 \approx 1 >> 10$ for rates of substitution; by the split p-orbitals method the order was $4 > 2 >> 1 \approx 3 >> 10$. Both sets of calculations predicted that electrophilic substitution should predominate at position 4 so that neither agrees with experiment, further emphasizing the difficulties attending theoretical treatments of heterocyclic systems.

The oxepin ring itself has been shown (18) to be olefinic in character but, in view of recent doubts about the interpretation of chemical shifts in terms of aromaticity especially in polycyclic hydrocarbons (19), it would seem dangerous to conclude from "ring-current" arguments based on the H (10,11) chemical shift alone that dibenz[*b*,*f*]-oxepin is weakly aromatic. However the LCAO bond order ot C (10-11) in dibenz[*b*,*f*]oxepin has been calculated from integrals recommended by Streitweiser (20), to be as high as 0.827, compared with 0.775 for the C (9-10) bond in phenanthrene (21). This high bond-order is consistent both with the coupling constant $J_{CH_3\text{-}H\ (11)}$ of 1.5 c/s for 10-methyldibenz[*b*,*f*]oxepin, compared with values of 1.1 c/s for 9-methylphenanthrene (14a, 22) and 1.7 c/s for propylene (23), and with the observation of a larger deshielding of H (11) by bromine

TABLE I

Chemical Shifts in Dibenz[*b*,*f*]oxepin and its Derivatives

| Compound | Conc. in | Shifts in p.p. m. ($\tau$ Scale) | |
|---|---|---|---|
| | $CS_2$ | H (11) | Aromatic |
| Dibenz[*b*,*f*]oxepin | I.D. | 3.39 | 2.62-3.07 |
| 10-Methyl (b) | 3% w/w (a) | 3.46 | 2.67-3.17 |
| 10-Nitro | I.D. | 2.03 | 2.50-2.92 |
| 10-Bromo | I.D. | 2.76 | 2.25-3.04 |
| 10-Cyano | 3% w/w (c) | 2.73-2.83 | (H(9) 2.38) 2.42-3.08 |

(a) Small sample (b) $\tau_{CH_3} = 7.73$ (c) Sparingly soluble I.D. - infinite dilution

in 10 bromodibenz[*b*,*f*]oxepin (-0.63 ppm.) than in either bromobenzene or 9-bromophenanthrene (14b).

The weakly aromatic character of dibenz[*b*,*f*]oxepin is reflected in its chemical properties, for example in the greater stability of its dibromo adduct (V) compared with that of phenanthrene. Further chemical evidence is provided by the ketone (IIIb) and its oxime (IIIa). Both exist in the ketonic forms, as shown by their infra-red and ultra-violet spectra and particularly clearly by their NMR spectra. In the latter, the H (11) signal in deuteriochloroform solution appears as a two-proton singlet at $\tau$ 6.02 for (IIIb) (c.f. (11)) and at $\tau$ 5.8 for (IIIa).

## EXPERIMENTAL

N.M.R. spectra were recorded on Varian A-60 or A-60A spectrometers and were calibrated against the separation between the resonances of a solution of 2% benzene, 2% TMS in carbon tetrachloride. For dibenz[*b*,*f*]oxepin and its 10-bromo- and nitro derivatives, peak positions were estimated from carbon disulfide solutions in the 2 to 20% w/w concentration range, followed by extrapolation to infinite dilution; for the 10-cyano- and 10-methyl- derivatives, poor solubility and small sample size, respectively, restricted maximum concentrations to 3% w/w.

UV spectra were recorded for solutions in ethanol, using a Beckman DK-2 spectrophotometer. The infrared spectra were recorded using a Beckman IR-9 spectrophotometer. Samples were prepared as Nujol mulls and, in the cases of (IIb) and (IIc), solutions in carbon disulfide and carbon tetrachloride. LCAO computations were carried out on the Bradford University ICT 1909.

Melting points were recorded using an 'Electrothermal' apparatus consisting of a gas-heated block equipped with a thermometer calibrated for stem-exposure. Microanalyses were carried out by Mr. M. J. Graham.

Dibenz[*b*,*f*]oxepin (I) was prepared from 9-xanthylmethanol by dehydration-rearrangement with phosphorous pentoxide (24). The product from large scale preparations was purified by successive chromatography (hexane-alumina), sublimation, and crystallization from ethanol, to give colorless needles (45-55%), m.p. 108-109°. (Lit. m.p. 109-110° (24)).

9-Xanthylmethyl *p*-Toluenesulfonate.

9-Xanthylmethanol was esterfied with *p*-toluenesulfonyl chloride in pyridine. The ester crystallized from hexane as long colorless needles (80%) m.p. 137-138°.

*Anal.* Calcd. for $C_{21}H_{18}O_4S$: C, 68.8; H, 4.95; S, 8.75. Found: C, 68.8; H, 5.03; S, 8.90.

Solvolysis in boiling formic acid gave dibenz[*b*,*f*]oxepin (35-50%) which also required extensive purification.

Dibenz[*b*,*f*]oxepin 2,4,7-Trinitrofluorenone Adduct.

This compound crystallized from acetic acid as brick red micro-needles, m.p. 124-125°.

*Anal.* Calcd. for $C_{27}H_{15}N_3O_8$: C, 63.7; H, 2.97; N, 8.25. Found: C, 63.6; H, 3.24; N, 8.19.

10-Methyl-10,11-dihydrodibenz[*b*,*f*]oxepin-10-ol.

The ketone (IIIb), (9), (0.7 g.) and ethereal lithium methyl gave the alcohol, which crystallized from hexane as massive irregular prisms (0.6 g., 79%), m.p. 133-134°.

*Anal.* Calcd. for $C_{15}H_{14}O_2$: C, 79.6; H, 6.24. Found: C, 79.8; H, 6.32.

10-Methyldibenz[*b*,*f*]oxepin.

The preceding alcohol was dehydrated by boiling under reflux with benzene and a crystal of iodine. Crystallization from methanol gave colorless needles, m.p. 58-59°, identical with a specimen prepared from xanthene (24).

10-Nitrodibenz[*b*,*f*]oxepin (IIa).

Fuming nitric acid (1.5 ml.) in acetic anhydride (5 ml.) was added dropwise to a stirred solution of dibenz[*b*,*f*]oxepin (5 g.) in acetic acid (50 ml.) and alcohol-free chloroform (50 ml.), cooled in an ice-bath. After 1 hour the resulting yellow solution was poured onto ice and extracted three times with methylene chloride. The combined extracts were washed with water and saturated sodium bicarbonate solution, dried over magnesium sulfate and evaporated. Crystallization from ethanol gave the nitro compound (1.32 g., 22%) as bright yellow prisms, m.p. 102-103°.

*Anal.* Calcd. for $C_{14}H_9NO_3$: C, 70.3; H, 3.79; N, 5.86. Found: C, 70.6; H, 3.82; N, 5.83.

The ethanol mother liquors were evaporated and the residue chromatographed from hexane-benzene (1:1) on alumina, giving dibenz[*b*,*f*]oxepin (3.1 g., 62%) and nitro compound (0.34 g., 5.5%). Thin layer chromatography of the crude nitration product and of crystallization fractions gave no evidence for additional nitro compounds.

10,11-Dihydrodibenz[*b*,*f*]oxepin-1-one Oxime (IIIa).

The nitro compound (IIa), (0.2 g.), in ethanol (15 ml.) was warmed with palladized charcoal and a few drops of hydrazine in the usual way (25). At the end of 40 minutes, the yellow color had disappeared. The catalyst was removed by filtration and the filtrate evaporated. Crystallization of the residue from benzene-hexane gave colorless prisms (0.11 g.), m.p. 136-137°.

The identity was established by comparison of infrared and ultraviolet spectra and m.p. and mixed m.p. determinations with an authentic specimen of the oxime (IIIa) (9). The NMR spectrum of a saturated solution in deuteriochloroform showed an eight-proton multiplet at $\tau$ 2.3-3.0, a broad one proton (OH) signal at $\tau$ 1.2 and a sharp two-proton singlet at $\tau$ 5.8 in agreement with structure IIIa. Ultraviolet $\lambda$ max (ethanol) m$\mu$ log $\epsilon$ 290 (3.48), 248 (3.98).

10,11-Dihydrodibenz[*b*,*f*]oxepin-10-one 2′,4′-Dinitrophenylhydrazone.

(a) The 2,4-dinitrophenylhydrazone, prepared from IIIb (9) and Brady's reagent in the usual way, separated from benzene-hexane as small orange needles, m.p. 237-238°.

*Anal.* Calcd. for $C_{20}H_{14}N_4O_5$: C, 61.5; H, 3.62. Found: C, 61.7; H, 3.73.

(b) The nitro compound (IIa), (0.1 g.), was reduced as described above. After removal of the catalyst, the solution was made just acid with dilute hydrochloric acid and warmed for 30 minutes. The solution was diluted and extracted with ether, evaporation of which left an amber oil. Infrared (film) $\nu$ C=O 1680 $cm^{-1}$.

The 2,4-dinitrophenylhydrazone was prepared and purified by chromatography (benzene-alumina), crystallization from benzene-hexane giving orange needles, m.p. and mixed m.p. 237-238°. The identity was confirmed by comparison of the infrared spectra.

10,11-Dibromo-10,11-dihydrodibenz[*b*,*f*]oxepin (V).

Bromine (4 g.) in chloroform (2 ml.) was added dropwise to a stirred solution of dibenz[*b*,*f*]oxepin (5 g.) in chloroform (10 ml.)

and ether (10 ml.) cooled in an ice bath. After 30 minutes the white crystals were collected and recrystallized from acetone-methanol to give rhombohedral plates (5.5 g., 61%), m.p. 152.5-153.5°, and a small quantity of prisms, m.p. 154.5-155°, not depressed when mixed with the plates.

*Anal.* Calcd. for $C_{14}H_{10}Br_2O$: C, 47.5; H, 2.84; Br, 45.1. Found: C, 47.5; H, 2.70; Br, 44.7.

Ultraviolet λ max (ethanol) mμ (log ε) 286.5 (4.50) with a broad shoulder at 250.

The dibromide was stable to at least 200°.

10-Bromodibenz[*b,f*]oxepin (IIb).

Potassium *t*-butoxide (1 g.) in *t*-butyl alcohol (15 ml.) was added to a hot solution of the dibromide (2.4 g.) in *t*-butyl alcohol (200 ml.). Separation of potassium bromide, which began immediately, was completed by warming for 30 minutes. The mixture was poured into water, extracted with ether and the extracts evaporated. The residual oil was distilled in a micro-distillation apparatus to give a colorless oil (1.2 g., 64%), b.p. 205-210°/10 mm.

*Anal.* Calcd. for $C_{14}H_9BrO$: C, 61.6; H, 3.32; Br, 29.3. Found: C, 61.2; H, 3.40; Br, 29.3.

The bromide crystallized below 0°. It formed intensely colored solutions with picric acid, trinitrobenzene, trinitrofluorenone and tetracyanoethylene, but crystalline complexes could not be isolated.

10-Cyanodibenz[*b,f*]oxepin (IIc).

The bromide (IIb), (0.7 g.), was boiled under reflux for 1 hour with cuprous cyanide (0.5 g.), dimethylformamide (3 ml.) and pyridine (1 drop). The mixture was poured into concentrated aqueous ammonia and extracted with methylene chloride. Evaporation of the extracts and crystallization from benzene-hexane gave the nitrile as pale yellow needles, (0.4 g., 71%), m.p. 159-160°. Ultraviolet λ max (ethanol), mμ (log ε); 231 (4.32), 297.5 (4.06) with shoulder at 328 and 330. Infrared (Nujol mull) ν C≡N 2220 $cm^{-1}$.

*Anal.* Calcd. for $C_{15}H_9NO$: C, 82.2; H, 4.14; N, 6.39. Found: C, 82.2; H, 4.27; N, 6.24.

Diphenylether-2,2′-dicarboxylic Acid.

The ketone (IIIb) was oxidized with potassium permanganate in acetone-water. The acid crystallized from acetone-benzene as needles, m.p. 235-237°, (lit. m.p. 231° (9)). The same acid, identified by melting point and mixed melting point determinations and by comparison of infrared spectra, was obtained by oxidizing the nitro and bromo compounds, (IIa) and (IIb).

Deuteration of Dibenz[*b,f*]oxepin.

Dibenz[*b,f*]oxepin (1 g.) and deuterated trifluoroacetic acid (2.5 g.) were heated in a sealed tube for 3 hours at 100°. After cooling, the contents of the tube were dissolved in chloroform, washed with water and the chloroform evaporated. The residue was chromatographed from hexane on alumina. The first fractions contained the deuterated dibenzo[*b,f*]oxepin (0.15 g.), identified by its melting point and infrared spectrum. Further elution with ether-hexane (1:1) gave an orange gum.

The NMR spectrum of the deuterated dibenz[*b,f*]oxepin showed the same bands as the starting compound but with peak areas in the ratio 8 to 1.65 rather than 8 to 2; this corresponds to 35% deuteration at C-10.

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