Removal of the solvent left 8 mg (90%) of a mixture of *anti*-(CH_3,Cl)B (27%) and (CH_3,Cl)(CH_3,Cl)lactone (73%) as determined by NMR.

Conversion of (CH_3,CH_3)(CH_3,CH_3)lactone to *anti*-(CH_3,CH_3)B. The lactone (28 mg, 0.15 mmol), initially a suspension, was stirred in sodium hydroxide (15 mL, 0.1 M, 1.5 mmol) for 2 h, the light yellow solution was acidified (ca. pH 2.5), the solution was stirred for a few hours and then extracted with $CHCl_3$, the extract was dried ($MgSO_4$), and the solvent was removed to yield 26 mg (93%) of *anti*-(CH_3,CH_3)B (90%) and lactone (10%) as shown by NMR.

A similar experiment with (CH_3CH_2,CH_3)(CH_3CH_2,CH_3)lactone yielded *anti*-(CH_3CH_2,CH_3)B (79%) and lactone (21%).

Rate Measurements. Low Rates. Bimane in CH_3CN (0.1 mL) was added to temperature-equilibrated buffer (3 mL) contained in a quartz cell. The absorption spectrum was measured with a Cary Model 17 spectrophotometer. For several *syn*-bimanes, fluorescence spectra were recorded with a Hitachi-Perkin-Elmer MPF 4.

High Rates. The bimane solution was added to the buffer being stirred by a small Teflon-coated bar moved by a small motor mounted below the cell holder with the chart paper running and the wavelength fixed at the absorption maximum. Smooth curves were usually observed after 1–2 s (mixing time). Sodium phosphate (pH 7–8) and sodium carbonate (pH 9–10) buffers were used. The pH values were measured at 25 °C and corrected to 50 °C with temperature factors recorded in the literature.[31]

Registry No. 4, 82666-04-4; 4a, 82666-05-5; 5, 82665-99-4; 6 (X = CH_2), 70090-46-9; 6 (X = NMe), 76421-32-4; 7, 82666-03-3; *anti*-(CH_3CH_2,CH_3)(CH_3CH_2,CH_3) B, 79746-62-6; *anti*-(benzo)(benzo)B, 18428-89-2; (CH_3CH_2)CH_3)(CH_3CH_2,CH_3)lactone, 79746-57-9; (benzo)(benzo)lactone, 3848-48-4; *syn*-(CH_3,Cl)(CH_3,Cl) B, 68654-19-3; *syn*-(CH_3,Br)(CH_3,Br) B, 74235-58-8; *syn*-(CH_3,I)(CH_3,I) B, 74235-76-0; *syn*-(CH_3,H)(CH_3,H) B, 74235-71-5; *syn*-(CH_3,CH_3)-(CH_3,CH_3)B, 68654-22-8; *syn*-(CH_3,CH_3)(CH_3,Cl)B, 68654-21-7; *syn*-(CH_3,H)(CH_3,Cl)B, 68654-24-0; *syn*-(CH_3,(CH_3)$_3$C)-(CH_3,CH_3)$_3$C)B, 82666-02-2; *syn*-(H,Cl)(H,Cl)B, 78763-68-5; *syn*-(H,H)(H,H)B, 79769-56-5; *syn*-(H,CH_3)(H,CH_3)B, 79746-89-7; *syn*-(H,H)(H,Cl)B, 79746-92-2; *syn*-($COOC_2H_5$,Cl)($COOC_2H_5$,Cl)B, 79746-74-0; *anti*-(CH_3,Cl)(CH_3,Cl)B, 68654-20-6; *anti*-(CH_3,Br)-(CH_3,Br) B, 74235-59-9; *anti*-(CH_3,CH_3)(CH_3,CH_3) B, 68654-23-9; *anti*-(CH_3,H)(CH_3,H)B, 74235-72-6; (CH_3,H)(CH_3,Cl)lactone, 82665-98-3; (CH_3,CH_3)(CH_3,CH_3)lactone, 79746-44-4; (CH_3,Br)-(CH_3,CH_3)lactone, 79746-50-2; (CH_3,CH_3)(CH_3,Br)lactone, 79746-49-9; (CH_3,Cl)(CH_3,CH_3)lactone, 79746-48-8; (CH_3,CH_3)(CH_3,Cl)-lactone, 79746-47-7; (CH_3,Cl)(CH_3,Cl)lactone, 79746-46-6; (CH_3,H)(CH_3,H)lactone, 74235-88-4; 2-(2-carboxyphenyl)benzopyrazoline-3-one, 18428-91-6; 2-(1,2-dimethyl-2-carboxyvinyl)-3,4-dimethyl-3-pyrazolin-5-one, 82666-00-0; 2-(1-ethyl-2-methyl-2-carboxyvinyl)-4-ethyl-3-methyl-3-pyrazolin-5-one, 82666-01-1; oxygen, 7782-44-7.

(31) (a) "Data for Biochemical Research"; Oxford University Press: Oxford, 1959; p 193. (b) "Handbook of Biochemistry and Molecular Biology"; 2nd ed.; CRC Press: Cleveland, 1970; pp 227–228.

Chemistry of Diazoacenaphthenones and Diazoacenaphthenes

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Wolff rearrangements do not occur in photolyses or thermolyses of diazoacenaphthenone (**1**), 2-diazo-5-nitroacenaphthenone (**2**), and 2-diazoaceanthrenone (**3**) in various environments. Thermal and photochemical decompositions of **1** in cyclooctane result in loss of nitrogen and formation of 2-cyclooctylacenaphthenone (**29**). In 2-propanol containing oxygen, **1** converts photolytically to acenaphthenone (**22**), acetone (**23**), and 1,8-naphthalic anhydride (**25**). Irradiation of **1** in *tert*-butyl alcohol/oxygen yields 2-*tert*-butoxyacenaphthenone (**28**) by solvent capture along with **25**. Diazo ketones **1–3** do not effect photochemical cyclopropanation of simple olefins; electronegatively substituted olefins such as acrylonitrile and methyl acrylate do give spirocyclopropanes however. Oxazoles are formed by 1,3-dipolar reactions of **1–3** with nitriles with loss of nitrogen. Acetylenes also react photolytically with **1–3** with nitrogen expulsion to yield furans regiospecifically. Thermolyses of **1–3** in acetylenes, however, result in initial 1,3-dipolar addition reactions to give spiropyrazoles which undergo spontaneous [1,5] sigmatropic migrations of their carbonyl groups to nitrogen to form isoquinolines. Diazoacenaphthene (**13**) decomposes carbenically to acenaphthylene (**66**). Similarly, 2-diazo-1,1-dimethylacenaphthene (**14**) converts to 8-methylcycloprop[*a*]acenaphthylene (**66**) which then isomerizes thermally to methylphenalenes (**70a–d**). Further, 2-diazoacenaphthenone ethylene acetal (**17**) thermolyzes and photolyzes with migration of one of its acetal oxygen moieties to yield 8,9-dihydroacenaphtho[1,2-*b*]-*p*-dioxin (**73**). Ring contraction does not occur in carbenic decompositions of **13**, **14**, and **17**.

A study is now summarized of various thermal, photolytic, metal ion catalyzed, and 1,3-dipolar reactions of diazoacenaphthenone (**1**), 2-diazo-5-nitroacenaphthenone (**2**), and 2-diazoaceanthrenone (**3**)[1] (Chart I). Thermolysis of **1** has been reported to yield biacenedione (**7**) and acenaphthenequinone monoazine[2] (minor). Of major interest to the present effort is that previous attempts to prepare (1*H*-cyclobuta[*de*]naphthalen-1-ylidene)methanone (**8**) from 2-oxoacenaphthenylidene (**10**) as generated thermally from **1** failed.[3,4] While the present investigation was in progress, photolysis of **1** in an argon matrix at 8 K was found to give **8**, as assigned by IR methods.[5] Because of

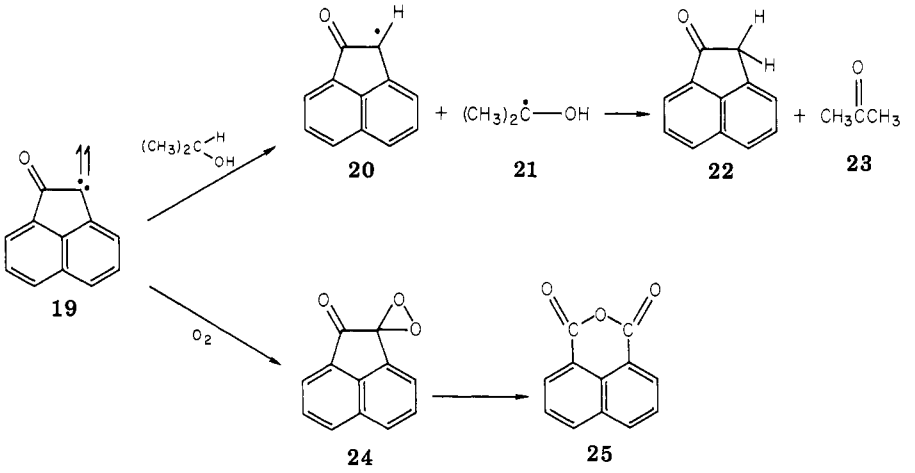
(1) Summarized in part from the Ph.D. Dissertations of (a) S.-J.C. (1979) and (b) B.K.R.S. (1981) at The Ohio State University.

(2) Tsuge, O.; Shinkai, I.; Koga, M. *J. Org. Chem.* **1971**, *36*, 745.

(3) (a) Cava, M. P.; Litle, R. L.; Napier, D. R. *J. Am. Chem. Soc.* **1958**, *80*, 2257. (b) Reid, W.; Lowasser, H. *Justus Liebigs Ann. Chem.* **1965**, *683*, 118. (c) DeJongh, D. C.; Van Fossen, R. Y. *Tetrahedron* **1972**, *28*, 3603.

(4) For reviews of the Wolff rearrangement see: (a) Meier, G. G.; Zeller, K. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 32. (b) Kirmse, W. "Carbene Chemistry", 2nd ed.; Academic Press: New York, 1971; pp 475–493. (c) Weygand, F.; Bestmann, H. J. *Angew. Chem.* **1960**, *72*, 535. (d) Rodina, L. L.; Korobitsyna, I. K., *Russ. Chem. Rev. (Engl. Transl.)* **1967**, *36*, 260. (e) Smith, P. A. S. In Mayo, P. "Molecular Rearrangements"; Interscience: New York, 1963, pp 528–550, 558–564.

0022-3263/82/1947-4226$01.25/0



(1)

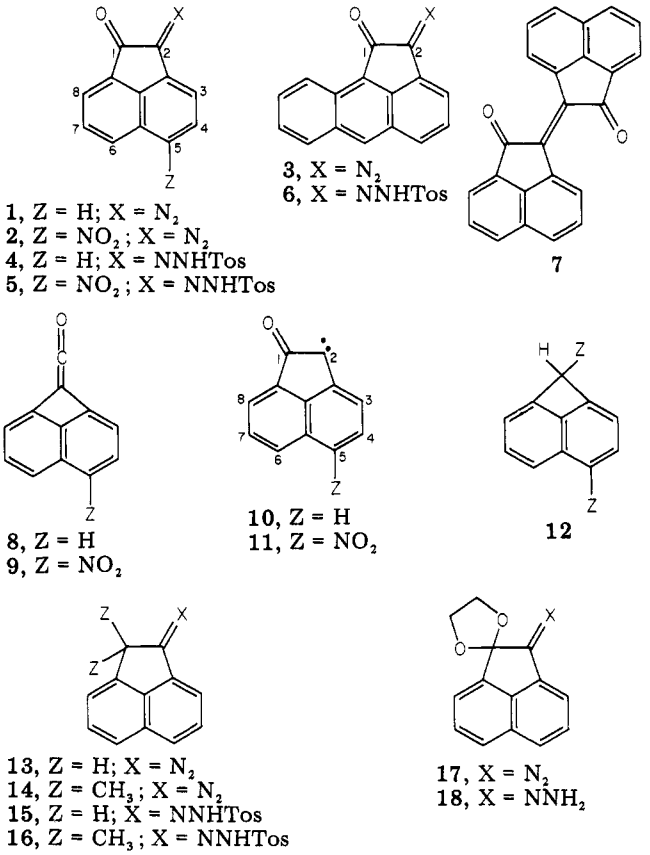
(2)

interests in the chemistry of α-diazo ketones and in particular improved synthesis of 1*H*-cyclobuta[*de*]naphthalene derivatives (**12**),[6] the behavior of **1–3** has been examined. As further possible entrees to derivatives of **12**, the carbenic decompositions of diazoacenaphthene (**13**), 2-diazo-1,1-dimethylacenaphthene (**14**), and 2-diazoacenaphthenone ethylene acetal (**17**) have also been studied.

Synthesis of 1–3, 13, 14, and 17. Diazo ketones **1–3**[7] were prepared by decomposition of acenaphthenequinone mono-*p*-tosylhydrazone (**4**), 5-nitroacenaphthenequinone 2-*p*-tosylhydrazone (**5**), and aceanthrenequinone 2-*p*-tosylhydrazone (**6**), respectively, with sodium hydroxide. Hydrazones **4–6** were obtained from their corresponding quinones and *p*-tosylhydrazine.[8] The structure of **2** is inferred on the basis that *p*-tosylhydrazine reacts preferentially with the carbonyl group at the 2-position in 5-nitroacenaphthenequinone because of electronic effects. The assignment of **5** is consistent with that for **2** in which the NMR of its proton at C-3 is shifted to higher field (δ 7.37) as compared to that in 5-nitroacenaphthenequinone (δ 8.18). The structure of **6** is based on the fact that the carbonyl group at C-2 in aceanthrenequinone is more exposed than that at C-1 to attack by *p*-tosylhydrazine. Along with elemental analysis, spectral data establish the structure of **3** in that the NMR for its hydrogen at C-3 comes at higher field (δ 7.40) than that at C-3 (δ 8.34) in aceanthrenequinone.

α-Diazoacenaphthenes **13** and **14** were generated in situ by base-catalyzed decomposition of acenaphthenone *p*-tosylhydrazone (**15**) and 2,2-dimethylacenaphthenone *p*-tosylhydrazone (**16**) as prepared from reactions of *p*-tosylhydrazine with acenaphthenone and 2,2-dimethylacenaphthenone. Condensation of hydrazine with acenaphthenequinone ethylene monoacetal and subsequent oxidation of acenaphthenequinone ethylene monoacetal hydrazone (**18**) with manganese dioxide yielded **17**.

Chart I



Reactions of 1–3. An initial purpose of this research was to prepare derivatives of **8** as possibly generated by Wolff rearrangement of **1**. Photolysis of **1** at 25 °C in 2-propanol which had not been deoxygenated resulted, however, in acenaphthenone (**22**, 44%), acetone (**23**, 43%), 1,8-naphthalic anhydride (**25**, 15%) and **7** (2%).[9] Products derived from **8** or by incorporation of 2-propanol in any direct manner were not found.[10]

Formation of **22** and **23** may occur by hydrogen abstraction from 2-propanol by **10** as triplet **19** to give the

(5) (a) Chapman, O. *Chem. Eng. News* **1978**, *56* (38), 17. (b) Hess, T. C., *Diss. Abstr. Int. B.* **1979**, *39* (10), 4893. (c) O. L. Chapman, *Pure Appl. Chem.* **1979**, *51*, 331.

(6) (a) Bailey, R. J.; Shechter, H. *J. Am. Chem. Soc.* **1974**, *96*, 8116. (b) Gessner, M.; Card, P.; Shechter, H.; Christoph, G. *Ibid.* **1977**, *99*, 2371. (c) Becker, J.; Wentrup, C. *J. Chem. Soc., Chem. Commun.* **1980**, 190. (d) Bailey, R. J.; Shechter, H. *J. Am. Chem. Soc.*, in press. (e) Card, P. J.; Friedli, F. E.; Shechter, H. *Ibid.*, in press. (f) Card, P. J.; Friedli, F. E.; Shechter, H. *Ibid.*, in press.

(7) Prepared (see Experimental Section) by extension of the method of ref 3a.

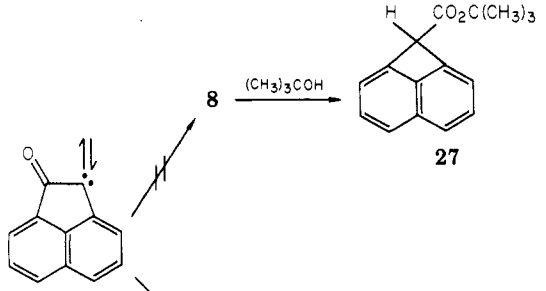
(8) (a) 5-Nitroacenaphthenequinone[8b,c] was obtained (53%) from acenaphthenequinone and nitric acid (1 equiv) at 0 °C. (b) Ruhemann, S. *Ber. Dtsch. Chem. Ges. B* **1920**, *52*, 287. (c) Rowe, F. M.; Davis, J. H. S. *J. Chem. Soc.* **1920**, 1344. (d) Aceanthrenequinone was synthesized from anthracene, oxalyl chloride, and aluminum chloride by a procedure (see Experimental Section) superior to that of: Liebermann, C.; Zusuffa, M. *Chem. Ber.* **1911**, *44*, 202.

(9) Okada, K.; Mukai, T. *Tetrahedron Lett.* **1980**, 359. These authors find as a result of a different mechanistic process that singlet oxygen, as produced by sensitization with *meso*-tetraphenylporphine, reacts with **1** to give acenaphthenequinone and **25**.

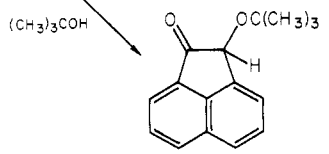
(10) The crude reaction product did not give any IR absorption for an ester function or for 2-propoxyacenaphthenone.

2-oxoacenaphthenyl radical (**20**, eq 1) which in turn abstracts hydrogen from the 2-hydroxy-2-propyl radical **21** previously generated.[11] Production of **25** is rationalized by reaction of **19** with (triplet) oxygen to possibly form dioxirane **24** which rearranges as in eq 2.[12] Dione **7** may arise from attack of **10** on **1** with loss of nitrogen and/or by more complex processes.[13]

Since 2-propanol led to reduction to **22**, **1** was then photolyzed in *tert*-butyl alcohol. The tertiary alcohol was not expected to undergo hydrogen abstraction as rapidly as 2-propanol, and the system might then allow **10** as singlet **26** (or even as excited **1** or **10**) to undergo Wolff rearrangement to **8** and thence conversion to *tert*-butyl 1*H*-cyclobuta[*de*]naphthalene-1-carboxylate (**27**, eq 3).



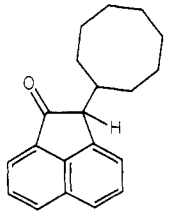
(3)



(4)

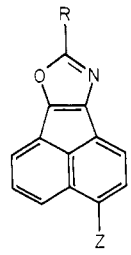
Irradiation of **1** in *tert*-butyl alcohol, however, resulted in 2-*tert*-butoxyacenaphthenone (**28**, 17%) and **7** along with intractables (eq 4). Ketene **8**, ester **27**, or any products containing an ester group were not identifiable in these experiments. Keto ether **28** presumably results from direct insertion of **26** into the O–H bond of *tert*-butyl alcohol[14] and/or from some competitive reaction mechanism.

Reactions of **10** in environments less nucleophilic than alcohols were then explored. Thus **1** was found to react photochemically and thermally (150 °C) in cyclooctane, from which oxygen had not been completely removed, to give 2-cyclooctylacenaphthenone (**29**; 52% and 62%, respectively) along with **25** (21% and 36%, respectively). Formation of **29** is explained by insertion into a C–H bond of cyclooctane by **10** possibly as singlet **26**; **25** might be produced as in eq 2.



29

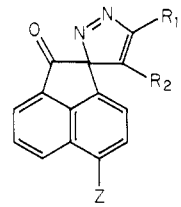
Decomposition of **1** was then investigated in benzonitrile and acetonitrile, polar solvents which might allow rearrangement to **8**. Thermolysis (160 °C) and photolysis of **1** in benzonitrile results, however, in 8-phenylacenaphth-[1,2-*d*]oxazole (**30**; 34% and 24%, respectively). Also,



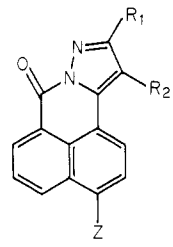
30, Z = H; R = C_6H_5
31, Z = H; R = CH_3
32, Z = NO_2; R = C_6H_5
33, Z = NO_2; R = CH_3

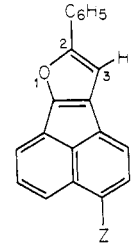
irradiation of **1** in acetonitrile yields 8-methylacenaphth-[1,2-*d*]oxazole (**31**, 62%). Similar cycloadditions have been reported for **1**.[15] α-Oxoazirenes, possible intermediates, were not detected. The behavior of **1** in benzonitrile containing cupric sulfate is modified, however, in that **7** (78%) is formed. In none of these experiments was there evidence for **8**.

Phenylacetylene adds regiospecifically to **1** with retention of nitrogen and rearrangement of **34** to give 10-phenyl-7*H*-benzo[*de*]pyrazolo[5,1-*a*]isoquinolin-7-one (**37**).[16] Photolysis of **1** in phenylacetylene differs, however,



34, Z = H; R_1 = C_6H_5; R_2 = H
35, Z = NO_2; R_1 = C_6H_5; R_2 = H
36, Z = NO_2; R_1 = R_2 = CO_2CH_3





37, Z = H; R_1 = C_6H_5; R_2 = H
38, Z = NO_2; R_1 = C_6H_5; R_2 = H
39, Z = NO_2; R_1 = R_2 = CO_2CH_3

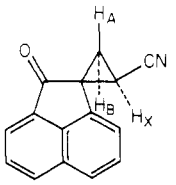
40, Z = H
41, Z = NO_2

in that nitrogen is lost and 8-phenylacenaphtho[1,2-*b*]furan (**40**, 21%) is formed. The behavior of **1** thus is as an electrophilic singlet (**26**) which undergoes net regiospecific 1,3-cycloaddition to phenylacetylene;[17] the intermediate α-oxocyclopropene cannot be ruled out, however, as a precursor to **40**. The structure of **40** (and thus the regiochemistry of addition) is assigned from its NMR singlet at δ 6.99 for the proton at C-3 of its furan nucleus. The

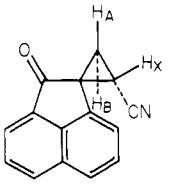
(11) Similar mechanisms for hydrogen abstraction by triplet α-keto carbenes have been reported by: (a) Padwa, A.; Layton, R. *Tetrahedron Lett.* **1965**, 2167. (b) Baumann, N. *Helv. Chim. Acta* **1972**, *55*, 274.
(12) Reference 5 has found that photolysis of **1** in argon matrix at 8–12 K in the presence of oxygen yields **25**.
(13) A possibility is reaction of **1** with excited **1**.
(14) Alternate possibilities include protonation of **26** or/and excited **1**, subsequent reaction with *tert*-butyl alcohol, and conversion to **28**.
(15) (a) After the present experiments were complete, it was reported[15b] that **1** (1) thermolyzes and photolyzes in benzonitrile to give **30** in 8% and 24% yields, respectively and (2) reacts photolytically with acetonitrile to form **31** (30%). (b) Tsuge, O.; Koga, M. *Heterocycles* **1977**, *6*, 411.
(16) Yamazaki, T.; Shechter, H. *Tetrahedron Lett.* **1972**, 4533.
(17) (a) Similar regiochemistry in cycloaddition is observed in the thermolysis of tetrachlorobenzene 1,2-diazooxide in phenylacetylene to give 4,5,6,7-tetrachloro-2-phenylbenzo[*b*]furan. (b) Huisgen, R.; Binsch, G.; Konig, H. *Chem. Ber.* **1964**, *97*, 2884.

chemical shift for this hydrogen compared to that of a β-proton in furan (δ 6.37) is attributed to the deshielding by the phenyl and acenaphthene groups. The NMR of the α-proton in furan comes at δ 7.42 and should be shifted to an even lower field if a phenyl group were adjacent.

Efforts to effect thermal or photolytic cyclopropanations of ethyl vinyl ether or cyclohexene with **1** or/and **10** have all been unsuccessful. Thermal decomposition or irradiation of **1** in acrylonitrile gives (*Z*)- and (*E*)- 2′-cyanospiro[acenaphthenone-2,1′-cyclopropanes] **42** and **43**.[18,19]



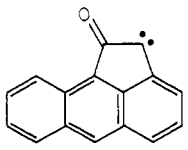
42



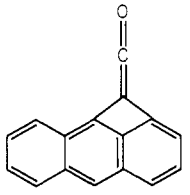
43

Thermolysis of **1** in acrylonitrile containing palladium acetate leads much more smoothly however to **42** (37%) and **43** (38%). The presumption is that **1** is converted by palladium acetate to an ylidic intermediate which then reacts with acrylonitrile to yield **42** and **43**, the structures of which have been assigned by NMR methods.[18,19]

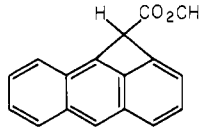
Investigation was then made of various reactions of **2** and **3**. Photolysis and thermolysis of **2** were studied on the basis that the nitro group at C-5 would make the carbene center (C-2) in **11** highly electron deficient. Therefore, migration would become more favorable, and rearrangement to ketene **9** might be induced. Possible strain relief leading to Wolff rearrangement in decomposition of **3**, a benzo analogue of **1**, was also explored. A purpose thus was to put a bulky group in the 8-position of a diazoacenaphthenone (see **1**) with the expectation that steric crowding would push the carbonyl group toward the subsequent carbenic center, thus making it easier in **44** for



44



45

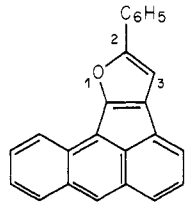


46

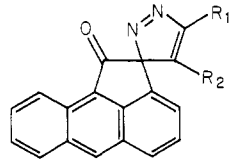
Wolff ring contraction to **45** occur. Photolysis of **2** in methylene chloride and in alcohols at −70 to +25 °C[20] as well as dry pyrolysis of **2** at 200 °C gave intractables however. There was no evidence for conversion of **2** to **9** in any of these experiments. Similarly, all efforts to effect photolytic conversion of **3** in methanol to methyl 1*H*-cyclobuta[*de*]anthracene-1-carboxylate (**46**)[20] as derived by trapping **45** failed.

Study was then directed to the chemistry of **2** and **3** in the presence of benzene, nitriles, acetylenes, and electro-

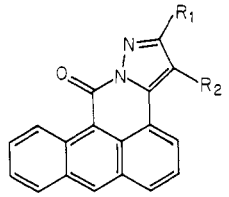
Chart II



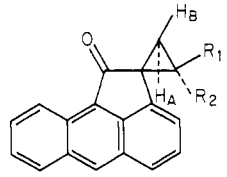
51



52, $R_1 = C_6H_5$; $R_2 = H$
53, $R_1 = R_2 = CO_2CH_3$

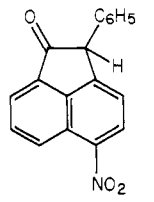


54, $R_1 = C_6H_5$; $R_2 = H$
55, $R_1 = R_2 = CO_2CH_3$

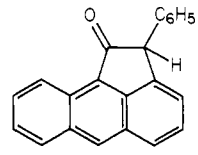


56, $R_1 = CN$; $R_2 = H_X$
57, $R_1 = H_X$; $R_2 = CN$
58, $R_1 = CO_2CH_3$; $R_2 = H_X$
59, $R_1 = H_X$; $R_2 = CO_2CH_3$

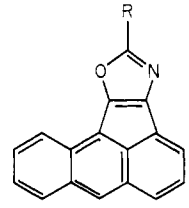
negatively substituted olefins. Irradiation of **2** and **3** in benzene results in aromatic substitution, yielding 5-nitro-2-phenylacenaphthenone (**47**, 55%) and 2-phenyl-



47



48



49, R = C_6H_5
50, R = CH_3

aceanthrenone (**48**, 68%), respectively.[21] In behavior similar to that of **1**, **2** reacts photolytically and thermally (191 °C)[22] in benzonitrile and photolytically in acetonitrile (apparently via **11**) to give 3-nitro-8-phenylacenaphth-[1,2-*d*]oxazole (**32**; 34% and 50%, respectively) and 8-methyl-3-nitroacenaphth[1,2-*d*]oxazole (**33**; 48%). Analogously, irradiation of **3** in benzonitrile and acetonitrile results in nitrogen expulsion and formation of 2-phenylaceanthryleno[2,1-*d*]oxazole (**49**, 11%) and 2-methylaceanthryleno[2,1-*d*]oxazole (**50**, 36%). In none of these experiments were rearrangements to **9** or **45** observable.

Again, **1**–**3** react photolytically with loss of nitrogen and regiospecific cycloaddition to phenylacetylene, giving 3-nitro-8-phenylacenaphtho[1,2-*b*]furan (**41**, 60%)[23] and 10-phenylaceanthro[1,2-*b*]furan (**51**,[24] Chart II). Further, **2** and **3** add thermally to phenylacetylene and dimethyl acetylenedicarboxylate with nitrogen retention and rear-

(18) It was reported[2] that thermolysis of **1** in acrylonitrile yields isomeric 2′-cyanospiro[acenaphthenone-2,1′-cyclopropanes]. The stereochemistry of the cyclopropanes was misassigned however.[19] It has been presently found that conversions to **42** and **43** are greatly improved upon reaction of **1** with acrylonitrile in the presence of palladium acetate.

(19) (a) The assignments of **42** and **43** exhibit clear ABX patterns for cyclopropyl protons. In **42**: $\delta(H_x)$ 2.54, $\delta(H_a)$ 1.98, $\delta(H_b)$ 2.16; $J_{ax} = 7$ Hz, $J_{bx} = 9$ Hz, $J_{ab} = 4$ Hz. In **43**: $\delta(H_x)$ 2.46, $\delta(H_a)$ 2.06, $\delta(H_b)$ 2.27; $J_{ax} = 9.6$ Hz, $J_{bx} = 6.9$ Hz, $J_{ab} = 3.6$ Hz. (b) Cis cyclopropyl protons exhibit larger coupling constants (8–10 Hz) than do trans protons (4–7 Hz). (c) Since a β-carbonyl group shields protons facing it, H_x of **42** is expected to come at lower field (higher δ value) than that of **43**. (d) The present assignments are opposite those previously proposed.

(20) The crude reaction products gave no IR or NMR evidence for ester derivatives.

(21) (a) Photolysis of **1** in benzene yields the spironorcaradiene adduct (84%) which is isomerized to 2-phenylacenaphthenone by acids or silver ion.[21b] In the present experiments with **2** and **3** in benzene, spironorcaradienes were not found. (b) Bannerman, C. G. F.; Cadogan, I. G.; Gosney, I.; Wilson, N. H. *J. Chem. Soc., Chem. Commun.* **1975**, 618.

(22) Cupric sulfate greatly accelerates reaction of **2** with benzonitrile to give **32**.

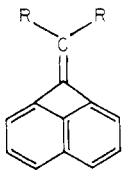
(23) The regiochemistry of addition to give **41** is assigned from its furan proton singlet at δ 7.10 upon comparison with the β-H resonance of 2,5-diphenylfuran at δ 6.71. Since the absorption of α-H for furans substituted by phenyl groups comes at lower field than δ 7.42, the regioisomer of **41** with the phenyl group at the 3-position is excluded.

(24) The NMR of **51** exhibits a singlet at δ 7.09 for hydrogen β to the furan oxygen. The resonance is thus similar to that of the β-proton of **40** (δ 6.99).

rangement (of **35**, **36**, **52**, and **53**) to produce 3-nitro-10-phenyl-7*H*-benzo[*de*]pyrazolo[5,1-*a*]isoquinolin-7-one (**38**, 67%),[25] 2-phenyl-12*H*-dibenzo[*de*,*h*]pyrazolo[1,5-*b*]isoquinolin-12-one (**54**, 98%),[26] dimethyl 3-nitro-7-oxo-7*H*-benzo[*de*]pyrazolo[5,1-*a*]isoquinoline-10,11-dicarboxylate (**39**, 83%),[27] and dimethyl 12-oxo-12*H*-dibenzo[*de*,*h*]-pyrazolo[1,5-*b*]isoquinoline-2,3-dicarboxylate (**55**, 100%)[28] efficiently. Presumed intermediates **35**, **36**, **52**, and **53** could not be detected because of their apparent spontaneous rearrangements. The utility of **3** as a reagent is revealed further by its reactions with acrylonitrile and methyl acrylate upon heating, yielding isomeric 2′-cyanospiro[aceanthrenone-2,1′-cyclopropanes] **56** (42%) and **57** (54%)[29] and 2′-(methoxycarbonyl)spiro[aceanthrenone-2,1′-cyclopropanes] **58** (39%) and **59** (51%).[30]

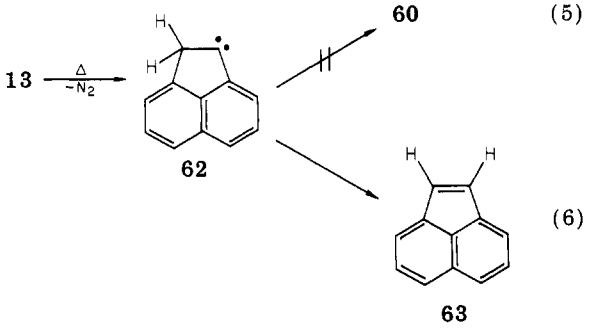
Attempts to effect preparative conversions of **1–3** in solution by photolysis or by thermolysis to **8**, **9**, and **45** and derivatives thereof have thus all failed. These results emphasize the importance of the low-temperature, matrix-isolation methodology to the successful conversion of **1** to **8**.[5] Efforts to study the preparative photochemistry of **1–3** in solution at reduced temperatures (−40 to −78 °C) have as yet been fruitless because of the poor solubilities of the diazo ketones in the solvents available.

Reactions of 13, 14, and 17. 1-Methylene-1*H*-cyclobuta[*de*]naphthalene (**60**), 1-isopropylidene-1*H*-cyclobuta[*de*]naphthalene (**61**), and their analogues have been prepared from (1*H*-cyclobuta[*de*]naphthalen-1-ylidene]-triphenylphosphorane and the requisite aldehydes or ketones.[6] The present methods, however, for synthesis of such olefins are lengthy and, as yet, unsuitable for large-scale purposes.



60, R = H
61, R = CH_3

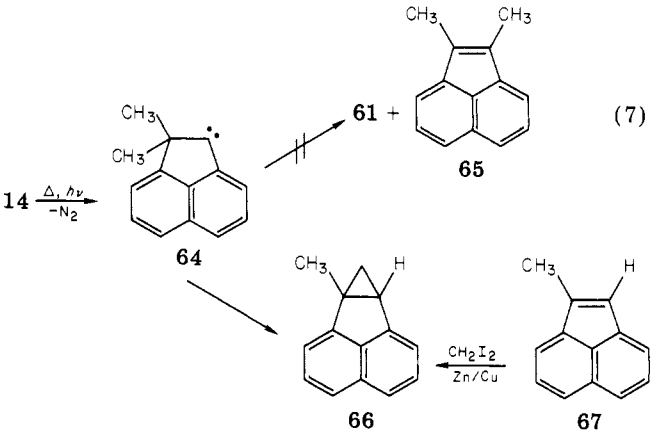
In many carbene systems migration of aryl groups to divalent carbon begins to compete effectively with rearrangement of hydrogen.[31] If **60** were to be formed even in low yield from decomposition of **13**, the synthesis would be extremely valuable. Thermolysis of **13**, as generated from the sodium salt of **15** at 100 or at 600 °C, is found, however, to give acenaphthylene (**63**) as the only product of isomerization of acenaphthylidene (**62**). Hydrogen migration (eq 6) rather than ring contraction (eq 5) thus occurs in rearrangement of **62**.



(5)

(6)

Aryl substituents undergo carbenic migration considerably more rapidly than do methyl groups.[31] Rearrangement of 2,2-dimethyl-1-acenaphthylidene (**64**) was thus examined as a source of **61** (eq 7). Decomposition



(7)

of **14**, as generated from the sodium salt of **16** under vacuum at 220–230 °C or in anisole at 154 °C, gives 8-methylcycloprop[*a*]acenaphthylene (**66**; 40% and 26%, respectively) as the only hydrocarbon carbenic product. Similarly, photolysis of the sodium salt of **16** gives **66** (16%). Isomerization of **64** thus did not yield **61** or 1,2-dimethylacenaphthylene (**65**). Insertion product **66** was identified upon synthesis from 1-methylacenaphthylene (**67**), methylene iodide, and zinc–copper couple.

Pyrolysis of **14** at much higher temperatures was then studied as an entree of **61**. Dropping the sodium salt of **16** at 0.05 mmHg through a quartz tube at 660 °C gave, however, methylphenalenes **70a–d**, and inseparable product apparently arising from rearrangement of **68**, and then **69** (eq 9). The product is similar to that from thermolysis of authentic **66** at 600 °C, and its gross structure is assigned from its NMR.[32] The thermal behavior of **66** thus resembles its facile rhodium(I)-catalyzed isomerizations to methylphenalenes.[33]

(25) (a) The UV spectrum of **38** (λ_{max} ($CHCl_3$) 248 and 385 nm) is similar to that of **37** (λ_{max} (EtOH) 252, 332, and 370 nm). Adduct **38** is recovered quantitatively after having been refluxed in chlorobenzene or irradiated in benzene for long periods. Since 3*H*-pyrazoles lose nitrogen readily upon photolysis and thermolysis, the stability of **38** eliminates **35** as an alternate structure.

(26) Quantitative analysis, spectral data, thermal and photolytic stability, and chemical properties establish **54**. The ^{13}C NMR of **54** exhibits a carbonyl carbon resonance at 162.08 ppm assignable to amide carbonyl. Ketones related to **52** show carbonyl resonances at 180–210 ppm.

(27) Isoquinoline **39** is thermally and photochemically stable, and its UV (EtOH) spectrum (λ_{max} 207 and 374 nm) is comparable to that of **38**.

(28) Isoquinoline **55** exhibits a ^{13}C NMR signal for carbonyl carbon at δ 162.88, similar to that of **39** (δ 163.42). Extended heating (refluxing toluene for 24 h) and irradiation (>3 h) do not alter **55**.

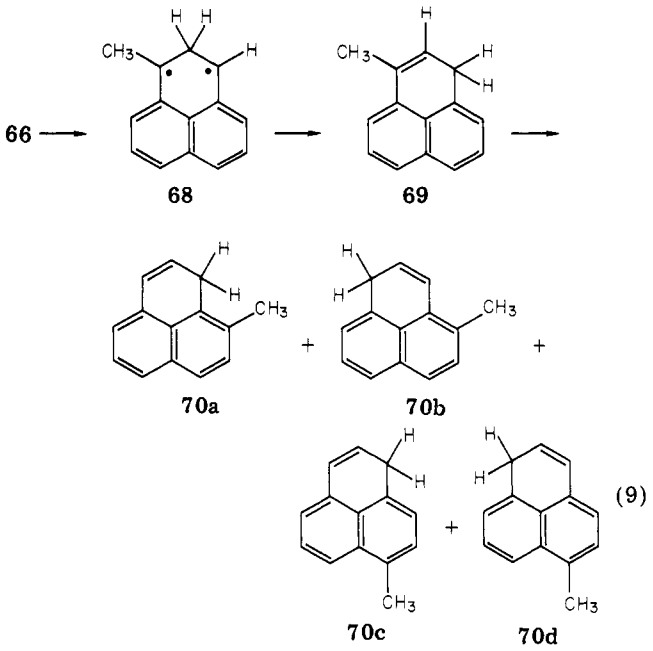
(29) (a) The stereochemistries of **56** and **57** are assigned on the basis that since H_x in **57** is syn to the carbonyl group, its $\delta(H_x)$ comes at higher field than that for **56**. The *J* values for **56** and **57** are also consistent with observations that larger coupling constants are exhibited by cis than by trans cyclopropyl protons.[29b,c] (b) Wiberg, K. B.; Nist, B. *J. J. Am. Chem. Soc.* **1963**, *85*, 2788. (c) Graham, J. D.; Rogers, M. T. *Ibid.* **1962**, *84*, 2249.

(30) Isomers **58** and **59** are distinguishable by NMR methods. In **59**: $\delta(H_x)$ 2.86, $\delta(H_a)$ 2.24, $\delta(H_b)$ 2.07; J_{ax} = 7 Hz, J_{bx} = 9 Hz, J_{ab} = 4 Hz. In **58**: $\delta(H_x)$ 2.90, $\delta(H_a)$ 2.60, $\delta(H_b)$ 2.08; J_{ax} = J_{bx} = 8 Hz, J_{ab} = 4 Hz.

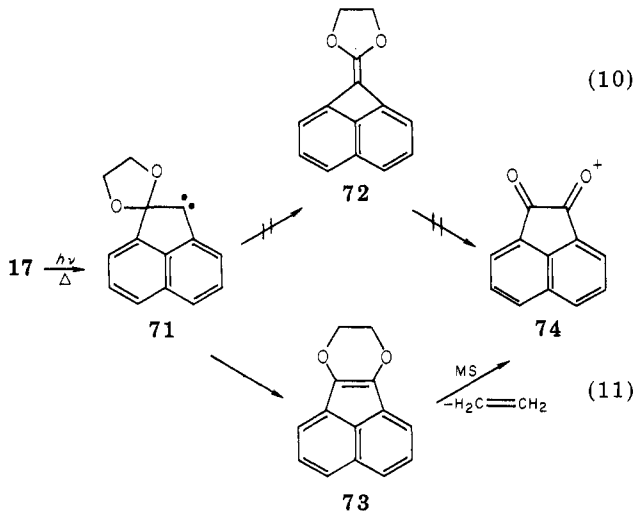
(31) (a) Kaufmann, G. M. Ph.D. Dissertation, The Ohio State University, 1967. (b) Philip, H.; Keating, J. *Tetrahedron Lett.* **1961**, 523. (c) Landgrebe, J. A.; Kirk, A. G. *J. Org. Chem.* **1967**, *32*, 3499. (d) Chang, K. T. Ph.D. Dissertation, The Ohio State University, Columbus, OH, 1978.

(32) The structures of the products of pyrolysis of the sodium salt of **16** and of authentic **66** are also consistent with their hydrogenation in methanol with platinum oxide to a mixture of 4- and 6-methylperinaphthanes: NMR ($CDCl_3$) δ 2.0 (m, CH_2), 2.4 (s, CH_3), 3.0 (m, benzylic H), 7.0–7.8 (m, aromatic); exact mass calcd for $C_{14}H_{14}$ *m/e* 182.109 544, found *m/e* 182.109 112. The NMR of the two methyl singlets in the hydrogenation products are very similar to those of 3- and 5-methylacenaphthylenes[32b] (δ 2.60 and 2.70, respectively). (b) Entwistle, I. D.; Jhonstone, R. A. W. *J. Chem. Soc.* C **1968**, 1821.

(33) Paquette, L. A.; Gree, R. *J. Organomet. Chem.* **1978**, *146*, 319.



Ether groups do not migrate readily to divalent carbon.[34] Decomposition of **17** was thus investigated as a source of (1*H*-cyclobuta[*de*]naphthalene-1-ylidene)methanone ethylene acetal (**72**, eq 10), a product of interest as a source



of 1*H*-cyclobuta[*de*]naphthalene-1-carboxylic acid upon hydrolysis. Photolysis of **17** in ethyl ether, however, results in 8,9-dihydroacenaphtho[1,2-*b*]-*p*-dioxin (**73**; eq 11, 51%), the product of migration of one of the acetal oxygen moieties in **71**. Similarly, decomposition of **17** in refluxing benzene yields **73** (31%). Ketene acetal **72** was not found in either experiment. *p*-Dioxin **73** is assigned from its varied spectra,[35] its exact mass, and, in particular, its mass spectral fragmentation pattern. Upon initial loss of 28 mass units, presumably for ethylene, the mass spectrum of **73** is identical with that of the acenaphthenequinone ion (**74**). Thus, mass spectral destruction of **73** apparently results in a reverse Diels–Alder reaction to give **74**. Fragmentation of **72** to **74** would be highly surprising.

Study of the chemistry of diazoacenaphthenones with substituents at their 5,6- and 3,8-positions has been initiated.

(34) Gould, K. Ph.D. Dissertation, The Ohio State University, Columbus, OH, 1978.

(35) The ^{13}C NMR of the product is totally consistent with the assignment of **73**.

Experimental Section

Photolysis of 1 in 2-Propanol. Irradiation[36] (3 h) of **1**[7] (0.4 g, 2 mmol) in 2-propanol, removal of the solvent, and chromatography (silica gel/benzene) yielded (1) biacenedione (**7**; 6 mg, 2%), (2) acenaphthenone [**22**: 84 mg (24%); exact mass calcd *m/e* 168.057 51, found *m/e* 168.057 90], and (3) 1,8-naphthalic anhydride (**25**; 59 mg, 15%) as identified by comparison with authentic samples.

Photolysis of 1 in *tert*-Butyl Alcohol. A *tert*-butyl alcohol solution of **1** (0.5 g, 2.57 mmol), on photolysis[36] (5 h), concentration, and chromatography (silica gel/benzene), gave (1) **7** [5 mg (2%); mp 292–295 °C (petroleum ether/toluene) (lit.[2] mp 294 °C); exact mass calcd for $C_{24}H_{12}O_2$ *m/e* 332.083 72, found *m/e* 332.084 42] and (2) 2-*tert*-butoxyacenaphthenone (**28**): 71 mg (17%); mp 212–214 °C (toluene); yellow crystals; IR (KBr) 1725 cm^{-1} (C=O, s); NMR ($CDCl_3$) δ 8.1–7.23 (m, 6 H, aromatic), 5.05 (s, 1 H, benzylic), 0.70 (br s, 9 H, 3 CH_3); exact mass calcd for $C_{16}H_{16}O_2$ *m/e* 240.115 02, found *m/e* 240.115 76.

Anal. Calcd for $C_{16}H_{16}O_2$: C, 80.00; H, 6.67. Found: C, 80.42; H, 6.12.

Photolysis of 1 in Cyclooctane. A solution of **1** (0.4 g, 2 mmol) in cyclooctane was photolyzed[36] (3 h), worked up, chromatographed (silica gel/hexane–benzene), and sublimed. 2-Cyclooctylacenaphthenone (**29**; 0.295 g, 52%) was obtained as a light yellow oil: IR (CH_2Cl_2) 2930–2860 (cyclooctyl CH, s), 1720 cm^{-1} (C=O, s); NMR ($CDCl_3$) δ 8.12–7.33 (m, 6 H, aromatic), 3.65 (d, 1 H, benzylic), 1.9–1.0 (br s, 15 H, cyclooctyl); mass spectrum, *m/e* 278 (M^+). (The 2,4-dinitrophenylhydrazone of **29** recrystallized from toluene/acetonitrile as red crystals, mp 234–236 °C dec.)

Anal. Calcd for $C_{20}H_{22}O$: C, 86.33; H, 7.91. Found: C, 86.47; H, 7.72.

Further elution with benzene and recrystallization from toluene/acetonitrile led to **25** [85 mg (21%); mp 266–269 °C (lit.[37] mp 267–269 °C)], identified by comparison with an authentic sample.

Thermolysis of 1 in Cyclooctane. Refluxing **1** (0.4 g, 2 mmol) in cyclooctane (100 mL) under nitrogen for 19 h, solvent removal under reduced pressure, and chromatography as in the previous photolysis yielded **29**, 0.357 g (62%). Further elution with benzene gave **25**, 0.146 g (36%).

Photolysis of 1 in Benzonitrile. Irradiation[36] of **1** (0.5 g, 2.57 mmol) in benzonitrile for 9 h, concentration, and chromatography (silica gel/benzene) yielded yellow crystals of 8-phenylacenaphth[1,2-*d*]oxazole (**30**): 0.165 g (24%); mp 217–218 °C (lit.[15b] mp 217–218 °C); exact mass calcd for $C_{19}H_{11}NO$ *m/e* 269.084 05, found *m/e* 269.084 69.

Anal. Calcd for $C_{19}H_{11}NO$: C, 84.76; H, 4.09; N, 5.20. Found: C, 84.51; H, 4.41; N, 5.28.

Thermolysis of 1 in Benzonitrile. A solution of **1** (0.5 g, 2.57 mmol) in benzonitrile (200 mL) was refluxed (160 °C) for 65 h. After vacuum concentration, the residue was chromatographed (silica gel/benzene) to yield **30** (0.245 g, 34%) as previously identified.

Thermolysis of 1 in Benzonitrile/Cupric Sulfate. A mixture of **1** (0.4 g, 2 mmol) and anhydrous cupric sulfate (0.2 g) in benzonitrile (50 mL) was refluxed (160 °C) for 24 h. After the copper sulfate was filtered, the workup resulted in **7**,[2] 0.27 g (78%).

Photolysis of 1 in Acetonitrile. An acetonitrile solution of **1** (1.0 g, 5.15 mmol), on irradiation (2.5 h), distillation, and chromatography on silica gel (benzene), gave 8-methylacenaphth[1,2-*d*]oxazole (**31**): 0.657 g (62%); mp 108–110 °C (lit.[15b] mp 115–116 °C); yellow crystals; NMR (acetone-d_6) δ 7.6–7.17 (m, 6 H, aromatic), 2.27 (s, 3 H, CH_3); exact mass calcd for $C_{14}H_9NO$ *m/e* 207.068 41, found *m/e* 207.068 76.

(36) Photolyses so indicated were conducted by irradiating the diazo compounds in the solvent (~220 mL) specified with a Hanovia 450-W medium-pressure lamp dipped in a Pyrex well. All solvents were dried and distilled. Nitrogen was bubbled through the solutions before and/or during photolysis. Photolyses were effected at room temperature unless otherwise indicated.

(37) Bun-Hoi, N. P.; Lavit, D., *Recl. Trav. Chim. Pays-Bas* **1958**, *77*, 724.

Anal. Calcd for $C_{14}H_9NO$: C, 81.16; H, 4.35; N, 6.76. Found: C, 81.41; H, 4.28; N, 6.83.

Photolysis of 1 in Phenylacetylene. Chromatography of a photolyzed solution (3 h) of **1** (0.5 g, 2.57 mmol) in phenylacetylene resulted in 8-phenylacenaphtho[1,2-*b*]furan (**40**): 0.147 g (21%); mp 130–131 °C (petroleum ether); orange crystals; NMR ($CDCl_3$) δ 7.85–7.15 (m, 11 H, aromatic), 6.99 (s, 1 H); exact mass calcd for $C_{20}H_{12}O$ *m/e* 268.088 81, found *m/e* 268.089 46.

Anal. Calcd for $C_{20}H_{12}O$: C, 89.55; H, 4.48. Found: C, 89.64; H, 4.45.

Thermolysis of 1 in Cyclohexene/Cuprous Bromide. A mixture of **1** (0.2 g, 1.03 mmol), a catalytic amount of cuprous bromide, and cyclohexene (40 mL) was refluxed under nitrogen for 2.5 h. Filtration, concentration, and chromatography (silica gel/chloroform) yielded **7**,[2] 0.131 g (77%).

Thermolysis of 1 in Acrylonitrile/Palladium Acetate. Refluxing (8 h) **1** (0.2 g, 1 mmol), palladium acetate (trace), and acrylonitrile (25 mL), product isolation, chromatography on silica gel, and elution with benzene gave (*Z*)-2′-cyanospiro[acenaphthenone-2,1′-cyclopropane] (**42**): 84 mg (37%); mp 115–116 °C (petroleum ether/toluene) (lit.[2] mp 118–119 °C); IR (KBr) 2250 C≡N, w), 1715 cm^{-1} (C=O, s); NMR ($CDCl_3$) δ 8.23–7.25 (m, 6 H, aromatic), 2.63–1.66 (m, 3 H, cyclopropyl C–H), J_{gem} = 4 Hz, J_{cis} = 9 Hz, J_{trans} = 7 Hz); exact mass calcd for $C_{15}H_9NO$ *m/e* 219.068 41, found *m/e* 219.069 05.

Further elution with chloroform yielded (*E*)-2′-cyanospiro-[acenaphthenone-2,1′-cyclopropane] (**43**): 87 mg (38%); mp 163–164 °C (lit.[2] mp 163–164 °C), isomeric with **42**; IR (KBr) 2260 (C≡N, w), 1715 cm^{-1} (C=O, s); exact mass calcd for $C_{15}H_9NO$ *m/e* 219.068 041, found *m/e* 219.069 05.

The stereochemical assignments of **42** and **43** are based on their NMR spectra and are opposite that previously given.[2]

5-Nitroacenaphthenequinone 2-*p*-Tosylhydrazone (5). A solution of 5-nitroacenaphthenequinone[8] (1.0 g, 4.4 mmol) and *p*-tosylhydrazine (0.84 g, 4.4 mmol) in tetrahydrofuran (30 mL) and concentrated hydrochloric acid (5 drops) was stirred 4 h. Crystallization of the precipitate from toluene/acetonitrile (1:1) yielded **5**: 1.22 g (70%); mp 208 °C dec; yellow prisms; NMR ($CDCl_3$) δ 12.68 (s, 1 H, NH), 9.11 (dd, 1 H), 8.67 (d, 1 H), 8.20–7.31 (m, 7 H), 2.42 (s, 3 H, CH_3).

Anal. Calcd for $C_{19}H_{13}N_3O_5S$: C, 57.97; H, 3.29; N, 10.63. Found: C, 57.85; H, 3.24; N, 10.37.

2-Diazo-5-nitroacenaphthenone (2). A mixture of aqueous sodium hydroxide (0.1 N, 13 mL, 1.26 mmol) and a methylene chloride (30 mL) solution of **5** (0.5 g, 1.26 mmol) was stirred overnight. The methylene chloride layer was washed with water, dried ($CaCl_2$), and concentrated. Crystallization of the yellow product gave **2**: 0.35 g (100%); mp 190 °C dec (toluene); IR (KBr) 2100 (=N_2, s), 1670 (C=O, s), 1480, 1320 cm^{-1} (NO_2, s); NMR ($CDCl_3$) δ 9.05 (dd, 1 H), 8.62 (d, 1 H), 8.16–7.87 (m, 2 H), 7.137 (d, 1 H).

Anal. Calcd for $C_{12}H_5N_3O_3$: N, 17.57. Found: N, 17.26.

Photolysis of 2 in Benzene. A benzene solution of **2** (0.4 g, 1.67 mmol), upon irradiation (3 h), rotary evaporation, and chromatography (silica gel/benzene), resulted in 5-nitro-2-phenylacenaphthenone (**47**): 0.263 g (55%); mp 153–154 °C dec (petroleum ether/toluene); yellow crystals; IR (KBr) 1730 (C=O, s), 1520, 1330 cm^{-1} (NO_2, s); NMR ($CDCl_3$) δ 9.06 (dd, 1 H), 8.6 (d, 1 H, benzylic); exact mass calcd for $C_{18}H_{11}NO_3$ 289.073 89, found *m/e* 289.074 59.

Anal. Calcd for $C_{18}H_{11}NO_3$: C, 74.74; H, 3.81; N, 4.84. Found: C, 74.74; H, 4.00; N, 4.99.

Photolysis of 2 in Benzonitrile. Photolysis of **2** (0.5 g, 2.1 mmol) in benzonitrile for 12 h, product concentration, and chromatography (silica gel/benzene) gave 3-nitro-8-phenylacenaphth[1,2-*d*]oxazole (**32**): 0.226 g (35%); mp 275–277 °C dec (petroleum ether/chloroform); red-brown crystals; IR (KBr) 1485, 1330 cm^{-1} (NO_2, s); NMR ($CDCl_3$) δ 8.94–7.25 (m, 10 H, aromatic); exact mass calcd for $C_{19}H_{10}N_2O_3$ *m/e* 314.069 14, found *m/e* 314.069 68.

Anal. Calcd for $C_{19}H_{10}N_2O_3$: C, 72.61; H, 3.18; N, 8.92. Found: C, 72.71; H, 2.94; N, 8.90.

Thermolysis of 2 in Benzonitrile. A mixture of **2** (0.4 g, 1.67 mmol) and benzonitrile (150 mL), after reflux (24 h), concentration, and chromatography, yielded **32**: 0.267 g (51%); mp 275–277 °C dec).

Photolysis of 2 in Acetonitrile. Irradiation of **2** (0.5 g, 2.1 mmol) in acetonitrile (1.5 h), concentration, and chromatography of the residue on silica gel (benzene) yielded red crystals of 8-methyl-3-nitroacenaphth[1,2-*d*]oxazole (**33**): 0.225 g (48%); mp 214–216 °C (petroleum ether/benzene); IR (KBr) 1510, 1320 cm^{-1} (NO_2, s); ($CDCl_3$) δ 8.62–8.50 (dd, 1 H), 8.45 (d, 1 H), 7.79 (d, 1 H), 7.7–7.5 (m, 2 H), 2.66 (s, 3 H, CH_3); exact mass calcd for $C_{14}H_8N_2O_3$ *m/e* 252.053 48, found *m/e* 252.053 98.

Anal. Calcd for $C_{14}H_8N_2O_3$: C, 66.66; H, 3.17; N, 11.11. Found: C, 66.64; H, 2.98; N, 10.96.

Photolysis of 2 in Phenylacetylene. Chromatography (silica gel/benzene) of the product of photolysis of **2** (0.5 g, 2.1 mmol) in phenylacetylene yielded dark brown crystals of 3-nitro-8-phenylacenaphtho[1,2-*b*]furan (**41**): 0.393 g (60%); mp 186–188 °C (petroleum ether/toluene); IR (KBr) 1515, 1330 cm^{-1} (NO_2, s); NMR ($CDCl_3$/Me_2SO-d_6) δ 8.30 (dd, 1 H), 7.90–7.30 (m, 9 H, aromatic), 7.10 (s, 1 H); exact mass calcd for $C_{20}H_{11}NO_3$ *m/e* 313.073 89, found *m/e* 313.074 44.

Anal. Calcd for $C_{20}H_{11}NO_3$: C, 76.68; H, 3.51; N, 4.47. Found: C, 76.91; H, 3.57; N, 4.65.

Thermolysis of 2 in Phenylacetylene. Phenylacetylene (2 mL) and **2** (0.3 g, 1.25 mmol) in chlorobenzene (20 mL) were refluxed under nitrogen for 19 h and concentrated. Chromatography (silica gel/chloroform) led to 3-nitro-10-phenyl-7*H*-benzo[*de*]pyrazolo[5,1-*a*]isoquinolin-7-one (**38**): 0.29 g (68%); mp 298 °C (chloroform); yellow crystals; IR (KBr) 1710 (C=O, s), 1520, 1350 cm^{-1} (NO_2, s); NMR ($CDCl_3$) δ 9.06–7.48 (m, 11 H, aromatic); exact mass calcd for $C_{20}H_{11}N_3O_3$ *m/e* 341.080 03, found *m/e* 341.080 57.

Anal. Calcd for $C_{20}H_{11}N_3O_3$: C, 70.38; H, 3.23; N, 12.32. Found: C, 70.43; H, 3.30; N, 12.39.

Thermolysis of 2 in Dimethyl Acetylenedicarboxylate. Removal of solvents and chromatography (silica gel/chloroform) of a mixture of **2** (0.2 g, 0.83 mmol) and dimethyl acetylenedicarboxylate (0.5 mL) in chlorobenzene (20 mL) which had been refluxed under nitrogen for 12 h yielded yellow crystals of dimethyl 3-nitro-7-oxo-7*H*-benzo[*de*]pyrazolo[5,1-*a*]isoquinoline-10,11-dicarboxylate (**39**): 0.265 g (83%); mp 235–238 °C (toluene/acetonitrile); IR (KBr) 1730 (C=O, br, s), 1530, 1350 cm^{-1} (NO_2, s); NMR ($CDCl_3$) δ 9.14–8.96 (m, 3 H), 8.41 (d, 1 H), 8.17–8.05 (m, 1 H), 4.06 (s, 3 H, OCH_3), 4.03 (s, 3 H, OCH_3); exact mass calcd for $C_{18}H_{11}N_3O_7$ *m/e* 381.05969, found *m/e* 381.06036.

Anal. Calcd for $C_{18}H_{11}N_3O_7$: C, 56.69; H, 2.89; N, 11.02. Found: C, 56.17; H, 2.85; N, 11.04.

Aceanthrenequinone.[8d] Oxalyl chloride (40 mL) was added slowly to a stirred mixture of anthracene (20 g, 86.2 mmol) and aluminum chloride (25.0 g) in carbon disulfide (200 mL) at 0–5 °C. Stirring was continued for 1 h at 0 °C and overnight at room temperature. The black tarry product was poured into ice–water, heated to remove carbon disulfide, cooled, and filtered. The orange product was then stirred in saturated sodium carbonate solution, filtered, washed with water, and dried. Recrystallization from toluene/acetonitrile produced aceanthrenequinone: 12.07 g (46%); mp 268–270 °C (lit.[8d] mp 270 °C); red crystals.

Aceanthrenequinone 2-*p*-Tosylhydrazone (6). A tetrahydrofuran (70 mL) solution of aceanthrenequinone (714 g, 32 mmol) and *p*-tosylhydrazine (6.53 g, 35 mmol) was refluxed 5 h. When the mixture was cooled, a yellow precipitate of **6** formed: 12.04 g (94%); mp 220–224 °C dec (toluene/acetonitrile).

Anal. Calcd for $C_{23}H_{16}N_2O_3S$: C, 69.00; H, 4.00; N, 7.00; S, 8.00. Found: C, 68.68; H, 3.92; N, 7.24; S, 7.97.

2-Diazoaceanthrenone (3). A mixture of aqueous sodium hydroxide (50 mL, 0.1 N, 5 mmol), methylene chloride (175 mL), and **6** (1.57 g, 3.9 mmol) was stirred overnight. The methylene chloride layer was washed with water, dried (Na_2SO_4), and evaporated. Chromatography (silica gel/benzene) of the residue gave yellow crystals of **3**: 0.61 g (63%); mp 130–131 °C (cyclohexane); IR (KBr) 2120 (=N_2, s), 1660 cm^{-1} (C=O, s); NMR ($CDCl_3$) δ 9.07 (dd, 1 H), 8.50 (s, 1 H), 8.07 (dd, 1 H), 7.80–7.15 (m, 5 H, aromatic).

Anal. Calcd for $C_{16}H_8N_2O$: C, 78.69; H, 3.28; N, 11.48. Found: C, 78.70; H, 3.48; N, 11.46.

Further elution yielded **6**, 0.47 g (30%).

Photolysis of 3 in Benzene. A benzene solution of **3** (0.5 g, 2 mmol) was irradiated 4 h. The concentrate, after chromatography on silica gel (hexane/benzene, 1:1), yielded yellow-orange

crystals of 2-phenylaceanthrenone (**48**): 0.41 g (68%); mp 210–212 °C dec (toluene/acetonitrile); IR (KBr) 1690 cm^{-1} (C=O, s); NMR ($CDCl_3$) δ 9.06 (dd, 1 H), 8.6 (s, 1 H), 8.2–7.2 (m, 11 H), 4.90 (s, 1 H); exact mass calcd for $C_{22}H_{14}O$ m/e 294.104 46, found m/e 294.105 12.

Anal. Calcd for $C_{22}H_{14}O$: C, 89.79; H, 4.76. Found: C, 89.98; H, 4.93.

Irradiation of 3 in Benzonitrile. A solution of **3** (0.4 g, 1.6 mmol) in benzonitrile was photolyzed 4 h, concentrated, and chromatographed (silica gel, hexane/benzene, 1:1) to give red-brown crystals of 2-phenylaceanthryleno[2,1-*d*]oxazole (**49**): 58 mg (11%); mp 160–165 °C (petroleum ether/toluene); NMR ($CDCl_3$) δ 8.33–7.17 (m, 13 H); exact mass calcd for $C_{23}H_{13}NO$ m/e 319.099 71, found m/e 319.100 48.

Anal. Calcd for $C_{23}H_{13}NO$: C, 86.52; H, 4.07; N, 4.39. Found: C, 86.69; H, 4.01; N, 4.21.

Photolysis of 3 in Acetonitrile. Irradiation of **3** (0.4 g, 1.6 mmol) in acetonitrile for 4 h, solvent removal, and chromatography (silica gel/benzene) resulted in 2-methylaceanthryleno[2,1-*d*]-oxazole (**50**): 0.153 g (36%); mp 132–135 °C (petroleum ether/toluene); red crystals; NMR ($CDCl_3$) δ 8.14–7.16 (m, 6 H, aromatic), 2.6 (s, 3 H, CH_3); exact mass calcd for $C_{18}H_{11}NO$ m/e 257.084 06, found m/e 257.084 52.

Anal. Calcd for $C_{18}H_{11}NO$: C, 84.05; H, 4.28; N, 5.45. Found: C, 83.85; H, 4.47; N, 5.54.

Photolysis of 3 in Phenylacetylene. A phenylacetylene solution of **3** (0.5 g, 2 mmol) was irradiated for 5 h. Vacuum evaporation and chromatography (silica gel/hexane) gave dark purple crystals of 10-phenylaceanthro[1,2-*b*]furan (**51**): 65 mg (10%); mp 176–178 °C (petroleum ether); NMR ($CDCl_3$) δ 8.47 (dd, 1 H), 8.30 (s, 1 H), 8.07–7.24 (m, 11 H, aromatic), 7.09 (s, 1 H); exact mass calcd for $C_{24}H_{14}O$ m/e 318.104 46, found m/e 318.105 25.

Anal. Calcd for $C_{24}H_{14}O$: C, 90.57; H, 4.40. Found: C, 90.25; H, 4.33.

Thermolysis of 3 in Phenylacetylene. A mixture of **3** (0.3 g, 1.2 mmol) and phenylacetylene (2 mL) in toluene (20 mL) was refluxed under nitrogen for 20 h. The residue, after removal of the solvent and chroamtography (neutral alumina), gave (1) **3** (11 mg, 4%) upon elution with benzene and, after elution with benzene/chloroform (1:1), (2) 2-phenyl-12*H*-dibenzo[*de*,*h*]-pyrazolo[1,5-*b*]isoquinolin-12-one (**54**): 0.418 g (98%); mp 222–222.5 °C (toluene/chloroform); red needles; IR (KBr) 1685 cm^{-1} (C=O, s); NMR ($CDCl_3$) δ 8.64–7.10 (m, 14 H, aromatic and pyrazole CH); exact mass calcd for $C_{24}H_{14}N_2O$ m/e 346.110 60, found m/e 346.111 11.

Anal. Calcd for $C_{24}H_{14}N_2O$: C, 83.24; H, 4.05; N, 8.09. Found: C, 83.32; H, 4.25; N, 8.29.

Thermolysis of 3 in Dimethyl Acetylenedicarboxylate. Dimethyl acetylenedicarboxylate (1 mL) and **3** (0.26 g, 1.04 mmol) in toluene (20 mL) were refluxed under nitrogen for 22 h and concentrated. Chromatography on neutral alumina (chloroform) yielded orange needles of dimethyl 12-oxo-12*H*-dibenzo[*de*,*h*]-pyrazolo[1,5-*b*]isoquinoline-2,3-dicarboxylate (**55**): 0.41 g (100%); mp 268–269 °C (toluene/acetonitrile); IR (KBr) 1750, 1720, 1710 cm^{-1} (C=O, s); NMR ($CDCl_3$) δ 8.92 (dd, 1 H), 8.67 (s, 1 H), 8.13–7.15 (m, 6 H, aromatic), 4.00 (s, 6 H, 2 CH_3; exact mass calcd for $C_{22}H_{14}N_2O_5$ m/e 386.090 26, found m/e 386.090 90.

Anal. Calcd for $C_{22}H_{14}N_2O_5$: C, 68.39; H, 3.63; N, 7.25. Found: C, 68.81; H, 3.74; N, 7.18.

Thermolysis of 3 in Acrylonitrile. A mixture of **3** (0.4 g, 1.6 mmol) and acrylonitrile (5 mL) in toluene (20 mL) was refluxed for 20 h. After evaporation, the residue was chromatographed on silica gel.

(a) Elution with benzene gave 2′-cyanospiro[aceanthrenone-2,1′-cyclopropane] (**56**): 0.185 g (42%); mp 199–200 °C (toluene); fluorescent yellow crystals; IR (KBr) 2250 (C≡N, w), 1700 cm^{-1} (C=O, s); NMR ($CDCl_3$) δ 9.20 (dd, 1 H), 8.73 (s, 1 H), 8.23–7.17 (m, 6 H, aromatic), 2.67–1.86 (m, 3 H, cyclopropyl CH), with $\delta(H_x)$ 2.56, $\delta(H_a)$ 2.14, $\delta(H_b)$ 1.98, J_{AX} = 9 Hz, J_{BX} = 7 Hz, J_{AB} = 5 Hz; exact mass calcd for $C_{19}H_{11}NO$ m/e 269.084 06, found m/e 269.084 69.

Anal. Calcd for $C_{19}H_{11}NO$: C, 84.76; H, 4.09; N, 5.20. Found: C, 84.74; H, 4.28; N, 5.56.

(b) Further elution with chloroform yielded 2′-cyanospiro-[aceanthrenone-2,1′-cyclopropane] (**57**): 0.236 g (54%); mp 195.5–197 °C (toluene/acetonitrile); IR (KBr) 2260 (C≡N, w), 1695 cm^{-1} (C=O, s); NMR ($CDCl_3$) δ 8.95 (dd, 1 H), 8.60 (s, 1 H), 8.14–7.20 (m, 6 H, aromatic), 2.60–2.00 (m, 3 H, cyclopropyl CH), with $\delta(H_x)$ 2.51, $\delta(H_a)$ 2.37, $\delta(H_b)$ 2.13, J_{AX} = 6.8 Hz, J_{BX} = 8.2 Hz, J_{AB} = 3.7 Hz; exact mass calcd for $C_{19}H_{11}NO$ m/e 269.084 06, found m/e 269.084 69.

Anal. Calcd for $C_{19}H_{11}NO$: C, 84.76; H, 4.09; N, 5.20. Found: C, 84.40; H, 4.05; N, 5.39.

Thermolysis of 3 in Methyl Acrylate. A solution of **3** (0.2 g, 0.82 mmol) and methyl acrylate (3 mL) in toluene (10 mL) was refluxed for 22 h. Concentration, chromatography on silica gel, elution with benzene, and recrystallization from petroleum ether (65–110 °C)/toluene (1:1) yielded 2′-(methoxycarbonyl)spiro-[aceanthrenone-2,1′-cyclopropane] (**58**): 0.127 g (51%); mp 158–159 °C; fluorescent yellow needles; IR (KBr) 1725, 1690 cm^{-1} (C=O, s); NMR ($CDCl_3$) δ 9.05 (dd, 1 H), 8.48 (s, 1 H), 8.1–7.2 (m, 2 H); exact mass calcd for $C_{20}H_{14}O_3$ m/e 302.094 28, found m/e 302.094 95.

Anal. Calcd for $C_{20}H_{14}O_3$: C, 79.47; H, 4.64. Found: C, 79.10; H, 4.53.

Further elution with chloroform led to 2′-(methoxycarbonyl)spiro[aceanthrenone-2,1′-cyclopropane] (**59**): 97 mg (39%); mp 173–174 °C (petroleum ether/toluene); IR (KBr) 1730, 1690 cm^{-1} (C=O, s); NMR ($CDCl_3$) δ 9.04 (dd, 1 H), 8.47 (s, 1 H), 8.1–6.84 (m, 6 H), 3.73 (s, 3 H, OCH_3), 2.9–2.36 (m, 2 H, cyclopropyl), 1.97–1.77 (2 d, 1 H); exact mass calcd for $C_{20}H_{14}O_3$ m/e 302.094 28, found m/e 302.094 95.

Anal. Calcd for $C_{20}H_{14}O_3$: C, 79.47; H, 4.64. Found: C, 79.42; H, 4.65.

Acenaphthenone *p*-Tosylhydrazone (15). Acenaphthenone (1 g, 5.9 mmol) and *p*-tosylhydrazine (1.20 g, 6.49 mmol) in hot methanol (30 mL), after cooling and recrystallization of the precipitate, yielded **15**: 1.5 g (76%); mp 203 °C; NMR ($CDCl_3$, Me_2SO-d_6) δ 2.3 (s, 3 H, CH_3), 3.92 (s, 2 H, benzylic), 7.2–8.0 (m, 10 H, aromatic); mass spectrum, m/e 336 (M^+).

Anal. Calcd for $C_{19}H_{16}N_2O_2S$: N, 8.32. Found: N, 8.13.

Thermolysis of the Sodium Salt of 15. Excess sodium hydride was added to **15** (336 mg, 1 mmol) in dry tetrahydrofuran (50 mL). After hydrogen evolution ceased, the mixture was concentrated at reduced pressure and then at 0.5 mmHg. The residue was heated at 300 °C for 5 min. TLC analysis of the distillate revealed one mobile fraction. Chromatography (silica gel/hexane) yielded acenaphthylene (**63**) as the only hydrocarbon product: 74.3 mg (49%); mp 88 °C (lit.[38] mp 88–91 °C); NMR ($CDCl_3$) δ 7.0 (s, 2 H, vinylic), 7.34–7.8 (m, 6 H, aromatic).

Pyrolysis of the Sodium Salt of 15. Sodium acenaphthenone *p*-tosylhydrazonate, as prepared from sodium hydride and **15** (500 mg, 1.5 mmol), was dropped through a quartz tube (2.5 cm × 30 cm) at 600 °C (0.05 mm). Chromatography on silica gel with hexane as the eluent gave **63**: [59 mg (26%); mp 88 °C (lit.[38] mp 89–91 °C)], identical with the previous product.

2,2-Dimethylacenaphthenone *p*-Tosylhydrazone (16). *p*-Tosylhydrazine (12.02 g, 0.065 mmol) and 2,2-dimethylacenaphthenone in benzene (75 mL) were refluxed overnight in a Dean–Stark apparatus. Removal of the solvent and recrystallization from ethanol gave **16**: 12 g (51%); mp 148 °C; NMR ($CDCl_3$, Me_2SO-d_6) δ 1.45 (s, 6 H, 2 CH_3), 2.3 (s, 3 H, Ar CH_3), 7.2–8.2 (m, 10 H, aromatic).

Anal. Calcd for $C_{21}H_{20}N_2O_2S$: C, 69.39; H, 5.26; N, 7.70. Found: C, 69.09; H, 5.64; N, 7.47.

Thermolysis of the Sodium Salt of 16 in Anisole. Excess sodium hydride was added to stirred **16** (364 mg, 1 mmol) in dichloromethane (10 mL). Upon evaporation of the mixture to dryness, anisole (20 mL) was added, and the solution was refluxed 90 min under nitrogen. Removal of the anisole under reduced pressure and chromatography (silica gel/hexane) allowed isolation of 8-methylcycloprop[*a*]acenaphthylene (**66**): 46.8 mg (26%); IR (neat) 3040, 2920, 1600, 825, 780 cm^{-1}; NMR ($CDCl_3$) δ 0.83 (dd, 1 H, J = 3, 4.5 Hz, H_A), 1.28 (dd, 1 H, J = 7.5, 4.5 Hz, H_B), 1.66 (s, 3 H, CH_3), 2.61 (dd, 1 H, J = 7.5, 3 Hz, H_X), 7.10 to 7.62 (m, 6 H, aromatic); mass spectrum, m/e 180 (M^+).

Vacuum Thermolysis of the Sodium Salt of 16. Excess sodium hydride was added in small portions to **16** (364 mg, 1

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mmol) stirred in dichloromethane (20 mL). After hydrogen evolution ceased (30 min), the solvent was removed at 0.1 mmHg, and the residue was heated at 230 °C. TLC analysis of the distillate revealed one mobile fraction. Chromatography as in the previous experiment yielded **66** (73.8 mg, 41%) identical with the previous sample.

Photolysis of the Sodium Salt of 16. A pentane slurry (200 mL) of the sodium salt of **16** [prepared from **16** (364 mg, 1 mmol), excess sodium hydride, and dichloromethane (20 mL) and then vacuum evaporation] was irradiated 3.5 h with a 450-W Hanovia 679A36 high-pressure mercury arc lamp under nitrogen. Filtration, solvent evaporation, TLC analysis, and chromatography revealed **66** (27.1 mg, 15%) as the only hydrocarbon product.

8-Methylcycloprop[*a*]acenaphthylene (66). An ethereal solution of 1-methylacenaphthylene (**67**; 170 mg, 1.22 mmol) and methylene iodide (2.68 g, 10 mmol) was added to zinc–copper couple [prepared from zinc dust (1.30 g, 20 mmol) and cuprous chloride (200 mg, 2 mmol)]. After the mixture had been refluxed 24 h, the ether solution was washed with 10% sodium thiosulfate and dilute hydrochloric acid, dried, concentrated, and distilled to give **66** (30 mg, 17%) identical with the hydrocarbon from the previous decompositions of **16**.

Pyrolysis of the Sodium Salt of 16 at 750 °C. The sodium salt of **16** [prepared from **16** (750 mg, 2.06 mmol) and sodium hydride in dichloromethane (20 mL)] was dropped gradually (0.05 mm) through a quartz tube at 750 °C. TLC analysis of the condensate revealed one mobile fraction. Chromatography (silica gel/hexane) gave a yellow oil (50.1 mg), a mixture of 1- (**69**), 4- (**70a**), 9- (**70b**), 6- (**70c**) and **7-methylphenalene (70d)**: IR (neat) 3020, 1600, 830, 795 cm^{-1}; NMR ($CDCl_3$) δ 2.0 (s, CH_3), 2.2 (s, CH_3), 2.3 (s, CH_3), 2.5 (s, CH_3), 3.2 (s), 4.0 (br s, benzylic H), 6.0 (m, olefinic H), 6.5 (m, olefinic H), 6.9–7.7 (m, aromatic).

Pyrolysis of 66 at 700 °C. Pure **66** (166.7 mg, 0.92 mmol) was passed through a quartz tube (2.5 cm × 30 cm) at 700 °C (0.4 mm). The dark condensate could not be separated chromatographically. Chromatography of the oily condensate gave a product mixture of **69** and **70a–d** (61.2 mg, 37%) with IR and NMR properties essentially identical with those of the product from pyrolysis of the sodium salt of **16** at 750 °C.

Acenaphthenequinone Ethylene Monoacetal Hydrazone (18). A solution of acenaphthenone ethylene monoacetal (1 g, 4.4 mmol), hydrazine hydrate (5 mL of 95% solution), and methanol (20 mL) was refluxed 3 h, cooled, and filtered. Recrystallization of the precipitate from ethanol yielded **18**: 669 mg (63%); mp 193 °C; NMR ($CDCl_3$) δ 4.46 (m, 4 H, $(CH_2)_2$), 6.0 (br, 2 H, NH_2), 7.3–8.0 (m, 6 H, aromatic).

Anal. Calcd for $C_{14}H_{12}N_2$: C, 69.98; H, 5.03; N, 11.65. Found: C, 69.98; H, 5.10; N, 11.68.

Photolysis of 2-Diazoacenaphthenone Ethylene Acetal (17). A mixture of **18** (240 mg, 1 mmol), activated manganese dioxide (870 mg, 10 mmol), ethyl ether (125 mL), and saturated ethanolic potassium hydroxide (0.15 mL) was stirred for 1 h, filtered, and rotoevaporated to give orange-red crystals of **17**: 215 mg (90%); IR (KBr) 2060 (s, >C=N_2), 1730 cm^{-1} (w, >C=O).

Diazo ketal **17** in ethyl ether (150 mL) was then irradiated under nitrogen in Pyrex for 1 h. After solvent removal, TLC analysis revealed two mobile fractions. Chromatography on silica gel with hexane/benzene (3:1 to 1:1) as the eluent gave (1) 8,9-dihydroacenaphtho[1,2-*b*]-*p*-dioxin [**73**: 80 mg (51%, corrected for **17** recovered); IR (neat) 3040, 1600, 1480, 1320, 1140, 1050, 960, 825, 775 cm^{-1}; NMR ($CDCl_3$) δ 4.26 (s, 5 H, $(CH_2)_2$), 7.26–7.73 (m, 6 H, aromatic); exact mass calcd for $C_{14}H_{10}O_2$ *m/e* 210.060816, found *m/e* 210.068650] and (2) recovered **17**: 57 mg (25%); IR (KBr) 3020, 2900, 1720 (>C=O), 1610, 1210, 1080, 840, 790 cm^{-1}.

Thermolysis of 17 in Benzene. A solution of **17** (220 mg) in dry benzene (20 mL) was refluxed 4 h under argon. Concentration and chromatography as in the previous experiment yielded **73** (58 mg, 30%, corrected for **17** recovered) and **17** (16 mg, 7%). The properties of **73** and **17** are identical with those of the previous experiment.

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Registry No. **1**, 2008-77-7; **2**, 81522-34-1; **3**, 81522-35-2; **4**, 66365-89-7; **5**, 81522-36-3; **6**, 81522-37-4; **7**, 13286-14-1; **13**, 79679-93-9; **14**, 81522-38-5; **15**, 81522-39-6; **15** Na, 81522-40-9; **16**, 81522-41-0; **16** Na, 81522-42-1; **17**, 81522-43-2; **18**, 81522-44-3; **22**, 2235-15-6; **22** ethylene ketal, 31445-81-5; **23**, 67-64-1; **25**, 81-84-5; **28**, 81522-45-4; **29**, 81522-46-5; **29** 2,4-dinitrophenylhydrazone, 81522-47-6; **30**, 63169-55-1; **31**, 63169-53-9; **32**, 81522-48-7; **33**, 81522-49-8; **38**, 81522-50-1; **39**, 81522-51-2; **40**, 81522-52-3; **41**, 81522-53-4; **42**, 27544-95-2; **43**, 27544-93-0; **47**, 81522-54-5; **48**, 81522-55-6; **49**, 81522-56-7; **50**, 81522-57-8; **51**, 81522-58-9; **54**, 81522-59-0; **55**, 81522-60-3; **56**, 81522-61-4; **57**, 81522-62-5; **58**, 81522-63-6; **59**, 81522-64-7; **63**, 208-96-8; **66**, 66622-83-1; **67**, 19345-99-4; **69**, 81522-65-8; **70a**, 72814-67-6; **70b**, 72814-49-4; **70c**, 72814-61-0; **70d**, 72814-55-2; **73**, 81626-25-7; benzonitrile, 100-47-0; acrylonitrile, 107-13-1; 5-nitroacenaphthenequinone, 24040-42-4; phenylacetylene, 536-74-3; dimethyl acetylenedicarboxylate, 762-42-5; oxalyl chloride, 79-37-8; anthracene, 120-12-7; aceanthrenequinone, 6373-11-1; methyl acrylate, 96-33-3; 2,2-dimethylacenaphthenone, 18086-43-6; acenaphthenequinone, 82-86-0; 4-methylperinaphthane, 68913-04-2; 6-methylperinaphthane, 81626-26-8.

Addition of Trifluoroacetic Acid to Substituted Styrenes

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The rates of addition of CF_3CO_2H to a series of ring-substituted styrenes $ArCH{=}CH_2$ with 100%, 50%, and 20% solutions of the acid in CCl_4 have been measured. The rates of addition of 100% CF_3CO_2H to the isomeric 1-phenylpropenes and the rate of *cis*- to *trans*-stilbene isomerization by this acid are also reported. The rates are correlated with σ^+ parameters of the substituents and with aqueous H_2SO_4-catalyzed hydrations of the same substrates. Deviations from the σ^+ correlation occur with substituents capable of strong hydrogen bonding to the acidic solvents; these deviations are attributed to a decrease in substituent electron-donating ability caused by this interaction. All of the evidence supports a mechanism of rate-determining protonation on carbon (the Ad_E2 mechanism), with no detectable effects from π complexation of the acids with the substrates.

Kinetic measurements of the rates of acid-catalyzed hydration of aryl-substituted styrenes have played a pivotal role in mechanistic studies of protonations of alkenes in general.[1,2] The results on nine different styrene systems

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