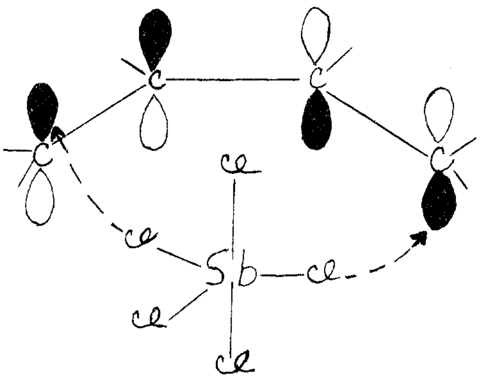

**Figure 1.** Intermediate for the formation of *cis*-1,4-dichlorobutene-2.

Two experiments point to reactant concentration as possible factor in isomer selectivity. The experiment in which the butadiene concentration was relatively high (mole fraction = 0.5) and $SbCl_5$ was added neat indicated relatively low **2**. Another experiment in which the concentration of both reactants were reduced by a factor of 2 relative to normal conditions in Table I had no significant effect on **2**, but the relative amount of **1** increased at the expense of **3**. In both cases, where chlorination occurred in the presence of relatively high concentrations of $SbCl_5$ (*i.e.*, neat $SbCl_5$ addition and reverse mixing of reactants), the isomer selectivity toward **2** was reduced.

The reaction mixture is stable toward isomerization. A sample remained at ambient lab conditions for 4 days with no significant change in the dichlorobutene isomer ratio. The presence of ambient light in the lab had no significant effect. The existence of the dichlorobutene isomers in the reaction mixture was determined by gc retention times relative to known isomer mixtures and verified semiquantitatively by nmr [multiplets at 3.6 and 4.0 ppm characteristic of terminal and allylic $CH_2Cl$ groups in **1** and (**2** + **3**), respectively]. Experiments were performed to demonstrate that alteration of the dichlorobutene isomer ratio does not occur either in the gc or by prolonged exposure to $SbCl_3$, a likely reaction product. The reaction product from one of the chlorinations in $CH_2Cl_2$ was mixed at the 50% level with a solution of known dichlorobutene isomer ratio and analyzed by gc with no significant difference observed. This virtually eliminated the possibility of isomerization catalysis by an unidentified reaction product. Solutions of known isomer ratio were dissolved in $SbCl_3$ + $CH_2Cl_2$ solutions in proportions comparable to those encountered in the chlorination experiments, allowed to stand at room temperature for several hours, and analyzed by gc. No significant change in isomer ratio was observed.

## Experimental Section

Solvents employed were of Spectrograde quality. $CH_2Cl_2$ was supplied by Fischer Scientific Co., $CHCl_3$ and $CCl_4$ by Matheson Coleman and Bell, as was 1,3-butadiene, instrument grade lecture bottle. $SbCl_5$ was supplied by Alpha Inorganic.

Karl Fischer reagent titration, employed to measure the amount of water in 1,3-butadiene and solvents, yielded the following: butadiene, <10 ppm; $CH_2Cl_2$, 39 ppm; $CCl_4$, 27 ppm; and $CHCl_3$, 330 ppm. Gc analysis was as follows: butadiene, 99.97%; $CH_2Cl_2$, 99.9%; $CCl_4$, 98.8%; and $CHCl_3$, 99.0% purity. The reaction system was maintained anhydrous by purging and blanketing with nitrogen having a water content of less than 0.001% by weight.

Conductivity data (Table V) clearly indicate that $SbCl_5$ was essentially anhydrous.

The dichlorobutene isomer equilibrium data[7] (Table IV) were obtained from the following starting mixtures: **1**, 0%; **2**, 5%; **3**, 95%; and from **1**, 95%; **2** and **3** combined 1%; impurities, mainly dichlorobutanes, 4%.

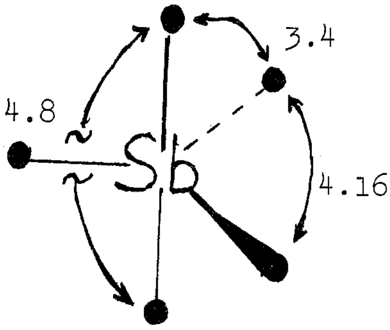

**Figure 2.** Approximate molecular dimensions of $SbCl_5$.

**Registry No.**—Chlorine, 7782-50-5; 1,3-butadiene, 106-99-0; antimony pentachloride, 7647-18-9; *cis*-1,4-dichlorobutene-2, 1476-11-5.

### References and Notes

(1) S. Uemura, O. Sasaki, and M. Okano, *Chem. Commun.*, 1064 (1971).
(2) M. L. Poutsma, *J. Org. Chem.*, **31**, 4167 (1966), and references cited therein.
(3) R. P. Vignes, unpublished data (see Table II).
(4) R. P. Vignes, unpublished data (see Table III).
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# Solvolysis of Xanthenyl and Fluorenyl Ion Pairs in 1,2-Dimethoxyethane

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An ostensibly routine attempt to prepare the xanthenylmethylamine derivative **4** from the corresponding amide **1** by hydride reduction in hot 1,2-dimethoxyethane (DME) led instead to an 83% yield of 9.9-dimethylxanthene (**2**),

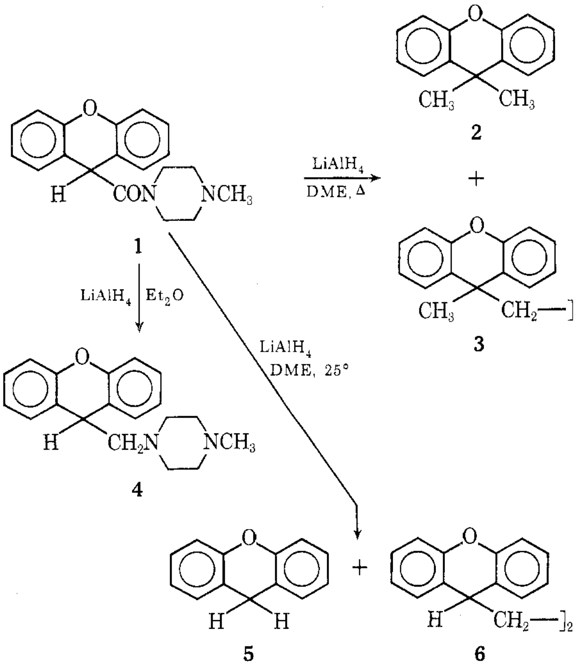
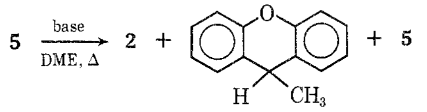


**Table I**
**Reactions of Xanthene with DME + Base**[a]



7

| Base | Mol ratio base:5 | Product composition, %[b] 2 | 7 | 5 |
|---|---|---|---|---|
| $LiAlH_4$ | 2:1 | >90 | 0 | <10 |
| $LiAlH_4$ | 1:1 | 54 | 30 | 16 |
| *n*-BuLi | 1:1 | 26 | 36 | 38 |
| *n*-BuLi | 3:1 | 30 | 40 | 30 |
| NaH | 2:1 | 9 | 13 | 78 |

[a] All reaction mixtures (0.01 mol of 5) were stirred and heated under reflux for 20 hr. [b] Yields of total product were 90–95%.

identical with material prepared[1] by a more conventional method. In contrast, when ethyl ether was used as solvent a nearly quantitative yield of the expected product 4 was obtained. Because a solvent effect of this kind had not been noted previously, a more detailed study was undertaken.[2]

Further investigation of the reaction in hot DME led to the additional isolation of a minor amount (17%) of the di(methylxanthenyl)ethane derivative **3**. With $LiAlD_4$ instead of $LiAlH_4$ neither deuterated nor nondeuterated **3** could be detected. However, 60% of the dimethylxanthene had one (and only one) methyl group completely deuterated. In cold (25°) DME with $LiAlH_4$, neither **2** nor **3** could be detected. Rather, the unmethylated xanthene **5** and the unmethylated dixanthylethane **6** were the only products formed in appreciable quantity. Therefore, attention was turned to the reactions of xanthene itself with various strong bases in hot DME. Results are summarized in Table I.

With xanthene as the starting material neither of the two dimeric compounds (**3**, **6**) could be detected (tlc, nmr) in the reaction mixture. The only observable products (in addition to unreacted xanthene) were monomethylxanthene **7** and dimethylxanthene **2**.

To test the generality of the reaction, fluorene also was treated with $LiAlH_4$ in hot DME. Under conditions that were optimum for dimethylation of xanthene (2:1 mol ratio), fluorene was monomethylated to the extent of only 20%, and barely dimethylated at all (~5%).

In all of the reactions leading to methylated products, the reaction mixtures initially developed deep red colors characteristic of the xanthenyl (or fluorenyl) carbanion. The color (sometimes with green fluorescence) usually persisted throughout the reaction, but was discharged on work-up.

## Discussion

Four items of evidence suggest that the ethylene group in **3** and **6** originates from a reductive dimerization of the amide **1** and not from the ethylene moiety of DME. (1) The dimers are formed only from **1** and not from xanthene (**5**). (2) Dimer **6** is formed from amide **1** even at room temperature. Under these conditions no *obvious* solvent participation in the form of methylation is observed. (3) No 9-(β-methoxyethyl)xanthene is detectable in any of the reactions even though this would be a more likely product than **6** if the ethylene moiety in **6** were indeed derived from the solvent. (4) Although **3** (either deuterated or nondeuterated) was not formed from **1** with $LiAlD_4$ in hot DME, the production of major amounts of trideuterated **2** under these conditions clearly shows that carbonyl reduction does indeed compete with the fragmentation process leading to xanthene (**5**).

Several conclusions are indicated by the data of Table I. The variation in product composition with change in cation strongly suggests the involvement of ion pairs. Furthermore, methylation is best promoted by the cations most able to coordinate with an oxygen atom of DME (*i.e.*, $LiAl^{n+} > Li^+ > Na^+$). The complex cations derived from $LiAlH_4$ assist most efficiently in the removal of the oxygen atom from a solvent methyl group as it is being attacked by the xanthenyl anion. Also, a relatively high order of nucleophilic reactivity seems to be required in the carbanion. The oxygen atom in xanthene destabilizes the corresponding carbanion relative to the fluorenyl anion with the result that, under comparable conditions, the xanthenyl anion is solvolyzed in DME to a much greater extent.

Finally, in view of the well-known[4] tendency of the fluorenyl anion (and presumably xanthenyl also) to form solvent-separated ion pairs in DME, it is tempting to suggest that such species are intimately involved in these solvolyses. They provide, *in the ground state,* the precise ternary system necessary for the "push-pull" mechanism suggested above.[5]

## Experimental Section[7]

**9,9-Dimethylxanthene (2) from 1-Methyl-4-xanthen-9-ylcarbonylpiperazine (1).** To a stirred suspension of $LiAlH_4$ (9.8 g, 0.26 mol) in DME (250 ml) was added dropwise a warm (35–45°) solution of **1** (40.3 g, 0.13 mol)[8] in DME (200 ml). The resulting deep-red solution was stirred and heated under reflux for 18 hr, during which time the color changed to a dark fluorescent green. To the cooled, stirred reaction mixture was added dropwise, successively, 30 ml of $H_2O$, 30 ml of 50% aqueous NaOH, and 30 ml of $H_2O$. The mixture was then stirred and heated under reflux for 0.5 hr and the hot DME solution was decanted from the gelatinous precipitate, which was washed with ether several times by decantation. The combined solutions were concentrated to dryness by distillation and the *neutral* residue (25.8 g) was distilled under reduced pressure to give 22.6 g (83%) of **2**: bp 114–115° (0.6 mm); $n^{25}\text{D}$ 1.5954; ir ($CHCl_3$) 890, 1580, and 1605 $cm^{-1}$; nmr ($CDCl_3$) δ 1.57 (s, 6, $CH_3$), 7.05 (m, 6, ArH), and 7.43 ppm (m, 2, ArH) [lit.[1] ir ($CHCl_3$) 878, 1575, and 1600 $cm^{-1}$; nmr ($CDCl_3$) δ 1.57 (s, 6), 7.02 (m, 6), and 7.47 ppm (m, 2)].

*Anal.* Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71; O, 7.61. Found: C, 85.99; H, 6.65; O, 7.80.

**1-Methyl-4-xanthen-9-ylmethylpiperazine (4) from 1.** When diethyl ether (250 ml) was substituted for DME in the foregoing procedure using 0.03 mol of **1** and heating under reflux for 48 hr, no red color developed, and a quantitative yield of crude basic product, mp 75–78°, was obtained. Recrystallization from hexane gave pure **4** (83% yield), mp 80–81°.

*Anal.* Calcd for $C_{19}H_{22}N_2O$: C, 77.51; H, 7.53; N, 9.52. Found: C, 77.46; H, 7.65; N, 9.46.

Dihydrochloride of **4** had mp 241–242° (from ethanol).

*Anal.* Calcd for $C_{19}H_{24}Cl_2N_2O$: C, 62.13; H, 6.58; N, 7.62. Found: C, 61.91; H, 6.58; N, 7.83.

**1,2-Di(9-methylxanthen-9-yl)ethane (3).** To a stirred suspension of $LiAlH_4$ (0.8 g, 0.02 mol) in DME (20 ml), under an atmosphere of $N_2$, solid **1** (3.08 g, 0.01 mol) was added in one portion. More DME (10 ml) was added and the red solution was stirred and heated under reflux for 22 hr. The reaction mixture was worked up in the usual way, but the neutral product (2.14 g) was not distilled. Rather it was kept in a vacuum oven overnight at 60°, during which time colorless prisms crystallized from the liquid dimethylxanthene (**2**) that constituted the bulk of the total product (1.95 g) as indicated both by tlc and nmr. The crystals were collected at the filter, washed with 95% ethanol, and recrystallized from benzene to give 0.35 g (17%) of pure **3**: mp 163–165°; ir ($CDCl_3$) 1040 (w), 1110 (w), 1270 (s), 1330 (s), 1450 (s), 1470 (s), 1495 (s), 1590 (m), and 1615 $cm^{-1}$ (w); nmr ($CDCl_3$) δ 1.32 (s, 6, $CH_3$), 1.52 (s, 4, $CH_2$), and 7.08 ppm (m, 16, ArH); high-resolution *m/e* of molecular ion, 418.1930 (calcd for $C_{30}H_{26}O_2$, 418.1933).

*Anal.* Calcd for $C_{30}H_{26}O_2$: C, 86.09; H, 6.26. Found: C, 86.34; H, 6.33.

**Xanthene (5) and 1,2-Dixanthen-9-ylethane (6) from 1.** The foregoing procedure was repeated except that the reactants were combined at ice-bath temperature and then stirred at room temperature for 24 hr. The crude product was separated into a glassy basic (0.20 g) and a semisolid neutral (1.44 g) fraction. Trituration of the neutral fraction with pentane followed by successive recrystallizations from cyclohexane (10 ml) and 2-butanone (3 ml) gave 0.10 g of pure **6**: mp 209–211°; ir ($CHCl_3$) 900 (m), 1100 (w), 1125 (w), 1260 (s), 1315 (m), 1465 (s), 1485 (s), 1585 (m), and 1605 $cm^{-1}$ (w); nmr ($CDCl_3$) $\delta$ 1.53 (m, 4, $CH_2$), 3.80 (m, 2, CH), and 7.00 ppm (m, 16, ArH); high-resolution *m/e* of molecular ion, 390.1603 (calcd for $C_{28}H_{22}O_2$, 390.1620).

*Anal.* Calcd for $C_{28}H_{22}O_2$: C, 86.12; H, 5.68. Found: C, 86.17; H, 5.81.

Combined residues (1.2 g) obtained from all mother liquors were dissolved in hot cyclohexane and chromatographed on a silica gel column (15 × 380 mm) using cyclohexane (500 ml) for elution. Concentration of the eluate to dryness in a rotary evaporator gave 0.30 g of white powder, mp 98–99°, identical (mixture melting point, ir, and nmr) with xanthene (**5**).

**Reaction of the Amide 1 with $LiAlD_4$.** When **1** was treated with $LiAlD_4$ in place of $LiAlH_4$ in hot DME exactly as described above for the preparation of **3**, there was obtained 1.93 g (92%) of a crude liquid product from which no solid deposited on standing. The nmr spectrum showed the presence of a single methyl species ($\delta$ 1.57 ppm) corresponding to **2** (no other peaks outside the aromatic region). However, the ratio of aromatic to methyl protons was roughly 2:1 instead of the 4:3 ratio required for pure **2**, suggesting the presence of deuterated material. (Treatment of a sample with excess *n*-BuLi in DME did not give a deep red color, thus eliminating 9,9-dideuterioxanthene as a possible component.) The nmr spectrum of a distilled sample of the product (>90% distillable) was nearly identical with that of the crude material. The pertinent mass spectrum follows: *m/e* (rel intensity) 213 (12), 210 (8), 198 (40), 195 (100). Of these four peaks only *m/e* 210 and 195 appeared in the mass spectrum of pure **2**. Thus, the nmr and mass spectra are uniquely consistent for a mixture composed of 40% **2** and 60% of the analog containing one completely deuterated methyl group.

**Reaction of Xanthene with $LiAlH_4$ in DME.** A 1.82-g (0.01 mol) sample of xanthene (**5**) was treated with $LiAlH_4$ (0.80 g, 0.02 mol) in hot DME in the usual way (20 hr under reflux). Work-up of the deep red reaction mixture gave 1.79 g (86% yield based on **2**) of light yellow oil consisting of >90% of dimethylxanthene **2** (by nmr). No peaks corresponding to **3** or **6** were observable in the nmr spectrum. The only sign of an impurity in the spectrum was a slight integral at 3.97 ppm corresponding to the presence of no more than 5–10% of starting xanthene (**5**).

When the reactants were stirred at room temperature for 20 hr, unchanged xanthene was recovered quantitatively.

When equimolar quantities (0.01 mol each) of the reactants were heated under reflux in DME for 20 hr, the nmr spectrum of the total product (1.86 g), essentially completely distillable in the boiling range of **2**, showed the presence of 9-methylxanthene (**7**) [$\delta$ 1.40 (d, $J$ = 7 Hz, $CH_3$) and 4.01 ppm (q, $J$ = 7 Hz, CH)] in addition to **2** and **5**. From the peak integrations the composition of the mixture could be calculated as 54% **2**, 30% **7**, and 16% **5**. (In a second identical experiment the calculated composition was 55, 29, and 16%, respectively.)

Because 9-methylxanthene is unreported in the literature, further characterization was carried out. A 200-$\mu$g sample of the product mixture was subjected to high-pressure liquid chromatography in a Waters Associates Model ALC 202/401 instrument. A 4 ft × 0.125 in. column packed with $C_{18}$/Corasil was used with 40:60 $CH_3CN-H_2O$ as solvent at a flow rate of 1.0 ml/min. Using ultraviolet (254 nm) detection, three well-resolved peaks were obtained, the first (18.6 min) and the third (30.6 min) corresponding to those observed for pure **5** and **2**, respectively. The eluate corresponding to the middle peak (23.6 min) was collected and the solute was analyzed in the high-resolution mass spectrometer: *m/e* of molecular ion, 196.0859 [calcd for $C_{14}H_{12}O$ (*i.e.*, **7**), 196.0888].

**Reactions of Xanthene with *n*-BuLi and NaH in DME.** Xanthene (0.01 mol) was heated under reflux in DME for 20 hr in the presence of these bases and worked up in the usual way. Product composition was determined by nmr. Results are summarized in Table I.

**Reaction of Fluorene with $LiAlH_4$ in DME.** Treatment of a 0.01-mol sample of fluorene with $LiAlH_4$ (0.02 mol) in hot DME for 23 hr gave an oily solid (93% recovery) whose nmr spectrum ($CDCl_3$) showed peaks for unreacted fluorene [$\delta$ 3.87 ($CH_2$)], 9-methylfluorene [$\delta$ 1.48 (d, $CH_3$, $J$ = 7 Hz) and ~3.88–3.90 ppm (q, half obscured by fluorene peak, CH, $J$ = 7 Hz)] [lit.[9] nmr ($CDCl_3$) $\delta$ 1.48 and 3.90 ppm ($J$ = 7.5 Hz)] and 9,9-dimethylfluorene [$\delta$ 1.45 ppm (s, $CH_3$)] [lit.[1] nmr ($CDCl_3$) $\delta$ 1.45 ppm]. Despite the close proximity of the methyl peaks, the composition of the mixture could be estimated as 75% fluorene, 20% monomethylfluorene, and 5% dimethylfluorene. A sample of the mixture was submitted to high-resolution mass spectral analysis: *m/e* of molecular ions, 166.0773 [calcd for $C_{13}H_{10}$ (fluorene), 166.0782]; 180.0922 [calcd for $C_{14}H_{12}$ (methylfluorene), 180.0939]; 194.1094 [calcd for $C_{15}H_{14}$ (dimethylfluorene), 194.1096]. Peak heights of the molecular ions, respectively, were in the ratio 75:22:3, in essential agreement with the nmr analysis.

**Registry No.—1,** 50507-10-3; **2,** 19814-75-6; **3,** 50507-13-6; **4,** 50507-11-4; 4 dihydrochloride, 50507-12-5; **5,** 92-83-1; **6,** 50507-14-7; **7,** 38731-93-0; fluorene, 86-73-7; 9-methylfluorene, 2523-37-7; 9,9-dimethylfluorene, 4569-45-3.

## References and Notes

(1) J. B. Chazan and G. Ourisson, *Bull. Soc. Chim. Fr.*, 1384 (1968).

(2) During the course of this work, Tomboulian and coworkers[3] reported some unexpected reactions resulting from the fragmentation of tetrahydrofuran in the presence of *n*-butyllithium and trityllithium.

(3) P. Tomboulian, D. Amick, S. Beare, K. Dumke, D. Hart, R. Hites, A. Metzger, and R. Nowak, *J. Org. Chem.*, **38**, 322 (1973).

(4) T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **88**, 307, 318 (1966); M. Szwarc, *Science*, **170** (3953), 23 (1970).

(5) The reactions of the present work are very likely related to those recently reported by Černý and Málek[6] in which diphenylmethane is alkylated by sodium bis(2-alkoxyethoxy)aluminohydrides at relatively high temperatures (140–170°) in aromatic solvents. Here the alkyl groups necessarily derive from the reducing agents rather than from the solvent. Also the more drastic conditions used led to more complex reaction mixtures (*i.e.*, appreciable amounts of a cyclopropane derivative were formed. Products of this type were not detectable in our crude reaction mixtures).

(6) M. Cerný and J. Málek, *Tetrahedron Lett.*, 691 (1972).

(7) Melting and boiling points are uncorrected. Spectra were recorded on a Perkin-Elmer Model 521 ir spectrophotometer, a Varian T-60 nmr spectrometer, and an AEI Model MS902 mass spectrometer. We wish to thank Mr. W. Washburn for the ir spectra, Dr. R. Egan and Mr. M. Cirovic for the nmr spectra, Dr. M. Levenberg, Mrs. S. Mueller and Mr. P. Goodley for the mass spectra, Ms. J. Hood for the microanalyses, and Dr. R. Hasbrouck for the high pressure liquid chromatography.

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(9) A. Mathieu, *Bull. Soc. Chim. Fr.*, 1526 (1971).

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# Photochemical Cycloaddition of Thiobenzophenone to Some Cyclic Polyolefins

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Thiobenzophenone has been found to undergo facile photochemical addition to diverse types of olefins to afford, in some cases, 1:1 adducts (thietanes) and in others 2:1 thione–olefin adducts (1,4-dithianes) depending on the exact structure of the olefinic substrate.[1,2] The factors governing the course of the reaction are both steric and electronic. In the case of 1,3-dienes a third type of reaction course, 1,4 addition of the thioketone to the diene system, is most often observed, with thietanes being found in some instances.[3]

The recent demonstration[4] that the 1:1 photoproduct from benzoquinone and cyclooctatetraene (COT) results from 1,4 rather than 1,2 addition to COT, as had been originally supposed,[5] prompts us to record our observations on the photochemical addition of thiobenzophenone to cyclooctatetraene, 6,6-diphenylfulvene, acenaphthylene, and norbornadiene.