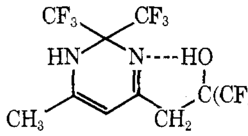
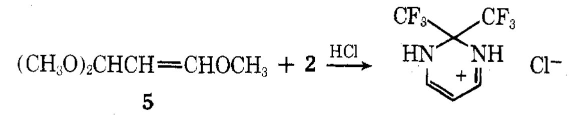


4

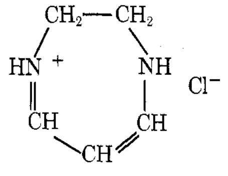
The dihydropyrimidine derivative **6** was prepared from **5** and **2**. This condensation worked well in benzene and hydrogen chloride in contrast to the reaction with acetylacetone, which gave a product that was difficult to purify.



5

6

Compounds **3** and **6** showed violet fluorescence in water and had only one absorption peak at 347 nm (ϵ 5000) and 355 (5000), respectively, in water. They fluoresce blue-violet in water, ethanol, and hexafluoro-2-propranol. The fluorescence maximum of **3** is at 398 nm in ethanol. On excitation with the second harmonic of a Q-switched ruby laser (λ 347 nm), **3** lases efficiently at 408 nm in water. The fluorescence of **3** and **6** is in direct contrast to the behavior of **7**, which shows no fluorescence in water or other solvents. The nonfluorescence of **7** probably is due to the nonplanarity of the molecule.



7

Attempts to prepare the N,N'-dimethyl derivative of **3**, either by methylation of a neutralized solution of **3** with methyl fluorosulfonate or by the condensation of acetylacetone and the N,N'-dimethyl derivative of **2**, were unsuccessful.

Experimental Section

Melting points were determined in a Mel-Temp apparatus and are uncorrected. Ultraviolet spectra were recorded on a Cary 14 spectrometer. Proton spectra were recorded with a Bruker HX-90 instrument and ^{13}C NMR spectra were recorded on a Bruker HX-90 equipped with a Digilab data system at 22.63 MHz. The NMR spectra were run in Me_2SO vs. Me_4Si.

4,6-Dimethyl-2,2-bis(trifluoromethyl)-1,2-dihydropyrimidinium Perchlorate (3). To a solution of 5 g (0.0274 mol) of **2** and 2.74 g (0.0274 mol) of acetylacetone in 25 ml of tetrahydrofuran was added 3.56 g (0.0274 mol) of 70% perchloric acid. The solution was allowed to stand in a 50-ml Erlenmeyer flask until the solvent had evaporated (about 2 weeks). The residue was extracted with 100 ml of hot isopropyl alcohol and filtered hot. The insoluble material (1.5 g) had an ir absorption curve that was identical with that of the perchlorate salt of the diamine **2**. The alcohol solution was evaporated to dryness and the residue was stirred with ether. The white, insoluble crystals of **3** were collected and recrystallized from 1,2,3-trichloropropane: yield 2.9 g; mp 198–200 °C. The ^1H NMR spectrum showed CH_3 (s, 6 H) at δ 2.18, CH (s, 1 H) at δ 5.4, and NH broad at δ 7.2 ppm.

Anal. Calcd for $C_8H_9ClF_6N_2O_4$: C, 27.7; H, 2.6; N, 8.1. Found: C, 27.5; H, 2.5; N, 8.2.

The ether filtrate was evaporated to dryness and the residue was recrystallized from heptane giving 3.2 g of **4**, mp 93–94 °C. The ^1H NMR spectrum showed CH_3 (s, 3 H) at δ 2.18, CH_2 (s, 2 H) at δ 2.98, CH (s, 1 H) at δ 5.05, and NH and OH broad at δ 5.0 and 8.1 ppm. The ^{13}C NMR spectrum showed C_4, 169; C_6, 155.4; CF_3 as two quartets centered at 123.5 and 121.5; C_5, 92.1, COH and C_2, multiplet centered at 76.7; CH_2, 34.0; and CH_3, 18.7 ppm.

Anal. Calcd for $C_{11}H_8F_{12}N_2O$: C, 32.1; H, 1.7; N, 6.8. Found: C, 31.9; H, 1.9; N, 6.8.

2,2-Bis(trifluoromethyl)-1,2-dihydropyrimidinium Chloride (6). Hydrogen chloride was passed through a solution of 5 g of **2** and 3.7 g of 1,3,3-trimethoxy-1-propene in 500 ml of dry benzene for 5 min. After the mixture had stood overnight, the solid was collected and washed with ether: yield 4 g; mp 185 °C dec. The ^{13}C NMR showed C_4 and C_6, 156; CF_3 as a quartet centered at 121; C_5, 91.8; and C_2, as a multiplet at 74.6 ppm.

Anal. Calcd for $C_6H_5ClF_6N_2$: C, 28.3; H, 2.0; N, 11.0. Found: C, 28.6; H, 2.3; N, 11.4.

Acknowledgment. We are grateful for the assistance of Dr. P. M. Henrichs, who interpreted the ^{13}C spectrum of **4** and suggested this structure.

Registry No.—**2,** 1737-80-0; **3,** 59389-77-4; **4,** 59389-78-5; **5,** 17576-35-1; **6,** 59389-79-6; acetylacetone, 123-54-6.

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Photochemical Transformation of 7-Benzoyl-7,8-epoxydibenzobicyclo[2.2.2]octa-2,5-diene

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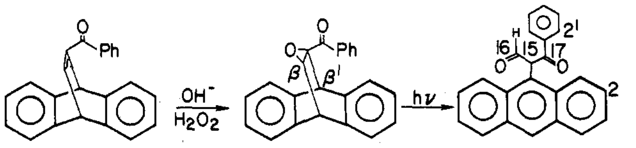
Investigations of a number of α,β-epoxy ketones have demonstrated that these species are exceptionally reactive under the influence of ultraviolet light. It has been shown that irradiation of these compounds may lead to geometrical isomerization, internal hydrogen abstraction, and rearrangement.[1] We have observed a novel, unanticipated photoisomerization of the title compound (**1**) which represents a new diversion in α,β-epoxy ketone rearrangement.

Base-catalyzed epoxidation of 7-benzoyldibenzobicyclo[2.2.2]octatriene[2] with hydrogen peroxide gave the title epoxy ketone (**1**), mp 191–192 °C. Irradiation of a 2% solution of the epoxy ketone **1** in dry benzene in a quartz reactor with unfiltered light from a medium-pressure lamp in a nitrogen atmosphere for 14 h yielded an isomeric (M^+ 324), golden yellow compound, mp 163–165 °C, in about 70% yield.



1

2

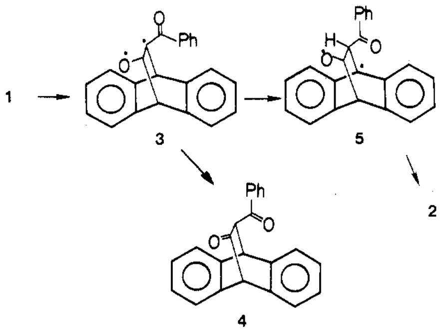
A complex absorption pattern at 1600 cm^{-1} in the infrared indicated an enolizable 1,3-dicarbonyl functionality in the photoproduct.[3] A broad band at 2850 cm^{-1} was suggestive of a possible C–H stretch of an aldehyde group. The electronic spectrum of the photoproduct was very similar to that of a 9-substituted anthracene.[4]

These data led to a tentative formulation of the product as **2**. This was further confirmed by a study of its ^1H and ^{13}C NMR spectra, which were as follows. ^1H NMR (220 MHz, $CDCl_3$) δ 8.64, d, 1 H, $C_{16}H$; 8.40, s, 1 H, $C_{15}H$; 7.45, m, 4 H, H at C_1, C_8, $C_{2'}$, and $C_{6'}$; 7.36, m, 4 H, H at C_{10}, $C_{3'}$, $C_{4'}$, and $C_{5'}$; 7.16, d, 2 H, C_4 H and C_5 H; 7.0, t, 2 H, C_2 H and C_7 H; 6.82, t, 2 H, C_3 H and C_6 H. Addition of D_2O caused sharpening of the doublet at δ 8.64 into a singlet, due apparently to a D_2O exchange with α-H to the carbonyl moieties causing decoupling of the aldehyde proton. Equilibration with water, however, caused broadening of the aldehyde proton. The ^1H NMR spectrum of the photoproduct in Me_2SO showed an apparent upfield shift of the aldehydic proton signal. This solvent effect was of the order of 60 Hz for a dilute sample. The remaining protons remained unaffected.

The ^{13}C NMR spectrum (Me_2SO-d_6) consisted of 191.7 (C_{17}), 164.5 (C_{16}), 138.7 ($C_{1'}$), 130.3 (C_9, $C_{4'}$), 129.5 ($C_{2'} = C_{6'}$), 129.4 ($C_{3'} = C_{5'}$), 128.6 (C_1, C_8), 127.6 ($C_{11} = C_{13}$), 127.3 ($C_{12} = C_{14}$), 125.4 (C_{10}), 125.0 ($C_4 = C_5$), 124.5 ($C_2 = C_7$), 124.1 ($C_3 = C_6$), and 115.0 ppm (C_{15}). The effect of the solvent (Me_2SO) may also be noted in the ^{13}C NMR spectrum where the aldehydic carbon signal appears at approximately −20 Hz from where normally expected. In addition, there is a broadening of the carbonyl C signals.

β-Keto aldehydes are reported to dissolve in Na_2CO_3 solution. The photoproduct (**2**) was allowed to stand with occasional shaking in a Na_2CO_3 solution; dissolution took place slowly.

The observed product (**2**) may arise from the common intermediate (**3**) via **5**. The diradical **3** is formed with a restricted configuration due to the bridge structure which allows for a small degree of rotational freedom thus permitting a higher degree of overlap with the bridgehead hydrogen ($C_{\beta'}$) over the groups at the C_β position. Migration of the bridgehead hydrogen would yield the biradical (**5**) which upon cleavage of the C_β–C_γ bond can rearrange to the observed product. The major driving force to the latter would appear to be the energy gained in the formation of the aromatic nucleus. The alternative of a cleavage of the C_β–C_γ bond *before* migration of the hydrogen at the bridgehead cannot be excluded.



The restricted geometry of the intermediate **3** may also be responsible for the apparent lack of geometrical isomerization and formation of the 1,3-diketone **4** which in turn can lead to **2** and the formation of lactones[5] as secondary photoproducts.

Fragmentation of diketones (α diketones) leading to aromatic nuclei upon irradiation have been reported.[6] Related photorearrangements again leading to aromatic derivatives have been reported by Becker et al.[7] in the photolysis of spiro epoxy substituted 2,4-cyclohexadienone Diels–Alder dimer.

Experimental Section

Melting points were determined in a Thomas-Hoover melting apparatus and are uncorrected. Elemental analysis and molecular weight determinations of the product was done by Galbraith Laboratories Inc., Knoxville, Tenn. Deuterium exchange was carried out in a Varian T-60 (60 MHz), ^1H NMR was obtained in a Varian HR-220 (220 MHz) (Me_4Si was used as internal standard), and ^{13}C NMR was run in a Bruker HFX-10 spectrometer with Me_2SO-d_6 as internal standard. The irradiation source was a Hanovia 450-W medium-pressure mercury arc lamp.

7-Benzoyl-7,8-epoxydibenzobicyclo[2.2.2]octa-2,5-diene (1). The reaction of 7-benzoyldibenzobicyclo[2.2.2]octatriene with hydrogen peroxide in the presence of a base yields epoxy ketone **1:** mass spectrum M^+ 324; ir spectrum 1610, 1450, 1290 cm^{-1}; ^1H NMR δ 3.95, d, 1 H, $J = 5$ Hz, C_8 H; 4.65, d, 1 H, $J = 5$ Hz, C_4 H; 5.2, s, 1 H, C_1 H; 7.1–7.65, m, 11 H, Ar; 7.8–8.1, m, 2 H, ortho protons of –COPh.

Physical Data of Photoproduct 2. Electronic spectrum λ_{max} (pentane) nm (log ϵ) 388 (4.1), 368 (4.12), 349 (4.1), 332 (4.17), 320 (4.2), 254 (5.2), and 220 (4.37); ir spectrum 2850, 1490, 1445, (m, –C═C–), 3060 (w, aromatic C–H), and 735 cm^{-1} (aromatic C–H); mol wt 325 ± 5 (average of two determinations using benzene as solvent); mass spectrum fragmentation pattern *m/e* 324 (M^+), 219 (M − C_6H_5CO), 202 (M − C_6H_5CO − OH), 191 (M − C_6H_5CO − CO), 178 (anthracenyl moiety), 105 (C_6H_5CO), 77 (C_6H_5). Anal. Calcd: C, 85.18; H, 4.94. Found: C, 85.19; H, 4.93.

Registry No.—**1,** 59434-22-9; **2,** 59434-23-0; 7-benzoyldibenzobicyclo[2.2.2]octatriene, 57757-84-3.

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