1 H, J = 6.0 Hz), 7.00–7.60 (m, 5 H); IR (film) 2090, 1700, 1650 cm^{-1}; chemical ionization mass spectrum, m/e 437 (M^+ + 2), 435 (M^+).

6-(3-Azidopropyl)-6-ethyl-3-(*N*-(methoxycarbonyl)anilino)cyclohex-2,4-dien-1-one (16a). To a solution of **15b** (15 g, 34 mmol) in acetone (200 mL) was added tetraethylammonium acetate (14.7 g, 78 mmol). The reaction mixture was heated to reflux for 1 h. Filtration and concentration gave an oil. Preparative HPLC (ethyl acetate–hexane; 1:1) gave **16a** (9.5 g, 79%): ^1H NMR ($CDCl_3$) δ 0.74 (t, 3 H, J = 7.0 Hz), 1.10–2.30 (m, 6 H), 3.00–3.40 (m, 2 H), 3.80 (s, 3 H), 5.70 (d, 1 H, J = 2.0 Hz), 6.22 (d, 1 H, J = 9.0 Hz), 6.80 (dd, 1 H, J = 9.0 Hz and 2.0 Hz), 7.05–7.60 (m, 5 H); IR ($CHCl_3$) 2090, 1725, 1640 cm^{-1}; UV (MeOH) λ_{max} 324 nm (ϵ 9200), 261 (7500), 222 (17 800), 204 (21 600).

6-(3-Azidopropyl)-6-ethyl-3-anilinocyclohex-2,4-dien-1-one (16b). To a solution of **16a** (136 mg, 0.384 mmol) in dry methanol (8 mL) was added sodium hydride (20 mg, 0.83 mmol) in several portions at 0 °C. The reaction mixture was stirred at room temperature for 2.5 h. After cooling to 0 °C, saturated ammonium chloride solution (3 mL) was added to the reaction mixture. The mixture was extracted with chloroform (3 × 10 mL) and the combined chloroform solution was washed with brine (2 × 10 mL). After drying ($MgSO_4$), the solvent was removed and the residue was chromatographed by preparative TLC (silica gel, ethyl acetate) to give **16b** (56 mg, 49%): ^1H NMR ($CDCl_3$) δ 0.70 (t, 3 H, J = 7.0 Hz), 1.10–2.40 (m, 6 H), 2.95–3.33 (m, 2 H), 5.70 (br s, 2 H), 7.00–7.45 (m, 5 H), 7.70 (br s, 1 H); IR ($CHCl_3$) 2100, 1650 cm^{-1}.

6a-Ethyl-5,6,6a,7,9a,9b-hexahydro-9-(*N*-(methylcarbonyl)anilino)-7-oxo-4*H*-1,2,3-triazolo[4,5,1-*ij*]quinoline (17a). Method A. A solution of **16a** (268 mg, 0.757 mmol) in benzene (25 mL) was heated to reflux for 3.5 h. Concentration and preparative TLC gave **17a** (179 mg, 67%).

Method B. A neat sample of **16a** (5 g, 14.1 mmol) was placed in a round-bottom flask and heated at 100–120 °C for 25 min; the sample was agitated by shaking occasionally. After cooling, the sample was recrystallized from ether to give **17a** (2 g); mp 164–165 °C. The mother liquor was concentrated and chromatographed by preparative HPLC (ethyl acetate–hexane 1:1) to yield **17a** (1.1 g, total yield 3.1 g, 62%). ^1H NMR ($CDCl_3$) δ 0.81 (t, 3 H, J = 7.0 Hz), 1.02–2.80 (m, 6 H), 3.17 (d, 1 H, J = 10 Hz), 3.73 (s, 3 H), 3.99–5.45 (m, 2 H), 5.28 (s, 1 H), 6.40 (d, 1 H, J = 10 Hz), 6.90–7.50 (m, 5 H); IR ($CHCl_3$) 1725, 1660 cm^{-1}; mass spectrum, m/e 354 (M^+), 326 (M^+ – 28); UV (MeOH) λ_{max} 286 nm (ϵ 11 800), 268 (11 200), 242 (13 000).

Anal. Calcd for $C_{19}H_{22}N_4O_3$: C, 64.39; H, 6.26; N, 15.81. Found: C, 64.40; H, 6.28; N, 15.76.

Preparation of Compound 17b. A solution of **16b** (140 mg, 0.473 mmol) in benzene (10 mL) was heated to reflux for 5 h. Concentration preparative TLC (ethyl acetate) gave **17b** (102 mg, 73%): mp 181–182 °C; ^1H NMR ($CDCl_3$) δ 0.82 (t, 3 H, J = 7.0 Hz), 1.20–2.20 (m, 6 H), 2.50–3.20 (m, 1 H), 3.38 (d, 1 H, J = 10 Hz), 4.05–4.50 (m, 1 H), 5.35 (d, 1 H, J = 10 Hz), 5.75 (s, 1 H), 7.00–7.60 (m, 5 H), 8.05 (br s, 1 H); IR ($CHCl_3$) 3200, 1605, 1590 cm^{-1}; UV (MeOH) λ_{max} 316 nm (ϵ 16 900), 236 (13 100), 225 (13 800), 205 (13 000).

Anal. Calcd for $C_{17}H_{20}N_4O$: C, 68.90; H, 6.80; N, 18.90. Found: C, 68.90; H, 6.82; N, 18.84.

Photolysis of 17a (Methanol Solution). Triazoline **17a** (40 mg, 0.11 mmol) in methanol (3 mL) was irradiated and worked up as described for preparation of **6a**. Chromatography (silica gel, ethyl acetate) gave **18** (30 mg, 75%): ^1H NMR ($CDCl_3$) δ 0.82 (t, 3 H, J = 7.0 Hz), 1.05–2.40 (m, 8 H), 3.67 (s, 3 H), 3.72 (s, 3 H), 3.50–3.90 (m, 1 H), 5.83 (m, 1 H), 6.45 (m, 1 H), 6.62 (m, 1 H), 7.15–7.40 (m, 5 H); IR ($CHCl_3$) 1710 cm^{-1}; chemical ionizaiton mass spectrum, m/e 359 (M^+ + 1).

Photolysis of 17a (Benzene Solution). A solution of **17a** (70 mg, 0.14 mmol) in spectrophotometric grade benzene (3 mL) was irradiated with Pyrex-filtered light for 30 min. Removal of solvent gave the ketene dimer (65 mg): ^1H NMR ($CDCl_3$) δ 0.92 (t, 6 H, J = 7.0 Hz), 1.00–2.90 (m, 12 H), 3.70 (s, 6 H), 3.50–4.10 (m, 4 H), 5.70–5.95 (m, 2 H), 6.31–6.50 (m, 2 H), 6.55–6.70 (m, 2 H), 7.10–7.55 (m, 10 H); IR ($CHCl_3$) 1810, 1710 cm^{-1}; chemical ionization mass spectrum, m/e 653 (M^+ + 1); ^{13}C NMR ($CDCl_3$) δ 215 (carbonyl carbon of the cyclobutane-1,3-dione ring system).

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Synthesis of a Dodecahydro-18,21-dioxoniakekulene

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Abstract: The synthesis of 1,2,4,5,7,8,10,11,13,14,24,25-dodecahydro-18,21-dioxonia-15,23:16,22-dimethenobenzo[1,2-*a*:5,4-*a'*]dipentaphene bis(trifluoromethanesulfonate) (**18**) is described. The key intermediate, 3,4,6,7,9,10-hexahydropentaphene-1,12(2*H*,11*H*)-dione (**6**), is prepared in seven steps from 9,10-dihydrophenanthrene in 32% yield via a double-Haworth synthesis. A Vilsmeier–Haack reaction on pentaphenedione **6** afforded 1,12-dichloro-3,4,6,7,9,10-hexahydro-2,11-pentaphenedicarboxaldehyde (**17**), which was condensed with pentaphenedione **6** in a convergent synthesis to afford the novel macrocyclic salt **18**. Spectral properties and transformations of macrocycle **18** are discussed.

The synthesis of macrocycles containing cavities solely on account of benzenoid ring fusion is a challenging and little-explored area of organic chemistry; hydrocarbons of this form have been referred to as "coronaphenes".[1] The a priori possibilities of annulenoid vs. benzenoid aromaticity render these macrocycles of considerable theoretical interest.[2] Questions regarding the ring strain resulting from polynuclear condensation and strain imposed by internal nonbonding interactions also arise.

Kekulene **1**, synthesized by Diederich and Staab,[3] represents the first and so far only example of a coronaphene. The minimal amount of angle strain and small nonbonding interactions in hydrocarbon **1** appeared to make attractive syntheses of heterokekulenes such as **2** and **4**.

We sought to develop an accessible route to heterokekulenes, with the possibility of converting bispyrylium salt **2** into hydrocarbon **1** via the known transformations of pyrylium salts into arenes.[4-7] A flexible route to diazakekulene **4** would allow the introduction of substituents and the testing of macrocycle **4** as a possible ligand for cations.[8]

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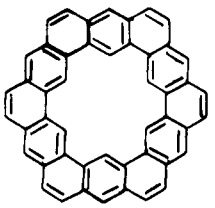

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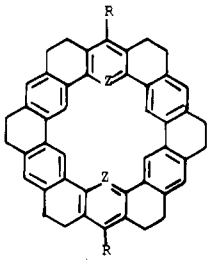
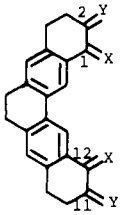


2, Z = $\overset{+}{O}$ X^-; R = H
3, Z = $\overset{+}{O}$ X^-; R = Ph
4, Z = N; R = H

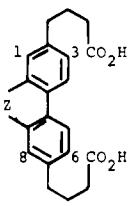
Synthetic Plan

Diederich and Staab[3] synthesized kekulene by the coupling of two dibenz[*a,j*]anthracene units, and subsequent stilbene-like photocyclization. The alternative convergent synthesis of hydrocarbon **1** involving two fragments would require pentaphene intermediates. Our interest in heterokekulenes suggested that bispyrylium salt **2** should be the target macrocycle, since efficient transformations of the pyrylium ring into heteroarenes are well-known.[4,9]

The extensive use of ketones in the synthesis of pyrylium salts[9] together with the greater stability and accessibility of diketone **6** as compared with diketone **5** suggested pentaphenedione **6** as



5, X = H_2; Y = O
6, X = O; Y = H_2



7, Z = CH=CH
8, Z = CH_2-CH_2

the key intermediate. Furthermore, diketone **6** should be capable of suitable fuctionalization exclusively at the 1,12- and 2,11-positions under mild conditions by nucleophiles and electrophiles, respectively.

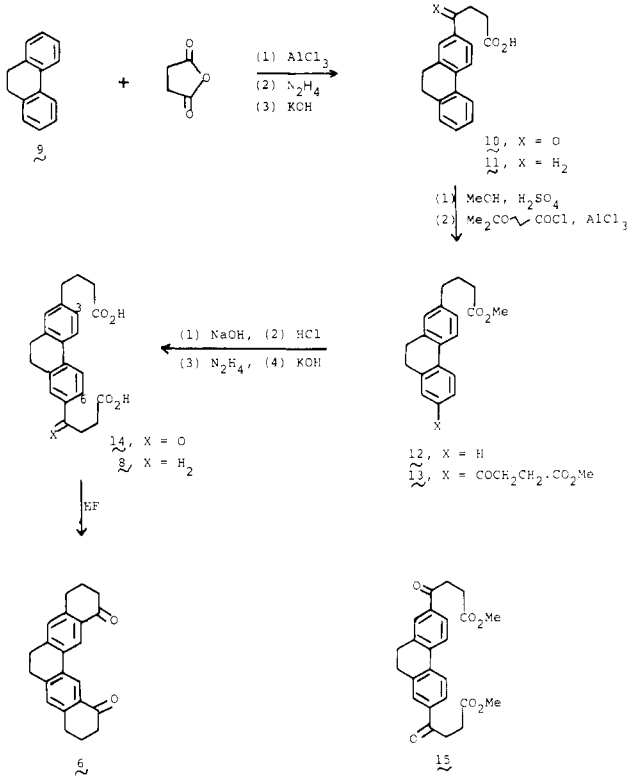
Existing routes[10] to the few known substituted pentaphene either are not general or require forcing conditions such as Elbs pyrolyses[11] under which functionality would be transformed. Hence, a double-Haworth synthesis of pentaphenedione **6** was considered. Phillips[12] has shown that diacid **7** cyclizes to give only C-1 + C-8 and C-1 + C-6 products. We therefore required diacid **8** in which the 9,10-ethano bridge was expected to direct the double intramolecular acylation predominantly to the 3- and 6-positions. Furthermore, it was necessary to start with 9,10-dihydrophenanthrene in order to observe initial diacylation at exclusively the 2- and 7-positions;[12] phenanthrene itself gives both 2- and 3-substituted products in Friedel–Crafts reactions.[13]

Results and Discussion

All attempts to prepare diester **15** by the method of Phillips[12] led to intractable isomeric mixtures, as shown by ^{13}C NMR studies. We therefore employed the known stepwise route to diacid **8**; considerable modification of it was found necessary (see Scheme I).

9,10-Dihydrophenanthrene **9** underwent monosuccinoylation to give acid **10**, according to the preparation of Burger and

Scheme I



6 15

Mosettig.[13] The reported[12] Huang–Minlon modification of the Wolff–Kishner reduction of keto acid **10** resulted in complex mixtures, shown by ^{13}C NMR studies; however, the Lock modification[14] of the Wolff–Kishner reduction afforded the required acid **11**. Acid **11** was esterified with methanol to give ester **12**, which was acylated exclusively at the 7-position with β-(methoxycarbonyl)propionyl chloride to afford keto diester **13**, both steps **11** → **12** and **12** → **13** proceeding as reported.[12]

The reported conversion[12] of keto diester **13** into diacid **8** in one step by a Huang–Minlon modification of the Wolff–Kishner reduction in our hands gave impure material of low melting point. However, saponification of keto diester **13**, followed by the Lock modification of the Wolff–Kishner reduction[14] gave satisfactorily diacid **8**. The advantage of the Lock procedure when applied to keto acids **10** and **14** lies in the ready formation of the corresponding hydrazones on stirring with hydrazine hydrate at 25 °C, and the smooth decomposition of the hydrazones to the corresponding carboxylates by KOH in the absence of solvent.

In order to form pentaphenedione **6** it was necessary to effect cyclodehydration of diacid **8** under conditions which preserved the 9,10-ethano bridge, which was to direct ring closure essentially to the 3- and 6-positions. Anhydrous hydrogen fluoride is known to be an efficient reagent for cycliacylation under mild conditions[15] and proved to be the reagent of choice; the novel pentaphenedione **6** was obtained from diacid **8** in 70% yield with HF, compared with 36% when sulfuric acid was employed. The resulting diketone **6**, after filtration through alumina and silica, was free from the two other possible isomers which might have been generated during ring closure, as shown particularly clearly by the ^{13}C NMR spectrum (see Experimental Section and Scheme II).

Since the condensation of ketones with arylidene ketones provides a common route to pyrylium salts,[9] we attempted to form the dioxoniakekulene system by condensing pentaphenedione **6** with dibenzylidene ketone **16**, itself obtained from ketone **6** and benzaldehyde. However, the bispyrylium salt **19** was never obtained pure, possibly because dibenzylidene ketone **16** is insuf-

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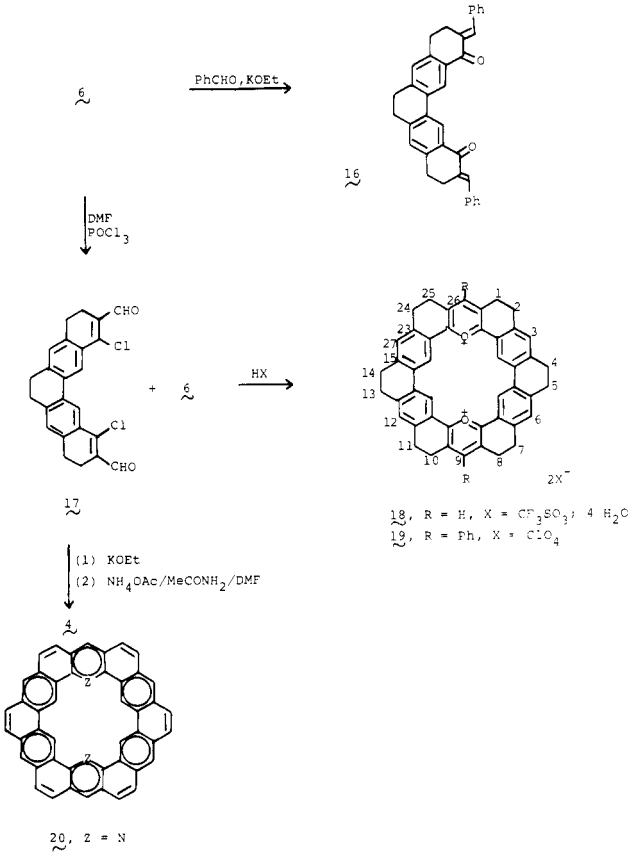
Table I. ^{13}C NMR Resonances of Pyrylium Salts 18 and 21 (in $CDCl_3/CF_3CO_2D$ at 20 °C; ppm from Me_4Si)

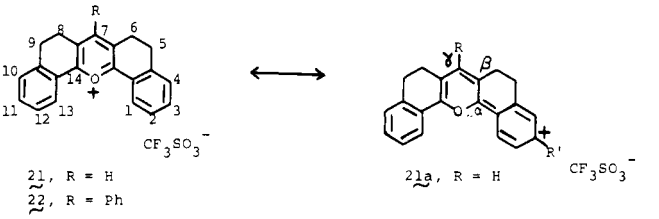
salt 18					salt 21				
signal	multiplicity[a]	δ	assignment	method of assignment[b]	signal	multiplicity[a]	δ	assignment	method of assignment[b]
1	s	166.2	17b, 18a, 20b, 21a	b	1	s	166.2	13b, 14a	c
2	d	152.5	9, 26	a, b	2	d	153.5	7	a
3	s	147.5	3a, 5a, 12a, 15	d	3	s	142.2	4a, 9a	a
4	s	142.8	2a, 6a, 11a, 23	b	4	d	135.9	3, 11	f
5	s	133.7	16, 16a, 19a, 19b	e	5	s	131.8	13a, 14b	c
6	s	131.6	17a, 18b, 20a, 22	c	6	d	129.4	1, 13	d
7	d	130.3	17, 19, 20, 22a	a, c	7	d	128.7	2, 12	d
8	s	124.4	8a, 9a, 25a, 26a	c	8	d	125.9	4, 10	c
9	d	120.3	3, 6, 12, 15a	a	9	s	125.2	6a, 7a	c, f
10	t	28.7	4, 5, 13, 14	d	10	t	26.1	5, 9	d
11	t	26.0	2, 7, 11, 24	b	11	t	25.5	6, 8	d
12	t	25.6	1, 8, 10, 25	b					

[a] s = singlet, d = doublet, t = triplet. [b] a, Off-resonance ^1H decoupling; b, comparison with salt **21**; c, comparison with 2-substituted-4-phenyl-5,6-dihydrobenzo[*h*]chromenylium salts; d, logical exclusion; e, comparison with 9,10-dihydrophenanthrene; f, comparison with salt **22**. A brace in the "assignment" column indicates that the assignment of these pairs may be reversed.

Scheme II



Scheme III



ficiently active to undergo the initial Michael addition. Another approach was to attempt to isolate the monobenzylidene derivative of diketone **6** and by self-condensation convert it into bispyrylium salt **19**. However, only the dibenzylidene ketone **16** could be obtained from diketone **6** under a variety of conditions.

General studies[16] on the synthesis of pyrylium salts have shown that it is the Michael addition of the ketonic fragment to the α,β-unsaturated ketone, rather than the subsequent (dehydrogenative) ring closure to the pyrylium nucleus that is often critical for success. The very reactive bis(β-chlorovinyl) dialdehyde **17** was therefore sought in the hope that the initial aldol condensation with pentaphenedione **6** would be facile, as would subsequent ring closure to the pyrylium ring, owing to the driving force provided by loss of hydrogen chloride. A Vilsmeier–Haack reaction on diketone **6** afforded, after systematic chromatography, the required bis(β-chlorovinyl) dialdehyde **17** which underwent condensation with pentaphenedione **6** to afford dark red dodecahydro-18,21-dioxoniakekulene bis(trifluoromethanesulfonate) **18** in 87% yield.

The dioxoniakekulene derivative **18** retained water tenaciously: its constitution was proved by mass spectral and NMR data. The mass spectrum generated by fast atom bombardment disclosed a peak at the expected molecular ion *m/e* 618: this molecular ion lost *both* the anions $CF_3SO_3^-$. Peaks *m/e* 619, 620, and 621 were in approximately the correct ratio (100:65:22:11) to that at 618 expected for the isotopic constitution (100:52:14:3), bearing in mind the background of ca. 10%. Moreover peaks were observed at all integral mass units from 618 down to 608, indicating the loss of up to 10 atoms of hydrogen.

The ^{13}C NMR spectrum (Table I) of dioxoniakekulene salt **18** shows no signals above 170 ppm, consistent with the reaction of all the C=O groups in both the diketone **6** and the dialdehyde **17**.

The two planes of symmetry orthogonal to the plane of the aromatic ring system in bispyrylium salt **18** imply a maximum of nine aromatic and three aliphatic signals; the ^{13}C NMR spectra of salts **18** and **21** both contain nine aromatic lines. While the α, β, and γ carbon atoms in salt **18** resonate at typical values for γ-H-pyrylium salts,[16] C-3a, -5a, -12a, and -15 appear at considerably lower field (147.5 ppm) than C-3 and -11 in pyrylium salt **21**; that is consistent with *p*-quinoid canonical forms lending more contribution to the distribution of charge in salt **18** than in salt **21** (Scheme III), on account of C-3a, -5a, -12a, and -15 being quaternary and C-3 and -11 being tertiary centers (R′ = H in **22a**).

That C-4, -5, -13, and -14 (28.7 ppm) are less shielded in salt **18** than C-1, -2, -7, -8, -10, -11, -24, and -25 (25–26 ppm) is also consistent with a considerable positive charge on C-3a, -5a, -12a, and -15. The high charge densities at C-2a, -3a, -5a, -6a, -11a, -12a, -15, and -23 account in part for the surprisingly shielded internal (130.3 ppm) and external (120.3 ppm) methine carbon atoms in salt **18**, those being similar to C-1 and -13 (129.4 ppm) and C-4 and -10 (125.9 ppm), respectively, in salt **21**.

The aromatic region of the ^1H NMR spectrum (Table II) of dioxoniakekulene salt **18** displays the expected three singlets for the γ, internal, and external hydrogen atoms. Of particular interest are the internal hydrogen atoms; their signal at δ 8.1

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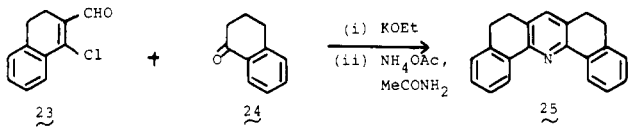
Table II. ^{1}H NMR Resonances of Pyrylium Salts 18 and 21 (in $CDCl_3/CF_3CO_2D$ at 20 °C; δ Values)

salt 18				salt 21			
H	multiplicity[a]	δ	assignment	H	multiplicity[a]	δ	assignment
2	s	8.7	9, 26	1	s	8.4	7
4	s	8.1	17, 19, 20, 22a	2	m	8.1	1, 13
4	s	7.2	3, 6, 12, 15a	6	m	7.5	2, 3, 4, 10, 11, 12
24	m	3.0–2.7	1, 2, 4, 5, 7 8, 10, 11, 13 14, 24, 25	8	s	3.2	5, 6, 8, 9

[a] s = singlet, m = multiplet.

Scheme IV



23 24 25

(compared with δ 8.1 in salt **21**) confirms both the presence of benzenoid as opposed to annulenoid aromaticity and the absence of significant internal nonbonding interactions in salt **18**.

Dibenz[*c,h*]acridine **25** was chosen as the model for pyridine **4** and was synthesized by condensing aldehyde **23** with 1-tetralone (**24**) under aldol conditions, followed by ring closure of the intermediate in an ammonium acetate–acetamide flux (see Scheme IV). An analogous condensation of dialdehyde **17** with ketone **6** afforded a highly insoluble yellow intermediate which was refluxed in dimethylformamide–ammonium acetate–acetamide; the mass spectrum of the final highly insoluble mixture showed a peak at *m/e* 614, probably corresponding to traces of M^+ of the novel diazakekulene **4**; peaks from *m/e* 614 down to 602 were also observed and are thought to be due to successive dehydrogenation of **4** to give, ultimately, the fully unsaturated azakekulene **20**.

Experimental Section

General Data. Melting points are uncorrected. ^{1}H NMR spectra (60 and 300 MHz) were obtained with Varian EM-360 and Nicolet NT-300 instruments, respectively; ^{13}C NMR spectra (25.00 and 75.46 MHz) were recorded with XL-100 and Nicolet NT-300 spectrometers. IR spectra were recorded on a Perkin Elmer 283-B spectrometer. Mass spectra were recorded on AEI MS30 at UF and AEI MS50 at the Middle Atlantic Mass Spectroscopy Facility (Johns Hopkins University), using the fast atom bombardment technique.

Literature Procedures. The following compounds were prepared by using standard literature methods: β-(methoxycarbonyl)propionyl chloride, bp 89–90 °C (15 mm) [lit.[17] bp 89–90 °C (15 mm)]; 9,10-dihydro-γ-oxo-2-phenanthrenebutanoic acid (**10**), mp 157–158 °C (lit.[13] mp 157.5–158.5 °C); methyl 9,10-dihydro-2-phenanthrenebutanoate (**12**), bp 200–202 °C (1.7 mm) [lit.[12] bp 205–207 °C (1.8 mm)]; dimethyl 9,10-dihydro-γ-oxo-2,7-phenanthrylenedibutanoate (**13**), mp 78–79 °C (lit.[12] mp 78.8–79.6 °C); 1-chloro-3,4-dihydro-2-naphthalenecarboxaldehyde (**23**), mp 34–35 °C (lit.[18] mp 37 °C).

Dimethyl 9,10-Dihydro-γ,γ′-dioxo-2,7-phenanthrylenedibutanoate (15). Attempts to repeat the preparation of **8** (mp 162 °C) by the method of Phillips[12] gave an inseparable mixture of products (mp 159–162 °C) which were not identified. ^{13}C NMR studies [$(CD_3)_2SO$; 20 °C; ppm from $SiMe_4$] showed 14 signals in the region 123–144 ppm (aromatic) together with 7 signals at 197.8, 197.7, 172.8, 51.3, 33.1, 28.2, and 27.6 ppm.

9,10-Dihydro-2-phenanthrenebutanoic Acid (11). All attempts to repeat the modified[19] Wolff–Kishner reduction[12] of **10** resulted in complex mixtures (^{13}C NMR studies). The following procedure was, however, successful. A stirred suspension of 30 g (0.113 mol) of **10** and 30 mL (0.618 mol) of hydrazine hydrate was heated under reflux in an oil bath at 150 °C for 25 min. KOH (60 g, 1.07 mol) was then added and the temperature kept at 170 °C for 30 min; after draining the condenser of water, heating was continued at 180 °C for a further 2 h. The residue was dissolved in 500 mL of water at 80 °C, diluted with 1 L of water, and neutralized with 10 M HCl; the resulting precipitate was kept overnight, filtered, washed with 1 L of water, and dried in air to give 28.5 g (100%) of **11**, suitable for esterification. Recrystallization from benzene–light petroleum gave pure **11** as needles: mp 91–92 °C (lit.[20] mp 92–92.5 °C).

9,10-Dihydro-γ-oxo-2,7-phenanthrylenedibutanoic Acid (14). A solution of 210 mL (2 M) NaOH and 16.1 g (40.9 mmol) of **13** was refluxed for 2 h. The cool solution was neutralized with 10 M HCl and the precipitate filtered and washed with 1 L of water to give 14.4 g (97%) of **14**, suitable for reduction, mp 146–150 °C. Analytically pure **14** recrystallized from acetone as plates: mp 157–159 °C; IR ($CHBr_3$) 3300–2600, 1710 (s), 1690 (s), 1600, 910, 895, 815 (s), 745 cm^{-1}; NMR ($CDCl_3/CF_3CO_2H$, 60 MHz) δ 2.15 (m, 2 H), 2.5–2.8 (m, 6 H), 2.93 (s, 4 H), 3.54 (t, *J* = 6 Hz, 2 H), 7.10 (m, 2 H), 7.83 (m, 4 H).

Anal. Calcd for $C_{22}H_{22}O_5$: C, 72.12; H, 6.05. Found: C, 71.96; H, 6.09.

9,10-Dihydro-2,7-phenanthrylenedibutanoic Acid (8). A stirred suspension of 14.3 g (39.0 mmol) of **14** and 21.5 mL (0.443 mol) of hydrazine hydrate was heated under reflux at 150 °C for 25 min. KOH (43 g, 0.768 mol) was then added and the temperature kept at 170 °C for 90 min; after the condenser was drained of water, further heating at 180 °C for 90 min was continued. The buff residue was dissolved in 150 mL of water at 80 °C and filtered, and the filtrate diluted with 400 mL of water. Neutralization with 10 M HCl afforded a precipitate which was kept overnight, filtered, washed with 1 L of water, and dried in air to give 13.5 g (98%) of crude **8**, mp 187–195 °C, suitable for cyclization. A sample crystallized from methanol as plates, mp 193–196 °C (lit.[12] mp 194–197 °C).

3,4,6,7,9,10-Hexahydropentaphene-1,12(2*H*,11*H*)-dione (6). To 150 mL of anhydrous HF at 0 °C (in a polythene bottle) was added 13 g (36.9 mmol) of **8** in portions over 20 min. After the mixture was stirred for 2 h at 20 °C, the HF was largely removed by passing a stream of air over the solution. The residue was triturated with 30 mL of 2 M sodium carbonate solution; extracting with 150 mL of CH_2Cl_2 (×3), washing with 200 mL of 2 M aqueous sodium carbonate, and drying (Na_2SO_4) gave a solution which was filtered through 20 g of neutral alumina and then through 30 g of silica. The eluate was dried (Na_2SO_4) and evaporated (50 °C (20 mm)) to give 8.2 g (70%) of **6**, mp 252–255 °C. Chromatography (neutral alumina, $CHCl_3$) afforded an analytical specimen of **6**, crystallized from AcOH as needles, mp 260–261 °C: IR ($CHBr_3$) 3010–2840 (m), 1675 (s), 1605 (m) cm^{-1}; NMR ($CDCl_3/CF_3CO_2H$, 60 MHz) δ 2.10 (m, 4 H), 2.4–3.1 (m, 12 H), 6.94 (s, 2 H), 8.29 (s, 2 H); ^{13}C NMR ($CDCl_3/CF_3CO_2H$, 25.05 MHz, ppm from $SiMe_4$) 22.8 (t), 28.6 (t), 29.0 (t), 38.2 (t), 112.8 (d), 128.9 (d), 130.4 (s), 132.3 (s), 145.3 (s), 146.1 (s), 204.5 (s).

Anal. Calcd for $C_{22}H_{20}O_2$: C, 83.52; H, 6.37. Found: C, 83.35; H, 6.39.

3,4,6,7,9,10-Hexahydro-2,11-bis(phenylmethylene)pentaphene-1,12-(2*H*,11*H*)-dione (16). A mixture of 0.190 g (0.60 mmol) of **6** and 0.130 g (1.23 mmol) of benzaldehyde were stirred with 0.3 mL of 4% ethanolic KOH for 3 h at 20 °C. Petroleum (bp 30–50 °C) was added, the suspension filtered and the solid chromatographed (neutral alumina; $CHCl_3$) to give 0.177 g (60%) of **16**, prisms from AcOH–$CHCl_3$, mp 264.5–265.5 °C: IR ($CHBr_3$) 3050–2830 (m), 1665 (s), 1610 (m), 1590 (s), 890, 800, 700 (s); NMR ($CDCl_3/CF_3CO_2H$, 60 MHz) δ 2.89 (s, 12 H), 7.20 (s, 2 H), 7.37 (m, 10 H), 7.88 (s, 2 H), 8.56 (s, 2 H); exact mass calcd for $C_{36}H_{28}O_2$, 492.2089; found, 492.2059.

1,12-Dichloro-3,4,6,7,9,10-hexahydro-2,11-pentaphenedicarboxaldehyde (17). To a stirred mixture of 0.657 g (9.00 mmol) of dimethylformamide and 2 mL of trichloroethylene at 5 °C in a flask equipped with a $CaCl_2$ drying tube was added 0.921 g (6.00 mmol) of $POCl_3$ over 20 min. A solution of 0.633 g (2.00 mol) of **6** in 4 mL of CH_2Cl_2 was then added and the mixture heated at 90 °C for 14 h. The residue was dissolved in 100 mL of 1:1 (v/v) CH_2Cl_2–NaOAc (10% aq) and the organic layer separated and dried over Na_2SO_4. Removal of solvent (60

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°C (20 mm)) gave a residue which was dissolved in 50 mL of CH_2Cl_2 and passed through 3 × 20 g of neutral alumina in three equal portions. A large yellow band was eluted first, the three fractions from these bands being combined and evaporated (50 °C (20 mm)) to give 0.460 g (56%) of **17**, mp 265-268 °C, suitable for condensation with **6**. A second chromatography provided an analytical sample as pale yellow prisms, mp 272-273 °C: IR ($CHBr_3$) 3010-2840 (m), 1660 (vs), 1610 (w), 1595 (s), 1555 (s), 1255 (s), 985, 890, 805, 735 cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 2.5-3.0 (m, 12 H), 7.04 (s, 2 H), 8.18 (s, 2 H), 10.30 (s, 2 H); ^{13}C NMR ($CDCl_3/CF_3CO_2H$, 25.05 MHz, ppm from $SiMe_4$) 21.5 (t), 26.6 (t), 28.7 (t), 122.4 (d), 128.4 (d), 130.8 (s), 131.4 (s), 133.1 (s), 139.9 (s), 143.1 (s), 152.4 (s), 195.0 (d).

Anal. Calcd for $C_{24}H_{18}Cl_2O_2$: C, 70.43; H, 4.43; Cl, 17.32. Found: C, 70.36; H, 4.45; Cl, 17.31.

1,2,4,5,7,8,10,11,13,14,24,25-Dodecahydro-18,21-dioxonia-15,23:16,22-dimethenobenzo[1,2-*a*:5,4-*a*]dipentaphene Bis(trifluoromethanesulfonate) (18). To a mixture of 46.0 mg (14.5 mmol) of **6** and 59.3 mg (14.5 mmol) of **17** was added 0.170 g (1.13 mmol) of CF_3SO_3H; the mixture was well stirred and heated at 100 °C for 2 h. The residue was triturated with 10 × 5 mL of Et_2O and filtered to give 124 mg (86%) of **18**, brownish-red microprisms, mp > 300 °C: IR ($CHBr_3$) 3500 (w, bd), 2950-2840, 1620 (m), 1560 (bd), 1475 (s), 1430, 1395, 1330 (w), 1260 (vs, v, bd), 1220, 1025 (s), 890 (bd, w), 870 (vw), 760 (vw), 740 (vw), 730 (vw) cm^{-1}; NMR ($CDCl_3/CF_3CO_2H$, 300 MHz) δ 2.5-3.1 (m, 24 H), 7.19 (s, 4 H, external), 8.11 (s, 4 H, internal), 8.66 (s, 2 H, γ in pyrylium ring); fast atom bombardment MS, M^+ 618 (100), 619 (65), 620 (22), 621 (11). $C_{46}H_{42}O_2$ requires M 618. No deductions of background (ca. 10%) have been made.

Anal. Calcd for the tetrahydrate $C_{48}H_{42}F_6S_2O_{12}$: C, 58.30; H, 4.28; S, 6.48. Found: C, 57.95; H, 3.78; S, 6.63.

5,6,8,9-Tetrahydrodibenzo[*c*,*h*]xanthylium Trifluoromethanesulfonate (21). To a mixture of 0.963 g (5.00 mmol) of **23** and 0.730 g (5.00 mmol) of 1-tetralone (Aldrich Co.) was added 0.750 g (5.00 mmol) of CF_3SO_3H; the mixture was well stirred and heated at 100 °C for 2 h. The residue was triturated with 3 × 50 mL of Et_2O and filtered to give 1.473 g (68%) of **21**. Recrystallization from HOAc gave orange needles, mp 204-206 °C: IR($CHBr_3$) 1610, 1560, 1475 (s), 1430 (s), 1420, 1350 (w), 1335 (w), 1265 (vs), 1225, 1190 (w), 1025 (s), 960 (w), 925 (bd, w), 890 (w), 735 (vs) cm^{-1}; NMR, see Table II.

Anal. Calcd for $C_{22}H_{17}F_3SO_4$: C, 60.83; H, 3.94; S, 7.38. Found: C, 60.81; H, 3.97; S, 7.41.

5,6,8,9-Tetrahydrodibenz[*c*,*h*]acridine (25). A mixture of 0.146 g of 1-tetralone (1.00 mmol), 0.193 g of 1-chloro-3,4-dihydro-2-naphthalenecarboxaldehyde and 0.3 mL of 4% ethanolic KOH were stirred at 20 °C for 4 h. Extraction with 20 mL of CH_2Cl_2 gave a solution which was washed with 3 × 20 mL of Et_2O, dried over $MgSO_4$, and evaporated (50 °C (20 mm)) to give 0.340 g of an oil; this was not identified but was refluxed with 0.500 g (6.49 mmol) of NH_4OAc and 0.500 g (8.47 mmol) of $MeCONH_2$ for 3 days. Addition of water, extraction with 3 × 20 mL of CH_2Cl_2, followed by washing with 3 × 20 mL of water, drying the organic layer over Na_2SO_4, and evaporating (50 °C (20 mm)) gave an oil which was chromatographed (alumina; 1:9 (v/v) EtOAc-light petroleum) to give 96.0 mg (33%) of **25**, crystallizing as needles from ethanol: mp 158-159 °C (lit.[21] 162 °C).

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Synthesis and Photoreactivity of Cholesteryl Diazoacetate: A Novel Photolabeling Reagent[1]

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Abstract: Cholesteryl diazoacetate (**1**), a new photolabeling reagent, has been synthesized for use in biological systems. Photolysis of the reagent proceeds by first-order kinetics at 254 and 350 nm. High-field ^1H and ^{13}C NMR spectroscopy allowed identification of separated products. The reagent undergoes intermolecular insertion reactions; C-H and O-H insertion are responsible for the major products when **1** is photolyzed in cyclohexane and methanol, respectively. Cholesterol and cholesteryl formate were unexpected side products of the cyclohexane reaction. Cholesterol was also a product of the photolysis in methanol, where O-H insertion was found to be favored by 16:1 over C-H insertion. In both solvents, photolysis produced little Wolff rearrangement.

Photoaffinity labeling, introduced with the photolysis of diazoacetylchymotrypsin,[2] has developed into a major technique for the investigation of biological systems.[3,4] An ideal photolabel should (a) be capable of introduction at a site of interest while remaining chemically "inert", (b) generate a highly reactive species upon photolysis which will react rapidly with the immediate environment to form a covalent bond, (c) react not only with nucleophiles, but also with hydrophobic regions (C-H bonds), and (d) generate a reactive species which is not readily deactivated by nonproductive side reactions such as H abstraction, intramolecular reaction, or rearrangement.[5]

Diazo compounds have demonstrated their utility as photolabels. Upon photolysis a molecule of N_2 is eliminated, followed by insertion of the resulting carbene into C-H or O-H bonds. α-Diazocarbonyl compounds are known, however, to undergo Wolff rearrangement to varying degrees, thereby wasting a percentage of the reactive carbene intermediate.[6] In the Wolff rearrangement an intermediate is formed[7] that may be relatively long lived and fail to react at the site where it was produced.

Cholesterol is the most abundant sterol found in mammalian cells. The molar ratio of cholesterol to phospholipid varies, de-

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