

965, 905, 855, 785, 745  $\text{cm}^{-1}$ ; HRMS calcd for  $\text{C}_{11}\text{H}_{22}\text{O}_3\text{P}$  (P -  $\text{NO}_2$ ) 233.13067, found 233.13089. Anal. Calcd for  $\text{C}_{11}\text{H}_{22}\text{NO}_5\text{P}$ : C, 47.31; H, 7.94; N, 5.01; P, 11.09. Found: C, 46.95; H, 8.06; N, 4.92; P, 11.26.

1-Cyclopropyl-1-nitro-1-(dimethoxyphosphinyl)ethane (14) was isolated by Kugelrohr distillation at 115 °C (0.4 torr):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.91 (d, 3,  $J_{\text{P}} = 10.9$  Hz), 3.88 (d, 3,  $J_{\text{P}} = 10.8$  Hz), 1.47 (d, 3,  $J_{\text{P}} = 14.6$  Hz), 1.0–0.2 (m, 4);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  90.06 (d,  $J_{\text{P}} = 153.8$  Hz, C-1), 54.44 (d,  $J_{\text{P}} = 6.12$  Hz,  $\text{OCH}_3$ ), 54.14 (d,  $J_{\text{P}} = 7.32$  Hz,  $\text{OCH}_3$ ), 14.84 (d,  $J_{\text{P}} = 10.37$  Hz, C-2), 3.87 (s), 1.44 (s), 1.00 (s); IR (neat) 1545 (s), 1460, 1390, 1335, 1260 (s), 1180, 1030 (s), 860, 830, 790, 770  $\text{cm}^{-1}$ ; HRMS calcd for  $\text{C}_7\text{H}_{14}\text{O}_3\text{P}$  (P -  $\text{NO}_2$ ) 177.06806, found 177.06779. Anal. Calcd for  $\text{C}_7\text{H}_{14}\text{NO}_5\text{P}$ : C, 37.67, H, 6.32. Found: C, 37.06; H, 6.68.

2-Nitro-2-(dimethoxyphosphinyl)hept-6-ene (15) was isolated by flash chromatography using hexane-ethyl acetate (1:1) as eluent:  $R_f$  0.24;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.74–5.61 (m, 1), 4.99–4.90 (m, 2), 3.81 (d, 3,  $J_{\text{P}} = 11.0$  Hz), 3.79 (d, 3,  $J_{\text{P}} = 11.0$  Hz), 1.72 (d, 3,  $J_{\text{P}} = 14.6$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  137.19 (s, C-6), 115.58 (s, C-7), 89.98 (d,  $J_{\text{P}} = 150.1$  Hz, C-2), 54.66 (d,  $J_{\text{P}} = 6.1$  Hz,  $\text{OCH}_3$ ),

54.39 (d,  $J_{\text{P}} = 6.1$  Hz,  $\text{OCH}_3$ ), 35.24 (s), 33.13 (s), 22.45 (d,  $J_{\text{P}} = 9.8$  Hz, C-1), 19.20 (s); IR (neat) 3090, 2975, 2870, 1645, 1550 (s), 1465, 1390, 1345, 1270 (s), 1190, 1055 (s), 1030 (s), 920, 840  $\text{cm}^{-1}$ ; HRMS calcd for  $\text{C}_9\text{H}_{18}\text{O}_3\text{P}$  (P -  $\text{NO}_2$ ) 205.09936, found 205.09984. Anal. Calcd for  $\text{C}_9\text{H}_{18}\text{NO}_5\text{P}$ : C, 43.03; H, 7.22; N, 5.58; P, 12.33. Found: C, 43.35; H, 7.25; N, 5.36; P, 12.05.

1-Cyclopropyl-1-nitro-1-(diethoxythiophosphinyl)ethane (16) isolated by Kugelrohr distillation bp 139 °C (0.9 torr);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.55–3.80 (m, 4), 1.81 (d, 3,  $J_{\text{P}} = 16.5$  Hz), 1.32 (t, 6,  $J_{\text{H}} = 6$  Hz), 1.0–0.3 (m, 4); IR (neat) 2950, 1545 (s), 1460, 1390, 1335, 1160, 1095, 1030 (s), 960 (s), 860, 835, 790, 675  $\text{cm}^{-1}$ ; HRMS calcd for  $\text{C}_9\text{H}_{18}\text{O}_2\text{PS}$  (P -  $\text{NO}_2$ ) 221.07652, found 221.07635.

The reaction of 2 with  $\text{Me}_3\text{C}(\text{O}^-)=\text{CH}_2$  yielded mainly 5-cyclopropyl-2,2-dimethyl-4-hexen-3-one which was isolated as a mixture of *E* and *Z* isomers in a ratio of 62:38 by Kugelrohr distillation at 50 °C (10 torr):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  6.28 (s, 1), 1.53 and 1.90 (d, 3,  $J = 1$  Hz), 1.16 (s, 9), 0.95–0.60 (m, 4); IR (neat) 2960 (s), 1665 (s), 1470, 1385, 1090, 1055, 1000, 910 (s), 870, 800  $\text{cm}^{-1}$ ; HRMS calcd for  $\text{C}_{11}\text{H}_{18}\text{O}$  166.13577, found 166.13584. Anal. Calcd for  $\text{C}_{11}\text{H}_{18}\text{O}$ : C, 79.46; H, 10.91. Found: C, 79.09; H, 10.68.

## Photochemical Transformations. 38. Novel Transformations of Diarobicyclo[3.2.1]octadienes to Phenanthrenes and Dihydrophenanthrenes<sup>1</sup>

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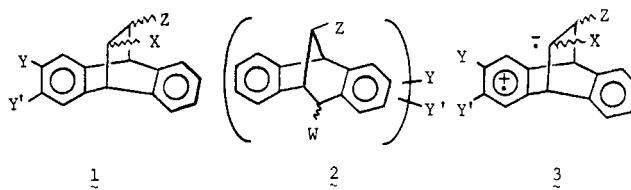
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Received November 30, 1984

Irradiation of 2,3;6,7-diarobicyclo[3.2.1]octadienes having nucleofugal groups at C-8, in an unprecedented rearrangement, produces 9-functionalized or 9,10-difunctionalized phenanthrenes (e.g., 8–11). The reactions involve triplet excited states, as demonstrated by acetone sensitization when the C-8 substituent was Cl or Br and by quenching studies when the C-8 substituent was  $\text{HgOAc}$ . When C-8 is unsubstituted, dihydrophenanthrenes, rather than phenanthrenes, are formed. The products of the latter reaction are presumably formed from a carbene intermediate resulting via a frustrated di- $\pi$ -methane rearrangement. On the other hand, the formation of the phenanthrene products is consistent with a pathway involving intramolecular electron transfer from the excited aromatic ring to the carbon-nucleofuge bond to form a zwitterionic biradical, loss of nucleofuge, and a convoluted rearrangement of the resulting biradical cation.

Our research group has been interested for some time<sup>2</sup> in photo-Wagner-Meerwein rearrangement and photo-solvolysis reactions, in which an aromatic ring is the light-absorbing chromophore and a remote carbon-X bond is subsequently activated and is ultimately cleaved to give  $\text{X}^-$  and a carbocation. Recently, our research<sup>1,3</sup> has led us to a fair degree of understanding of the general requirements for such reactions to occur.

Much of the work has been carried out with diarobicyclo[2.2.2]octadiene systems 1, in which variations in the



nature of the auxochromic groups Y and Y' and of the nucleofugal group X, as well as of the stereochemistry of the nucleofugal group X with respect to the light-absorbing Y-substituted ring, have been studied.

Considerations of stereochemistry, of the electron-donating ability (oxidation potential) of the photoactivated ring, and of the electron-accepting ability (reduction potential) of the carbon-nucleofuge bond have allowed considerable speculation about the course of the reactions leading to the photo-Wagner-Meerwein rearranged products 2. Thus, we have proposed<sup>1,3</sup> that electron transfer from a  $\pi, \pi^*$  activated arene ring to the  $\sigma^*$  orbital of the carbon-nucleofuge bond is required for photoac-

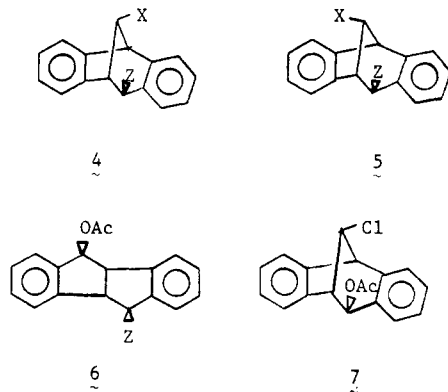
(1) Paper 37: Cristol, S. J.; Bindel, T. H.; Hoffmann, D.; Aeling, E. O. *J. Org. Chem.* 1984, 49, 2368. A portion of this work was reported at the Midwest Regional Meeting of the American Chemical Society at Lawrence, KS, Nov 3–4, 1983.

(2) Cristol, S. J.; Mayo, G. O.; Lee, G. A. *J. Am. Chem. Soc.* 1969, 91, 214.

(3) (a) Cristol, S. J.; Opitz, R. J.; Bindel, T. H.; Dickenson, W. A. *J. Am. Chem. Soc.* 1980, 102, 7977. (b) Cristol, S. J.; Graf, G. A. *J. Org. Chem.* 1982, 47, 5186. (c) Cristol, S. J.; Dickenson, W. A.; Stanko, M. K. *J. Am. Chem. Soc.* 1983, 105, 1218. (d) Cristol, S. J.; Seapy, D. G.; Aeling, E. O. *Ibid.* 1983, 105, 7337. (e) Cristol, S. J.; Ali, M. Z. *Tetrahedron Lett.* 1983, 24, 5839.

tivity, resulting in a zwitterionic biradical **3**. Fragmentation of **3**, with loss of  $X^-$ , in some cases accompanied by migration of the syn aryl ring or, in other cases, followed by migration of either ring, ultimately followed by decay to a ground-state carbocation, to give the solvolysis and rearranged products, was proposed to rationalize the stereochemical results, which differed greatly from those of ground-state solvolyses.

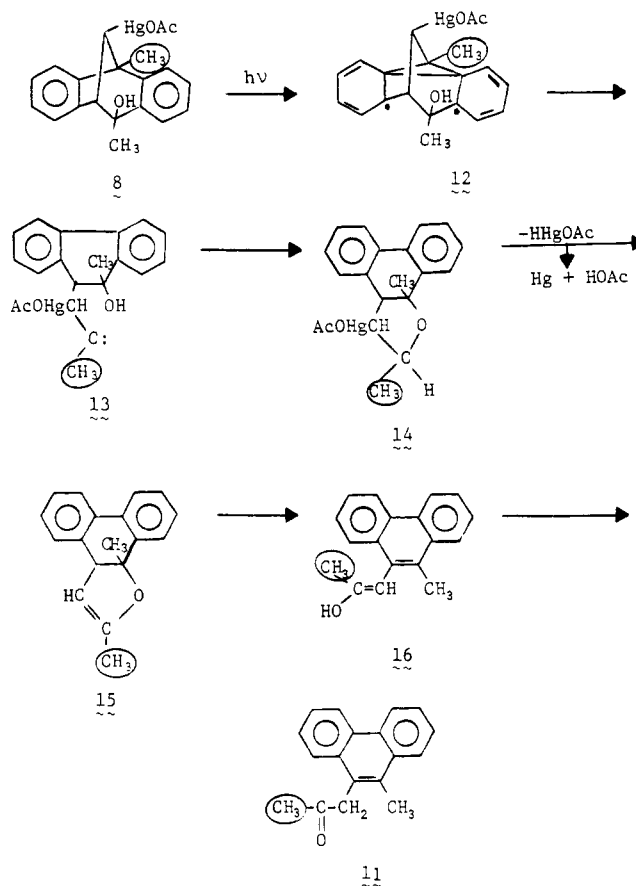
Two decades ago, members of our research group<sup>4</sup> had studied the solvolysis of 8-substituted dibenzobicyclo-[3.2.1]octadienes. Carbonium ion intermediates were produced from a variety of both syn (**4**) and anti (**5**) sub-



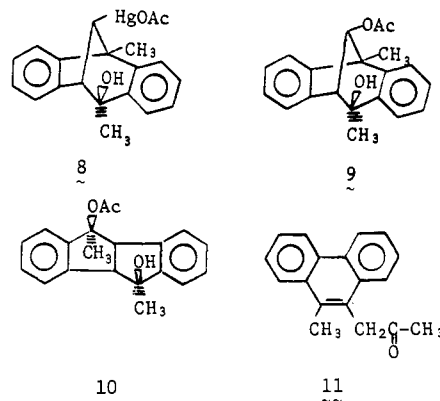
stituted compounds, but the products of reaction made it clear that the intermediates from the syn and anti epimers were distinct and noninterconvertible. Thus, for example, treatment of the *syn*-8-iodo 4-acetate (**4**,  $X = I$ ;  $Z = OAc$ ) with silver acetate in acetic acid led to the unrearranged diacetate of retained configuration (**4**,  $X = Z = OAc$ ), as did deamination of the amide **4** ( $X = NHAc$ ;  $Z = OAc$ ) in acetic acid. On the other hand, deamination of the anti epimer **5** ( $X = NHAc$ ;  $Z = OAc$ ) gave the rearranged [3.3.0] diacetate **6** ( $Z = OAc$ ), and treatment of the anti chloride **5** ( $X = Cl$ ;  $Z = H$ ) also gave rise to rearranged [3.3.0] acetate **6** ( $Z = H$ ). These results were rationalized<sup>4</sup> on the assumption of anti participation of the  $\pi$ -electron cloud<sup>5,6</sup> for the syn epimers and anti migration of the aryl group<sup>7</sup> for the anti epimers, consistent with the geometries of these systems. It was of obvious interest to irradiate compounds of types **4** and **5**, to learn what stereochemistries might be observed, in particular to see if syn migration or syn participation would be observed in these systems. As described below, the anticipated photosolvolyses were not observed. Rather, novel and unexpected rearrangements occurred. This paper describes these results and those of experiments devised in our attempt to delineate the reaction course.

Although earlier experiments had suggested that the 8-chloro [3.2.1] acetate **7** did not show photoactivity, with chloride loss, when irradiated in acetic acid, our recent observation<sup>8</sup> that electron transfer occurs readily from an excited benzene ring to a carbon-mercury bond, leading to the formation of a carbocation and an  $HgX^-$  species, which gives metallic mercury and  $X^-$ , suggested a study of 8-mercuri substituents in the [3.2.1] system. It seemed reasonable to assume that replacement of chlorine by the more readily reducible<sup>8</sup> carbon-mercury bond might lead to photoactivity in the **4** or **5** systems, which are  $\beta$ -aryl

## Scheme I



mercurials, similar to that observed in the [2.2.2] systems **1** ( $X = HgOAc, HgCl$ ). Our first experiment was done on compound **8**, a compound that had been prepared earlier<sup>9</sup>



in our laboratory. As expected, compound **8** was photoactive, when irradiated in acetic acid with 254-nm light, and metallic mercury was formed. However, neither of the plausible solvolysis products **9** or **10** was formed. Instead the product, formed in good isolable yield, was the completely unanticipated 9,10-difunctionalized phenanthrene **11**.

In spite of the attractiveness of the idea of intramolecular electron transfer following excitation, it seemed reasonable to consider alternative reaction paths possibly leading from **8** to **11**. One of these is given in Scheme I, which finds its basis in the work of Iwamura<sup>10</sup> and of

(4) Cristol, S. J.; Mohrig, J. R.; Parungo, F. P.; Florde, D. E.; Schwarzenbach, K. *J. Am. Chem. Soc.* **1963**, *85*, 2675.

(5) Winstein, S.; Shatavsky, M.; Norton, C.; Woodward, R. B. *J. Am. Chem. Soc.* **1955**, *77*, 4183.

(6) Bartlett, P. D.; Giddings, W. P. *J. Am. Chem. Soc.* **1960**, *82*, 1240.

(7) Winstein, S.; Stafford, E. T. *J. Am. Chem. Soc.* **1957**, *79*, 505.

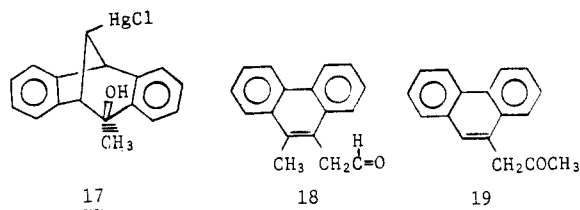
(8) Hush, N. S.; Oldham, K. B. *J. Electroanal. Chem.* **1963**, *6*, 34.

(9) Cristol, S. J.; Perry, J. S., Jr.; Beckley, R. S. *J. Org. Chem.* **1976**, *41*, 1912.

(10) (a) Iwamura, H.; Yoshimura, K. *J. Am. Chem. Soc.* **1974**, *96*, 2652.

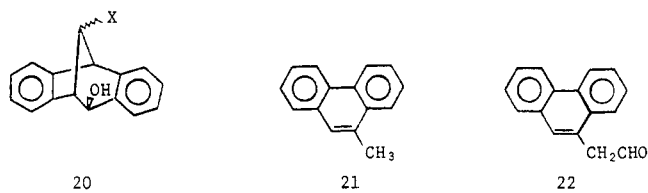
(b) Iwamura, H. *Chem. Lett.* **1974**, 5. (c) Iwamura, H.; Tukada, H. *Tetrahedron Lett.* **1978**, *37*, 3451.

Hemetsberger,<sup>11</sup> who demonstrated the photoinduced extrusion of carbenes from triptycenes<sup>10</sup> or from ethanodihydroanthracenes<sup>11</sup> with carbon-carbon bond formation in frustrated di- $\pi$ -methane rearrangements. All of the other steps in Scheme I have reasonable analogies in ground-state chemistry. Scrutiny of Scheme I shows that the methyl group remote from the hydroxyl group (i.e., the encircled one) becomes the one attached to the carbonyl carbon atom, while that initially on the carbinol carbon atom becomes the methyl attached directly to the 10-position of the phenanthrene ring. Accordingly, we decided to test this postulated mechanism by a study of compound 17,<sup>9</sup> missing the methyl group at C-1 of 8. If the mecha-



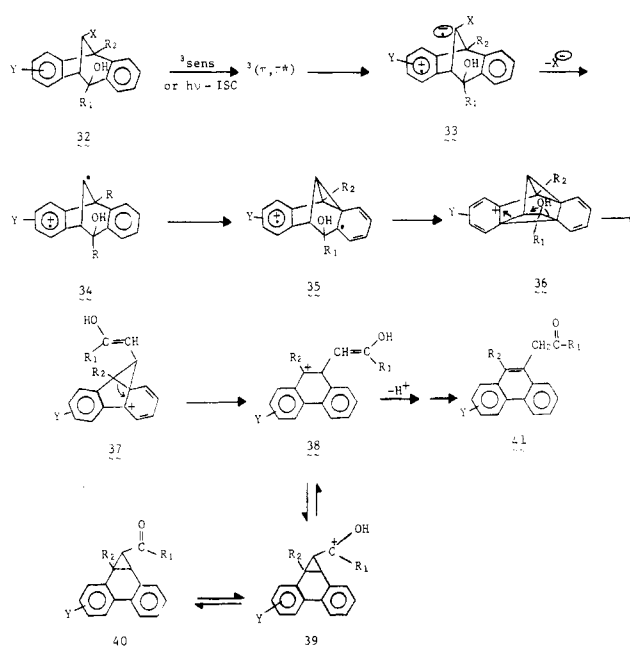
nism in Scheme I was operable, the aldehyde 18 (or its decarbonylation product) would be anticipated. In fact, this was not produced; irradiation of 17 gave the ketone 19. Clearly the methyl group at C-1 in 8 became the C-10 methyl group in 11, and the carbene mechanism of Scheme I is thus eliminated.

At this stage in our work, we observed that when a nucleofugal group at C-8 was one other than the mercuri function, that is, when chlorine or bromine was present (i.e., with 20-Cl or 20-Br), irradiation of an acetone solution

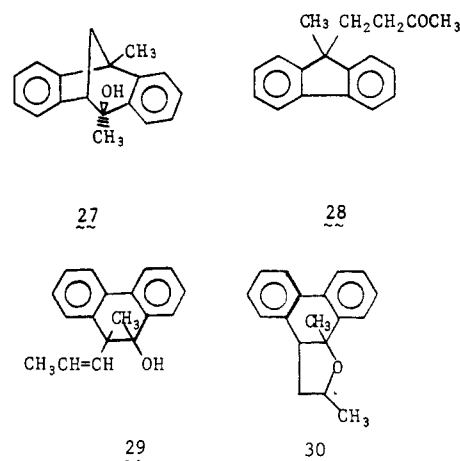


with 300-nm light led to the formation of 9-methylphenanthrene 21, presumably by photoinduced decarbonylation of 9-phenanthrylacetaldehyde 22. As 20 species are transparent in dilute solution to 300-nm light and as these species are only slightly reactive on direct irradiation (254-nm light), the intervention of excited-state triplets may be assumed. It seemed reasonable that intersystem crossing of the mercurial might also lead to a reactive triplet intermediate. To check this, quenching studies, with *cis*-piperylene as the triplet quencher, were performed. It was shown that formation of the phenanthrene 11 was quenched by *cis*-piperylene. Stern-Volmer analysis<sup>12</sup> of the quenching data on 8 gave a triplet lifetime of about 2 ns. The discovery that triplet excited states were involved raised the question again that the principal function of the halogen atom in the 20 compounds which showed low reactivity upon direct irradiation or of the mercury in 8 or 17 was to promote intersystem crossing, rather than to be involved in the early stages of the photochemistry. This suggested the plausible reaction path of Scheme II, having the photochemistry of a frustrated di- $\pi$ -ethane rearrangement<sup>13</sup> to give 24, followed by frag-

## Scheme II



mentation to give the fluorene 25. The carbenium ion conversion of a species such as 25 to a phenanthrene is well documented<sup>14</sup> in ground-state chemistry. Predictions from Scheme II suggest that triplet sensitization of a compound without a nucleofugal group at C-8 should lead to a stable fluorene; that is, compound 27 should give 28.



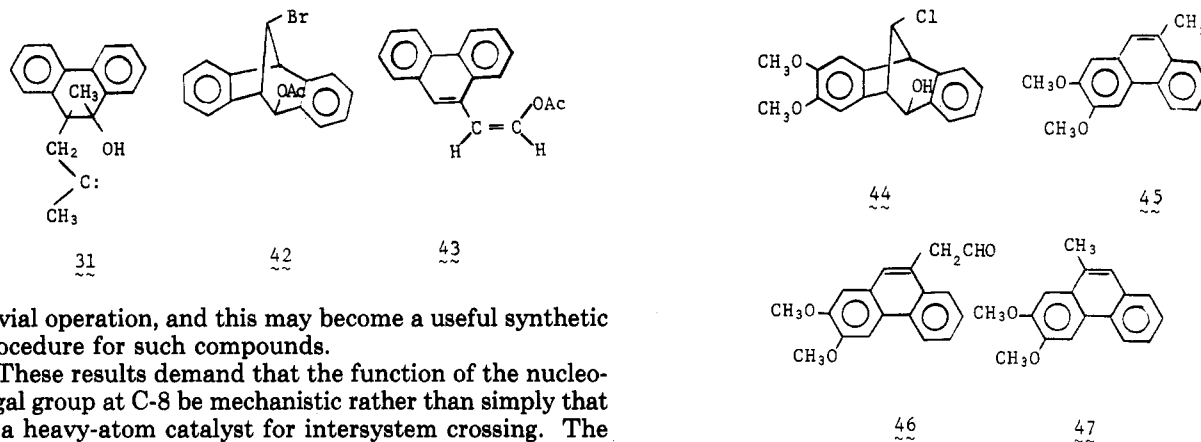
In fact, however, irradiation of 27<sup>9</sup> in acetic acid led not to 28 but to a mixture of the dihydrophenanthrenes 29 and 30. There would appear to be little question as to the origination of each atom in 29 or 30, and it should be noted that these are quite different from the phenanthrene-producing rearrangements. It is reasonable to assume that the frustrated di- $\pi$ -methane carbene extrusion process envisaged in other systems by Iwamura<sup>10</sup> and Hemetsberger<sup>11</sup> is operative here. Thus, this process would give, as outlined in the first steps of Scheme I, the intermediate carbene 31. Insertion into the hydrogen-oxygen bond would give the furan 30, while hydrogen transfer would give 29. While this experiment demonstrates that the mechanism of Scheme II is not operative for the phenanthrene-producing process, the preparation of 9- and 10-substituted 9,10-dihydrophenanthrenes is often not a

(11) Hemetsberger, H.; Brauer, W.; Tartler, D. *Chem. Ber.* **1977**, *110*, 1586. Hemetsberger, H.; Holstein, W.; Warres, F. *Tetrahedron* **1983**, *39*, 1151.

(12) Stern, O.; Volmer, M. *Phys. Z.* **1919**, *20*, 183.

(13) Schumann, W. C.; Vashi, D. B.; Ross, J. A.; Binkley, R. G. *J. Org. Chem.* **1972**, *37*, 21.

(14) See, for example: (a) Werner, A.; Grob, A. *Ber.* **1904**, *37*, 2887. (b) Bachmann, W. E. *J. Am. Chem. Soc.* **1933**, *55*, 3857.



trivial operation, and this may become a useful synthetic procedure for such compounds.

These results demand that the function of the nucleofugal group at C-8 be mechanistic rather than simply that of a heavy-atom catalyst for intersystem crossing. The possibility that the  $\pi, \pi^*$  excited state suffers energy transfer followed by bond homolysis to give a radical site at C-8 may be disregarded, as such radicals are known to undergo atom-transfer reactions without rearrangement.<sup>15</sup> Further, energy transfer followed by bond heterolysis to give a cation with the positive charge at C-8 would certainly lead to one or both of the fates described above for 4 and 5 and therefore must be disregarded as well. Accordingly, we propose, as we did for other systems,<sup>1,3</sup> an intramolecular electron-transfer mechanism, from an excited state,<sup>16</sup> to give a  $\pi, \sigma^*$  zwitterionic biradical, such as 33, whose transformation to phenanthrene is postulated to follow the pathway indicated in Scheme III. Evidence for the intermediacy of the dihydrophenanthryl cation 38 was seen in the observation that, after a short-time irradiation of 8, the product mixture contained, in addition to phenanthrene 11, the dibenzonorcaradiene 40 ( $R_1 = R_2 = \text{CH}_3$ ). This compound was isolated and was found to be converted to 11, both thermally and photochemically, in acetic acid. When the 8-bromo 4-acetate 42 was irradiated in acetone, the enol acetate 43 was obtained (along with 9-methylphenanthrene (21), its hydrolysis and decarbonylation product), also consistent with the path outlined in Scheme III. Finally, one notes that we have assumed that the process assumes that the arene ring on the six-membered-ring side of the [3.2.1] system is that involved in the initial bonding to the radical site. This gives a 3/5 ring fusion rather than a 3/4 ring fusion, with consequently less strain, although it is possible to conceive of an alternative process involving the other arene ring.

A first test of this was conducted by irradiation of 44 in acetone with 300-nm light. As anticipated from the mechanism of Scheme III, only 9-methyl-2,3-dimethoxyphenanthrene (45) was formed (by photochemical decarbonylation of 46). No isomeric 47 was produced. The structure of the product was adduced by comparison with an authentic sample.<sup>17</sup> It is necessary to be cautious in interpreting this result, however, as scrambling via a norcaradiene species such as 40 would undoubtedly also lead to 46 and 45, rather than to the carbocation progenitor of 47 (and its aldehyde progenitor). However, it should be noted that, while the norcaradiene was formed and isolated in the irradiation of 8, none was observed in the irradiation of 44 or of other species without methyl groups at C-4, that is, 20 species. The formation of 40 from 38

must, of course, compete with loss of a proton to give 41 and presumably proceeds via the cyclopropylcarbinyl cation 39. The homoallyl-to-cyclopropylcarbinyl rearrangement should be favored by the additional stabilization afforded to the latter cation by  $R_1 = \text{CH}_3$  rather than  $R_1 = \text{H}$ , and this would explain the failure to see the norcaradiene when  $R_1 = \text{H}$ . While it is possible that the norcaradiene is a participant in the reaction when  $R_1 = \text{H}$ , it does not seem likely that the norcaradiene from 20 species should be more labile than that from 8, where the norcaradiene can be intercepted.

It is clear that additional work is required to substantiate the mechanism of Scheme III in detail or to discard it, but it is difficult to avoid the conclusion that intramolecular electron transfer from a photoexcited aromatic ring to a readily reduced carbon-nucleophile bond is the key factor in the phenanthrene formation.

In summary, we have extended our studies on photoinduced intramolecular electron transfers from the diarobicyclo[2.2.2]octadiene system to the diarobicyclo[3.2.1]octadiene system. In contrast to the solvolyses and Wagner-Meerwein rearrangements observed in the former system, much more extensive rearrangement occurs when a nucleofugal group is present at C-8 in the [3.2.1] system. These unprecedented rearrangements lead to 9-functionalized or 9,10-difunctionalized phenanthrenes. When no nucleofuge is present at C-8, a fundamentally different reaction occurs, producing dihydrophenanthrenes, presumably via carbene intermediates. We anticipate that these reactions may find utility in the synthesis of functionalized phenanthrenes and dihydrophenanthrenes, and we are currently exploring these reactions further.

### Experimental Section

All melting points were determined with a Thomas-Hoover apparatus and were corrected. <sup>1</sup>H NMR spectra were obtained with the use of a Varian Associates EM-390 or a Bruker WM-250 instrument. Chemical shifts are reported in parts per million relative to tetramethylsilane. Mass spectra were obtained with the use of a Varian MAT CH-5 spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc. Irradiations with 254- and 300-nm light were carried out in a Srinivasan-Griffin photochemical reactor, hereafter referred to as a "Rayonet". All solvents and reagents were commercially available and reagent grade and were used without further purification unless otherwise stated.

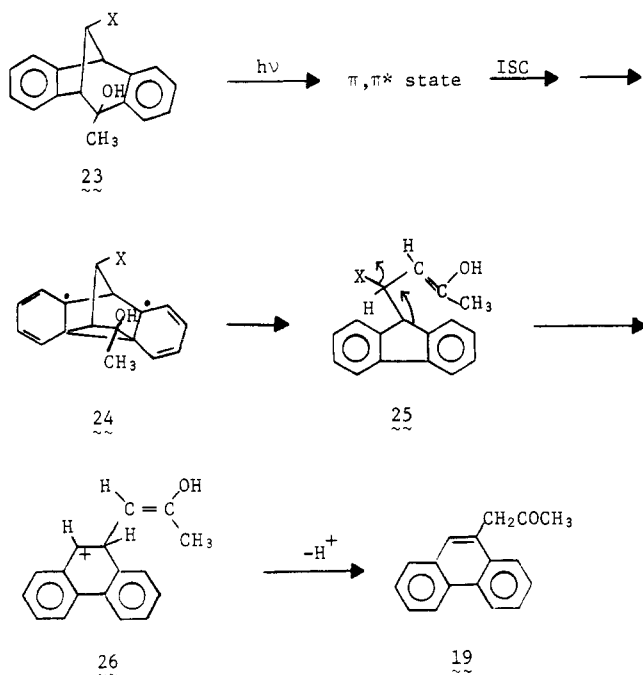
**Irradiation of Mercurial 8 in Acetic Acid.** A solution of 250 mg (0.49 mmol) of *syn*-8-(acetoxymercuro)-1,*endo*-4-dimethyldibenzobicyclo[3.2.1]octa-2,6-dien-*exo*-4-ol (8)<sup>9</sup> in 40 mL of glacial acetic acid was placed in a quartz tube. The sample was capped and deoxygenated by bubbling nitrogen gas through the solution for 45 min. The void space was wrapped with aluminum foil, and the sample was irradiated with 254-nm light in a Rayonet for 15 h. The precipitated metallic mercury was filtered

(15) Cristol, S. J.; Parungo, F. P.; Plorde, D. E. *J. Am. Chem. Soc.* **1965**, *87*, 2870.

(16) In the [2.2.2] system, the electron transfers were generally from the singlet excited states,<sup>1,3</sup> while in the 8-substituted [3.2.1] system, triplets are involved. We trust that further work will clarify this distinction.

(17) Dyke, S. K.; Marshall, A. R.; Watson, J. P. *Tetrahedron* **1966**, *22*, 2515.

Scheme III



(glass wool) and was washed with chloroform (10 mL). The solvents were evaporated in vacuo at  $\leq 40^\circ\text{C}$  to give 95 mg of a brown paste.  $^1\text{H}$  NMR spectroscopy revealed that compound 8 had been  $\geq 95\%$  converted to new products. The crude product mixture was chromatographed on a 20 cm  $\times$  20 cm  $\times$  2 mm silica gel thin-layer chromatography (TLC) plate with hexane/ether (10:1) as the eluent to give 71 mg (58%) of 10-methyl-9-phenanthryl)acetone (11) as a pale yellow solid. Recrystallization from 95% ethanol gave a white solid: mp  $156\text{--}157^\circ\text{C}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.85–8.60 (m, 2 H, H-4, H-5), 8.25–7.80 (m, 2 H, H-1, H-8), 7.75–7.40 (m, 4 H, H-2, H-3, H-6, H-7), 4.23 (s, 2 H, methylene H), 2.66 (s, 3 H, 10-methyl), 2.08 (s, 3 H,  $\text{C}(=\text{O})\text{CH}_3$ ); mass spectrum,  $m/e$  (major peaks) 248, 205. Anal. Calcd for  $\text{C}_{18}\text{H}_{16}\text{O}$ : C, 87.06; H, 6.49. Found: C, 86.92; H, 6.49.

In a similar irradiation as above, compound 8 (219 mg, 0.43 mmol) was irradiated in acetic acid (40 mL) for 2.5 h and worked up as above.  $^1\text{H}$  NMR spectroscopy revealed that about 40% of compound 8 had converted to product. A portion of the crude product mixture was chromatographed on a 20 cm  $\times$  20 cm  $\times$  2 mm silica gel thin-layer chromatography (TLC) plate with hexane/ether (10:1) as the eluent to give 10 mg of 11 and 23 mg of 9-methyl-9,10-dihydro-9,10-acetomethano phenanthrene, an oil whose  $^1\text{H}$  NMR spectrum is that of 40 ( $\text{R}_1 = \text{R}_2 = \text{CH}_3$ ;  $\text{Y} = \text{H}$ ):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.32–7.91 (m, 2 H, H-4, H-5), 7.79–7.18 (m, 6 H, Ar H), 3.24 (d, 1 H, H-10,  $J_{10,11} = 5$  Hz), 2.21 (s, 3 H,  $\text{C}(=\text{O})\text{CH}_3$ ), 1.74 (s, 3 H, 9- $\text{CH}_3$ ), 1.54 (d, 1 H, H-11,  $J_{10,11} = 5$  Hz). On the basis of the H-10–H-11 coupling constant, the aceto group at C-11 may be tentatively assigned the endo structure. Compound 40 (15 mg, 0.06 mmol) was dissolved in 0.6 mL of deuterioacetic acid and was irradiated with 254-nm light through a quartz NMR tube. The progress of the reaction was monitored by  $^1\text{H}$  NMR spectroscopy and it was observed that compound 40 was gradually converted to compound 11 as the sole product (complete conversion to 11 in 15 h). In another experiment, compound 40 (12 mg, 0.05 mmol) was dissolved in 0.5 mL of deuterioacetic acid in an NMR tube and the solution was covered by aluminum foil. Monitoring of the progress of the reaction by  $^1\text{H}$  NMR spectroscopy revealed that 40 was slowly converted to 11 (complete conversion to 11 in 5 days).

**Irradiation of Mercurial 17 in Acetic Acid.** A solution of 101 mg (0.21 mmol) of *syn*-8-(chloromercurio)-4-*endo*-methyl-dibenzobicyclo[3.2.1]octa-2,6-dien-4-ol (17)<sup>9</sup> in 20 mL of acetic acid was placed in a quartz tube. Sample preparation, irradiation (254-nm light), and workup were similar to those described for 8. Silica gel thin-layer chromatography gave 20 mg (40%) of (9-phenanthryl)acetone (19), mp  $96\text{--}98^\circ\text{C}$ , after recrystallization from 95% ethanol (lit.<sup>18</sup> mp  $98.5\text{--}99^\circ\text{C}$ ):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$

8.75 (m, 2 H, H-4, H-5), 8.05–7.55 (m, 7 H, arom H), 4.11 (s, 2 H,  $\text{CH}_2$ ), 2.11 (s, 3 H,  $\text{CH}_3$ ).

**Acetone-Sensitized Irradiation of 20-Br.** A solution of 12 mg (0.04 mmol) of *syn*-8-bromodibenzobicyclo[3.2.1]octa-2,6-dien-4-ol (*syn*-20-Br)<sup>15</sup> in 10 mL of acetone in a Pyrex tube was deoxygenated by bubbling nitrogen gas through the solution for 30 min. The sample was irradiated with 300-nm light in a Rayonet for 12 h. The acetone was evaporated in vacuo, and to the residue was added chloroform and water. The chloroform layer was separated, washed with water, and dried over anhydrous  $\text{MgSO}_4$ . Evaporation of the solvent in vacuo left 9 mg of 9-methylphenanthrene (21)<sup>19</sup> as the only product, identified by comparison of its  $^1\text{H}$  NMR spectrum with the reported  $^1\text{H}$  NMR spectrum.

A similar result was obtained when *syn*-20-Cl<sup>20</sup> was irradiated in acetone. However, the rate of conversion to 21 was slow compared with that of *syn*-20-Br.

**Irradiation of 1,endo-4-Dimethyl-exo-4-dibenzobicyclo[3.2.1]octa-2,6-dienol (27) in Acetone with 300-nm Light.** Compound 27 (236 mg, 0.94 mmol) was dissolved in 50 mL of acetone in a Pyrex tube, and 2 mL of water was added. The solution was deoxygenated by bubbling nitrogen gas through the solution for 45 min and then irradiated with 300-nm light in a Rayonet for 40 h. The acetone was evaporated in vacuo, and 50 mL of chloroform was added to the residue. The solution was washed with water and dried ( $\text{MgSO}_4$ ). Evaporation of the solvent in vacuo gave 205 mg of a brown oil. The crude product mixture was chromatographed on a 20 cm  $\times$  20 cm  $\times$  2 mm silica gel TLC plate with hexane/ether (5:1) as the eluent to give 36 mg (15%) of 30 and 25 mg (10.6%) of 9-methyl-10-(1'-propenyl)-9,10-dihydrophenanthren-9-ol (29) along with a fraction (56 mg) which contained starting alcohol 27 and unidentified compounds. Compound 30, upon recrystallization from ethanol, had mp  $100\text{--}101^\circ\text{C}$ :  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.90–7.15 (m, 8 H, Ar H), 4.34 (m, 1 H, HCO), 3.17 (dd, 1 H, H-10,  $J = 13$  Hz,  $J = 7$  Hz), 2.28 (m, 1 H,  $\text{CH}_2$ ), 1.55 (m, 1 H,  $\text{CH}_2$ ), 1.40 (s, 3 H,  $\text{CH}_3$ ), 1.10 (d, 3 H,  $\text{CH}_3$ ,  $J = 6$  Hz); mass spectrum,  $m/e$  (major peaks) 250, 235, 194, 193, 191, 178. Anal. Calcd for  $\text{C}_{18}\text{H}_{18}\text{O}$ : C, 86.36; H, 7.25. Found: C, 86.50; H, 7.17. Compound 29 was obtained as a pasty mass and was not crystallized:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.90–7.14 (m, 8 H, Ar H), 5.73 (m, 1 H, olefinic), 5.1 (m, 1 H, olefinic), 3.38 (d, 1 H, H-10,  $J = 10$  Hz), 2.18 (s, 1 H, OH), 1.59 (dd, 3 H,  $J = 7$  Hz,  $J = 2$  Hz,  $\text{CH}_3$ ), 1.30 (s, 3 H,  $\text{CH}_3$ ); mass spectrum,  $m/e$  (major peaks) 250, 235, 233, 207, 195; IR ( $\text{CCl}_4$ ) 3580 (s sharp), 3050 (s), 3015 (m), 2950 (s), 2910 (m)  $\text{cm}^{-1}$ .

**Conversion of 29 to 10-Methyl-9-propylphenanthrene.** Compound 29 (60 mg, 0.24 mmol) was treated with 5 mL of 10% sulfuric acid in acetic acid for 2–3 min at room temperature after which the solution was poured onto a mixture of 100 mL of water and 30 mL of ether. The ether layer was separated, washed with water and aqueous sodium bicarbonate, and dried ( $\text{MgSO}_4$ ). The ether was removed in vacuo to give 54 mg of 9-(1'-propenyl)-1-methylphenanthrene as a pasty mass, which crystallized upon standing, mp  $99\text{--}100^\circ\text{C}$  (after recrystallization from ethanol):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.76–8.68 (m, 2 H, H-4, H-5), 8.16–8.06 (m, 2 H, H-1, H-8), 7.67–7.50 (m, 4 H, H-2, H-3, H-6, H-7), 6.78 (d, 1 H,  $J = 16.5$  Hz, H-1'), 5.80 (m, 1 H, H-2'), 2.74 (s, 3 H, 10- $\text{CH}_3$ ), 2.08 (dd, 3 H,  $J = 5$  Hz,  $J = 2$  Hz, H-3'). Reciprocal coupling between H-1' and H-3' is not clearly observed from H-1' at  $\delta$  6.78 because of the lack of resolution at the peaks of the doublet; however, the peak width at half-height was 5 Hz. A  $^1\text{H}$  decoupling experiment (irradiation at  $\delta$  2.08) revealed that only the trans isomer was present. Mass spectrum,  $m/e$  (major peaks) 232, 217, 191. Anal. Calcd for  $\text{C}_{18}\text{H}_{16}$ : C, 93.06; H, 6.94. Found: C, 92.84; H, 6.97.

To a solution of 27 mg (0.12 mmol) of this olefin in 5 mL of glacial acetic acid was added a small amount of 10% Pd on C catalyst. The solution was frozen in liquid  $\text{N}_2$  and degassed. The flask was then filled with hydrogen (about 1.5 atm), and the flask was closed. The solution was allowed to warm to room temperature and stirred for 5 days (the reaction may have been over in a much shorter time). The catalyst was filtered, and the solvent

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was removed in vacuo to give 25 mg of a yellow paste. The crude product mixture was chromatographed on a 20 cm × 20 cm × 1 mm silica gel TLC plate with hexanes as eluent to give 10 mg (37%) of 10-methyl-9-propylphenanthrene, mp 92–93 °C (after recrystallization from ethanol) (lit.<sup>21</sup> mp 92.5–93.5 °C): <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.72 (m, 2 H, H-4, H-5), 8.10 (m, 2 H, H-1, H-8), 7.61 (m, 4 H, H-3, H-4, H-6, H-7), 3.16 (dd, 2 H, average *J* = 8 Hz, H-1'), 2.76 (s, 3 H, C-10 CH<sub>3</sub>), 1.75 (m, 2H, H-2'), 1.12 (t, 3 H, *J* = 8 Hz, H-3').

**Irradiation of Mercurial 8 in Acetic Acid in the Presence of *cis*-Piperylene as the Quencher.** In each of two photolyzing tubes was placed 92 mg (0.18 mmol) of mercurial 8. To the first tube was added 20 mL of glacial acetic acid, and to the second tube were added 19.8 mL of glacial acetic acid and 0.2 mL of *cis*-piperylene (0.1 M). The solutions were capped and deoxygenated by bubbling nitrogen gas through the solution for 30 min. The samples were then irradiated at 254 nm (Rayonet) in a merry-go-round apparatus for 2.5 h. The solutions were filtered through glass wool to remove metallic mercury, and the filtrates were rotary evaporated in vacuo at ≤40 °C. <sup>1</sup>H NMR spectroscopy revealed that the amount of phenanthrene compound 11 produced in the presence of *cis*-piperylene was half of that produced in the absence of *cis*-piperylene. While the bubbling undoubtedly removed some of the piperylene, if the assumptions are made that (a) no piperylene was removed and (b) the rate constant<sup>22</sup> for triplet quenching by piperylene is  $5 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ , calculation from the Stern–Volmer equation<sup>12</sup> gives a value for the lifetime of triplet 8 of 2 ns. This value then represents a minimum value. When this experiment was repeated at 0.05 M *cis*-piperylene (except that deoxygenated piperylene was added to the deoxygenated solution of 8 in acetic acid) 37% of product formation was quenched. This leads to a value for the lifetime of triplet 8 of 2.4 ns.

**Irradiation of *syn*-8-Chloro-14,15-dimethoxy-2,3:6,7-dibenzobicyclo[3.2.1]octa-2,6-dien-*exo*-4-ol (44).**<sup>3d</sup> A solution of 70 mg (0.23 mmol) of compound 44 in 200 mL of acetone was placed in a thick-walled (3.5 mm) Pyrex tube. The solution was deoxygenated (N<sub>2</sub> bubbling) and then irradiated with 300-nm light in a Rayonet for 20 h. The solvent was evaporated in vacuo. <sup>1</sup>H NMR spectroscopy revealed that 44 had been 40% converted to new products. The crude product mixture was chromatographed on a 20 cm × 20 cm × 2 mm silica gel TLC plate with hexane/ether (5:1) as the eluent to give 9 mg of 2,3-dimethoxy-9-methylphenanthrene (45), mp 138.5–139.5 °C (after recrystalli-

zation from 95% ethanol). Compound 45 was synthesized by the procedure of Dyke, Marshall, and Watson.<sup>17</sup> The photochemical and the literature procedures gave the identical compound (melting point, mixed melting point, and <sup>1</sup>H NMR). The <sup>1</sup>H NMR spectrum of the photoproduct showed only one methyl resonance before and after recrystallization (250-MHz NMR). Thus, it is assumed that only the 9-methyl isomer 45 was present in both recrystallized and nonrecrystallized product. The isomeric structure was confirmed by doing a <sup>1</sup>H NMR NOE experiment. This gave a NOE of 18% for H-10 and 11% for H-8 for both the photoproduct and the synthetic product.

**Irradiation of *syn*-8-Bromodibenzobicyclo[3.2.1]octa-2,6-dien-4-ol Acetate (42).**<sup>15</sup> Compound 42 (21.5 mg, 0.06 mmol) was dissolved in 10 mL of acetone, and 20 mg of NaOAc was added (most of it remained insoluble). After deoxygenation of the solution (N<sub>2</sub> bubbling), the solution was irradiated with 300-nm light for 6 h. The solution was filtered to remove NaOAc, and the filtrate was evaporated in vacuo at ≤40 °C. The residue was dissolved in dichloromethane/water, and the dichloromethane layer was separated. After drying (MgSO<sub>4</sub>) and solvent removal in vacuo, <sup>1</sup>H NMR spectroscopy revealed that 42-Br was 85% converted to 9-methylphenanthrene (21) (70%) and 9-(2'-acetoxynyl)phenanthrene (43) (15%). Compound 43 is tentatively assigned from the acetate methyl resonance at δ 2.10 and the *cis* structure from the olefinic resonance at δ 6.23 (H-2', *J* = 7 Hz) in the <sup>1</sup>H NMR spectrum. Mass spectral analysis of the crude reaction mixture revealed the presence of a molecular ion peak at 262 for 43; also, there was a peak at 203, which presumably arises by the loss of the acetoxy group from 43.

**"Dark Reactions" of 8, 17, 20-Br, 27, 42, and 44.** "Dark reactions" were performed simultaneously with all six irradiations. Solutions were made up with similar concentrations, placed in similar tubes wrapped in aluminum foil, and placed in the Rayonet beside the "light reactions". The "dark reactions" remained in the Rayonet for as long as the "light reactions". All "dark reactions" were worked up (if a workup was involved) in the same way as the "light reactions". For all six compounds 8, 17, 20-Br, 27, 42, and 44, no reaction was observed in the dark.

**Acknowledgment.** We are indebted to the National Science Foundation (Grants CHE80-11933 and CHE83-09927) for support of this work.

**Registry No.** 8, 96444-77-8; 11, 96444-78-9; 17, 58426-59-8; 19, 58443-80-4; *syn*-20 (X = Br), 2734-12-5; 21, 883-20-5; 27, 58426-62-3; 29, 96444-80-3; 30, 96444-81-4; 40 (R<sub>1</sub> = R<sub>2</sub> = CH<sub>3</sub>; Y = H), 96444-79-0; 42, 2831-72-3; 43, 96444-83-6; 44, 87567-84-8; 45, 789-48-0; 9-(1'-propenyl)-1-methylphenanthrene, 96444-82-5; 10-methyl-9-propylphenanthrene, 66553-00-2.

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