colorless liquid which decomposed on standing. It could be stored by keeping it in the cold and in the dark.

2-Phenyltetrahydrofuran.—Phenylmagnesium bromide was prepared from 0.75 g of bromobenzene and 0.3 g of magnesium. To the Grignard reagent was added 0.5 g of 2-chlorotetrahydrofuran in ether and the mixture was refluxed for 1 hr. It was then cooled, poured onto ice, and acidified with 5% sulfuric acid. The layers were separated and the ether layer was washed with water and was dried. The ether was removed by distillation, giving 0.9 g of crude product. 2-Phenyltetrahydrofuran was isolated by gas chromatography (silicone rubber, 140°). The nmr spectrum showed absorptions at τ 7.75 (5 H, singlet), 5.19 (1 H, triplet, J = 7 cps), 6.05 (2 H, multiplet), and 8.00 (4 H, multiplet).

2-Benzyltetrahydrofuran.—2-Benzyltetrahydrofuran (**12**) was prepared from 0.86 g of 2-chlorotetrahydrofuran and benzylmagnesium chloride. Isolation of the product as described before gave 1.1 g of crude product. The pure sample was isolated by gas chromatography (silicone, rubber, 120°). The nmr spectrum showed absorptions at τ 2.87 (5 H, singlet), 6.26 (3 H, a broad multiplet), 7.25 (2 H, triplet, J = 5 cps), and 8.28 (4 H, multiplet). Gas chromatography also indicated that small amounts of two other products were present, one of which had the same retention time as biphenyl.

Reaction of 1-Phenyl-1-butanol with LTA.—A mixture of 1.0 g of 1-phenyl-1-butanol, prepared from benzaldehyde and propylmagnesium bromide, 2.94 g of LTA, and 25 ml of benzene was refluxed for 18 hr. The crude product was isolated as described before and distillation through a short-path distillation column gave 0.52 g of product, bp 33–105° (0.2 mm). Gas chromatography (silicone rubber, programmed from 100 to 261°) showed ten components, three of which were identified[11] as benzaldehyde (**16**, 28%) phenyl propyl ketone (**17**, 47%), and 1-phenyl-1-butyl acetate (**18**, 10%).

Reaction of 1-Phenyl-2-pentanol with LTA.—A mixture of 2.67 g of LTA, 1.0 g of 1-phenyl-2-pentanol, and 25 ml of benzene was refluxed for 18 hr. The crude product was distilled through a short-path distillation column, giving 0.41 g of product, bp 32–152° (0.2 mm). Gas chromatography (silicone rubber, programmed from 100 to 261°) showed six components which were identified[11] as benzyl acetate (**19**, 14%), benzyl propyl ketone (**20**, 7%), 1-phenyl-2-pentanol (**15**, 48%), 1-phenyl-2-pentyl acetate (**21**, 22%), 1-phenyl-1-pentyl acetate (**22**, 5%), and 2-(1-phenylpentyl) benzyl ether (**23**, 4%).

2-(1-Phenylpentyl) Benzyl Ether.—A mixture of 0.13 g of sodium, 1.0 g of 1-phenyl-1-pentanol, and 40 ml of benzene was refluxed for 20 hr. It was cooled to room temperature and 0.75 g of benzyl chloride was added. The mixture was then stirred for 5 min and refluxed for 23 hr. After cooling to room temperature, 1.0 ml of methanol was added. This solution was washed with water until the washings were neutral. After drying over anhydrous magnesium sulfate, the benzene was removed by distillation. Gas chromatography (silicone rubber, 175°) indicated the presence of 2-(1-phenylpentyl) benzyl ether as well as some residual starting material. The nmr spectrum had absorptions at τ 2.80 (10 H, singlet), 5.60 (2 H, singlet), 6.42 (1 H, multiplet), 7.22 (2 H, doublet, J = 5 cps), 8.59 (4 H, multiplet), and 9.11 (3 H, multiplet).

10,12-Dihydrocyclohept[*b*]fluorene and Other Derivatives of Cyclohept[*f*]indene[1]

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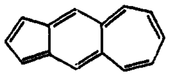
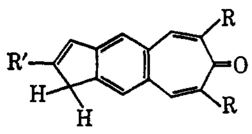
Received June 2, 1967

A synthesis of 10,12-dihydrocyclohept[*b*]fluorene (**9**) and cationic (**10**) and anionic (**12**) derivatives is reported. Delocalization energies, charge densities, and bond orders were calculated for cyclohept[*f*]indene (**1**) and for cyclohept[*b*]fluorene (**4**). The theoretical results suggest that **1** and **4** should have as much aromatic character as azulene, although **4** may have more polyolefinic character. Attempts at formation of **4** by elimination of HBF_4 from **10** or by reaction of **10** with **12** were unsuccessful. The electronic spectra of **10** and **12** are related to those of fluorene and **9** and show significant bathochromic and hypsochromic effects.

In recent years several attempts at synthesis of the cyclohept[*f*]indene (**1**) system have been reported. Derivatives such as **2** and **3** have been prepared by Bertelli[2,3] ($R = C_6H_5$, $R' = H$) and by Bordwell and Winn[4] ($R = CH_3$, $R' = C_6H_5$). Neither ketone displayed any tendency to exist in the enol form, according to nmr and infrared spectra. Furthermore the tropylium salts, **3**, reacted with trimethylamine to produce polymeric material, rather than the fully unsaturated hydrocarbon formed by the elimination of HA.



1



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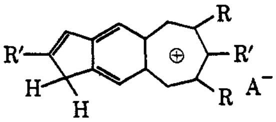
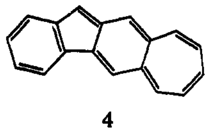


3

This paper is a report on compounds related to a benzo derivative of **1**, cyclohept[*b*]fluorene (**4**).



4

Hückel and SCF Calculations.—In Table I are listed theoretical delocalizations energies (DE's) for **1** and **4**; naphthalene and azulene are included for comparison. The values for DE per electron indicate that **1** and **4** should have at least as much resonance stabilization as azulene, although still less than ordinary benzenoid systems.

The Hückel and self-consistent field (SCF) charge densities and bond orders for azulene, cyclohept[*f*]-indene, and cyclohept[*b*]fluorene are recorded in Tables II–IV. The densities and bond orders of **1** are very similar to those of azulene, a stable nonbenzenoid

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(1) From the Ph.D. Thesis of M. G. G., June 1967.

(2) D. J. Bertelli, *J. Org. Chem.*, **29**, 3032 (1964).

(3) D. J. Bertelli, *ibid.*, **30**, 891 (1965).

(4) F. G. Bordwell and M. Winn, *ibid.*, **32**, 42 (1967).

TABLE I

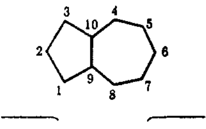
DELOCALIZATION ENERGIES[a,b]

Compound	Empirical RE	Ring strain[b,c] energy	HMO[d] DE	DE per electron
Naphthalene	61	0	61	6.1
Azulene	30–32	16	40	4.0
1	...	22	59	4.2
4	...	25	85	4.7

[a] Delocalization energies were computed according to the Hückel molecular orbital method. All energies are in kcal/mole. [b] A. Streitweiser, Jr. "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 239. [c] Reference 2, and H. J. Dauben, Jr., private communication. [d] $\beta = -16.5$ kcal/mole.

TABLE II

π-ELECTRON DENSITIES AND BOND ORDERS FOR AZULENE[a]

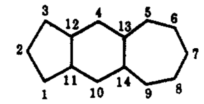


π-Electron density			π-Electron density		
Atom	Huckel	SCF	Bond	Huckel	SCF
1	1.173	1.107	1–2	0.656	0.657
2	1.047	1.004	1–9	0.596	0.611
4	0.855	0.892	4–10	0.586	0 607
5	0.986	1.020	4–5	0.664	0.655
6	0.870	0.924	5–6	0.639	0.645
9	1.027	1.017	9–10	0.401	0.310

[a] All bond distances were taken as 1.39 A and regular polygon angles were assumed. Zero differential overlap was used, the repulsion integrals were computed by means of the Mataga equation (N. Mataga and K. Nishimoto, *Z. Physik. Chem.* (Frankfurt), **13**, 140 (1957)) and core matrix elements were evaluated according to the Pariser–Parr procedure (R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466 (1955); *ibid.*, 767 (1955)).

TABLE III

π-ELECTRON DENSITIES AND BOND ORDERS FOR CYCLOHEPT[*f*]INDENE[a]



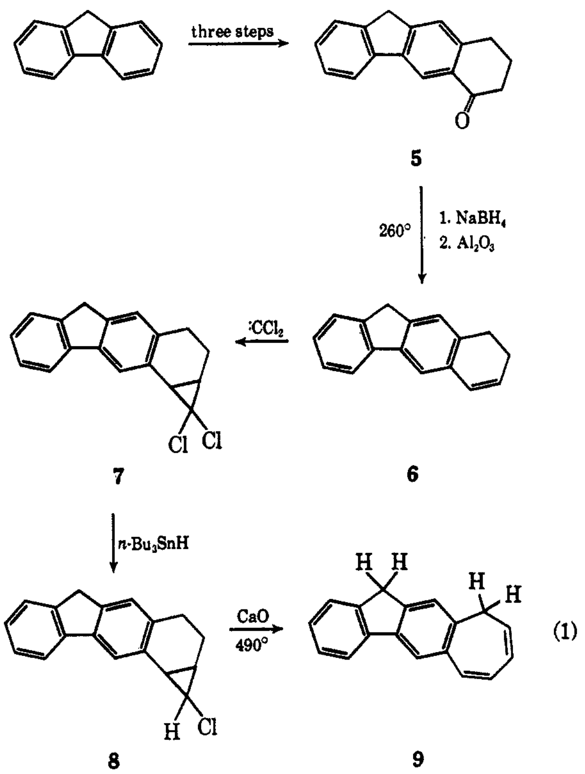
π-Electron density			π-Electron density		
Atom	Huckel	SCF	Bond	Huckel	SCF
1	1.236	1.145	1–2	0.656	0.654
2	1.065	1.006	1–11	0.568	0.599
4	0.995	0.987	4–12	0.603	0.615
5	0.816	0.866	4–13	0.615	0.615
6	0.970	1.024	5–6	0.670	0.652
7	0.825	0.891	5–13	0.555	0.594
11	1.050	1.010	6–7	0.629	0.639
13	0.988	1.020	11–12	0.428	0.325
			13–14	0.426	0.332

[a] See footnote *a*, Table II.

aromatic hydrocarbon. For both molecules the SCF densities tend to be closer to unity than the Hückel densities and the peripheral bond orders tend more to an average 0.62–0.63. This smoothing-out process is an expected consequence of the explicit inclusion of electron-repulsion interactions in the SCF calculations. For **4**, the charge densities are also closer to unity in the SCF treatment, but the bond orders become more alternating. Although the bond orders are still far from pure single or double bond values (0.0 or 1.0), they nevertheless suggest the polyolefinic Kekule structure given for **4**.

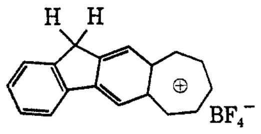
The theoretical predictions for aromatic character for **4**, one based on resonance energy and the other on bond orders and charge densities, are somewhat contradictory. A more satisfactory theoretical study of its chemical stability, as well as that of **1**, probably would be based on localization energies, in which the energies of transition states of reactions the molecule might undergo would be computed.

We had chosen to study the cyclohept[*f*]indene system as a derivative of fluorene for synthetic advantages and also because the additional benzene ring might serve to stabilize the fully unsaturated system, if formed. The synthetic route to the dehydro derivative of **4** is illustrated by equation 1. 10,12-Dihydrocyclohept[*b*]fluorene (**9**) was prepared by an eight-step synthesis from fluorene. The ketone, **5**, was made by succinoylation of fluorene,[5] followed by Clemmenson reduction[5] of the keto acid and ring closure with anhydrous HF.[6] Reduction of the ketone with $NaBH_4$ and vapor-phase dehydration provided



the olefin, **6**. The dichloro compound, **7**, formed by the addition of dichlorocarbene to **6**, was reduced to the monochloride with tri-*n*-butyltin hydride. The hydrocarbon, **9**, was obtained from **7** by pyrolytic ring opening and dehydrohalogenation. Such ring-opening dehydrohalogenation reactions of norcaranes to give seven-membered ring compounds are well known;[7,8] however, the present synthesis appears to be the first example for a 7-chloronorcarene.

Synthesis.—The tropylium salt, **10**, was formed by hydride abstraction with triphenylcarbonium fluoroborate in acetonitrile–carbon tetrachloride solution. The salt precipitated from the solution as small or-



10

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[5] C. F. Koelsch, *J. Am. Chem. Soc.*, **55**, 3885 (1933).

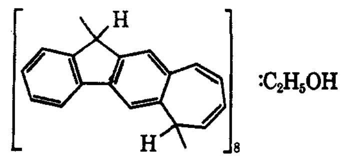
[6] W. C. Lothrop and J. A. Coffman, *ibid.*, **63**, 2564 (1941).

[7] G. C. Robinson, *J. Org. Chem.*, **29**, 3433 (1964).

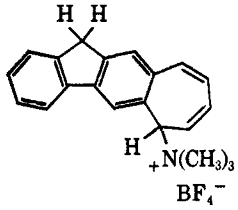
[8] W. E. Parham, D. A. Bolon, and E. E. Schweizer, *J. Am. Chem. Soc.*, **83**, 603 (1961).

ange-red needles, which were very stable and unreactive to atmospheric moisture.

Deprotonation of such tropylium salts with trimethylamine has been shown by Dauben and Bertelli[9,10] to be a valuable synthetic method in heptafulvene chemistry. Application of this method to **10**, however, failed to lead to a monomeric unsaturated hydrocarbon. The reaction of **10** with trimethylamine in chloroform at 0°, in the absence of oxygen, rapidly produced a yellow solution, which slowly precipitated $HN(CH_3)_3BF_4$ with a slight deepening in color. Addition of ethanol to the solution caused the precipitation of a light-colored powder, whose elemental analysis and molecular weight is consistent with an octamer of the type



Formation of such a polymer does not necessarily require the intermediate existence of free **4**. The initial reaction with amine to form a yellow solution, followed by a slow deposition of $HN(CH_3)_3BF_4$, indicates that an adduct of trimethylamine and the tropyium fluoroborate salt is first formed.



A polymerization step involving bimolecular elimination of $HN(CH_3)_3BF_4$ from two such species is easily formulated.

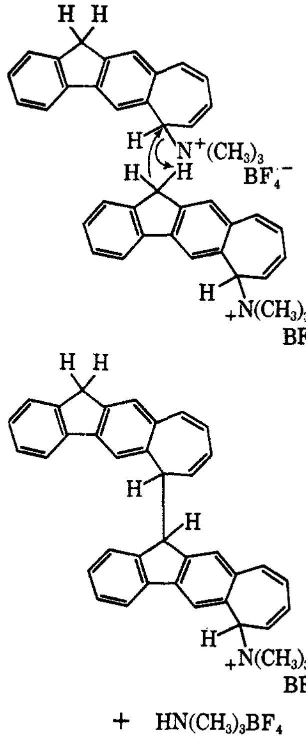
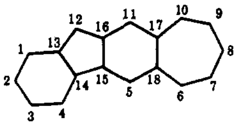


TABLE IV

π-ELECTRON DENSITIES AND BOND ORDERS FOR CYCLOHEPT[*f*]INDENE[a]



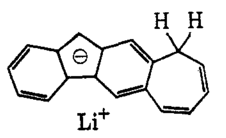
Atom	π-Electron density Huckel	SCF	Bond	π-Electron density Huckel	SCF
1	1.053	1.016	1–2	0.709	0.702
2	1.011	1.005	1–13	0.560	0.581
3	1.068	1.037	2–3	0.615	0.625
4	0.993	0.996	3–4	0.694	0.692
5	0.962	0.979	4–14	0.596	0.603
6	0.831	0.918	5–15	0.661	0.735
7	0.963	0.999	5–18	0.576	0.509
8	0.838	0.923	6–7	0.646	0.565
9	0.963	1.012	6–18	0.582	0.672
10	0.831	0.892	7–8	0.652	0.725
11	1.050	1.034	8–9	0.607	0.540
12	1.290	1.126	9–10	0.693	0.752
13	1.033	0.995	10–17	0.530	0.473
14	1.099	1.065	11–16	0.572	0.495
15	1.032	0.967	11–17	0.636	0.718
16	1.028	1.026	12–13	0.551	0.479
17	0.979	1.033	12–16	0.604	0.710
18	0.978	0.977	13–14	0.506	0.546
			14–15	0.462	0.408
			15–16	0.437	0.367
			17–18	0.433	0.362

[a] See footnote *a*, Table II.

A similar polymer would be expected from self-polymerization of free **4**, perhaps initiated by nucleophilic addition of amine. In both cases, ethanolysis of the product should result in addition of one molecule of ethanol to each polymer molecule and elimination of any amine. The yield of $HN(CH_3)_3BF_4$ (63%) suggests that a significant amount of the inorganic salt remained with the polymer; for an octamer, 12.5% should remain, according to the simultaneous elimination–polymerization mechanism.

These results are in substantial agreement with the findings of Bertelli,[3] and Bordwell and Winn,[4] for other derivatives of the 1H-cyclohept[*f*]indenium system. It appears that the cyclohept[*b*]fluorene system is a high-energy species relative to the amine–tropylium adduct, as seen in the rapid formation and slow decomposition of the adduct, and also high in energy relative to the polymer, as shown by the formation of polymer. These deductions make use of the reasonable assumption that the products of such reactions are energetically similar to the transition states.

Reaction of **9** with *n*-butyllithium in tetrahydrofuran (THF) gave a deep red solution of the lithium salt (**12**). Addition of heptane to the THF solution



12

caused precipitation of an amorphous, deep red solid. The solid was collected and placed under vacuum for several hours. The resultant powder had a neutralization equivalent of 343, corresponding to a complex having the ratio $THF:C_{18}H_{13}Li$ of 1.48:1. Similar

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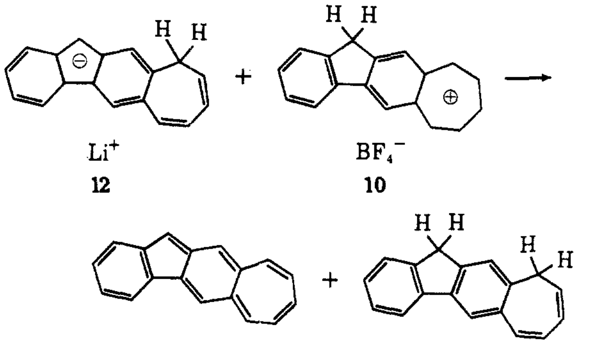
[9] H. J. Dauben and D. J. Bertelli, *J. Am. Chem. Soc.*, **83**, 4659 (1961).

[10] D. J. Bertelli and C. C. Ong, *ibid.*, **87**, 3719 (1965).

THF:RLi ratios have been reported for fluorenyllithium,[11] and the amount of THF in the complex was a function of the vacuum used in removing the solvent.

A reaction of the cation **10** with the anion **12** was carried out with the hope of effecting an elimination reaction to produce **4** (eq 2). The reaction could proceed by hydride abstraction by the cation or proton abstraction by the anion. Either route should afford one molecule of **9** for each of **4**. In an inert atmosphere, in THF, at room temperature or −60°, the reaction proceeded with rapid formation of a yellow solution. Nmr spectra of the reaction mixture, or of the residue, obtained by evaporation of the THF, and re-solution in deuteriochloroform, showed only peaks similar to the dihydro compound **9**. However, an attempt at sublimation of the reaction product under conditions at which **9** is known to sublime produced no trace of sublimate. Apparently a simple acid–base addition reaction had occurred between **10** and **12**.



12 **10** **4** **9** (2)

This result is additional confirmation for the lack of tendency for derivatives of cyclohept[*f*]fluorene to undergo simple elimination reactions which would lead to the fully conjugated nonbenzenoid system. The body of experimental information which purports to illustrate the instability of **1** is at present in conflict with theoretical predictions for this system. This conflict will hopefully be resolved as more complete theoretical treatments become available.

Ultraviolet and Visible Spectra.—In Table V are listed the ultraviolet and visible absorptions for 10,12-dihydrocyclohept[*b*]fluorene, some of the synthesis intermediates, and the cationic and anionic derivatives. These compounds form a group whose members are closely related to the fluorene π-electron system. Since the members differ principally in degree of extension of the fluorene unsaturated system, they form a "variconjugate sequence"[12] and accordingly should have closely related electronic spectra. In particular, the spectrum of the dichloro compound **7** is very similar to that of fluorene, and the band assignments and nomenclature of Platt[12] may be directly applied.

The effect of addition of a conjugated double bond to the fluorene system can be seen in the spectrum of the dihydrobenzofluorene **6**. The ^1L_b band is only slightly effected, but the short-wavelength bands are considerably enhanced, in agreement with the assigned longitudinal polarization of these transitions. Generally such extension of conjugation will also shift the band to a longer wavelength; however, in this case the ^1L_a band is moved to shorter wavelength by 10 mμ. In **9** increased conjugation has led to substantial bathochromic shifts for the ^1B_b and ^1L_a bands. The ^1L_a band is now quite broad and apparently has buried the ^1L_b band. Models show that the seven-membered ring is far from planar, which may account for the lack of intensification of the bands.

The ions show the most dramatic changes. In the cation **10** both the ^1B_b and ^1L_a bands shifted to longer wavelengths, and the intensification of both bands due to the large longitudinal dipole results in the strongest bands of the series. The intensity of the ^1L_b band is relatively unaffected but its position is shifted into the violet portion of the visible spectrum giving rise to the orange color of the cation. In the anion **17** the charge is more centrally located and produces a smaller dipole, and consequently the short-wavelength bands are reduced in intensity relative to the cation. The long-wavelength band, although reduced in intensity, now absorbs in the green and accounts for the blood-red color of the anion.

TABLE V
ELECTRONIC SPECTRA OF
10,12-DIHYDROCYCLOHEPT[*b*]FLUORENE
AND RELATED COMPOUNDS

	Transition[a,b]		
Compound	$^1B_b \leftarrow {}^1A$	$^1L_a \leftarrow {}^1A$	$^1L_b \leftarrow {}^1A$
Fluorene[c]	222	263	289,294,300
	(19,000)	(20,000)	(10,000)
7[d]	235	267	298,303,310
	(21,000)	(20,000)	(11,000)
6[d]	247	256	282,287,300,313,326
	(31,000)	(40,000)	(8,700)
9[d]	253	321	
	(19,000)	(21,000)	
10[d]	269	333	398,480
	(34,000)	(50,000)	(8,100)
12[e]	254	337	458,503,535
	(20,000)	(33,000)	(4,300)

[a] The notation for the excited states is that of Platt.[12] [b] The transition energies λ_{max}, are given in millimicrons and the number in parentheses is the extinction coefficient. For the ^1L_b band, the peaks due to vibrational structure are given and the extinction coefficient is that for the peak at longest wavelength. [c] R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951; the solvent is 95% ethanol. [d] In acetonitrile. [e] In tetrahydrofuran.

Experimental Section[13]

6,7,8,9-Tetrahydro-6-hydroxy-11H-benzo[*b*]fluorene (13) from 5.—A solution of 72 g (0.31 mole) of **5** and 17 g (0.45 mole) of sodium borohydride in 3200 ml of absolute ethanol was refluxed for 6 hr. After cooling to room temperature, the solution was poured into 7 l. of water and filtered to give 65.2 g (90%) of colorless plates, mp 132–134° (ethanol).

Anal. Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.83. Found: C, 86.65; H, 6.88.

8,9-Dihydro-11H-benzo[*b*]fluorene (6) from 13.—Sixty grams (0.25 mole) of **13** was distilled at 0.1 mm nitrogen pressure over a period of 1 hr through a 19-mm diameter tube containing 26 g of $^1/_8$-in. pellets of alumina, heated to 265°. The colorless

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[11] J. A. Dixon, P. A. Gwinner, and D. C. Lini, *J. Am. Chem. Soc.*, **87**, 1379 (1965).

[12] J. R. Platt, *J. Chem. Phys.*, **19**, 101 (1951).

[13] Melting points were determined with a Nalge hot-stage microscope and are corrected. The ultraviolet spectra were recorded by a Cary Model 15 recording spectrometer. Nmr spectra were obtained at 60 or 100 Mc on a Varian Model A-60 or HA-100 spectrometer. Peak positions are reported in parts per million downfield from internal tetramethylsilane. Elemental analyses were performed by Midwest Microlab, Inc., Indianapolis, Ind.

distillate was recrystallized from absolute ethanol, giving 48.6 g (89%) of white plates, mp 151–154°.

Anal. Calcd for $C_{17}H_{14}$: C, 93.54; H, 6.47. Found: C, 93.70; H, 6.33.

1,1-Dichloro-1a,2,3,5,10b-pentahydro-1H-cyclopropa[*l*]benzo-[*b*]fluorene (7) from 6.—A mixture of 25 g (0.11 mole) of **6**, 21 g (0.39 mole) of sodium methoxide, 525 ml of benzene, and 90 ml of pentane, in a nitrogen atmosphere, was cooled to 0°. To the stirred mixture was added 43 ml (0.31 mole) of ethyl trichloroacetate over a period of 1 hr.[14] After stirring for 5 hr at 0°, the orange benzene solution was decanted from the inorganic salts, washed with water, and dried over magnesium sulfate. After filtration and evaporation on a steam bath, the carbonic esters were removed by evacuation at 0.05 mm in a vacuum desiccator. Sublimation of the tan powder at 130° (0.01 mm), followed by recrystallization from ethanol, gave 24.0 g (73%) of white plates, mp 138–140°. The nmr spectrum in deuteriochloroform showed three sets of protons: (1) the five-membered ring protons give a singlet at 3.72; (2) the two protons at the 3 position give a triplet, centered at 2.68 (J = 0.09 ppm), and superimposed on this triplet is a singlet at 2.65 due to the 10b proton; and (3) from 1.8 to 2.3 is a complex multiplet due to the protons at the 1a and 2 positions.

Anal. Calcd for $C_{18}H_{14}Cl_2$: Cl, 23.59. Found: Cl, 23.55.

1-Chloro-1a,2,3,5,10b-pentahydro-1H-cyclopropa[*l*]benzo-[*b*]fluorene (8) from 7.—A mixture of 10 g (33 mmoles) of **7** and 9.6 g (33 mmoles) of tri-*n*-butyltin hydride[15] was heated at 130° for 3 hr with stirring.[16] The extent of reaction was followed by monitoring the Sn–H infrared absorption at 5.54 μ. The flask contents were poured into 75 ml of methanol. A light yellow oil separated and slowly solidified. Residual tri-*n*-butyltin chloride was removed from the solid by chromatography on alumina with chloroform. The resultant ivory powder was recrystallized twice (hexane–carbon tetrachloride), giving 4.5 g (51%) of white powder, mp 140–145°. An additional recrystallization from hexane provided the analytical sample of small colorless prisms, mp 145–147°. The nmr spectrum in deuteriochloroform showed a singlet at 3.75, corresponding to the five-membered ring protons, and a triplet at 3.15 (J = 0.05 ppm) due to the proton at the 1 position (*cis* isomer).[16] The remaining aliphatic protons appeared as an unresolved multiplet from 1.6 to 2.7. From the nmr peak areas, the ratio of *cis*:*trans* isomer is estimated to be 3.0:1.

Anal. Calcd for $C_{18}H_{15}Cl$: C, 81.04; H, 5.67. Found: C, 80.89; H, 5.60.

10,12-Dihydrocyclohept[*b*]fluorene (9) from 8.—Five grams of **8** was distilled at 0.07 mm nitrogen pressure over a period of 1 hr through a 19-mm diameter, horizontal Pyrex tube containing 20 g of lump calcium oxide, heated to 490°. The tan pyrolysate was sublimed at 100° (0.01 mm) and recrystallized twice from carbon tetrachloride to give 1.7 g (39%) of white powder, mp 135–155°. Two additional recrystallizations from carbon tetrachloride gave small white plates, mp 165–167.5°, whose elemental analysis, nmr, and infrared spectra were virtually identical with the crude powder. Apparently the powder is **9**, contaminated by small amounts of double bond isomers. The nmr spectrum in deuteriochloroform consisted of a doublet at 3.11 (A) (J = 0.10 ppm) due to the seven-membered ring methylene protons, a singlet at 3.80 (B) due to the fluorenyl methylene protons, a complex multiplet at 5.6–6.6 (C) due to the olefinic protons, and a series of aromatic bands from 7.0 to 7.8 ppm. The integrated areas gave for the ratios of A:B and C:B the values of 0.94 and 1.97, respectively (theoretical 1.0 and 2.0).

Anal. Calcd for $C_{18}H_{14}$: C, 93.87; H, 6.13. Found: C, 93.77; H, 6.24.

12H-Cyclohept[*b*]fluorenium Fluoroborate (10) from 9.—To a mixture of 0.9 g (3.9 mmoles of **9** and 1.29 g (3.9 mmoles) of triphenylcarbonium fluoroborate[17] was added a solution of 35 ml of acetonitrile and 15 ml of carbon tetrachloride. The solution was stirred at room temperature for 2 hr during which time red needles of **10** separated from solution. A 25-ml aliquot of carbon tetrachloride was added and stirring was continued for 2 hr in ice. After further cooling overnight the red needles were filtered and washed with carbon tetrachloride, giving 0.79 g (64%) of the fluoroborate salt. The nmr spectrum was taken at 100 Mc in fluorosulfonic acid at −20°, with tetramethylammonium chloride as the internal standard (3.10 ppm from tetramethylsilane).[18] The spectrum shows peaks at 6.44, 6.69, 7.48, 7.91, 8.22, and 8.59. The ultraviolet spectrum (Table V) was obtained in a flask fitted with a quartz cell side arm.[19] Acetonitrile was distilled into the flask from triphenylmethylcarbonium fluoroborate, using vacuum-line technique.

Anal. Calcd for $C_{18}H_{13}BF_4$: C, 68.39; H, 4.15. Found: C, 68.59; H, 4.32.

10H-Cyclohept[*b*]fluorenyllithium (11) from 9.—A small, modified Schlenk tube[20,21] was used for the reaction with *n*-butyllithium. The Schlenk tube consisted of two one-necked flasks connected by a length of glass tubing containing a fritted disk. The reaction was carried out in one of the flasks, and any precipitated product was separated by merely tilting the apparatus, to allow the liquid to filter through the fritted disk and into the other flask. All manipulations were carried out in a drybox, the helium atmosphere of which, as well as all apparatus and reagents, was thoroughly freed of oxygen and moisture. A 0.50-g (2.2-mmole) sample of **9** was dissolved in 7 ml of THF in the Schlenk tube, which was equipped with a magnetic stirrer bar and two vacuum stopcocks. Using a syringe, 1.50 ml (2.2 mmoles) of 1.46 N *n*-butyllithium in hexane was added to the THF solution, which immediately turned deep red. After stirring for 10 min, 30 ml of heptane was added, and an amorphous, deep-red solid was precipitated. Stirring was continued for an additional 5 min, and filtration was begun by tilting the assembly. Over a period of 25 min, the solid was washed with 5 ml of heptane, then with a solution of 1 ml of *n*-butyllithium solution in 5 ml of heptane, and finally with 5 ml of heptane. The red filtrates were emptied from the Schlenk tube, which was then evacuated overnight at 0.1 mm. The yield of deep-red powder was 0.65 g. The neutralization equivalent of the powder was 343, corresponding to a ratio of THF:$C_{18}H_{13}Li$ of 1.48:1. The nmr spectrum in THF showed a complex series of bands from 5.3 to 7.8. The spectrum was significantly different from **9**, indicating substantial delocalization of charge, as in the cation **10**. The spectrum could not be analyzed below 4 ppm because of the strong solvent peaks.

Reaction of 10 with Trimethylamine.—A flask containing 0.43 g (1.4 mmoles) of **10** was connected to a vacuum line and evacuated. Chloroform (25 ml) was vacuum distilled from phosphorous pentoxide into the flask with the fluoroborate salt (cooled to Dry Ice temperature), followed by 0.5 ml of trimethylamine which was distilled from lithium aluminum hydride. Magnetic stirring was begun at 0°. The mixture rapidly formed a yellow solution; stirring was continued in ice for several hours, with no apparent change in appearance of the solution. After standing for 2 days under nitrogen, at room temperature, a slight deepening in the yellow color was accompanied by a slow precipitation of a semicrystalline solid. Filtration afforded 0.13 g (63%) of essentially pure trimethylammonium fluoroborate (identified by infrared spectrum). An equal volume of ethanol was added to the chloroform filtrate and caused the precipitation of 0.20 g of a pale pink powder.

Anal. Found: C, 92.47; H, 5.76; residue, 0.93; mol wt (determined by a Mechrolab Model 301A osmometer), 1861 ± 80.

After correction for the residue (presumably trimethylammonium fluoroborate) the elemental analysis was slightly changed.

Anal. Found: C, 93.4%; H, 5.8%.

An octomer formed from eight molecules of **4** and one of ethanol has a molecular weight of 1872 and an elemental content of 93.7% carbon and 5.5% hydrogen.

Reaction of 10 with 11.—In the drybox, 0.10 g (0.32 mmole) of **10** and 0.11 g (0.32 mmole) of **11** were placed in a small vial. One milliliter of benzene-d_6 was added, but both reactants were so insoluble that no reaction occurred. After addition of 0.5 ml

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of THF, reaction occurred over a period of a few minutes, resulting in an orange solution with a small amount of precipitate. A portion of the solution was removed for nmr analysis, and the remainder was placed in a vacuum sublimator. The nmr spectrum could not be examined below 4 ppm because of the strong THF peaks, but the aromatic and olefinic region was rather similar to that obtained for **9**, although poorly resolved. There were two broad olefinic peaks at 5.7 and 6.4 and a series of diffuse aromatic peaks from 6.8 to 7.8. The solvent was evaporated from the sample in the sublimator and the apparatus evacuated to below 0.005 mm. The sample was heated at 100° for 24 hr, but there was no trace of sublimate at the end of this period. Since **9** is known to sublime readily under these conditions, it may be concluded that none was formed by the reaction. A second reaction was run on the vacuum line in degassed THF at −60 to −65°. The initial red color changed to orange over a period of 30 min. After stirring for 5 hr, a small amount of orange solid gradually formed, although the appearance of the solution remained about the same. The solvent was removed under vacuum, and the resultant orange solid was left below 0.01 mm overnight. Addition of deuteriochloroform to the solid gave an orange solution with an insoluble residue. The residue was largely inorganic, as determined by an ignition test. The nmr spectrum of the solution was virtually identical with the previous spectrum in the olefinic and aromatic regions. Residual THF gave rise to multiplets at 1.8 and 3.7, but additional small, broad aliphatic peaks could be discerned at 3.1 and 4.1.

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Pyrolysis of Benzoyl-α-benzaldoximes.
I. The Effect of Substitution, Solvents, and Catalysts

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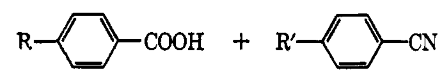
The pyrolytic elimination of benzoic acid from eight substituted benzoyl-α-benzaldoximes to yield the corresponding substituted benzonitriles shows first-order kinetics in five solvents. The plot of log k_1 *vs.* σ is linear for this reaction in the solvents tetralin, *o*-dichlorobenzene, dimethyl sulfoxide, and N-methylacetamide but not N,N-dimethylformamide, in which competing base catalysis by the solvent occurs. Thermodynamic parameters and small negative values for ρ indicate that the reaction mechanism is essentially synchronous. Catalysis by a wide range of metal salts was observed.

Of the many reactions available for the conversion of oximes to nitriles the pyrolysis of acyl-α-aldoximes (*syn* isomers) has been one of the least used.[2] This reaction occurs at moderate temperatures (100–150°) and has been shown to be first order when carried out in xylene using several different acyl groups.[3,4] The relatively low temperatures required for this pyrolysis allowed us to study further the kinetics of this reaction in a range of solvents. In addition, the effect of substituents and catalysts on the kinetics of reaction was investigated by us to gain insight into the reaction mechanism. We chose the benzoyl derivatives for this investigation because they are easily prepared and purified, and the benzoic acid produced on pyrolysis can be readily titrated in aqueous solution.

The benzoyl-α-benzaldoximes, I–VIII, used in this study were prepared by previously described methods[5] and, with the exception of VI which was photosensitive, were stable when stored *in vacuo* over potassium hydroxide. Pyrolyses were carried out at 123° and 142° in the absence of any solvent and at these same two temperatures after solution in each of five solvents: tetralin (TET), *o*-dichlorobenzene (DCB), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and N-methylacetamide (NMA).



I, R = H; R′ = NO_2
II, R = H; R′ = Cl
III, R = R′ = H
IV, R = H; R′ = CH_3
V, R = H; R′ = OCH_3
VI, R = H; R′ = $N(CH_3)_2$
VII, R = NO_2; R′ = OCH_3
VIII, R = R′ = OCH_3

When heated in the absence of solvent at 142° for about 48 hr, all the benzoyl-α-benzaldoximes yielded stoichiometric amounts of benzoic acid, which was assayed by titration. Gas chromatography of the residues left after extraction of the benzoic acid with dilute carbonate showed that only one component was present in each residue. This component had the same retention time as the expected authentic nitrile. The benzoic acid free residues showed no N—H or C═O absorptions in the infrared, thus ruling out the formation of amides during pyrolysis by a Beckmann type of rearrangement. Heating for 48 hr in the presence of solvents also yielded essentially stoichiometric amounts of benzoic acid. When the solvent was water miscible (DMF, NMA, DMSO), work-up of the reaction consistently yielded better than 85% of the expected nitrile, the infrared spectrum of which was always superimposable on that of the corresponding authentic nitrile. Pyrolyses in water-immiscible

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