

# Photolytic, Thermal, Addition, and Cycloaddition Reactions of 2-Diazo-5,6- and -3,8-disubstituted Acenaphthenones

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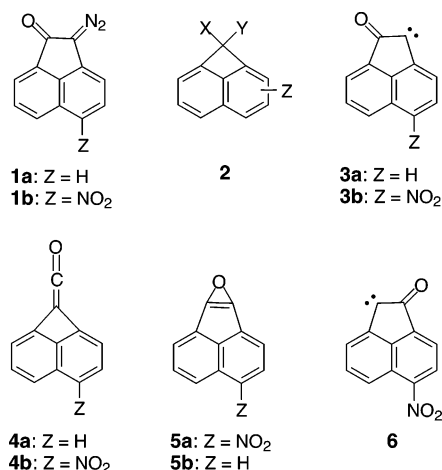
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Preparation and varied thermal and photolytic reactions of 2-diazo-5,6-(disubstituted)acenaphthenones (**11a–d**) and 2-diazo-3,8-dimethoxyacenaphthenone (**12**) are reported. Alcohols react thermally and photolytically with **11a–c** with losses of N<sub>2</sub> to yield 2-alkoxynaphthenones (**24a,b** and **47a,b**) and acenaphthenones (**25** and **48a,b**). Aniline and diphenylamine are converted by **11a–c** at 180 °C to acenaph[1,2-*b*]indoles (**29a,b** and **53a,b**). Thermolyses of **11a–c** at ~450 °C (0.15 mmHg) yield reduction products **25** and **48a,b**, respectively. Wolff rearrangements to 1,8-naphthylideneketenes (**15a–d**) and/or their derivatives are not observed in the above experiments. Oxygen converts **11a–c** thermally to acenaphthenequinones (**19a–c**) and/or 1,8-naphthalic anhydrides. Insertion, addition, substitution, and/or isomerization reactions occur upon irradiation of 2-diazoacenaphthenones in cyclohexane, benzene, and tetrahydrofuran. Photolysis of **11d** in benzene in the presence of O<sub>2</sub> yields the insertion–oxidation product 2-hydroxy-5,6-dinitro-2-phenylacenaphthenone (**60**). Photolyses of **11a–c** in nitriles result in N<sub>2</sub> evolution and dipolar cycloaddition to give acenaph[1,2-*d*]oxazoles (**41** and **61a,b**). Acetylenes undergo thermal and photolytic cycloaddition/1,5-sigmatropic rearrangement reactions with **11a–d** with N<sub>2</sub> retention to give pyrazolo[5,1-*a*]quinolin-7-ones (**69f–j**). 2-Diazoacenaphthenones **1a** and **11a** react thermally and photolytically with electronegatively-substituted olefins with N<sub>2</sub> expulsion to yield (*E*)- and (*Z*)-2-oxospiro[acenaphthylene-1(2*H*),1'cyclopropanes] **73a–c** and **74a–c**, respectively. The mechanisms of the reactions of **1a**, **11a–d**, and **12** reported are discussed.

## Introduction

Photolytic, thermal, acid- and metal-ion catalyzed, and cycloaddition reactions of 2-diazoacenaphthenone (**1a**)<sup>1a–o</sup> and 2-diazo-5-nitroacenaphthenone (**1b**)<sup>11</sup> have been reported. Important with respect to the need for improved syntheses of 1*H*-cyclobuta[*de*]naphthalenes (**2**)<sup>2</sup> and practical preparative methods for decomposing stable α-diazoketones thermally or photolytically in solvents or in the gas phase at various temperatures and pressures is that 2-oxoacenaphthenylidene (**3a**) as formed under such conditions from **1a** does not undergo Wolff rearrangement<sup>3</sup> to 1,8-naphthaleneketene (**4a**).<sup>1a–d,1–o</sup> Further,

6-nitro-2-oxoacenaphthenylidene (**3b**) as generated by heating or photolytically in solution or thermally at reduced pressures from **1b** does not isomerize to 4-nitro-1,8-naphthaleneketene (**4b**) or give products from 5-nitro-2-oxoacenaphthenylidene (**6**) as formed from oxirene **5a** by rearrangement.<sup>11,3</sup> The inabilities of *syn*-α-diazo-

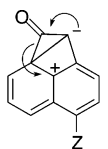


- (1) (a) Horner, L.; Kirmse, W.; Muth, K. *Chem. Ber.* **1958**, *91*, 430. (b) Cava, M. P.; Litle, R. L.; Napier, O. R. *J. Am. Chem. Soc.* **1958**, *80*, 2257. (c) Ried, W.; Lohwasser, H. *Justus Liebigs Ann. Chem.* **1965**, *683*, 118. (d) DeJongh, D. C.; Van Fossen, R. Y. *Tetrahedron* **1972**, *28*, 3603. (e) Tsuge, O.; Shinkai, M.; Koga, M. *J. Org. Chem.* **1971**, *36*, 745. (f) Yamazaki, T.; Shechter, H. *Tetrahedron Lett.* **1972**, 4533. (g) Bannerman, C. G. F.; Cadogan, J. I. G.; Gosney, I. G.; Wilson, N. H. J. *Chem. Soc., Chem. Commun.* **1975**, 618. (h) Tsuge, O.; Koga, M. *Heterocycles* **1977**, *6*, 411. (i) Chapman, O. L. *Chem. Eng. News* **1978**, Sep 18, 17. (j) Chapman, O. L. *Pure Appl. Chem.* **1979**, *51*, 331. (k) Okada, K.; Mukai, T. *Tetrahedron Lett.* **1980**, 359. (l) Chang, S.-J.; Ravi Shankar, B. K.; Shechter, H. *J. Org. Chem.* **1982**, *47*, 2226. (m) Maier, G.; Reisenauer, H. P.; Sayrac, T. *Chem. Ber.* **1982**, *115*, 2192. (n) Hayes, R. A.; Hess, T. C.; McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* **1983**, *105*, 7786. (o) McMahon, R. J.; Chapman, O. L.; Hayes, R. A.; Hess, T. C.; Krimmer, H. P. *J. Am. Chem. Soc.* **1985**, *107*, 7597.

(2) For present methodologies for preparing 1*H*-cyclobuta[*de*]naphthalenes and their cyclobuta derivatives, see: Engler, T. A.; Shechter, H. *J. Org. Chem.* **1999**, *64*, 4247 and references therein.

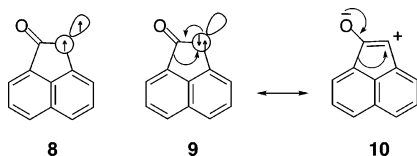
ketones **1a**<sup>4</sup> and **1b**<sup>4</sup> to rearrange to ketenes **4a** and **4b**, respectively, in the above experiments are interpreted

to arise from strains in singlet state ( $S^1$ ) isomerizations of **3a** and **3b** as in **7a** and **7b**.<sup>11,n,o</sup> In a profound series of



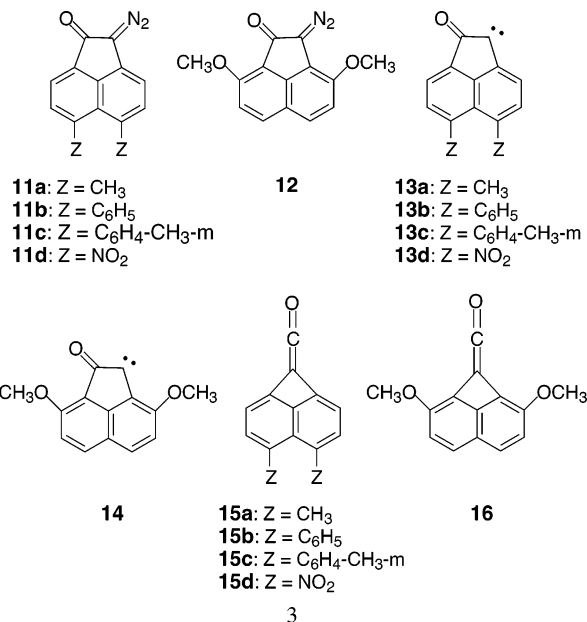
**7a**: Z = H  
**7b**: Z = NO<sub>2</sub>

mechanism studies, Chapman et al. have found that photolysis ( $365 \pm 8$  nm) of **1a** in frozen argon at 10–15 °K gives triplet 2-oxoacenaphthenylidene [**8**,  $T^0$ ] as assigned spectrally and which is converted by matrix O<sub>2</sub> to 1,8-naphthalic anhydride.<sup>11,j,n,o</sup> Matrix irradiation ( $625 \pm 8$  nm) of triplet 2-oxocarbene **8**, after generation from **1a** in solid argon at 10–15 K, then yields naphthaleneketene **4a** as assigned in the matrix by IR methods.<sup>1,j,n,o</sup> Oxirene **5b** is not detected spectrally.<sup>1,j,n,o</sup> Photolytic ring contraction of oxocarbene **3a** in matrix to ketene **4a** is interpreted to arise from in-planar Wolff rearrangement of the excited carbene in its  $S^{11}$  singlet state (**9** and **10**).<sup>1n,o</sup>



Studies are now reported of the syntheses and various reactions of 2-diazo-5,6-dimethylacenaphthenone (**11a**), 2-diazo-5,6-diphenylacenaphthenone (**11b**), 2-diazo-5,6-di(*m*-tolyl)acenaphthenone (**11c**), 2-diazo-5,6-dinitroacenaphthenone (**11d**), and 2-diazo-3,8-dimethoxyacenaphthenone (**12**). Of interest is whether 5,6- (**13a–d**) and/or 3,8-disubstituted (**14**) 2-oxoacenaphthenylidenes as generated thermally, photolytically, or catalytically in solution or by low-pressure pyrolyses of **11a–d** and **12**, respectively, convert preparatively to their corresponding ketenes, **15a–d** and **16**, and/or products thereof.<sup>5</sup> Repulsion interactions between the *peri* 5,6-dimethyl, -diphenyl, -di(*m*-tolyl), and -dinitro substituents in carbenes

**13a–d**, respectively, and the crowding effects of the *ortho* (3,8)-dimethoxy groups in **14** might lead to Wolff rearrangements by compressing, twisting, and reducing the stabilizing delocalizations in their 5-membered ring,  $\alpha$ -ketocarbonyl moieties, and subsequent strain accommodation.<sup>6</sup> Conversions to ketenes **15d** and/or **16**, respectively, should also be facilitated by the enhanced electron deficiency at the carbene center in **13d** arising from its 5,6-dinitro groups and/or by the increased migratory ability of the naphthyl group in **14** resulting from electron donation by its 3-methoxy group. As will be described, the 5,6- and/or the 3,8-disubstituent effects in **11a–d** and **12**, respectively, do not lead to preparative syntheses of ketenes **15a–d** and **16** and/or their derivatives. The facts that **11a–d** and **12** do not undergo thermal and photolytic Wolff rearrangements readily allow the diazo compounds to be used effectively for valuable and certain unique syntheses. The studies also provide information with respect to the generation, behavior, and mechanisms of various reactions of non-rearranging *syn*- $\alpha$ -oxocarbenes **13a–d** and **14**. Preparation and the varied chemistries of 2-diazoacenaphthenones **11a–d** and **12** are now described.



(3) Wolff rearrangements and related chemistry of  $\alpha$ -diazoketones have been reviewed by: (a) Kirmse, W. *Eur. J. Org. Chem.* **2002**, 2193. (b) Toscano, J. P. In *Advances in Carbene Chemistry*; Brinker, V. H., Ed.; JAI Press, Inc.: Stamford, CT, 1998; Vol. 2, p 215. (c) Tidwell, T. T. *Ketenes*; Wiley: New York, 1995; p 77. (d) Zollinger, H. *Diazo Chemistry II*; VCH: Weinheim, 1995; p 344. (e) Ye, M. A.; McKerverey, A. *Chem. Rev.* **1994**, 94, 1091. (f) Gill, G. B. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Pattenden, G., Eds.; Pergamon: Oxford, 1991; Vol. 3, p 887 and (g) references therein.<sup>3a,g</sup>

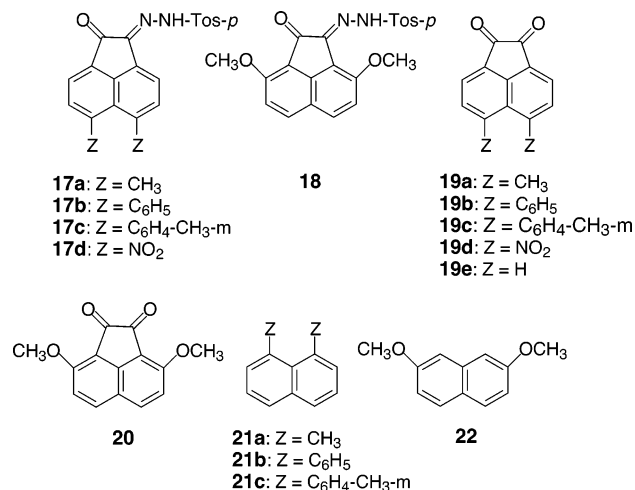
(4) (a) In concerted Wolff rearrangements  $\alpha$ -diazoketones of *s*-Z stereochemistry are believed to react more rapidly than their *s*-E conformers because the migrating group attacks preferentially the carbon atom bonded to the diazo group from the backside from which nitrogen is expelled.<sup>4b,c</sup> (b) Kaplan, F.; Meloy, G. K. *J. Am. Chem. Soc.* **1966**, 88, 950. (c) Kaplan, F.; Mitchell, M. L. *Tetrahedron Lett.* **1979**, 759. (d) For summaries and discussions of steric aspects and mechanism complications in decompositions and in Wolff rearrangements of  $\alpha$ -diazocarbonyl compounds, see ref 3a,b and references therein. (e) In Wolff rearrangements of  $\alpha$ -diazoaldehydes and ketones in the presence of alcohols and amines, the migratory aptitudes of various groups may be significantly affected by solvation or more intimate coordination of the carbonyl groups of the  $\alpha$ -diazo compounds with the nucleophilic solvents.<sup>4d</sup> (f) Jordon, D. M. Ph.D. Dissertation, The Ohio State University, Columbus, OH, 1965.

## Results and Discussion

**Syntheses of 11a–d and 12.** 2-Diazoacenaphthenones **11a–d**<sup>7,8</sup> and **12**<sup>7,8</sup> are presently prepared efficiently by reactions of NaOH or NaOCH<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> with acenaphthenequinone mono-*p*-tosylhydrazones **17a–d**<sup>8</sup> and **18**,<sup>8</sup> respectively, as obtained from acenaphthenequinones **19a–d** and **20**<sup>8</sup> with *p*-tosylhydrazine (1.0 equiv) in refluxing CH<sub>3</sub>OH. The 2-diazoacenaphthenones are stable, high-melting solids and can be recrystallized from hot CH<sub>3</sub>CN, benzene, and toluene in ordinary light without decomposition. Acenaphthenequinones **19a–c**<sup>8</sup> and **20**,<sup>8</sup>

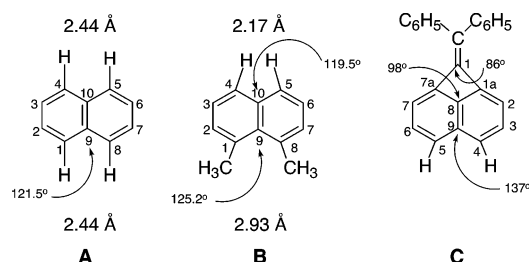
(5) (a) Many examples of cyclic  $\alpha$ -diazoketones that undergo Wolff rearrangements to yield highly strained, small-ring ketenes and/or their derivatives are given in ref 3a–e. (b) Photosensitization eliminates or greatly minimizes Wolff rearrangements of  $\alpha$ -diazocarbonyl compounds,<sup>3,5c</sup> and thus, such methodologies have not been presently investigated for decompositions of **1a,b**, **11a–d**, and **12**. (c) Padwa, A.; Layton, R. *Tetrahedron Lett.* **1965**, 2167.

respectively, are obtained by condensations of 1,8-dimethyl- (**21a**), 1,8-diphenyl- (**21b**), 1,8-di(*m*-tolyl)- (**21c**), and 2,7-dimethoxynaphthalenes (**22**), respectively, with oxalyl chloride (>2 equiv) and AlCl<sub>3</sub> (>2 equiv) in CS<sub>2</sub> at -78 to +25 °C. Dinitration [HNO<sub>3</sub> (>2 equiv)/H<sub>2</sub>SO<sub>4</sub>] of acenaphthenequinone (**19e**) at 0 °C yields 5,6-dinitroacenaphthenequinone (**19d**).<sup>9</sup>



**Reactions of 11a–d and 12.** Initial efforts in the present studies involved possible practical photo- and thermal-Wolff rearrangements of 5,6-dimethyl- $\alpha$ -diazo-ketone **11a** in alcohol and in amine solvents at various temperatures to give 4,5-dimethyl-1,8-naphthaleneketene

(6) (a) X-ray structural analyses reveal *peri* effects of hydrogens in naphthalene (**A**) and of methyl groups in 1,8-dimethylnaphthalene (**B**) as shown.<sup>6b</sup> The carbon skeleton in **B** is essentially planar with no bending of its methyl groups out of the plane of its naphthalene ring.<sup>6b</sup> The C(1)–C(9)–C(8) bond angle in **B** is 125.2°. <sup>6b</sup> (b) Bright, D.; Maxwell, I. E.; de Boer, J. *J. Chem. Soc., Perkins Trans. 2* **1973**, 2101. (c) Of note with respect to possible conversions of **1a**, **11a–d**, and **12** to cyclobutaketenes **4a**, **b**, **15a–d**, and **16**, respectively, is that 1-alkylidene-1*H*-cyclobuta[*de*]naphthalenes are preparable and quite stable.<sup>6d</sup> In crystalline 1-(diphenylmethylene)-1*H*-cyclobuta[*de*]naphthalene (**C**), the bond angles in its C(1a)–C(1)–C(7a) and C(1a)–C(8)–C(7a) units are ca. 86° and 98°, respectively, the cyclobuta bond distances for C(1)–C(1a) and C(1)–C(7a) are only 1.53–1.54 Å and thus shorter (~0.03 Å) than such bonds in planar cyclobutanes, and, of particular significance, its C(4)–C(9)–C(5) bond angle is 137°. <sup>6e</sup> Also, the C(4)–C(9)–C(5) angle in 1-bromo-1*H*-cyclobuta[*de*]naphthalene is 138°. <sup>6f</sup> The abilities of naphthalene rings to adjust to strains from *peri*-cyclobuta interactions are impressive. (d) Card, P. J.; Friedli, F. E.; Shechter, H. *J. Am. Chem. Soc.* **1983**, *105*, 6104. (e) Kumar, A.; Friedli, F. E.; Hsu, L.; Card, P. J.; Mathur, N.; Shechter, H. *J. Org. Chem.* **1991**, *56*, 1663. (f) Gessner, M.; Card, P.; Shechter, H.; Christoph, G. *J. Am. Chem. Soc.* **1977**, *99*, 2371.

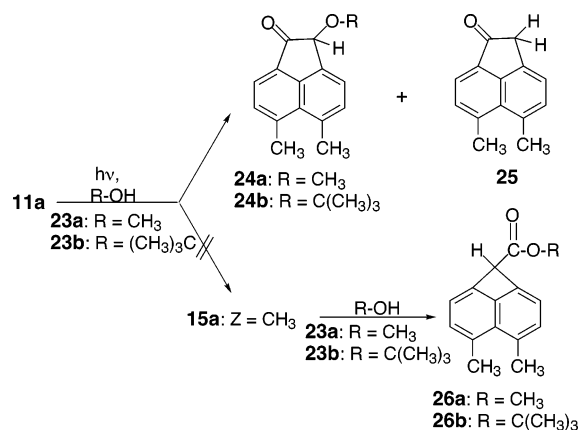


(7) The syntheses of **11a–d** and **12** from mono-*p*-tosylhydrazones **17a–d** and **18**, respectively, are extensions of that for **1a** and **1b** in ref 1b and 1l, respectively.

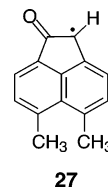
(8) The products designated are of proper elemental analyses and spectra (mass, IR, and NMR). See the Experimental Section or Supporting Information.

(9) (a) Ruhemann, S. *Chem. Ber.* **1920**, *52B*, 287. (b) Rowe, F. M.; Davis, J. H. S. *J. Chem. Soc.* **1920**, 1344.

## SCHEME 1



(**15a**) that then undergoes additions of the solvents. Photolysis of **11a** (medium-pressure Hg lamp) in CH<sub>3</sub>-OH (**23a**) at 25 °C under N<sub>2</sub> through Pyrex occurs smoothly, however, with loss of N<sub>2</sub> to give (Scheme 1) 2-methoxy-5,6-dimethylacenaphthenone (**24a**, >61%) and the reduction product 5,6-dimethylacenaphthenone (**25**, >9%).<sup>8</sup> Methyl 4,5-dimethyl-1*H*-cyclobuta[*de*]naphthalene-1-carboxylate (**26a**, Scheme 1), the product expected by addition of **23a** to ketene **15a** if generated, is not detected (see the Experimental Section and Supporting Information). Formation of 2-methoxyacenaphthenone **24a** (R = CH<sub>3</sub>) is presumed to occur by (1) reaction(s) of CH<sub>3</sub>OH (**23a**) with excited **11a** with loss of N<sub>2</sub> and/or (2) loss of N<sub>2</sub> and then reaction(s) of singlet carbene **13a** with **23a**. The photolytic reduction product, 5,6-dimethylacenaphthenone (**25**), from **11a** and **23a** is apparently produced by hydrogen abstraction reactions of excited **11a** and/or carbene **13a** as triplets (T°) with **23a**, the hydroxymethyl radical (·CH<sub>2</sub>OH) after formation from **23a**, reaction product **24a**, and/or initial **11a** to give 2-oxoacenaphthenyl radical **27** which then abstracts hydrogen from (any of) the above hydrogen atom donors.



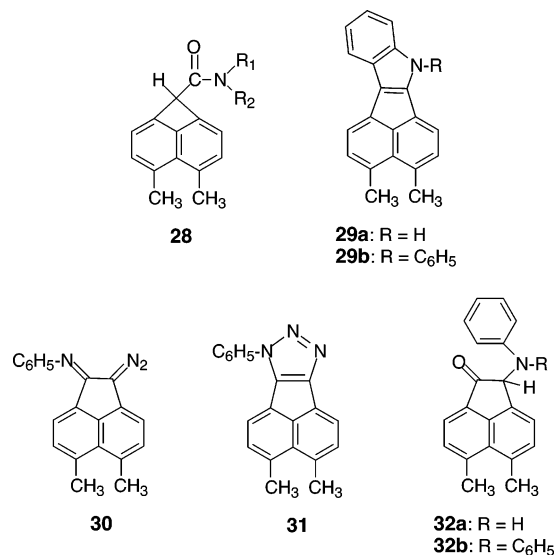
In further attempts to bring about Wolff rearrangement to ketene **15a** and minimize reduction to dimethylacenaphthenone **25**, **11a** was photolyzed in *tert*-butyl alcohol [**23b**, R = (CH<sub>3</sub>)<sub>3</sub>C]. Capture product, 2-*tert*-butoxy-5,6-dimethylacenaphthenone [**24b**, R = C(CH<sub>3</sub>)<sub>3</sub>, Scheme 1, 22%],<sup>8</sup> reduction product **25** (Scheme 1, 23%), and intractables are obtained, however. There is no evidence for formation of *tert*-butyl 4,5-dimethyl-1*H*-cyclobuta[*de*]naphthalene-1-carboxylate (**26b**, Scheme 1) from ketene **15a** and alcohol **23b** [R = (CH<sub>3</sub>)<sub>3</sub>C] in these experiments. Photolysis of **11a** in *tert*-butyl alcohol (**23b**) to give **25** (Scheme 1) as a major product is of interest. Since *tert*-alcohol **23b** is expected to be a poor hydrogen-transfer reagent, formation of reduction product **25** is presumed to arise primarily upon hydrogen abstraction reactions of photolysis triplet **11a** and/or triplet carbene **13a** (T°) with capture product **24b** [R = C(CH<sub>3</sub>)<sub>3</sub>] and/or



initial  $\alpha$ -diazoketone **11a**. Of relevance, as will be detailed later, is that photolysis of **11a** in cyclohexane results in carbenic C–H insertion into the solvent rather than reduction (dihydrogen abstraction) to give **25**.

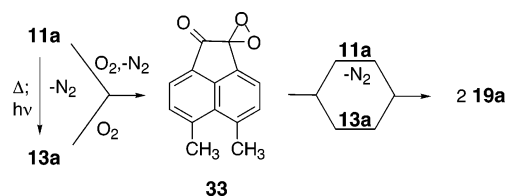
$\alpha$ -Diazoketones in alcohols frequently undergo Wolff rearrangements to ketenes at elevated temperatures<sup>4c</sup> and as catalyzed by silver ion.<sup>3</sup> The ketenes generated are then usually efficiently trapped by the alcohols. In present studies,  $\alpha$ -diazoketone **11a** reacts slowly in refluxing  $\text{CH}_3\text{OH}$  (**23a**,  $\text{R} = \text{CH}_3$ ) and in refluxing **23a** containing silver oxide to yield (Scheme 1) the  $\text{CH}_3\text{OH}$  capture product **24a** and reduction product **25**. Methyl dimethylcyclobutacarboxylate **26a** (Scheme 1) is not obtained. Further, decompositions of **11a** in cyclohexanol at 140 °C or in benzyl alcohol at 180 °C do not yield cyclohexyl or benzyl 4,5-dimethyl-1*H*-cyclobuta[*de*]naphthalene-1-carboxylates, products derivable from additions of the alcohols to ketene **15a**.

Thermolyses of **11a** were then conducted in solution in primary and in secondary amines at elevated temperatures (140–180 °C) in efforts to generate and convert ketene **15a** to its corresponding 4,5-dimethyl-*N*-substituted 1*H*-cyclobuta[*de*]naphthalene-1-carboxamides (**28**). Reactions of **11a** in refluxing aniline (bp 184 °C) under  $\text{N}_2$  which are not completely free of  $\text{O}_2$  give, however, 3,4-dimethylacenaphth[1,2-*b*]indole (**29a**, > 27%),<sup>8</sup> 5,6-dimethylacenaphthenequinone (**19a**, 32%), and intrac-tables. Formation of **29a** is the first example of reaction of an  $\alpha$ -diazoketone with an aniline to give an indole.



4,5-Dimethyl-*N*-phenyl-1*H*-cyclobuta[*de*]naphthalene-1-carboxamide (**28**;  $\text{R}_1 = \text{H}$ ,  $\text{R}_2 = \text{C}_6\text{H}_5$ ) is not a reaction product. At temperatures of ~80 °C for 48 h, diazoketone **11a** is stable and does not react with aniline. 1-Diazo-5,6-dimethyl-2-phenyliminoacenaphthalene (**30**) and/or its ring-closure isomer, 3,4-dimethylacenaphth[4,5-*b*]-*N*(1)-phenyl-1,2,3-triazole (**31**), products expected upon addition–elimination reactions of the carbonyl group in **11a** with the amino group in aniline at 80 to ~184 °C, are not found. Formation of indole **29a** apparently occurs upon reaction of **11a** with heated aniline and then loss of  $\text{N}_2$  and/or decomposition of **11a** to **13a** followed by carbenic insertion into the amino group in aniline to give **32a** ( $\text{R} = \text{H}$ ) and its tautomers that undergo intramo-

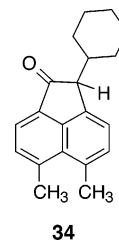
## SCHEME 2



lecular ortho ring-closure with elimination of  $\text{H}_2\text{O}$ . Indole **29a** and acenaphthenequinone **19a** are also obtained upon photolysis of **11a** in aniline in which  $\text{O}_2$  is present. Quinone **19a** is presumed to be formed (Scheme 2) by reaction(s) of  $\text{O}_2$  with **11a** and/or its subsequent carbene (**13a**) in its triplet state to give  $\alpha$ -ketodioxirane **33**, which then oxidizes **11a** and/or carbene(s) **13a**. No attempts have been made to increase the yields of indole **29a** by thermolysis or photolysis of **11a** in aniline in which  $\text{O}_2$  is totally absent.

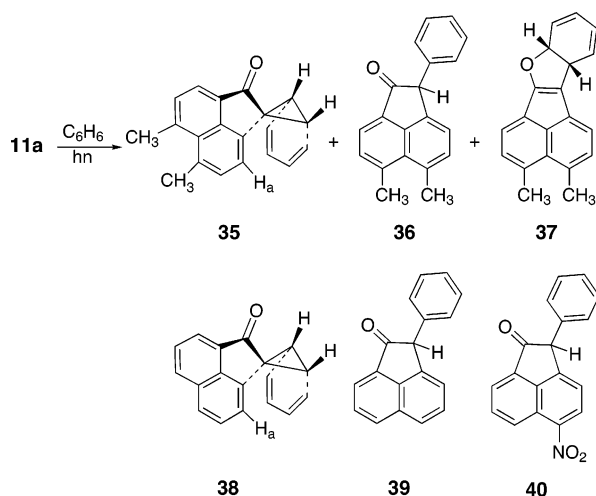
Of further interest is that reactions of **11a** with molten diphenylamine at 295 °C yield 3,4-dimethyl-*N*-phenyl-acenaphth[1,2-*b*]indole (**29b**)<sup>8</sup> and reduction (dihydrogen abstraction) product, acenaphthenequinone **25**. Reaction of diphenylamine, a secondary amine, with **11a** to yield **29b** cannot occur upon initial elimination of  $\text{H}_2\text{O}$  to give Schiff base intermediates as considered for aniline and **11a**. Indole **29b** is presumed to be obtained thermally by (1) loss of  $\text{N}_2$  from **11a**, insertion of carbene **13a** into the N–H bond in diphenylamine to give  $\alpha$ -aminoketone **32b** and its tautomers, and then heterocyclization by elimination of  $\text{H}_2\text{O}$  and/or (2) nucleophilic addition of diphenylamine to **11a** to yield (*E*)- and (*Z*)-aminoazo intermediates which lose nitrogen to form **32b** and/or its tautomers followed by dehydrative indolization. Reduction product **25** is possibly formed by hydrogen atom transfer to the 2-oxoacenaphthenyl radical (**27**) as generated by hydrogen abstraction processes similar to those proposed for photolyses of **11a** in **23a** and **23b** and/or by homolytic decomposition of the **32b** ( $\text{R} = \text{C}_6\text{H}_5$ ) initially produced thermally from **11a** and diphenylamine with loss of  $\text{N}_2$ .

Photolyses of **11a** in very poorly nucleophilic solvents were then investigated. Irradiation of **11a** in cyclohexane yields 2-cyclohexyl-5,6-dimethylacenaphthene (**34**, 70%).<sup>8</sup> Ketone **34** is presumably formed by insertion of carbene **13a** in its singlet state into a C–H bond of cyclohexane. There is no evidence for generation of ketene **15a** in these experiments. Reduction product **25a** is not detected.



Further, irradiation of **11a** in benzene (Scheme 3) gives (*E*)-*cis*-5,6-dimethylspiro[acenaphthene-1,7'-[2,4]norcaradiene]-2-one (**35**, 20%),<sup>10</sup> 5,6-dimethyl-2-phenylacenaphthene (**36**, 20%),<sup>8</sup> and *cis*-7a,11a-dihydro-3,4-dimethylacenaphtho[1,2-*b*]benzo[*d*]furan (**37**, 40%).<sup>8</sup> Ketene **15a** and/or its products are not observed. Spiro[norcaradiene

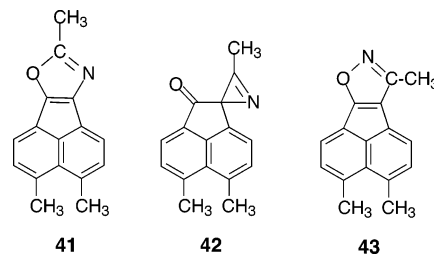
## SCHEME 3



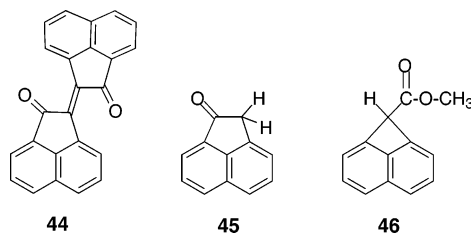
**35** is thermally unstable and converts quantitatively to **36** on standing and in refluxing xylenes. Photolysis of **11a** in benzene to give **35**, **36**, and **37** and isomerization of **35** to **37** provide additional information as to the behaviors of 2-oxoacenaphthenylidenes with benzene in that it has been previously reported that irradiation of (1) **1a** in benzene yields (*E*)-spironorcaradiene adduct **38** (84%) which is isomerized by acids or silver ion to 2-phenylacenaphthene (**39**)<sup>1g</sup> and (2) **1b** in benzene results in aromatic substitution of the solvent to give 5-nitro-2-phenylacenaphthene (**40**, 55%).<sup>11</sup> The fact that spironorcaradiene **38** is more stable thermally than **35** suggests that the *peri*-methyl groups in **35** cause destabilization, presumably by the steric compression and twisting in its spironorcaradiene section. In the present experiments formation, without catalysis, of **36** and **37**, both of which should be less strained than **35**, is thus facilitated.

Of value with respect to synthesis and reaction mechanism is that photolysis of **11a** in CH<sub>3</sub>CN yields 3,4,8-trimethylacenaph[1,2-*d*]oxazole (**41**, 52%)<sup>8,11</sup> presumably as formed by addition of excited **11a** to the nitrile, loss of N<sub>2</sub>, and ring-closure, and/or generation and then reaction(s) of oxocarbene **13a** with the cyano group of the CH<sub>3</sub>CN.<sup>12</sup> Ketene **15a** or its derivatives, azirene **42**, or

isoxazole **43** are not found in any of the present experiments.

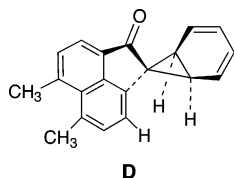


Possible thermal conversions of **1a** to ketene **4a** have been previously investigated.<sup>1c,d</sup> Decomposition of molten **1a** at 160 °C yields (*E*)-[Δ<sup>1,1</sup>]biacenaphthene-2,2'-dione (**45**, 75%).<sup>1c,d</sup> Gas-phase decomposition of **1a** at 400 °C gives intractables.<sup>1c,d</sup> Ketene **4a** and/or its transformation products are not found in these experiments.<sup>1c,d</sup> Study has now been made of the behaviors of **11a** and **1a**, respectively, upon dropping the finely ground, solid 2-diazoacenaphthenones at various rates directly into vertical, packed quartz tubes at 0.15 mm Hg pressure and 450 °C and rapidly condensing the volatile products at -78 °C or in CH<sub>3</sub>OH (**23a**) at <-78 °C. Such vacuum pyrolyses of **11a** give the reduction product, 5,6-dimethylacenaphthene (**25**, 14%), and non-chromatographable materials. Further, vacuum thermolyses of **1a** at 450 °C/0.10 mm Hg as above result in formation of the reduction product, acenaphthene (**45**, 16%), and intractables. There is no evidence in the present decomposition or capture experiments (see the Experimental Section) for conversions of (1) **11a** to ketene **15a** or cyclobuta ester **26a** and/or (2) **1a** to ketene **4a** or methyl 1*H*-cyclobuta[*de*]naphthalene-1-carboxylate (**46**).<sup>13</sup> As will be described, reduction (double hydrogen transfer) reactions also occur in decompositions of **11b** and of **11c** upon being heated to ~450 °C at 0.10–0.15 mm Hg pressures as for **11a**.



Studies were then initiated of the photolytic and thermal behaviors of **11b** and **11c**.<sup>7</sup> Of importance is

(10) (a) Because of its instability and difficulties in its separation from **36** and **37**, (*E*)-**35** was not isolated analytically pure. The assignment of the product as (*E*)-**35** rather than **D** is based on its IR and mass spectra, its NMR spectrum as compared to that of (*E*)-**38** as prepared by photolysis of **1a** in benzene,<sup>1g</sup> and expectation that, because of steric effects from the carbonyl group(s) in carbene(s) **13a**, addition of the carbene(s) to a double bond in benzene will occur preferentially to give the cyclopropane now reported. (b) Reference 1g has emphasized that H<sub>a</sub> in **30** is highly shielded and exhibits NMR absorption at 6.8–6.9 δ.

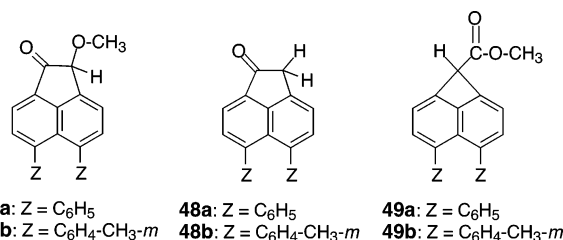


(11) (a) Important to the assignment is that **41** does not exhibit IR absorption for a carbonyl group and its methyl group has the same NMR chemical shift, δ = 2.61, as that in 8-methylacenaphth[1,2-*d*]oxazole.<sup>11,11b</sup> (b) Ibata, T.; Sato, R. *Chem. Lett.* **1978**, 10, 1129.

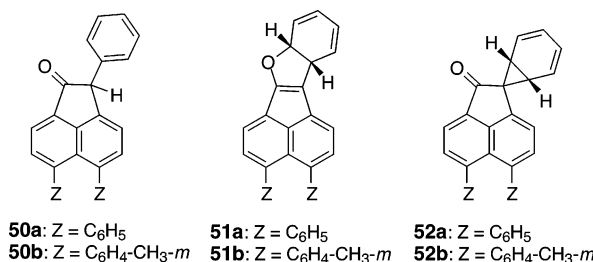
(12) Many reactions of **11a–d** of the present studies with nitriles, acetylenes, and olefins involve possible 1,3-dipolar and related cycloaddition processes. For comprehensive reviews of such reactions of diazo compounds see (a) Huisgen, R. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: N. Y., 1984; Vol. 1, pp 1–176. (b) Regitz, M.; Heydt, H. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; Vol. 1, pp 393–558. (c) Maas, G. In *Synthetic Applications of 1,3-Dipolar Cycloaddition Chemistry Toward Heterocycles and Natural Products*; Padwa, A., Pearson, W. A., Eds.; Wiley: New York, 2002; pp 539–622 and (d) references therein.

(13) Ester **46** is prepared<sup>6d</sup> by (1) photolysis of 8-bromo-1-naphthyl diazomethane, (2) reaction of the resulting 1-bromo-1*H*-cyclobuta[*de*]naphthalene with Mg, (3) conversion of the Grignard reagent formed by CO<sub>2</sub> and then acidification to 1*H*-cyclobuta[*de*]naphthalene-1-carboxylic acid, and (4) esterification of the carboxylic acid with diazomethane.

whether the steric repulsions of the *peri*-phenyl groups in **11b** and/or the *peri*-*m*-tolyl groups in **11c** are sufficient to compress, twist, and strain the diazoketone moieties in the 2-diazoacenaphthenones such that photolytic losses of N<sub>2</sub> and ring-shrinking rearrangements to ketenes **15b** and/or **15c** will occur. Photolysis of **11b** in CH<sub>3</sub>OH (**23a**) yields, however, the **23a** capture product 2-methoxy-5,6-diphenylacenaphthenone (**47a**, 33%)<sup>8</sup> and the reduction (dihydrogen transfer) product 5,6-diphenylacenaphthenone (**48a**, 15%).<sup>8</sup> Similarly, irradiation of **11c** in **23a** gives 2-methoxy-5,6-di(*m*-tolyl)acenaphthenone (**47a**, 36%)<sup>8</sup> and 5,6-di(*m*-tolyl)acenaphthenone (**48b**, 16%).<sup>8</sup> Photolytic conversions of **11b** and **11c**, respectively, in **23a** to ketenes **15b** and **15c** and/or their CH<sub>3</sub>OH adducts **49a** and **49b** are not observed. The behaviors of **11b** and **11c** upon irradiation in **23a** are thus essentially identical with that of **11a** under similar conditions.

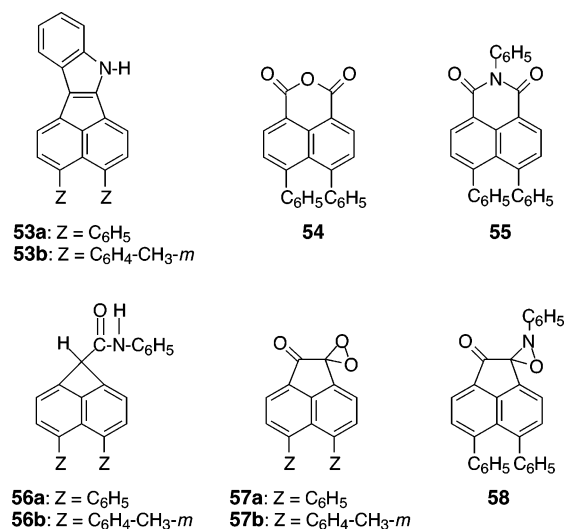


Photolyses of **11b** and **11c**, respectively, in benzene were then investigated. Irradiation of **11b** in benzene yields the carbenic capture products: 2,5,6-triphenylacenaphthenone (**50a**, 25%)<sup>8</sup> and *cis*-7a,11a-dihydro-3,4-diphenylacenaphtho[1,2-*b*]benzo[*d*]furan (**51a**, 44%)<sup>8</sup>; *cis*-5,6-diphenylspiro[acenaphthene-1,7'-[2,4]norcaradiene]-2-one (**52a**), ketene **15b**, and reduction product **48a** are not found. In present experiments essentially identical with that described earlier for **11a**, photolysis of **11c** in benzene gives 2-phenyl-5,6-di(*m*-tolyl)acenaphthenone (**50b**, 13%)<sup>8</sup>, *cis*-7a,11a-dihydro-3,4-di(*m*-tolyl)acenaphtho[1,2-*b*]benzo[*d*]furan (**51b**, 39%)<sup>8</sup> and reduction product **48b** (13%); spironorcaradiene **52b** and ketene **15c** are not obtained. Because of its strain **52b**, if formed, is expected to isomerize readily to **50b** and/or **51b**. As in photolysis of **11a** in benzene to give reduction (dihydrogen abstraction) product **25**, there are many routes by which **48b** might be formed upon photolysis of **11c** in benzene.



Investigations of thermal and photolytic reactions of **11b** and of **11c** were continued. Heating **11b** in refluxing aniline (~180 °C) under N<sub>2</sub> in which O<sub>2</sub> is not completely purged yields 3,4-diphenylacenaphth[1,2-*b*]indole (**53a**, 17%)<sup>8</sup> along with 4,5-diphenyl-1,8-naphthalic anhydride (**54**, 20%)<sup>8</sup> and 5,6-diphenylacenaphthenequinone (**19b**, 48%). Further, irradiation of **11b** in aniline at ~25 °C in

which O<sub>2</sub> is deliberately added gives *N*,4,5-triphenyl-1,8-naphthalimide (**55**, 15%)<sup>8</sup> along with indole **53a**. In no experiment is carboxamide **56a**, as possibly formed from ketene **15a** and aniline, found. The thermal and the photolytic behaviors of the **11b**/aniline system are very sensitive to O<sub>2</sub> even in trace amounts. Anhydride **54** is presumed to be formed by rearrangement of dioxirane **57a** as produced thermally from **11b** and O<sub>2</sub>. Anthraquinone **19b** apparently results from thermal reactions of dioxirane **57a** and/or O<sub>2</sub> with **11b** and/or its carbenes (**13b**). Naphthalimide **55** as obtained photochemically from **15b**, aniline, and O<sub>2</sub> presumably arises by reaction of aniline with anhydride **54** and/or rearrangement of oxazirane **58** as generated from aniline and dioxirane **57a**.



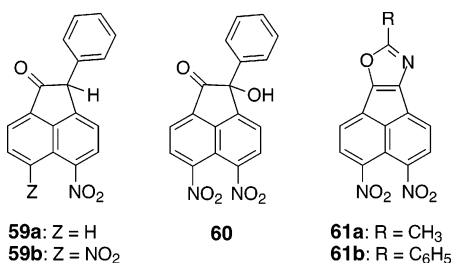
Of further interest is that heating **11c** with aniline at 180 °C under N<sub>2</sub> in which a trace of O<sub>2</sub> is present yields 3,4-di(*m*-tolyl)acenaphth[1,2-*b*]indole (**53b**, 36%)<sup>8</sup> and 5,6-di(*m*-tolyl)acenaphthenequinone (**19d**, 32%). Carboxamide **56b** is not obtained. The reactions of **11c** are thus similar to that of **11b** and **11a** with aniline/O<sub>2</sub> at 180 °C. Formation of indoles **29a**, **53a**, and **53b**, respectively, from thermal reactions of **11a**–**c** with aniline is of synthesis value.

The behaviors of **11b** and **11c** at high temperatures, short contact times, and reduced pressures were then determined. As discussed previously for **11a** and **1a**, finely ground solid **11b** and **11c** were each dropped directly into evacuated quartz tubes at ~450 °C/0.15 mm Hg pressure, and the exit products were condensed rapidly at –78 °C or in **23a** at –78 °C and separated and/or analyzed by chromatographic methods. Such decompositions of **11b** and **11c** give the reduction (double hydrogen abstraction) products **48a** (7%) and **48b** (11%), respectively, along with inseparable, complicated materials. The above thermolyses of **11b** and **11c** give no evidence for formation of ketenes **15b** and **15c** and/or their respective ketene-CH<sub>3</sub>OH adducts **49a** and **49b**. As in pyrolysis of **1a** to reduction product **45**, thermolysis of **11b** requires transfer of two hydrogen atoms by two or more molecular events to yield **48a**.

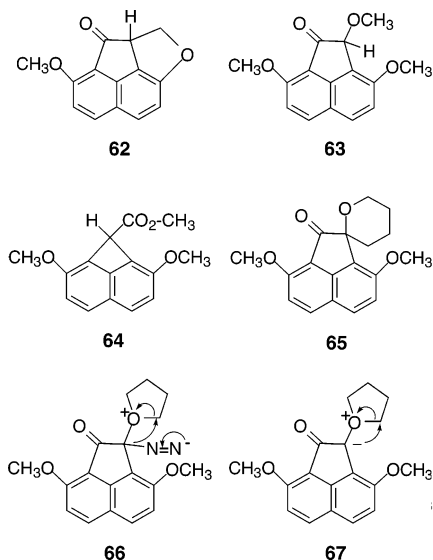
Various nitrogen-extrusion reactions of **11d** were then investigated. Diazodinitroacenaphthenone **11d** is a high-melting solid (mp 234–236 °C) that decomposes with



evolution of  $N_2$  on melting, vacuum pyrolysis, and thermally and photolytically in solution in various solvents. Thermolyses and photolyses of **11d** do not give cyclobutaketene **15d**. Photolyses of benzene solutions of **1b** under  $N_2$  containing small amounts of  $O_2$  yield 5-nitro-2-phenylacenaphthenone (**35a**);<sup>11</sup> under similar conditions, **11d** gives 2-hydroxy-5,6-dinitro-2-phenylacenaphthenone (**60**)<sup>8</sup> as a principal product (45%). Oxidation of **59b** presumably yields **60**. Of value for synthesis is that photolyses of **11d** in  $CH_3CN$  and in benzonitrile occur with loss of  $N_2$  to yield the products of cycloaddition–capture by the nitrile groups: 8-methyl-(3,4-dinitro-acenaphth)[1,2-*d*]oxazole (**61a**, 67%)<sup>8</sup> and 3,4-dinitro-8-phenylacenaphth[1,2-*d*]oxazole (**61b**, 26%),<sup>8</sup> respectively. 5,6-Dinitro analogues of **42** and **43** are not detected.



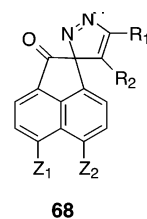
The thermal and the photolytic behaviors of 2-diazo-3,8-dimethoxyacenaphthenone (**12**) were then investigated. Diazoketone **12** does not convert to ketene **16**, insertion product **62**, or products resulting from attack on oxygen of its 3-methoxy group when heated as a solid, on melting (mp 145–146 °C), or in solution. Photolysis of **12** in  $CH_3OH$  (**23a**) yields 2,3,8-trimethoxyacenaphthenone (**63**, >78%)<sup>8</sup> preparatively. Methyl 2,7-dimethoxy-1*H*-cyclobuta[*de*]naphthalene-1-carboxylate (**64**) is not detected. A further example that **12** does not convert



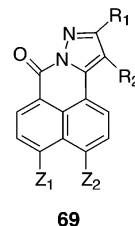
to a Wolff rearrangement product readily is irradiation of the diazoketone in tetrahydrofuran to give spiro[3,8-dimethoxyacenaphthenone-2,2'-tetrahydropyran] (**65**)<sup>8</sup> in 53% yield. Formation of **65** presumably occurs by (1) nucleophilic reaction of tetrahydrofuran with excited singlet **12** and decomposition with loss of  $N_2$  as in **66** and/or (2) rearrangement of **67** as generated from **66** by loss

of  $N_2$ , or more likely, by photolytic conversion of **12** to singlet carbene **14** followed by nucleophilic addition of tetrahydrofuran. Photochemical nucleophilic-rearrangement reactions similar to that for **12** with tetrahydrofuran have been previously found for other  $\alpha$ -diazocarbonyl compounds with oxiranes and other ethers.<sup>14</sup> The present photolytic reaction of **12** and tetrahydrofuran to give **65** is significant in that coordinative electrophilic attack on ethereal oxygen and rearrangement occur so much more extensively than carbenic insertions into any of the 8 carbon–hydrogen bonds of the cyclic ether.

The products and the mechanisms of thermal and photolytic reactions of various 2-diazoacenaphthenones with acetylenes continue to be of interest.<sup>12</sup> 2-Diazoacenaphthenone (**1a**) is reported to react with diethyl acetylenedicarboxylate and with phenylacetylene in refluxing benzene by 1,3-dipolar cycloaddition processes to yield spiro[acenaphthenone-2,3'-(3'*H*)-pyrazoles **68a** (80%) and **68b** (25%), respectively.<sup>1e</sup> In studies in this laboratory, reactions of **1a** with dimethyl acetylenedicarboxylate and phenylacetylene in refluxing benzene (bp 80 °C) are found to give 7*H*-benzo[*de*]pyrazolo[5,1-*a*]isoquinolin-7-ones **69c** (89%) and **69b** (82%), respectively.<sup>11</sup> The structures of the **69c** and **69b** as thus obtained are established by independent syntheses of the isoquinolin-7-ones, and the properties of the **69b** prepared are identical with that reported for **68b**.<sup>1e</sup> Efforts to detect **68c** and **68b** as cycloaddition products in the above experiments were unsuccessful.<sup>11</sup> Spiropyrazoles **68c**, **68b**, and presumably **68a** as formed by 1,3-dipolar



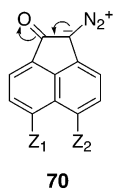
- 68a**: R<sub>1</sub> = R<sub>2</sub> = CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>; Z<sub>1</sub> = Z<sub>2</sub> = H  
**68b**: R<sub>1</sub> = C<sub>6</sub>H<sub>5</sub>; R<sub>2</sub> = H; Z<sub>1</sub> = Z<sub>2</sub> = H  
**68c**: R<sub>1</sub> = R<sub>2</sub> = CO<sub>2</sub>CH<sub>3</sub>; Z<sub>1</sub> = Z<sub>2</sub> = H  
**68d**: R<sub>1</sub> = R<sub>2</sub> = CO<sub>2</sub>CH<sub>3</sub>; Z<sub>1</sub> = H; Z<sub>2</sub> = NO<sub>2</sub>  
**68e**: R<sub>1</sub> = C<sub>6</sub>H<sub>5</sub>; R<sub>2</sub> = H; Z<sub>1</sub> = H; Z<sub>2</sub> = NO<sub>2</sub>  
**68f**: R<sub>1</sub> = C<sub>6</sub>H<sub>5</sub>; R<sub>2</sub> = H; Z<sub>1</sub> = Z<sub>2</sub> = CH<sub>3</sub>  
**68g**: R<sub>1</sub> = R<sub>2</sub> = CO<sub>2</sub>CH<sub>3</sub>; Z<sub>1</sub> = Z<sub>2</sub> = CH<sub>3</sub>  
**68h**: R<sub>1</sub> = R<sub>2</sub> = CO<sub>2</sub>CH<sub>3</sub>; Z<sub>1</sub> = Z<sub>2</sub> = C<sub>6</sub>H<sub>5</sub>  
**68i**: R<sub>1</sub> = R<sub>2</sub> = CO<sub>2</sub>CH<sub>3</sub>; Z<sub>1</sub> = Z<sub>2</sub> = C<sub>6</sub>H<sub>4</sub>-CH<sub>3</sub>-*m*  
**68j**: R<sub>1</sub> = R<sub>2</sub> = CO<sub>2</sub>CH<sub>3</sub>; Z<sub>1</sub> = Z<sub>2</sub> = NO<sub>2</sub>



- 69a**: R<sub>1</sub> = R<sub>2</sub> = CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>; Z<sub>1</sub> = Z<sub>2</sub> = H  
**69b**: R<sub>1</sub> = C<sub>6</sub>H<sub>5</sub>; R<sub>2</sub> = H; Z<sub>1</sub> = Z<sub>2</sub> = H  
**69c**: R<sub>1</sub> = R<sub>2</sub> = CO<sub>2</sub>CH<sub>3</sub>; Z<sub>1</sub> = Z<sub>2</sub> = H  
**69d**: R<sub>1</sub> = R<sub>2</sub> = CO<sub>2</sub>CH<sub>3</sub>; Z<sub>1</sub> = H; Z<sub>2</sub> = NO<sub>2</sub>  
**69e**: R<sub>1</sub> = C<sub>6</sub>H<sub>5</sub>; R<sub>2</sub> = H; Z<sub>1</sub> = H; Z<sub>2</sub> = NO<sub>2</sub>  
**69f**: R<sub>1</sub> = C<sub>6</sub>H<sub>5</sub>; R<sub>2</sub> = H; Z<sub>1</sub> = Z<sub>2</sub> = CH<sub>3</sub>  
**69g**: R<sub>1</sub> = R<sub>2</sub> = CO<sub>2</sub>CH<sub>3</sub>; Z<sub>1</sub> = Z<sub>2</sub> = CH<sub>3</sub>  
**69h**: R<sub>1</sub> = R<sub>2</sub> = CO<sub>2</sub>CH<sub>3</sub>; Z<sub>1</sub> = Z<sub>2</sub> = C<sub>6</sub>H<sub>5</sub>  
**69i**: R<sub>1</sub> = R<sub>2</sub> = CO<sub>2</sub>CH<sub>3</sub>; Z<sub>1</sub> = Z<sub>2</sub> = C<sub>6</sub>H<sub>4</sub>-CH<sub>3</sub>-*m*  
**69j**: R<sub>1</sub> = R<sub>2</sub> = CO<sub>2</sub>CH<sub>3</sub>; Z<sub>1</sub> = Z<sub>2</sub> = NO<sub>2</sub>

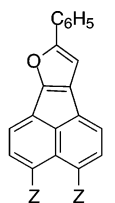
cycloaddition reactions of dimethyl acetylenedicarboxylate, phenylacetylene, and diethyl acetylenedicarboxylate with **1a** are surmised to undergo rapid, thermally allowed, and sterically-favored 1,5-sigmatropic rearrangements to **69c**, **69b**, and **69a**, respectively.<sup>16</sup> Further, dimethyl acetylenedicarboxylate and phenylacetylene react with **1b** in chlorobenzene at 130 °C to yield **69d** (83%) and **69e** (68%), respectively, presumably by isomerizations of cycloadducts **68d** and **68e** as initially formed.<sup>11</sup>

Studies have now been made of the addition reactions of 2-diazoanthrones **11a–d** with phenylacetylene and/or dimethyl acetylenedicarboxylate in warm toluene (~111 °C) in efforts to control formation of spiropyrazoles **68** and isoquinolin-7-ones **69** by steric and/or electronic effects. In all of the present experiments with **11a–d**, the only products isolable are the respective isoquinolin-7-ones **69f–j** (74–100% yields)<sup>8</sup> as presumably formed by rearrangements of the initial spiropyrazoles **68f–j**. Of importance in these experiments is that (1) 2-diazoanthrones **11a–d** react as 1,3-dipolar reagents expressed as **70a–d** to give **69f–j** in excellent yields and (2) the electron-attracting effects of the CO<sub>2</sub>CH<sub>3</sub> groups in **68g–j**, the compressions caused by steric repulsions of the *peri*-substituents in **68f–j**, and the electron-donations to the carbonyl groups by the Z<sub>1</sub> substituents in **68f–i** are insufficient to stop formation of **69f–i**.

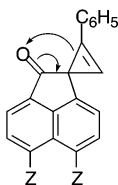


**70a:** Z<sub>1</sub> = Z<sub>2</sub> = CH<sub>3</sub>  
**70b:** Z<sub>1</sub> = Z<sub>2</sub> = C<sub>6</sub>H<sub>5</sub>  
**70c:** Z<sub>1</sub> = Z<sub>2</sub> = C<sub>6</sub>H<sub>4</sub>-CH<sub>3</sub>-*m*  
**70d:** Z<sub>1</sub> = Z<sub>2</sub> = NO<sub>2</sub>

Photolyses of **11a** and **11d** in phenylacetylene differ, however, from thermolyses in that N<sub>2</sub> is extruded and net regiospecific cycloadditions occur to give acenaphtho[1,2-*b*]furans **71a** (61%) and **71b** (48%), respectively. The overall photolytic reactions of **11a** and **11d** with phenylacetylene and with CH<sub>3</sub>CN are thus similar. The photochemical reactions of **11a** and **11d** are presumed to involve generation of electrophilic carbenes **13a** and **13d**, respectively, which undergo net, directed 1,3-dipolar reactions with phenylacetylene to yield **71a** and/or **71b**. The α-oxocyclopropenes **72a** and **72b**, respectively, as possibly formed by additions of **13a** and **13d** to phenylacetylene, are not found as reaction intermediates but, as yet, cannot be excluded as precursors to **71a** and **71b**.



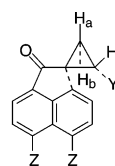
**71a:** Z = CH<sub>3</sub>  
**71b:** Z = NO<sub>2</sub>



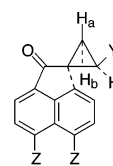
**72a:** Z = CH<sub>3</sub>  
**72b:** Z = NO<sub>2</sub>

Of further interest is that **1a** reacts thermally (~80 °C, 10 h)<sup>1h,i</sup> and photolytically<sup>11</sup> with acrylonitrile and

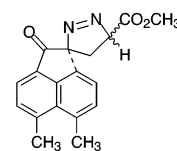
with ethyl acrylate, highly electronegatively-substituted olefins, with loss of N<sub>2</sub> to give the corresponding (*E*)- and (*Z*)-spiro[acenaphthenone-2,1'-cyclopropanes] **73a**<sup>15</sup> and **74a**<sup>15</sup> and **73b** and **74b**, respectively. Reactions of **1a** with acrylonitrile as catalyzed by palladium acetate yield **73a** and **74a** more rapidly and in higher yields.<sup>11</sup> Of importance with respect to preparation and mechanisms of formation of cyclopropyl derivatives from 2-diazoacenaphthenones and olefins is that **11a** does not react with cyclohexene at 85 °C or on storage with the electron-rich olefin, ethyl vinyl ether. Reactions of **11a** occur efficiently, however, with methyl acrylate at 80 °C (<12 h) and, of mechanistic significance, at 20–25 °C (24 h) to give methyl (*E*)- (**73c**, 50%) and (*Z*)-5,6-dimethyl-2-oxospiro[acenaphthylene-1(2*H*),1'-cyclopropane]-2'-carboxylates (**74c**, 39%).<sup>16</sup> Thus, **11a** reacts as a nucleophile with methyl acrylate at room temperature without initial loss of N<sub>2</sub>. 1,3-Dipolar cycloadducts **75** are not detected as yet however as reaction intermediates. That (*E*)- and (*Z*)-**75** are not obtained as stable intermediates or that such intermediates, if formed, undergo prototopic rearrangements with retention of nitrogen allow simple syntheses of **73c** and **74c**. An important aspect of nucleophilic reactions of **1a** and **11a** with acrylonitrile and acrylic esters is ready loss of N<sub>2</sub> to give cyclopropane derivatives which have bisected stereochemistries and are stabilized by spiroconjugation.



**73a:** Z = H; Y = CN  
**73b:** Z = H; Y = CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>  
**73c:** Z = CH<sub>3</sub>; Y = CO<sub>2</sub>CH<sub>3</sub>



**74a:** Z = H; Y = CN  
**74b:** Z = H; Y = CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>  
**74c:** Z = CH<sub>3</sub>; Y = CO<sub>2</sub>CH<sub>3</sub>



## Conclusions

Sterically strained 2-diazoacenaphthenones photolyze in solution with loss of N<sub>2</sub> and without rearrangement in reactions with alcohols, cyclohexane, tetrahydrofuran, benzene, nitriles, and acetylenes. Thermal decompositions of the 2-diazoacenaphthenones in solution or at low pressures do not yield ketenes and/or products thereof preparatively. Thermolyses of 2-diazoacenaphthenones in aniline and in diphenylamine result in N<sub>2</sub> loss from the diazo compounds, insertions into the N–H groups of the amines, *ortho* ring closures, and eliminations of H<sub>2</sub>O to give novel acenaph[1,2-*b*]indoles (**29a,b** and **54a,b**). 2-Diazoacenaphthenones react rapidly with O<sub>2</sub> on heating

(14) (a) Nozaki, H.; Takaya, H.; Noyori, R. *Tetrahedron Lett.* **1965**, 2563. (b) Nozaki, H.; Takaya, H.; Noyori, R. *Tetrahedron* **1966**, 22, 3393. (c) Kirmse, W.; Lelgemann, R.; Friedrich, K. *Chem. Ber.* **1991**, 124, 1853.

(15) Upon reinvestigation of their NMR, the spirocyclopropanes from **1a** and acrylonitrile<sup>16</sup> are reassigned stereochemically as **73a** and **74a**.<sup>11</sup>

(16) Assignment of the structures of **73c** and **74c** have been made upon comparison of their spectra with that of **73b** and **74b** as prepared by heating **1a** in ethyl acrylate.<sup>11</sup> Spirocyclopropane **73b** has IR absorptions for its carbonyl groups at 1728 and 1710 cm<sup>-1</sup> which compare to 1730 and 1700 cm in **73c**. The ABX patterns in the NMR spectra of **73c** and **73b** are identical. Spirocyclopropane **74b** exhibits IR carbonyl absorptions at 1740 and 1713 cm<sup>-1</sup> compared to 1745 and 1710 cm<sup>-1</sup> in **74c**. The ABX portions of the NMR of **74c** and **74b** are identical. The actual values of the chemical shifts and coupling constants of **73c** and **74c** are not calculated because portions of their ABX patterns are buried beneath that for their *peri*-methyl groups.



and upon photolysis. In hydrogen-atom donor environments, thermal and photolytic reduction reactions of 2-diazoacenaphthenones may become prominent. Acetylenes undergo nucleophilic additions to 2-diazoacenaphthenones (**1a**, **b**, **11a–c**, and **12**) with retention of N<sub>2</sub> and 1,5-sigmatropic rearrangements to yield pyrazolo[5,1-*a*]-quinolin-7-ones (**69**). Electronegatively-substituted olefins such as methyl acrylate and acrylonitrile undergo thermal and photochemical addition reactions of their olefinic groups with 2-diazoacenaphthenones (**1a** and **11a**) with loss of N<sub>2</sub> and without rearrangements to give (*E*)- and (*Z*)-spirocyclopropyl derivatives (**73a–c** and **74a–c**). Carbenic reactions of 2-diazo-5,6-bis(trisubstitutedsilyl)-acenaphthenones and more highly compressed 2-diazo-acenaphthenones are of present interest.

## Experimental Section

**5,6-Dimethylacenaphthenequinone (19a).** Oxalyl chloride (5 mL, *D* = 1.46, 57 mmol) was added to a stirred slurry of AlCl<sub>3</sub> (6.0 g, 45 mmol) in CS<sub>2</sub> (30 mL) at –78 °C. Solid 1,8-dimethylnaphthalene (2.5 g, 16 mmol)<sup>17</sup> was then added. The thick, dark-red solution was allowed to warm and then stirred for 3 h at –10 °C and for 1 h at ~25 °C, followed by slow addition of H<sub>2</sub>O. The CS<sub>2</sub> was removed by heating. The resulting yellow solid was filtered, dried, and recrystallized from toluene/CH<sub>3</sub>CN (1:1) to give **19a** (1.8 g, 54%, mp 232–235 °C) as long yellow needles: IR (KBr, cm<sup>–1</sup>) 1723, 1715 (C=O, s); NMR (CDCl<sub>3</sub>, δ) 7.69 (d of d, 4H, naphthyl), 3.07 (s, 6H, 2 CH<sub>3</sub>); MS *m/e* 210 (M<sup>+</sup>). Anal. Calcd for C<sub>14</sub>H<sub>10</sub>O<sub>2</sub>: C, 79.99; H, 4.80. Found: C, 80.02; H, 4.91.

**5,6-Dimethylacenaphthenequinone 2-*p*-Tosylhydrazine (17a).** *p*-Tosylhydrazine (9.75 g, 48 mmol) was added to a suspension of 5,6-dimethylacenaphthenequinone (**19a**, 8.75 g, 42 mmol) in boiling CH<sub>3</sub>CN (200 mL). The resulting mixture was refluxed 0.5 h. The yellow crystals obtained upon cooling were filtered and dried to yield **17a** (13.1 g, 83%, mp 121–123 °C): IR (KBr, cm<sup>–1</sup>) 3193 (NH, w), 1681 (C=O, s), 1392, 1170 (SO<sub>2</sub>, s); NMR (CDCl<sub>3</sub>, δ) 8.37 (bs, 1H), 8.03–7.13 (m, 8H), 2.90 (d, 6H), 2.36 (s, 3H). Anal. Calcd for C<sub>21</sub>H<sub>18</sub>N<sub>2</sub>SO<sub>3</sub>: N, 7.40; S, 8.47. Found: N, 7.25; S, 8.30.

**2-Diazo-5,6-dimethylacenaphthene (11a).** A CH<sub>2</sub>Cl<sub>2</sub> (90 mL) solution of **17a** (1.58 g, 4.2 mmol) and aqueous NaOH (46 mL, 0.1 N, 4.6 mmol) was vigorously stirred overnight. The H<sub>2</sub>O layer was extracted several times with CH<sub>2</sub>Cl<sub>2</sub>. The combined CH<sub>2</sub>Cl<sub>2</sub> extracts were washed with H<sub>2</sub>O and dried over Na<sub>2</sub>SO<sub>4</sub>. Removal of CH<sub>2</sub>Cl<sub>2</sub> and chromatography (neutral alumina, CH<sub>2</sub>Cl<sub>2</sub>) yielded **11a** (0.73 g, 79%, mp 128–129 °C) as light orange needles after recrystallization from toluene/petroleum ether: IR (KBr, cm<sup>–1</sup>) 2085 (=N<sub>2</sub>, s), 1682 (C=O, s); NMR (CDCl<sub>3</sub>, δ) 7.65 (d of d, 2H), 7.20 (d, 2H), 2.90 (d, 6H). Anal. Calcd for C<sub>14</sub>H<sub>10</sub>N<sub>2</sub>O: C, 75.66; H, 4.54; N, 12.60. Found: C, 75.41; H, 4.56; N, 12.37.

**Search for Wolff Rearrangement Products in Reactions of 2-Diazoacenaphthenones 11a–c and 12, Respectively, with Alcohols and Amines.** The reactions of **11a–c** and **12**, respectively, with alcohols were carefully examined for Wolff rearrangement products. Important to these analyses is that methyl 1*H*-cyclobuta[*de*]naphthalene-1-carboxylate (**46**)<sup>6d</sup> is a stable, chromatographable liquid prepared as in ref 13. The properties of **46** which are reliably determined are its exact mass, its IR absorption for its ester carbonyl group at 1735 cm<sup>–1</sup>, and its NMR at δ = 5.94 for one cyclobuta proton.<sup>6d</sup>

Cyclobuta ester **46** is readily detected spectrally in low concentrations in admixture with its isomer, 2-methoxyacenaphthenone, along with acenaphthenone. In photolyses of **11a** in **23a** and in **23b** there is no spectral evidence for cyclobuta ester **26a** and **26b**, respectively, in the crude or the purified reaction products. Similarly, spectral analyses of the products of thermolyses of **11a** in cyclohexanol at 240 °C and in benzyl alcohol at 180 °C do not indicate the presence of cyclohexyl or benzyl ester analogues of **26a** and **26b**. The MS, IR, and NMR methods for **46** were also used to determine that Wolff rearrangement products are not obtained from reactions of **11b–c** and of **12** with alcohols. When these analytical methods are extended to the products of reactions of **11a–c** with amines, there is no evidence for formation of amides resulting from capture of ketenes arising from Wolff rearrangements.

**Photolysis of 11a in Methanol (23a).** A solution of **11a** (0.51 g, 2.3 mmol) in **23a** (225 mL) was photolyzed 3 h. The residue obtained upon removal of solvent under vacuum and chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether 1:1) yielded two products:

(1) 5,6-dimethylacenaphthene (**25**, 50 mg, 9%, mp 164–165 °C) obtained as pink crystals after recrystallization from hexane: IR (KBr, cm<sup>–1</sup>) 1700 (C=O, s); NMR (CDCl<sub>3</sub>, δ) 7.90–7.23 (m, 4H), 3.70 (s, 2H), 2.91 (d, 6H). Anal. Calcd for C<sub>14</sub>H<sub>12</sub>O: C, 85.68; H, 6.16. Found: C, 85.42; H, 6.21 and (2) 2-methoxy-5,6-dimethylacenaphthene (**24a**, 0.32 g, 61%, mp 130–131 °C) which was recrystallized from hexane to give pale yellow crystals: IR (KBr, cm<sup>–1</sup>) 2815 (OCH<sub>3</sub>, w), 1718 (C=O, s); NMR (CDCl<sub>3</sub>, δ) 7.90–7.23 (m, 4H), 5.00 (s, 1H), 3.57 (s, 3H), 2.93 (d, 6H). Anal. Calcd for C<sub>15</sub>H<sub>14</sub>O<sub>2</sub>: C, 79.62; H, 6.24. Found: C, 79.49; H, 6.40. There was no evidence for **26a** in the reaction products.

**Photolysis of 11a in *tert*-Butyl Alcohol (23b).** Photolysis of **11a** (0.5 g, 2.2 mmol) in **23b** (225 mL) was effected for 26 h. Vacuum removal of the **23b** yielded a brown semi-solid which was chromatographed on silica gel (benzene). The first compound eluted was reduction product **25** (0.1 g, 23%, mp 164–165 °C) as characterized previously. The next compound eluted was 2-*tert*-butoxy-5,6-dimethylacenaphthene (**24b**, 0.13 g, 22%, mp 136–136.5 °C (benzene/petroleum ether) as off-white needles: IR (KBr, cm<sup>–1</sup>) 1721 (C=O, s), no absorption assignable to **26b** resulting from addition to **15a**, the possible ketene, from Wolff contraction of **11a**; NMR (CDCl<sub>3</sub>, δ) 7.77–7.13 (m, 4H), 5.10 (s, 1H), 2.89 (d, 6H), 1.49 (s, 9H); *m/e* calcd for C<sub>18</sub>H<sub>20</sub>O<sub>2</sub>: 268.14632, obsd 268.14542. Anal. Calcd for C<sub>18</sub>H<sub>20</sub>O<sub>2</sub>: C, 80.56; H, 7.51. Found: C, 80.48; H, 7.71.

**Thermolysis of 11a in Aniline.** A solution of **11a** (0.5 g, 2.2 mmol) in aniline (5 mL) was heated to 180 °C for 0.25 h and then refluxed (~180 °C) for 1 h. The dark red solution was allowed to cool to room temperature, poured into a concentrated HCl–ice slurry, and extracted with benzene. The organic layer was dried over MgSO<sub>4</sub> and concentrated to a dark orange semisolid. Chromatography on silica gel (benzene) yielded 3,4-dimethylacenaphth[1,2-*b*]indole (**28**, 0.16 g, 27%, mp 272–274 °C (benzene)), as light orange crystals: IR (KBr, cm<sup>–1</sup>) 3417 (NH, s); NMR (CDCl<sub>3</sub>, δ) 8.48 (bs, 1H), 7.96–6.93 (m, 8H), 2.83 (s, 6H); *m/e* calcd for C<sub>20</sub>H<sub>15</sub>N 269.12044, obsd 269.12112. Anal. Calcd for C<sub>20</sub>H<sub>15</sub>N: C, 89.19; H, 5.6; N, 5.20. Found: C, 88.88; H, 5.75; N, 5.03. The second product isolated was **25** (0.15 g, 32%, mp 232–235 °C) as previously characterized. [Similar results were obtained upon submerging a solution of **11a** in aniline in a silicone bath at 180 °C and refluxing the mixture for 1 h.]

**Thermolysis of 11a in Diphenylamine.** Diphenylamine (5 g) was melted (mp 54 °C) and **11a** (0.3 g, 1.4 mmol) was added. The mixture was heated for 10 min in a salt bath (47% NaNO<sub>2</sub>, 7% NaNO<sub>3</sub>, 46% KNO<sub>3</sub>) at 295 °C and then cooled to room temperature. Ethyl ether was added, and the dark red solution was poured into a concentrated HCl–ice slurry. The H<sub>2</sub>O layer was extracted several times with benzene. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under vacuum. The red, oily concentrate (5.27 g) was primarily

(17) (a) 1,8-Dimethylnaphthalene was prepared by (1) reduction of 1,8-naphthalic anhydride with LiAlH<sub>4</sub> to 1,8-bis(hydroxymethyl)-naphthalene,<sup>17b</sup> (2) conversion of the diol by PBr<sub>3</sub> to 1,8-bis(bromomethyl)-naphthalene,<sup>17c</sup> and (3) reaction of the dibromide with LiAlH<sub>4</sub>.<sup>17d</sup> (b) Boekelheide, V.; Vick, G. K. *J. Am. Chem. Soc.* **1956**, *78*, 653. (c) Mitchell, W. J.; Sondheimer, F. *Tetrahedron* **1968**, *34*, 1397. (d) Mitchell, W. J.; Topsom, R. D.; Vaughan, J. *J. Chem. Soc.* **1940**, 2526.

diphenylamine and eventually solidified. Chromatography of the solid concentrate on silica gel (benzene/petroleum ether 1:1) yielded 3,4-dimethyl-*N*-phenylacenaphth[1,2-*b*]indole (**29b**, 60 mg, 12%, mp 191–192 °C) which was recrystallized from benzene:petroleum ether to give shiny red crystals: NMR (CDCl<sub>3</sub>,  $\delta$ ) 8.23–7.23 (m, 13H), 3.03 (s, 6H); *m/e* calcd for C<sub>26</sub>H<sub>19</sub>N: 345.15174, obsd: 345.15257. Anal. Calcd for C<sub>26</sub>H<sub>19</sub>N: C, 90.40; H, 5.54; N, 4.06. Found: C, 90.38; H, 5.65; N, 3.96.

Diphenylamine, contaminated with a small amount of **29b**, was next eluted on chromatography (diphenylamine and **29b** have similar *R<sub>f</sub>* values). Further elution produced **25** (20 mg, 7%, mp 164–165 °C) as characterized previously.

**Photolysis of 11a in Cyclohexane.** Diazoacenaphthenone **11a** (0.52 g, 2.3 mmol) in cyclohexane (225 mL) was photolyzed 3 h and then concentrated to dryness. Chromatography of the crude product on silica gel (benzene) yielded 2-cyclohexyl-5,6-dimethylacenaphthenone (**34**, 0.39 g, 70% based on reacted starting material, mp 115–116 °C). Recrystallization of **34** from benzene:hexane (1:1) gave tiny orange crystals: IR (CCl<sub>4</sub>, cm<sup>-1</sup>) 1712 (C=O, s); NMR (CDCl<sub>3</sub>,  $\delta$ ) 7.82–7.10 (m, 4H), 3.43 (d, 1H, *J* = 1.5), 2.80 (d, H), 1.87–0.57 (bm, 11H); *m/e* calcd for C<sub>20</sub>H<sub>22</sub>O 278.16706, obsd 278.16770. Anal. Calcd for C<sub>20</sub>H<sub>22</sub>O: C, 86.29; H, 7.96. Found: C, 86.45; H, 8.02. Further elution resulted in recovery of **11a** (80 mg, 15%) as identified by comparison with an authentic sample.

**Photolysis of 11a in Benzene.** A benzene (225 mL) solution of **11a** (1.0 g, 4.5 mmol) was irradiated 3 h. The benzene was removed under vacuum and the residue chromatographed on silica gel (benzene). Three compounds were isolated:

(1) 5,6-Dimethyl-2-phenylacenaphthenone (**36**, 0.25 g, 20%, mp 142–143 °C) which sublimates as a light yellow solid: IR (KBr, cm<sup>-1</sup>) 1715 (C=O, s); NMR (CDCl<sub>3</sub>,  $\delta$ ) 7.67 (d of d, 2H), 7.38–7.00 (m, 7H), 4.83 (s, 1H), 3.00 (d, 6H); *m/e* calcd for C<sub>20</sub>H<sub>16</sub>O 272.12010, obsd 272.12081. Anal. Calcd for C<sub>20</sub>H<sub>16</sub>O: C, 88.20; H, 5.92. Found: C, 88.08; H, 6.08. (2) (*E*)-*cis*-5,6-Dimethylspiro[acenaphthene-1,7'-[2,4]norcaradien]-2-one (**35**, 0.24 g, 20%, mp 165–167 °C) as a light yellow solid: IR (KBr, cm<sup>-1</sup>) 1688 (C=O, s); NMR (CDCl<sub>3</sub>,  $\delta$ ) 7.94–7.00 (m, 4H), 6.90–6.00 (m, 4H), 3.26 (t, 2H), 2.90 (d, 6H); *m/e* calcd for C<sub>20</sub>H<sub>16</sub>O 272.1201077, obsd 272.1208065. (3) *cis*-7a,11a-Dihydro-3,4-dimethylacenaphtho[1,2-*b*]benzo[*d*]furan (**37**, 0.47 g, 40%, mp 181–183 °C) as light orange crystals when recrystallized from benzene: IR (KBr, cm<sup>-1</sup>) 1628 (C = C, s), no carbonyl; NMR (CDCl<sub>3</sub>,  $\delta$ ) 8.74–7.36 (m, 5H), 7.06–6.20 (m, 2H), 6.00–5.53 (m, 1H), 3.17 (d, 2H), 2.98 (s, 6H); *m/e* calcd for C<sub>20</sub>H<sub>16</sub>O 272.12010, obsd 272.12081. Anal. Calcd for C<sub>20</sub>H<sub>16</sub>O: C, 88.20; H, 5.92. Found: C, 88.05; H, 6.15.

Norcaradiene **35** is highly unstable and must be stored at low temperature. The norcaradiene (**35**) was isomerized quantitatively to **36** upon refluxing in xylene for 4 h. The product (**36**) was isolated upon cooling and evaporating the solution, chromatography of the residue on silica gel (CH<sub>2</sub>Cl<sub>2</sub>), and recrystallization from benzene.

**Photolysis of 11a in Acetonitrile.** A solution of **11a** (0.51 g, 2.3 mmol) in CH<sub>3</sub>CN (225 mL) was irradiated 3 h. Following removal of the CH<sub>3</sub>CN at reduced pressures, the residue was chromatographed (silica gel, benzene) to yield 3,4,8-trimethylacenaphth[1,2-*d*]oxazole (**41**, 0.28 g, 52%, mp 195–196 °C) as yellow crystals after sublimation: NMR (CDCl<sub>3</sub>,  $\delta$ ) 7.77–7.13 (m, 4H), 2.82 (s, 6H), 2.61 (s, 3H); *m/e* calcd for C<sub>16</sub>H<sub>13</sub>NO 235.09971, obsd 235.10033. Anal. Calcd for C<sub>16</sub>H<sub>13</sub>NO: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.22; H, 5.74; N, 5.83.

**Thermal Decomposition of 11a.** Finely powdered **11a** (0.3 g, 1.4 mmol) was placed in a scoop fitted in an inverted Erlenmeyer flask attached to the top of an insulated quartz pyrolysis tube (43 × 2.5 cm) in which the top one-third was packed with glass wool. At the bottom of the pyrolysis tube was a receiving flask cooled to –78 °C attached to a vacuum system. The pyrolysis equipment was evacuated (0.15 mm Hg) and heated externally to ~450 °C.

The **11a** was dropped slowly into the pyrolysis tube by gradually turning the scoop in the Erlenmeyer flask. The condensable volatile products were collected in the receiving flask and, after 30 min, the pyrolysis equipment was allowed to cool. Anhydrous CH<sub>3</sub>OH (**23a**, 20 mL) was added to the condensate at –78 °C in the receiving flask. The light orange **23a** solution was allowed to warm to room temperature and evaporated. Chromatography of the light orange film on alumina (benzene) yielded **25** (40 mg, 14%, mp 164–165 °C), identical with an authentic sample. There was much dark material on the walls of the pyrolysis tube.

Similar results were obtained from vacuum pyrolysis of **11a** when **23a** was placed in the receiving flask.

**Photolysis of 11a in Phenylacetylene.** A solution of **11a** (0.5 g, 2.2 mmol) in phenylacetylene (225 mL) was photolyzed 24 h. The phenylacetylene was removed under vacuum, leaving a brown oil which was chromatographed on silica gel (benzene/hexane 1:1) to give 3,4-dimethyl-8-phenylacenaphtho[1,2-*b*]furan (**71a**, 0.4 g, 61% based on reacted starting material, mp 186–188 °C) as orange crystals when recrystallized from petroleum ether: NMR (CDCl<sub>3</sub>,  $\delta$ ) 7.93–7.12 (m, 9H), 6.97 (s, 1H), 2.83 (s, 6H). Anal. Calcd for C<sub>22</sub>H<sub>16</sub>O: C, 89.16; H, 5.44. Found: C, 89.21; H, 5.30.

**Thermolysis of 11a in Phenylacetylene.** A mixture of **11a** (0.3 g, 1.4 mmol) and phenylacetylene (1 mL) in toluene (15 mL) was refluxed 28 h. After the mixture was cooled, the orange crystals formed were filtered to give 3,4-dimethyl-10-phenyl-7*H*-benzo[*de*]pyrazolo[5,1-*a*]isoquinoline-7-one (**69b**, 0.35 g, 79%, mp 244–247 °C): IR (KBr, cm<sup>-1</sup>) 1699 (C=O, s); NMR (CDCl<sub>3</sub>,  $\delta$ ) 8.54–7.20 (m, 9H), 6.98 (s, 1H), 2.90 (d, 6H); *m/e* calcd for C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>O 324.12626, obsd 324.12679. Anal. Calcd for C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>O: C, 81.46; H, 4.97; N, 8.64. Found: C, 81.15; H, 5.03; N, 8.65.

**Thermolysis of 11a in Dimethyl Acetylenedicarboxylate.** 2-Diazoacenaphthenone **11a** (0.3 g, 1.4 mmol) was dissolved in toluene (15 mL) containing dimethyl acetylenedicarboxylate (1 mL) and the mixture was refluxed 24 h. Upon concentrating the solution to a small volume, orange crystals formed which, after filtration, were identified as dimethyl 3,4-dimethyl-7-oxo-7*H*-benzo[*de*]pyrazolo[5,1-*a*]isoquinoline-10,11-dicarboxylate (**69g**, 0.49 g, 100%, mp 240–241 °C): IR (KBr, cm<sup>-1</sup>) 1745, 1732, 1712 (C=O, s), 1237, 1218 (C–O–C, s); NMR (CDCl<sub>3</sub>,  $\delta$ ) 8.49 (d of d, 2H), 7.54–7.15 (m, 2H), 4.03 (s, 6H), 2.92 (d, 6H); *m/e* calcd for C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O<sub>5</sub> 364.10591, obsd 364.10658. Anal. Calcd for C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O<sub>5</sub>: C, 65.93; H, 4.43; N, 7.69. Found: C, 65.91; H, 4.60; N, 7.64.

**Thermolysis of 11a in Methyl Acrylate.** A toluene (15 mL) solution of **11a** (0.4 g, 1.8 mmol) and methyl acrylate (1 mL) was refluxed overnight. Removal of the solvent under vacuum produced a light orange solid which was chromatographed on silica gel (benzene).

The first product obtained was methyl (*E*)-5,6-dimethyl-2-oxospiro[acenaphthylene-1(2*H*),1'-cyclopropane]-2'-carboxylate (**73c**, 0.26 g, 50%, mp 163–164 °C) as off-white needles when recrystallized from toluene/petroleum ether (1:1): IR (KBr, cm<sup>-1</sup>) 1730, 1700 (C=O, s), 1207, 1177 (C–O–C, s); NMR (CDCl<sub>3</sub>,  $\delta$ ) 7.94–7.10 (m, 4H), 3.67 (s, 3H), 2.85 (d, 6H), 2.85–2.57, 2.33–1.83 (m, 3H); *m/e* calcd for C<sub>18</sub>H<sub>16</sub>O<sub>3</sub> 280.10994, obsd 280.11090. Anal. Calcd for C<sub>18</sub>H<sub>16</sub>O<sub>3</sub>: C, 77.12; H, 5.76. Found: C, 77.28; H, 5.90.

Further elution with CHCl<sub>3</sub> yielded methyl (*Z*)-5,6-dimethyl-2-oxospiro[acenaphthylene-1(2*H*),1'-cyclopropane]-2'-carboxylate (**74c**, 0.2 g, 39%, mp 145.5–146.5 °C) which was recrystallized from toluene/petroleum ether (1:1) to give off-white needles: IR (KBr, cm<sup>-1</sup>) 1745, 1710 (C=O, s), 1210, 1179 (C–O–C, s); NMR (CDCl<sub>3</sub>,  $\delta$ ) 7.27 (d of d, 2H), 7.27 (d of d, 2H), 3.74 (s, 3H), 2.80 (d, 6H), 2.80–2.27, 1.98–1.67 (m, 3H); *m/e* calcd for C<sub>18</sub>H<sub>16</sub>O<sub>3</sub> 280.10994, obsd 280.11090. Anal. Calcd for C<sub>18</sub>H<sub>16</sub>O<sub>3</sub>: C, 77.12; H, 5.76. Found: C, 77.06; H, 5.79.

When a solution of **11a** (0.1 g, 0.45 mmol) in methyl acrylate (10 mL) was stirred at room temperature for 24 h, no **11a**

remained. Purification and chromatography of the crude product led to isolation of **73c** and **74c** in excellent yields.

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**Supporting Information Available:** Procedures involving (1) methods and materials; (2) syntheses of 1,8-diphenylnaphthalene, 1,8-di(*m*-tolyl)naphthalene, 2,7-dimethoxynaph-

thalene, quinones **19b–d** and **20**, *p*-tosylhydrazones **17b–d** and **18**, diazoacenaphthenones **11b–d** and **12**; (3) reactions of **11b** and **12** in various environments; and (4) preparation of **47a,b**, **48a,b**, **49a**, **50a,b**, **51a,b**, **53a,b**, **54**, **55**, **60**, **61a,b**, **63**, **64**, **69h–j**, **70b**, 3,3'-dimethylbiphenyl, and 8,8'-di(*m*-tolyl)-1,1'-dinaphthyl. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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