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 ($CDCl_3$) δ 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 (δ 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**) [δ 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-μg 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 [δ 3.87 (CH_2)], 9-methylfluorene [δ 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 ($CDCl_3$) δ 1.48 and 3.90 ppm (J = 7.5 Hz)] and 9,9-dimethylfluorene [δ 1.45 ppm (s, CH_3)] [lit.[1] nmr ($CDCl_3$) δ 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.

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(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).
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(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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Photochemical Cycloaddition of Thiobenzophenone to Some Cyclic Polyolefins

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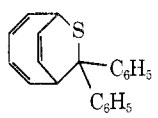
Thiobenzophenone has been found to undergo facile photochemical addition to diverse types of olefins to afford, in some cases, 1:1 adducts (thietanes) and in others 2:1 thione–olefin adducts (1,4-dithianes) depending on the exact structure of the olefinic substrate.[1,2] The factors governing the course 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.

Irradiation of thiobenzophenone (1) with light of ≥340 nm in excess COT gave a single product, the 1,4 adduct **2**, in 58% yield. Its structure was assigned on the basis of spectral and analytical data. Of particular help in deciding between **2** and the isomeric structure **3** was information from the 220-MHz nmr spectrum of the adduct. At this frequency the bridgehead hydrogens appeared as two nonoverlapping apparent triplets of J = 4.2 and 3.6 Hz at τ 5.84 and 5.98, respectively. The lack of mutual coupling seen (and substantiated by appropriate decoupling experiments on **2** and on the corresponding sulfone, **4**)[6] is in accord with structure **2**, in which the two bridgehead hydrogens should both be strongly coupled to the two adjacent vinyl hydrogens, but not with structure **3**, in which the bridgehead hydrogens are on adjacent carbons and have a dihedral angle near 0°, and should therefore be mutually coupled.



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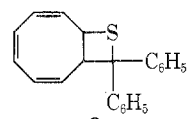

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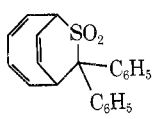

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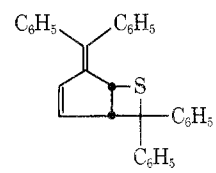
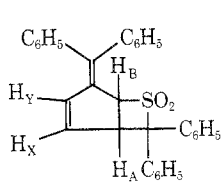
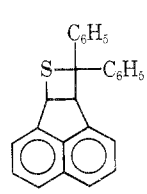


5

Irradiation of **1** with 6,6-diphenylfulvene gave a modest yield of 1:1 adduct, assigned structure **5** on the basis of its uv and nmr spectral properties. The uv absorption maximum (298 nm, ϵ 22,000) is reasonably similar to that exhibited by the parent 3-benzyhydrylidenecyclopentene,[7] but quite different from that expected for a 1,1-diphenylethylene chromophore which would be present in a 1,4-addition product. [For 1,1-diphenylethylene, λ_{max} is 251 nm (ϵ 10,500).] The nmr chemical shifts and splitting constants of the four hydrogens of **5** derived from the fulvene ring system (see Experimental Section) show a strong resemblance to the data reported for the [2 + 2] cycloadduct of dichloroketene and diphenylfulvene.[8] The orientation of **5** is assigned on the basis of the very close correspondence of the couplings between the four aliphatic hydrogens and those of the ketene adducts of diphenylfulvene described in ref 8. The complete parameters were elucidated by means of decoupling experiments on **5** and on the corresponding sulfone, **6**. The orientation of **5** is that predicted by analogy with known reactions of fulvenes with radicals or radical-like reagents which proceed *via* initial attack at the 2 position of the fulvene ring.[9]



6



7

Addition of **1** to acenaphthylene gave a low yield of the expected 1:1 adduct, **7**, identified on the basis of spectral and analytical data. The remainder of the starting compounds were converted to intractable material. No well-defined product could be isolated from irradiated solutions of **1** and norbornadiene.

No reaction was observed when cyclooctatetraene, diphenylfulvene, or acenaphthylene were treated in the dark with solutions of thiobenzophenone. Thus, the products described here are of photochemical, and not thermal, origin. In previous studies of the addition of free radicals and radical-like species to cyclooctatetraene, it has been found that 2-cyano-2-propyl radicals,[10a] N_2O_4,[9c] and N_2F_4[10b] all add in 1,4 fashion. Photoexcited thiobenzophenone can now be added to this list of reagents.

Experimental Section

Infrared spectra were run on a Perkin-Elmer Model 257 instrument and nmr spectra on either a Varian A-60 or HR-220 spectrometer. Mass spectra were obtained at 70 eV on a Consolidated Model 202-1.

Melting points are uncorrected. Irradiations were performed on argon-flushed solutions using light from a Hanovia 450-W medium-pressure mercury arc, filtered through uranium glass (transmits >330 nm).

Photochemical Reaction of Thiobenzophenone (1) with Cyclooctatetraene. A solution of thiobenzophenone (3.3 g, 16 mmol) in freshly distilled cyclooctatetraene (120 ml) was irradiated in the standard manner for 6 hr, during which time the color of the reaction mixture changed from blue-green to deep orange. Excess COT was removed by distillation at reduced pressure [bp 28–34° (8 mm)] and the residue was dissolved in benzene–hexane and cooled to −15°. During 2 days, a total of 2.6 g (58%) of adduct **2** precipitated as a tan solid. Recrystallization of this material from 3:1 hexane–benzene at 0°, keeping the solution under argon, gave pure **2** as off-white needles: mp 162–163.5°; ir (KBr) 1600 (w), 1448 (m), 1495 (m), 758 (s), 740 (s), 700 cm^{-1} (s); nmr ($CDCl_3$, 220 MHz) τ 2.5–2.9 (10 H, m), 4.05 (4 H, m), 4.42 (2 H, m), 5.90 (2 H, 2 t, J = 4.2 and 3.6 Hz); uv max (EtOH) 261 nm (ϵ 4300) and 300 (sh, 1200); mass spectrum m/e (rel intensity) 303 (P + 1, 20), 302 (P, 72), 205 (5), 198 (98), 167 (100), 165 (100), 121 (88), 104 (95), and 91 (82). *Anal.* Calcd for $C_{21}H_{18}S$: C, 83.47; H, 5.96. Found: C, 83.64; H, 5.87.

Oxidation of Sulfide 2 to Sulfone 4. A solution of **2** (0.30 g, 1.0 mmol) and *m*-chloroperbenzoic acid (0.20 g, 1.0 mmol) in methylene chloride (8 ml) was allowed to stand at room temperature for 20 hr. The solution was then washed three times with 10% sodium carbonate solution, followed by two washings with water. After drying of the solution and evaporation of the solvent, the residue was recrystallized from chloroform–hexane to give sulfone **4** as white needles: mp 203–204° (0.22 g, 65%); ir (KBr) 1290 and 1108 cm^{-1}; nmr ($CDCl_3$) τ 2.4–2.8 (10 H, m) 3.8–4.3 (6 H, m), 5.53 (1 H, t, J = 4.5 Hz), 5.99 (1 H, t, J = 3.8 Hz); mass spectrum m/e (rel intensity) 334 (P, 1), 270 (36), 193 (91), 192 (100), 191 (89), 179, (63), and 178 (160).

Photochemical Addition of 1 to 6,6-Diphenylfulvene. A solution of **1** (1.0 g, 5 mmol) and 6,6-diphenylfulvene (2.2 g, 9.5 mmol) in benzene (120 ml) was irradiated under the standard conditions for 5 hr. After evaporation of the solvent, the brownish residue was triturated with hexane–benzene and allowed to stand overnight. Filtration of the slurry gave 1.4 g of tan solid, mp 142–146°. Two recrystallizations of this material from 2:1 hexane–benzene at −5° gave adduct **5** as off-white rhombs: mp 147–148° (1.1 g); uv (EtOH) 298 nm (ϵ 22,100); nmr ($CDCl_3$) τ 2.6–3.0 (20 H, m), 3.54 (1 H, d of m, J = 5.6 Hz), 4.31 (1 H, 2 d, J = 5.6, J' = 3.0 Hz), 5.11 (1 H, m), and 5.55 (d, J = 5.6 Hz); mass spectrum m/e (rel intensity) 428 (P, 0.2), 230 (5), 186 (12), 185 (16), 91 (48), 78 (100). *Anal.* Calcd for $C_{31}H_{24}S$: C, 86.95; H, 5.60. Found: C, 86.90; H, 5.43.

Oxidation of Adduct 5 to Sulfone 6. To a solution of **5** (0.43 g, 1.0 mmol) in methylene chloride (10 ml) was added over 30 min a solution of *m*-chloroperbenzoic acid (85%, 0.40 g, 2 mmol). The reaction mixture was stirred at room temperature for 20 hr, then washed three times with 5% sodium bicarbonate and once with water and dried. Evaporation of the solvent and recrystallization of the residue from chloroform–hexane gave the sulfone **6** as colorless needles: mp 107–108; ir (KBr) 1298 and 1130 cm^{-1}; nmr ($CDCl_3$) τ 2.5–2.8 (20 H, m), 3.38 (1 H, H_Y, 2 d, J = 6.8, J' = 2.0 Hz), 4.03 (1 H, H_X, 2 d, J = 6.8, J' = 0.9 Hz), 4.56 (1 H, H_B, 2 d, J = 7.2, J' = 0.9 Hz), and 5.26 (1 H, H_A, 2 t, J = 7.2, J' = 2.3 Hz). Decoupling led to the following assignments: J_{XY} = 6.8, J_{AY} = −2.0, J_{AX} = 2.3, J_{BX} = 0.9, and J_{AB} = 7.2 Hz. *Anal.* Calcd for $C_{31}H_{24}SO_2$: C, 80.91; H, 5.21. Found: C, 80.60; H, 5.07.

Photochemical Reaction of 1 with Acenaphthylene. A solution of **1** (1.5 g) and acenaphthylene (3.0 g) in benzene (120 ml) was irradiated in the usual fashion for 5 hr. The residue remaining after evaporation of the solvent was chromatographed on a column of activity I alumina (2.0 × 25 cm). Elution with 25% benzene–hexane gave two fractions containing an off-white solid,

which after recrystallization from benzene–hexane gave adduct 7 as white prisms: mp 217–218° (0.18 g, 7%); nmr ($CDCl_3$) τ 2.4–2.9 (16 H, m), 5.5 and 5.7 (2 H, AB, $J \cong 7$ Hz); mass spectrum m/e (rel intensity) 350 (34, P), 317 (20), 239, (27), 198 (19), 152 (100), and 78 (55). *Anal.* Calcd for $C_{25}H_{18}S$: C, 85.74; H, 5.15. Found: C, 85.56; H, 5.31.

Acknowledgments. I am deeply grateful to the following individuals at the National Institutes of Health: Dr. Hermann Ziffer for 220-MHz nmr spectra; Dr. Herman Yeh for decoupling experiments; and Mr. Bill Landis for the mass spectra of the compounds reported.

Registry No.—1, 1450-31-3; 2, 49746-16-9; 4, 49746-17-0; 5, 49746-18-1; 6, 49746-19-2; 7, 49746-20-5; cyclooctatetraene, 629-20-9; 6,6-diphenylfulvene, 2175-90-8; acenaphthylene, 208-96-8.

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Preparation of Benzoate Esters of Tertiary Alcohols by Transesterification[1]

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Standard procedures for esterification are usually not adequate for the synthesis of esters of tertiary alcohols.[2] Although several methods have been developed, they either suffer from lack of generality or present new disadvantages.[3] For example, procedures utilizing such intermediates as acid chlorides[4] or trialkyloxonium salts[5] require additional synthetic and purification steps, with consequent decreases in yield.

The finding that phenyl benzoate readily reacts with potassium 2-propoxide in liquid ammonia to give 2-propyl benzoate in high yield[6] prompted us to investigate the generality of the reaction. It offered promise as a method for the preparation of benzoate esters of tertiary alcohols. Accordingly we did a few experiments, now reported, which demonstrate the practicability of the method.

Operationally, the method involves two steps. First, phenol is converted to the desired benzoic ester through reaction with an appropiate benzoic acid in toluene, catalyzed by boric–sulfuric acid[7] (eq 1). This reaction gives good yields with all the acids so far studied (70–90%).

$$ArCO_2H + PhOH \longrightarrow ArCO_2Ph + H_2O \quad (1)$$

Second, the phenyl benzoate so obtained reacts with the potassium salt of the desired tertiary alcohol in liquid ammonia, giving an alkyl benzoate and potassium phenoxide (eq 2).

$$ArCO_2Ph + RO^- \longrightarrow ArCO_2R + PhO^- \quad (2)$$

Table I
Transesterification of Phenyl Benzoates by Alkoxide Ions in Liquid Ammonia

$ArCO_2Ph$		RO^-K^+		$ArCO_2R$ yield,
Ar	Mmol	R	Mmol	%
C_6H_5	41	*tert*-Butyl	42	91[a]
	35	Isopropyl	39	92[a]
	85	*tert*-Amyl	88	62[a]
	13	*tert*-Amyl	26	86[a]
	75	Isobutyl	90	89[a]
	5	*n*-Butyl[b]	9	90[c]
o-$CH_3OC_6H_4$	5	*tert*-Butyl	10	76[c]
	9	*tert*-Amyl	30	83[c]
3,5-$(NO_2)_2C_6H_3$	6	*tert*-Butyl	13	0[a]
m-ClC_6H_4	8.5	*tert*-Butyl	25	80[c]

[a] Determined by glpc. [b] Potassium *tert*-butoxide (9 mmol) also was present. No *tert*-butyl benzoate was found. [c] Isolated and weighed.

Potassium alkoxides are readily formed *in situ* by the iron-catalyzed reaction of potassium metal with tertiary alcohols in liquid ammonia.[8]

The second step is quite fast, and the conversion is complete in about 45 min. As expected, with primary alcohols the transesterification is even faster, as was demonstrated by an experiment in which equal amounts of primary and tertiary alkoxides were allowed to compete with phenyl benzoate. No tertiary ester was found, but *ca.* 90% of the primary ester was formed. In the cases we have examined the yields of the second step are 80–90%. Results obtained are summarized in Table I.

In the second step, two main factors cause the reaction to proceed in the desired direction. First, the phenoxide anion is a better leaving group (lower pK_a) that any aliphatic alkoxide. Second, potassium phenoxide appears to be less soluble in the reaction medium; we observed that at the end of the reaction a white precipitate is present, presumably potassium phenoxide.

Among others, this method has the advantage that the two operational steps are easy to perform, quickly, and since the solvent is ammonia the product is easily isolated from the reaction mixture. Small-scale preparations are feasible with this method because the reaction is very clean and the corresponding benzamide (2–10%) is the only contaminating product. This impurity is very easy to remove (see Experimental Section).

Substituents such as alkoxy and halogen in the aromatic moiety survive, as probably would also alkyl, aryl, and aryloxy groups. Also, alcohols sensitive to heat or acids would survive under our reaction conditions.

When an attempt was made to utilize phenyl 3,5-dinitrobenzoate in this synthesis, a deep red color was formed immediately after mixing the reagents, probably due to σ-complex formation,[9] and no transesterification product was found.

Experimental Section

Phenyl benzoates were prepared by the method of Lawrence.[7] The structures of the esters were established by melting point, nmr, ir, and agreement of physical constants with published data. Benzoic acids were all commercially available materials. Boiling and melting points are uncorrected. Infrared spectra were recorded on a Beckman IR-8 spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian T-60 spectrometer, using carbon tetrachloride as solvent and TMS as internal standard. Gas chromatographic analyses were performed on an F