Mechanisms of Photochemical Reactions in Solution. LVII.[1] The Photorearrangement of 1,4-Epoxy-1,4-dihydronaphthalene to Benz[*f*]oxepin

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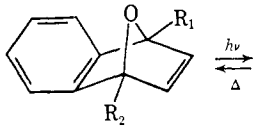
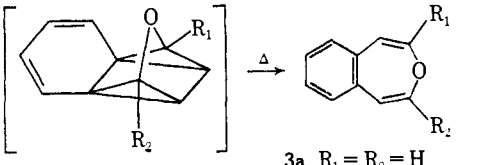
Abstract: The title reaction has been shown to proceed *via* an oxaquadricyclic intermediate. The quantum yield for benz[*f*]oxepin formation is 0.10 ± 0.01. Quenching studies indicate that the benz[*f*]oxepin is formed from an excited singlet state. When the reaction is run under triplet sensitized conditions no benz[*f*]oxepin is formed, instead a cyclobutane dimer and a large amount of polymer are isolated.

We have recently reported the direct photoisomerization at 2537 Å of 1,4-epoxy-1,4-dihydronaphthalene (**1a**) to benz[*f*]oxepin (**3a**)[3] *via* **2**, thus adding another example to the apparently general photoisomerization of norbornadiene analogs to their corresponding quadricyclic compounds.[4] We have studied the details of the direct and sensitized reactions of **1a** and our results are presented here:



1a, $R_1 = R_2 = H$
b, $R_1 = R_2 = D$
c, $R_1 = H$; $R_2 = CH_3$



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3a, $R_1 = R_2 = H$
b, $R_1 = R_2 = D$
c, $R_1 = H$; $R_2 = CH_3$

Results

Direct irradiation at 2537 Å of **1a** in ether, cyclohexane, or absolute ethanol gave **3a** in 4% yield or 6% in sealed degassed tubes. The structure of **3a** was established by comparison of its physical properties with those reported by Dimroth, *et al.* (see Experimental Section). The photolysis of **1b** and **1c** similarly produced **3b** and **3c**.

The quantum yield for formation of **3a** was measured by following the increase in optical density at 445 nm. This technique relies on the fact that no other species present in solution contribute significantly to the optical density at this wavelength. Control experiments have shown this to be the case if analyses are performed immediately after irradiation. We were unable to develop a suitable vapor phase chromatographic analysis because of the similarity in retention times of **1a** and **3a** and because measurements must be made at very low conversions.

Tables I and II present the quantum yields for formation of **3a** as a function of time and starting material concentration. The solvent in all cases was absolute ethanol and excitation was effected by direct absorption of 2537-Å light.

Table I. Quantum Yields for Formation of Benz[*f*]oxepin[a] as a Function of Irradiation Time

Irradiation time, min	Φ[b]
25	0.10 ± 0.01
100	0.08 ± 0.01
200	0.10 ± 0.01
300	0.10 ± 0.01

[a] Concentration of starting material was 0.25 *M*. [b] Average of at least two determinations.

Table II. Quantum Yields for Formation of Benz[*f*]oxepin as a Function of Concentration of Starting Material

[**1a**], *M*	Φ[a]
0.10	0.10 ± 0.01
0.20	0.10 ± 0.01
0.30	0.08 ± 0.01
0.40	0.09 ± 0.01
0.50	0.12 ± 0.01

[a] Average of at least two determinations.

Tables III and IV present data obtained from runs with added cyclohexene and added piperylene.

When a solution of **1a** was irradiated[5] in the presence of sensitizers[6] **3a** was not isolated. Instead an 8%

(1) Part LVI: S. Murov and G. S. Hammond, *J. Phys. Chem.*, **72**, 3797 (1968).
(2) National Institutes of Health Postdoctoral Fellow, 1967–1968.
(3) G. R. Ziegler and G. S. Hammond, *J. Am. Chem. Soc.*, **90**, 513 (1968).
(4) (a) S. J. Cristol and R. L. Snell, *ibid.*, **80**, 1950 (1958); (b) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961); (c) G. S. Hammond, N. J. Turro, and A. Fischer, *J. Am. Chem. Soc.*, **83**, 4674 (1961); (d) H. G. Richey, Jr., and N. C. Buckley, *ibid.*, **85**, 3057 (1963); (e) P. R. Story and S. R. Fahrenholtz, *ibid.*, **86**, 1270 (1964); (f) P. G. Gassman, D. H. Aue, and D. S. Patton, *ibid.*, **86**, 4211 (1964); (g) D. M. Lemal, R. A. Lovald, and R. W. Harrington, *Tetrahedron Letters*, 2779 (1965); (h) H. Tanida, Y. Hata, Y. Matsui, and I. Tanaka, *J. Org. Chem.*, **30**, 2259 (1965); (i) H. Prinzbach, M. Arguelles, and E. Druckrey, *Angew. Chem. Intern. Ed. Engl.*, **5**, 1039 (1966); (j) E. Payo, L. Cortés, J. Mantécon, C. Rivas, and G. de Pinto, *Tetrahedron Letters*, 2415 (1967); (k) H. Prinzbach and J. Rivier, *Angew. Chem. Intern. Ed. Engl.*, **6**, 1068 (1967); (l) H. Prinzbach, M. Arguelles, P. Vogel, and W. Eberbach, *ibid.*, **6**, 1070 (1967); (m) H. Prinzbach and J. Rivier, *Tetrahedron Letters*, 3713 (1967); (n) W. Eberbach and H. Prinzbach, *Helv. Chim. Acta*, **50**, 2490 (1967); (o) H. Prinzbach, *Chimia*, **21**, 194 (1967); (p) H. Prinzbach, P. Vogel, and W. Auge, *ibid.*, **21**, 469 (1967).
(5) A 450-W Hanovia mercury lamp with a Pyrex sleeve was used.
(6) Acetophenone, benzophenone, xanthone, acetone, and triphenylene were used as sensitizers.

Table III. Quantum Yields for Benz[*f*]oxepin Formation in the Presence of Cyclohexene

[Cyclohexene], *M*	Φ^a
0.01	0.10 ± 0.02
0.05	0.10 ± 0.01
0.10	0.10 ± 0.01
0.20	0.09 ± 0.01

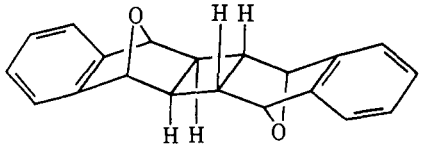
[a] Average of two determinations.

Table IV. Quantum Yields for Benz[*f*]oxepin Formation in the Presence of Piperylene

[Piperylene], *M*	Φ^a
0.00[b]	0.10 ± 0.01
0.0001	0.10 ± 0.01
0.001	0.11 ± 0.01
0.005	0.10 ± 0.01
0.01	0.09 ± 0.01
0.10	0.10 ± 0.01

[a] Average of two determinations. [b] Control tubes.

yield of a dimer, **4**, was formed along with an 80% yield of an intractable material, **5**, having properties suggesting that it is polymeric. The symmetrical nature of the dimer was demonstrated by its nmr



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spectrum consisting of three groups of signals: τ 2.77 (m), 4.78 (s), 7.89 (s) in the ratio of 2:1:1. Since the protons at τ 7.89 (assigned to the cyclobutane ring) appear as a singlet, they must reside in equivalent environments. There are four possible structures: *exo-trans-exo*, *exo-cis-exo*, *endo-trans-endo*, and *endo-cis-endo*. With the aid of a crystal structure determination,[7] dimer **4** was identified as having the *exo-trans-exo* configuration.

Attempts to elucidate the structure of **5** have been unsuccessful. It is sparingly soluble in common solvents, tends to form oils on attempted recrystallization, has only broad nmr resonances and a wide melting point range. Control experiments have shown that no sensitizer units become incorporated into the polymer **5**.

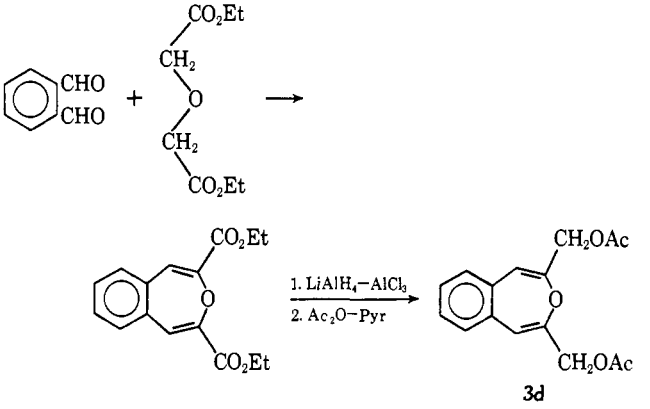
Discussion

Direct irradiation of **1a** produced as the only primary photoproduct **3a**. In order to elucidate the detailed mechanism of this transformation **1b** and **1c** were synthesized and photoisomerized. It is expected that the benz[*f*]oxepins are separated from their arene oxide tautomers by a relatively high energy barrier and that the nmr spectra are due only to the benzoxepin forms. If this is true, the anomalous shifts observed in the spectrum of oxepin itself[8] should not be observed. We therefore assign the downfield portion of the $(AB)_2$ pattern to the α-hydrogens (those adjacent to the oxygen) and the upfield portion to the β hydrogens. The nmr spectra of **3b** and **3c** show the upfield portion to be the larger (see Experimental Section). The spectra thus show that substituents attached to bridgeheads in the starting materials, **1**, appear in the α positions in the benzoxepins, **3**. This skeletal change is easily explained by the mechanistic sequence **1** → **2** → **3** and is difficult to rationalize by any mechanism involving bond breaking and migration of groups by 1,2 shifts.

Since the entire mechanistic argument rests on the interpretation of the nmr spectra in a series of compounds where little literature data are available it seemed wise to obtain confirmatory evidence based on more well-known synthetic reactions. Two alternatives were available to us: (1) prepare **3b** or **3c** by an independent procedure and demonstrate equivalence, or, (2) prepare a previously reported benz[*f*]oxepin by our photoisomerization reaction and demonstrate equivalence. We chose the second alternative.

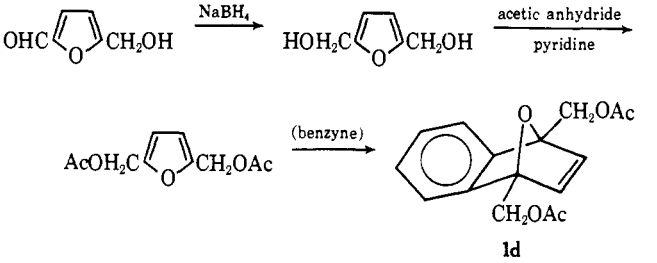
Jorgenson[9] had prepared 1,3-diacetoxymethylbenz[*f*]oxepin (**3d**) by Scheme I. Our task therefore was to

Scheme I



prepare **3d**, by the photoisomerism reaction and show that indeed substituents which originated at the bridgeheads were found in the α positions, thus confirming our nmr interpretation and validating our inferences as to the mechanistic pathway of the rearrangement. Scheme II shows the methed used to prepare the desired starting material, **1d**.

Scheme II



Photolysis of **1d** in absolute ethanol gave a product, **3d**, which was shown to be identical with 1,3-diacetoxymethyl benz[*f*]oxepin prepared by Jorgenson.

Having settled the over-all rearrangement pattern we next turned to the photochemical details of the reaction.

From the data in Tables I and II we see that the quantum yield for formation of **3a** is 0.10 ± 0.01 and

(7) J. Bordner, R. H. Stanford, and R. E. Dickerson, *Acta Cryst.*, in press.

(8) E. Vogel and H. Günther, *Angew. Chem. Intern. Ed. Engl.*, **6**, 385 (1967).

(9) M. J. Jorgenson, *J. Org. Chem.*, **27**, 3224 (1962).

is insensitive to starting material concentration and time over the ranges examined. The data in Tables III and IV indicate that no quenching occurs with cyclohexene or piperylene. Cyclohexene, being a poor quencher, did not behave unexpectedly. At the concentrations used piperylene is known to be a good triplet quencher[10] but only a poor singlet quencher.[11] These results, along with those obtained by sensitization experiments, suggest that in the direct irradiations of **1a** the oxepin, **3a**, is formed from an excited singlet state of **1a** and that direct excitation of **1a** does not lead to any significant yield of triplets. Under the conditions of direct irradiation described here, the oxepins appear to be the only primary photoproducts formed. However, high conversions cannot be obtained because of competitive light absorption by the reaction products, a process which leads to slow photochemical destruction of the benzoxepins.

Attempts to trap the intermediate, **2**, have thus far been unsuccessful. Photolysis of **1a** in the presence of dimethylacetylene dicarboxylate led only to polymeric material. Photolysis of **1a** at 77°K in an absolute ethanol glass followed by immediate crushing in a blender containing dimethylacetylene dicarboxylate gave no reaction. However, when the photolyzed tube was crushed in the presence of TCNE, a vigorous reaction occurred which did not occur with **1a** or **3a** under the same conditions. This suggests the presence of a new species, possibly **2**. It was not possible, however, to isolate a product from the TCNE reaction although several concentrations of TCNE were used. In one experiment the irradiated tube was attached to a vacuum line while still at 77°K and by vacuum line techniques TCNE was admitted to the tube. A reaction did take place but no product could be isolated.

We next ask the question why is the quantum yield for benzoxepin production only 0.10? Two answers seem reasonable. (1) **1a** absorbs the 2537-Å light and is excited to its singlet state which radiationlessly decays back to its ground state 90% of the time (no fluorescence or phosphorescence of **1a** was observed) and goes on to **2** 10% of the time. By analogy to other reactions the conversion of **2** → **3** could rapidly occur thermally.[4] (2) **1a** absorbs the 2537-Å light and is excited to its singlet state which goes on to **2** with high efficiency (say >90%). However the thermal conversion **2** → **3** does not compete favorably with the thermally possible reverse reaction **2** → **1**. Thus the observed quantum yield for production of **3** is low.

While we have no direct evidence in this system to support either choice, one piece of data that lends some support to the second choice is that norbornadiene is converted to quadricyclane with a quantum yield of 0.9 in experiments with acetophenone as a sensitizer.[12]

The sensitized photoreactions of **1a** appear to lead to entirely different products. That this type reaction is occurring *via* the triplet state of **1a** is shown by the fact that **1a** efficiently quenches the phosphorescence of acetophenone. Several exciting wavelengths were used to rule out the role of impurities. We also find that **1a** gives no detectable fluorescence. Benzene and many of its derivatives have easily observable fluorescence. Consequently, we infer that the excited singlet state of **1a** must find some unusually rapid path for nonradiative decay. Although the additional unsaturated center in **1a** could be responsible for catalysis of nonradiative decay without being involved in bond formation, mechanism 2 provides an attractive "chemical" path for nonradiative relaxation.[13]

Dimer formation has analogies in the norbornene and norbornadiene systems.[14] The mechanism of formation of the polymeric material is an open question. Sensitized irradiation of **1a** may lead directly to **5** or may lead to some intermediate which, under the reaction conditions, goes on to polymer. Indeed this intermediate might be benz[*f*]oxepin as it is unstable to the reaction conditions. In a separate experiment, irradiation of a solution of **3a** and xanthone, under conditions where the xanthone absorbs >95% of the light, resulted in disappearance of **3a** with the concurrent formation of polymeric material. These results are consistent with, but do not require, the presence of **3a** as an unstable intermediate in the sensitized irradiation of **1a**.

Experimental Section

Melting and boiling points are uncorrected. Infrared spectra were obtained with a Perkin-Elmer Model 257 spectrophotometer. Ultraviolet spectra were obtained with a Cary 14 spectrophotometer. Nuclear magnetic resonance spectra were taken with a Varian A60A spectrometer. Analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Fluorescence and phosphorescence measurements were made with an Aminco spectrofluorimeter.

Materials. Acetophenone, benzophenone, xanthone, acetone, and triphenylene were purified by distillation or recrystallization before use as sensitizers. Piperylene was distilled from lithium aluminum hydride prior to use. Absolute ethanol was used as commercially available.

Procedures. All quantum yield measurements were run in 12-mm quartz tubes using the merry-go-round apparatus described.[10] After solutions of the proper concentrations had been prepared, 3 ml of each was placed in a tube, and the tubes were degassed three or four times to 5×10^{-4} torr in freeze–thaw cycles and finally sealed *in vacuo*. Duplicate or triplicate tubes were used for all quantum yield determinations. The contents of the tubes were analyzed by measuring the optical densities at 445 nm.

Benzenediazonium-2-carboxylate hydrochloride was prepared by a modification of the method of Friedmann and Logullo.[15] To a magnetically stirred, cold solution of anthranilic acid (55 g, 0.4 mol) in absolute ethanol (600 ml) contained in a 2-l. beaker was added concentrated hydrochloric acid (45 ml) followed by isoamyl nitrite (100 ml). The mixture was stirred for 10 min and ether (600 ml) was added. Stirring was continued for 5 min. The crystals were collected by suction filtration, washed with ether (250 ml), and air dried giving 65 g (87%) of benzenediazonium-2-carboxylate hydrochloride.

Furan-2,5-d_2. Furan (68 g, 1 mol) and a solution of *n*-butyllithium in ether (2 mol in 200 ml) were heated under reflux for 4 hr and then quenched with deuterium oxide (50 ml). Distillation of the mixture afforded an ethereal solution of furan-2,5-d_2 along with some furan-2-*d* and undeuterated furan. The solution had the following nmr: τ 3.75 (singlet, β protons) and 2.65 (multiplet, α protons). The area for the α protons was about 30% of the area for the β protons.

1,4-Epoxy-1,4-dihydronaphthalene (1a) was prepared *via* the reaction of benzyne with furan. Benzenediazonium-2-carboxylate hydrochloride (60 g, 0.32 mol), furan (68 g, excess), propylene oxide (90 g, excess) and 1,2-dichloroethane (2 l.) were heated under reflux

(10) G. S. Hammond, *et al.*, *J. Am. Chem. Soc.*, **86**, 3197 (1964).
(11) L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *ibid.*, **88**, 3665 (1966).
(12) S. Murov and G. S. Hammond, data in ref 1.
(13) A. A. Lamola, G. S. Hammond, and F. B. Mallory, *Photochem. Photobiol.*, **4**, 259 (1965).
(14) D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Am. Chem. Soc.*, **87**, 2596 (1965).
(15) This modification was communicated to Professor A. Streitwieser, Jr., who passed it on to the author: L. Friedman and F. M. Logullo, *J. Am. Chem. Soc.*, **85**, 1549 (1963).

until a clear, maroon solution was obtained. The solution was cooled and filtered. The solvents were removed under reduced pressure (aspirator). The dark red liquid was taken up in ether (*ca.* 150 ml) and washed with ten 1000-ml portions of 1 *N* sodium hydroxide followed by sufficient washings with water to remove the base. Removal of the ether yielded a tan solid. Sublimation of this solid (0.1 mm of Hg, 50°) gave 20 g (44%) of white material, mp 55–56° (lit.[16] 55–56°). Vpc and uv data indicate that the material was free from α-naphthol and of a purity >99.9%. The nmr spectrum of **1a** was as follows: τ 2.6–3.2 (multiplet, six protons) and 4.34 (triplet, J = 1 cps, two bridgehead protons).

1,4-Epoxy-1,4-dihydro-1,4-d_2-naphthalene (1b) was prepared in an analogous manner to the preparation of **1a**. The nmr spectrum was as follows: τ 2.5–3.2 (multiplet) and 4.35 (singlet of low relative intensity).

1-Methyl-1,4-epoxy-1,4-dihydronaphthalene (1c) was prepared from 2-methylfuran and benzenediazonium-2-carboxylate hydrochloride in a manner analogous to the preparation of **1a**. The yield was 47% of material having bp 68–70° (0.5 mm).[16] The nmr spectrum was as follows: τ 2.85–3.5 (multiplet, six protons), 4.75 (doublet, one proton, J = 2 cps), and 2.8–3.6 (singlet, three protons).

Benz[*f*]oxepin (3a). A 2% solution of **1a** in absolute ethanol was placed in a vessel surrounding a quartz immersion well and irradiated for 24 hr with a Hanovia low-pressure mercury resonance lamp. This lamp has 90% of its output at 2537 Å. After irradiation the solvent was removed on a rotary evaporator, and the residue was chromatographed on silica gel or neutral alumina. During chromatography the starting material, **1a**, was converted to α-naphthol and was held tightly on the column. A 5% benzene in petroleum ether (bp 30–60°) mixture eluted the desired benzoxepin. A 6% yield of **3a** was formed. It displayed the following data: mp 80–81°; nmr, τ 3.1–3.5 (multiplet, four protons) and 4.25–5.10 [$(AB)_2$ quartet, four protons, J = 7.5 Hz]; λ_{max}^{EtOH} 445 (ϵ 44) and 415 nm (ϵ 167). These data are in agreement with those reported in the literature.[17]

Benz[*f*]oxepin-2,4-d_2 (3b) was formed as the major product in the direct irradiation of **1b**. Irradiation and purification were carried out as above to give **3b** in comparable yield. The nmr spectrum of **3b** was the same as **3a** except that the downfield portion of the $(AB)_2$ pattern was greatly reduced in area.

2-Methylbenz[*f*]oxepin (3c) was formed in the direct irradiation of **1c**. Irradiation and purification were carried out as above. From 8 g of **1c** 186 mg (2%) of purified **3c** was obtained. It displayed the following physical data; mp 44–45°; nmr, τ 2.85–3.65 (multiplet, four protons), 4.29 (doublet, one proton, J = 7.5 cps), 5.10 (unsymmetrical doublet, two protons), and 8.28 (singlet, three protons); ir, ν_{max} 1050 and 1665 cm^{-1}.

Anal. Calcd for $C_{11}H_{10}O$: C, 83.51; H, 6.37. Found: C, 83.31; H, 6.44.

Dimer 4 was formed in 5–8% yield by the sensitized reaction of **1a**. After irradiation, the polymer formed was removed by filtration; evaporation of the solvent gave a red oil containing some solid. The solid was collected by suction filtration and was washed with acetone to give white crystals identified as **4**. The material did not melt but sublimed at about 300°. The nmr spectrum consisted of three regions: τ 2.70–2.80 (multiplet), 4.78 (singlet), and 7.89 (singlet) in the ratio of 2:1:1.

Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 82.80; H, 5.35.

2,5-Furandimethanol. 5-Hydroxymethylfurfural (10 g, 0.08 mol) in methanol (100 ml containing 2 ml of 0.1 *N* sodium hydoxide) was added to a 300-ml, round-bottomed flask equipped with a reflux condenser. The solution was cooled to 0°, and a solution of sodium borohydride (1.52 g, 0.04 mol) in methanol (50 ml containing 0.5 ml of 0.1 *N* sodium hydroxide) was added over a 10-min period. The mixture was allowed to warm to room temperature and the exothermic reaction kept the solution at reflux for 30 min. After the reaction had ceased the methanol was removed under vacuum and water (20 ml) was added. The water solution was extracted with ether in a continuous liquid–liquid extractor. Evaporation of the ether gave 6 g (60%) of the diol, mp 73–74° (lit.[18] 73–74°); nmr spectrum: τ 3.79 (s), 5.52 (s), and 6.2 (broad s) in the ratio of 1:2:1.

2,5-Furandimethanol Diacetate. 2,5-Furandimethanol (5 g, 0.04 mol), acetic anhydride (15 ml), and pyridine (100 ml) were heated at reflux for 4 hr and cooled, and the mixture was poured onto ice and water. The white precipitate formed was collected by suction filtration giving the diacetate (5 g, 60%), mp 62–63° (lit.[18] 62–64°); nmr spectrum: τ 3.51 (s), 4.93 (s), and 7.90 (s) in the ratio of 1:2:3.

1,4-Epoxy-1,4-dihydro-1,4-diacetoxymethylnaphthalene (1d). Using the method described for the preparation of **1a**, 2,5-furandimethanol diacetate (3 g, 0.014 mol) and benzenediazonium-2-carboxylate hydrochloride (3.5 g, excess) yielded a red oil (1.4 g, 35%). Upon standing for 2 days, crystals formed. The crystals were collected by suction filtration and recrystallized from hexane giving 1,4-epoxy-1,4-dihydro-1,4-acetoxymethylnaphthalene (310 mg, 8%), a white solid, mp 80–80.5°; nmr spectrum: τ 2.9 (multiplet with a singlet inside at 3.02), 5.00 (s), and 7.95 (s) in the ratio of 3:2:3.

Anal. Calcd for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found: C, 66.76; H, 5.59.

1,3-Diacetoxymethylbenz[*f*]oxepin (3d). A sealed, degassed quartz tube containing **1d** (100 mg) in absolute ethanol (3 ml) was taped to the outside wall of a quartz immersion well with a Hanovia low-pressure mercury resonance lamp for 8 hr. The solvent was removed on a rotary evaporatory and the residue was chromatographed in benzene on alumina (activity III). This yielded a yellow oil which when dissolved in petroleum ether and cooled to liquid nitrogen temperature precipitated a white solid which was collected by suction filtration. A second "recrystallization" cycle gave a white solid (5 mg, 5%), mp 36–39° (lit.[9] 45°). The nmr spectrum of this solid was identical to that of 1,3-diacetoxymethylbenz[*f*]oxepin prepared by Jorgenson.[9]

Acknowledgment. The author wishes to express his thanks to Professor George Hammond for his continued interest and enthusiasm in this work. This work was supported by the National Science Foundation.

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