overall reaction becomes very slow when all the amine oxide is phosphorylated (see Experimental Section).

The reaction was followed in carbonate buffer with *p*-NPDPP in excess over DDMAO in CTABr. (It was necessary to use excess CTABr to solubilize the substrate). The reactions followed reasonably good first-order kinetics for approximately two half-lives, and the first-order rate constants decreased with increasing [CTABr] (Table IV). Values of k_ψ varied linearly with [DDMAO]/[CTABr], i.e., with the concentration of amine oxide in the comicelle. The absorbance after ca. 7 half-lives was approximately 60% of that calculated for complete decomposition of *p*-NPDPP (Experimental Section), so that there is apparently a small contribution from reaction with OH^- or buffer or some turnover of phosphorylated amine oxide. Despite these complications values of k_ψ in the comicelles agree reasonably well with those in DDMAO alone.

Substrate should be fully bound at the higher [CTABr], and under these conditions k_ψ is given by eq 3[1b,e,17] and

$$k_\psi = k_M[\text{DDMAO}]/([\text{CTABr}] + [\text{DDMAO}]) \quad (2)$$

from the data in Table IV, $k_M \approx 2.4 \times 10^{-3}$ s^{-1}, which is similar to that of $k_M = 1.5 \times 10^{-3}$ s^{-1} for reaction in DDMAO (Figure 1). The higher value in the comicelles is probably due to incursion of reaction with buffer or OH^-. The rate constant depends upon reagent concentration at the micellar surface and micellar charge has little or no effect.

Experimental Section

Materials. Dodecyldimethylamine oxide (DDMAO) (Aldrich) was purified by recrystallization (EtOAc). This and unpurified material gave the same values of k_ψ for reaction in NaOH. The preparation or purification of the other materials has been described.[11,15] Reactions were followed in redistilled, deionized, CO_2-free water.

Kinetics. The reaction was followed spectrophotometrically at 405 nm or at the isosbestic point between *p*-nitrophenol and phenoxide ion, 347 nm. Except where noted the substrate concentration was 10^{-5} M, and substrate was added in MeCN so that the reaction solution contained 0.3% MeCN. The first-order rate constants, k_ψ, are in reciprocal seconds.

The reaction was followed with 3×10^{-4} M *p*-NPDPP, 1.5×10^{-4} M DDMAO, and 0.01 M carbonate buffer, pH 7.0 with 0.003, 0.005, and 0.01 M CTABr, and after ca. 7 half-lives absorbances at 347 nm were respectively 60%, 70%, and 62% of those of solutions in which *p*-NPDPP was replaced by equimolar *p*-nitrophenol. In the reactions in buffer 3 mL of reaction solution contained 1 mL of carbonate of the specified pH.

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The Bis Cycloadduct of Hexamethyl-2,4-cyclohexadienone and a 1,4-Benzadiyne Equivalent

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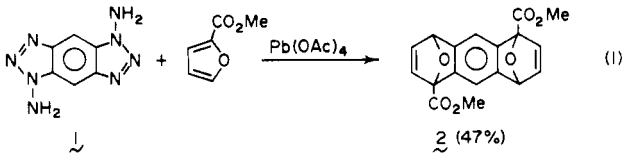
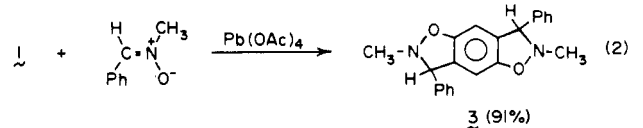
A single bis adduct **5** (*anti*-1,2,3,4,5,6,7,8,12,12,14,14-dodecamethyl-1,4:5,8-diethano-1,4,5,8-tetrahydroanthracene-11,13-dione) was obtained from the reaction of 1,4-benzadiyne equivalent **1** (1,5-diamino-1,5-dihydrobenzo[1,2-*d*:4,5-*d*']bistriazole) with hexamethyl-2,4-cyclohexadienone (**4**) and lead tetraacetate. Possible reasons for this remarkable regioselectivity in an aryne cycloaddition are discussed. Bis adduct **5** rearranges in neat trifluoroacetic acid to a mixture of isomeric diketones **13–16**. Irradiation of **16** through Pyrex gives the novel heptacyclic diketone **17**.

DABT (1,5-diamino-1,5-dihydrobenzo[1,2-*d*:4,5-*d*']bistriazole, **1**) is a useful 1,4-benzadiyne equivalent.[1] On treatment with dienes or 1,3-dipoles and lead tetraacetate, DABT gives good yields of bis(aryne) adducts. With unsymmetric dienes or 1,3-dipoles, the cycloadditions may be quite regioselective, as illustrated in eq 1 and 2. Although some secondary questions remain about the full structures of the adducts (oxygens syn or anti in **2**, phenyls cis or trans in **3**), the regiochemistry with regard to the cycloaddition was unequivocally established in both exammples. The cycloadditions to **1** probably occur stepwise, the observed regioselectivity arising in the second cycloaddition step.



(1)

1 **2** (47%)



(2)

3 (91%)

Many aryne cycloadditions occur without a high degree of selectivity.[2] In those examples where the regioselectivity is high, the factors which control it are still not entirely understood and are a matter of current interest.[2,3] We report here an example of truly remarkable regioselectivity in a cycloaddition involving benzadiyne equivalent **1**.

Results and Discussion

Cycloaddition of Hexamethyl-2,4-cyclohexadienone (4) with 1. Treatment of **1** with 2 equiv of **4**[4] and slightly

(1) Hart, H.; Ok, D. *Tetrahedron Lett.* **1984**, *25*, 2073. Hart, H.; Ok, D. *J. Org. Chem.* **1986**, *51*, 979.

(2) Pollart, D. J.; Rickborn, B. *J. Org.* Chem. **1987**, *52*, 792 and references cited therein.

(3) Gribble, G. W.; Keavy, D. J. *Abstracts of Papers*, 193rd National Meeting of the American Chemical Society, Denver, Colorado; American Chemical Society: Washington, DC, 1987; ORGN 153.

(4) Hart, H.; Lange, R. M.; Collins, P. M. *Organic Syntheses*; Wiley: New York, **1973**; Collect. Vol. V, p 598.

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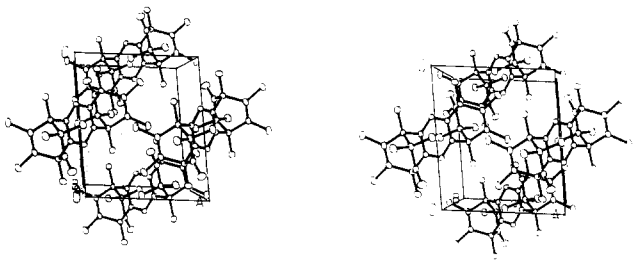
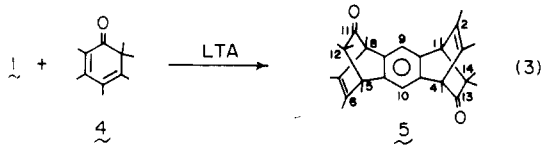


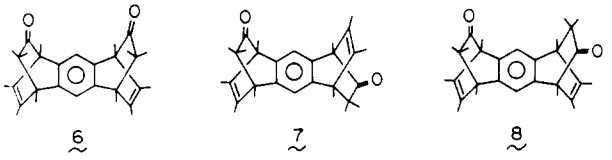
Figure 1.

over 2 equiv of lead tetraacetate (LTA) in tetrahydrofuran gave a single crystalline bis adduct **5**, mp 338 °C dec, in 79% yield. Four regioisomers are possible in this reaction



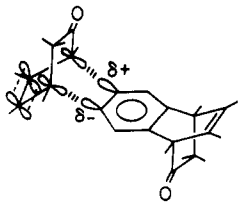
(3)

(**5-8**). The aromatic protons in the product appeared as a sharp singlet (δ 7.00), which suggested that structures **6** and **7** could probably be excluded. Barring coincidence,



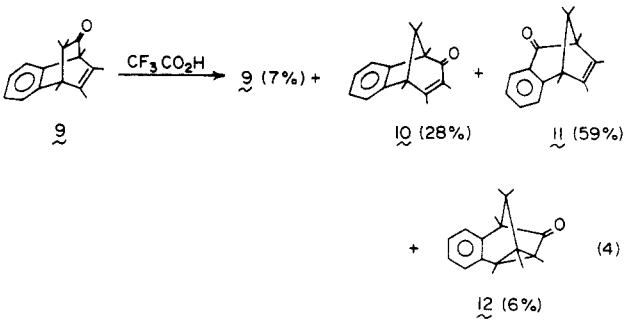
only the "anti" orientation of the carbonyl groups in **5** or **8** is consistent with this observation. The rest of the ^1H NMR spectrum consisted of singlets at δ 0.49 and 1.07 for the *gem*-dimethyl group, singlets at δ 1.62 and 1.67 for the bridgehead methyls, and mutually coupled signals at δ 1.69 and 1.78 (J = 1 Hz) for the allylic methyl protons. Through the use of deuteriated dienones, it was possible to unequivocally assign each of these methyl signals (see Experimental Section). Nevertheless, the spectrum could not distinguish between structures **5** and **8**. The matter was settled in favor of **5** by an X-ray crystal structure (Figure 1).

The cycloaddition is thus highly regioselective, being anti with respect to the orientation of the carbonyl group dipoles and anti with respect to the carbonyl-containing bridges. At present, the reasons for this regioselectivity can only be speculative. If we reasonably assume that the addition proceeds stepwise, then the orientation depicted below of the intermediate aryne and the second dienone moiety must be preferred over the three other possible orientations. One factor that might contribute to this



preference is a polarization of the aryne bond in the direction shown as a consequence of electron withdrawal by the carbonyl substituent. The cycloaddition, then, might take on some of the characteristics of a nucleophilic addition to the dienone. Another factor which could favor the anti arrangement of the carbonyl bridges might be a minimization of dipole–dipole interactions. Clearly, additional work is needed to resolve these questions.

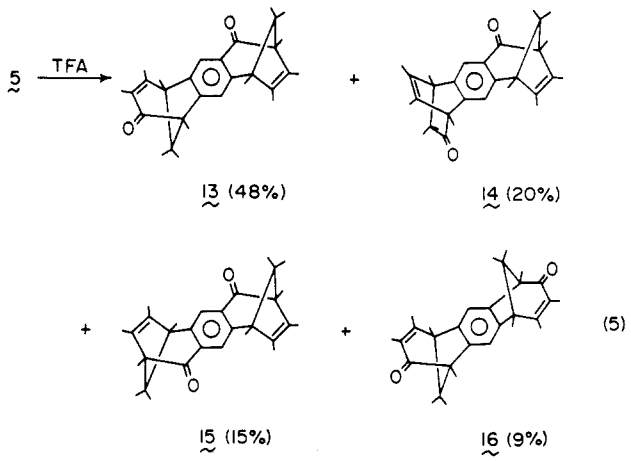
Acid-Catalyzed Rearrangements of 5. Some years ago we prepared the simple benzyne adduct of **4** (i.e., **9**[5]) and found[6] that it rearranged in acid to an equilibrium mixture of **9–12** (eq 4). It seemed of some interest to study



(4)

the analogous rearrangements of **5**, to determine whether similar products would be obtained and whether the transformations would occur on one or both "sides" of the arene ring.

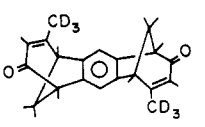
Diketone **5** was heated at reflux in neat trifluoroacetic acid (TFA) for 21 h to give a mixture of four isomeric diketones **13–16** (92% yield), together with 8% of unidentified minor products. The same equilibrium mixture



(5)

was obtained when each of the diketones was separately treated with TFA. Each diketone was isolated as a crystalline solid, and the assigned structures are based on spectra, on deuterium-labeling experiments, and by analogy with the rearrangement of **9**.

The ^1H and ^{13}C NMR spectral data of **5** and **13–16** are shown in Table I. Compounds **15** and **16** have C_i symmetry and, therefore, have half the number of ^1H and ^{13}C NMR signals as their isomers **13** and **14**. Both **15** and **16** are conjugated ketones. The carbonyl frequency is lower for **16** (1650 cm^{-1}) than for **15** (1670 cm^{-1}), consistent with double bond and aromatic conjugation, respectively. In addition, the aromatic protons in **15** appear at much lower field (δ 7.77) than in **16** (δ 6.74), consistent with their location adjacent to a carbonyl group in **15**. Finally, treatment of **16** with CH_3ONa in excess CH_3OD gave **16**-d_6, whose ^1H NMR spectrum was identical with that of **16** except that the signal at δ 1.86 was absent and the peak at δ 1.61 had sharpened to a singlet. No analogous exchange occurred with **15**.



(5) Gripper Gray, A. C.; Hart, H. *J. Am. Chem. Soc.* **1968**, *90*, 2569.
(6) Hart, H.; Love, G. M. *Tetrahedron Lett.* **1971**, 2267. Hart, H.; Love, G. M. *J. Am. Chem. Soc.* **1971**, *93*, 6264.

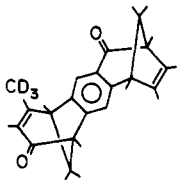
Table I. NMR Spectra of Diketones 5 and 13–16

	^{1}H NMR, δ			
		methyls[a,b]		
compd	Ar	allylic	bridgehead	*gem*
5	7.00	1.69, 1.78	1.62, 1.67	0.49, 1.07
13	6.90, 7.64	1.44 (6 H), 1.61, 1.88	1.14, 1.23, 1.37 (6 H)	0.71, 0.78, 1.01 (6 H)
14	6.83, 7.88	1.30, 1.43, 1.46, 1.53	1.15, 1.17, 1.22, 1.25	0.41, 0.72, 0.98, 1.03
15	7.77	1.44, 1.45	1.16, 1.30	0.73, 1.03
16	6.74	1.61, 1.86	1.29, 1.31	0.77, 0.99

	^{13}C NMR[c] δ			
compd	C=O	vinyl and Ar	quaternary	methyls
5	199.51	115.40, 132.00, 138.28, 140.34, 143.16	45.19, 50.42, 58.42	12.18, 12.56, 13.08, 15.30, 23.54, 24.14
13	197.39, 198.39	118.70, 119.77, 125.45, 129.38, 131.45, 147.61, 148.04, 149.34, 149.93, 157.95	55.48, 56.47, 57.33, 62.32, 64.46, 66.52	9.76, 10.06, 10.66, 11.34 (2), 12.50, 13.26, 16.36, 16.74, 17.92, 21.15, 21.72
14	191.25, 197.21	117.03, 122.53, 128.80, 129.23, 130.86, 131.32, 136.78, 142.28, 146.84, 147.66	42.00, 42.25, 45.13, 55.36, 57.29, 66.47	5.49, 7.72, 9.73, 9.92, 10.00, 11.29, 13.03, 13.66, 17.26, 17.88, 21.66, 22.96
15	197.00	121.90, 130.84, 132.96, 147.22, 148.34	56.19, 57.21, 66.77	9.75, 10.01, 11.40, 12.35, 17.98, 21.57
16	199.36	116.93, 125.10, 143.64, 150.29, 157.30	55.47, 62.34, 63.59	11.34 (2), 13.29, 16.40, 16.89, 21.26

[a] All peak areas are consistent with the structures. [b] All peaks are singlets except for the allylic methyls, which may show homoallylic coupling, $J \simeq 1$ Hz. [c] Overlapping signals are indicated by (2).

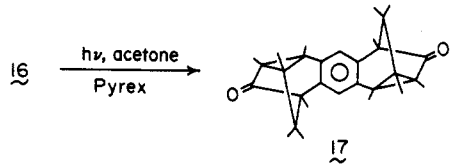
Diketone **13** has a strong carbonyl absorption at 1655 cm^{-1}, whereas **14** shows both conjugated (1670 cm^{-1}) and nonconjugated (1720 cm^{-1}) carbonyls. Treatment of **13** with CH_3ONa in excess CH_3OD resulted in **13**-d_3, whose ^{1}H NMR spectrum differed from that of **13** only in the disappearance of the signal at δ 1.88 and the sharpening of the signal at δ 1.61 to a singlet. No analogous exchange



13-d_3

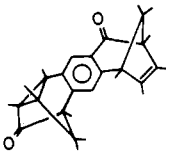
occurred with **14**. Other data which support structure **14** (in contrast, for example, with a structure on the "left" side of the arene ring analogous to the cyclopropyl ketone structure **12**) are the ^{13}C NMR spectrum, which shows six (*not* eight) quaternary carbons, and the mass spectrum. Diketone **14** is the only isomer which shows a substantial fragmentation peak at *m/e* 360 corresponding to the loss of dimethylketene. This process is prominent in the mass spectra of **5** and **9**.

To establish the structure more securely, we studied briefly the photoisomerization of **16**. We had shown earlier[7] that **10** photoisomerizes quantitatively to **12**. We now find that analogous irradiation of **16** (acetone, Pyrex) gives a nearly quantitative yield of **17**. The structure of **17** is



16 → **17**

clear from its spectra. It shows a single carbonyl band at 1715 cm^{-1}. The ^{1}H NMR spectrum shows only one aromatic proton singlet (δ 6.89) and six aliphatic methyl singlets consistent with the C_i symmetry. The ^{13}C NMR spectrum of **17** shows one carbonyl signal (δ 199.03), three aromatic carbons, five quaternary aliphatic carbons (from δ 35.97 to 54.70), and six methyl signals (from δ 5.60 to 23.00). By comparison with the spectra of **14**, we can unequivocally rule out the alternative structure **14'** for this diketone.



14'

The structures of **13–16** thus seem on fairly firm ground, particularly with regard to the bicyclic ring structure on either side of the arene ring. We have assumed and not proved, however, that the bridges are anti, as they are in the precursor **5**. The mechanisms by which **13–16** are formed are no doubt analogous to those for the rearrangement of **9**.[6]

To summarize, we have shown that 1,4-benzadiyne equivalent **1** adds to cyclohexadienone **4** to give the bis cycloadduct **5**, whose structure was established via spectra and an X-ray structure. Possible factors responsible for this highly regioselective aryne cycloaddition are briefly discussed. In acid, **5** rearranges to an equilibrium mixture of isomeric diketones **13–16**.

Experimental Section[8]

***anti*-1,2,3,4,5,6,7,8,12,12,14,14-Dodecamethyl-1,4:5,8-diethano-1,4,5,8-tetrahydroanthracene-11,13-dione (5).** To a mixture of DABT (**1**) (1.10 g, 5.78 mmol) and hexamethyl-2,4-cyclohexadienone (**4**) (2.06 g, 11.57 mmol) in 200 mL of dry THF at room temperature was added, in portions, 5.65 g (12.73 mmol) of LTA in 100 mL of THF over 30 min. After 20 min of additional stirring of the mixture, the lead diacetate was filtered, and the filtrate was diluted with 500 mL of water and extracted with methylene chloride (3 × 100 mL). The combined extracts were washed with saturated $NaHCO_3$ solution and saturated NaCl solution and dried ($MgSO_4$). Removal of the solvent (rotary evaporation) gave a yellow residue, which was flash chromatographed over silica gel (1:1 ethyl acetate–hexane eluent) to give 1.95 g (79%) of **5**. An analytical sample was obtained by recrystallization from ethanol: mp 338 °C dec; ^{1}H and ^{13}C NMR, see Table I; mass spectrum, *m/e* (relative intensity) 430 (M^+, 1), 360 (M^+ – dimethylketene, 10), 290 (M^+ – 2 dimethylketene, 100), 275 (9), 260 (3), 215 (1), 70 (23); IR (KBr) 2980, 2940, 1710, 1600, 1585, 1460, 1440, 1386, 1265 cm^{-1}. Anal. Calcd for $C_{30}H_{38}O_2$: C,

(7) Hart, H.; Love, G. M. *Tetrahedron Lett.* **1971**, 3563.

(8) For general procedures, see the second paper in ref 1.

83.67; H, 8.89. Found: C, 83.59; H, 8.79.

Use of 2,4,5,6,6-pentamethyl-3-methyl-d_3-2,4-cyclohexadienone (**4**-d_3)[9] in place of **4** gave **5**-d_6 as white needles, mp 331 °C dec, whose ^{1}H NMR spectrum differed from that of **5** in that the peak at δ 1.69 was absent and the peak at δ 1.78 sharpened to a singlet. Therefore, these peaks can be assigned to the C3, C7 and C2,C6 methyls, respectively: mass spectrum (CI), *m/e* (relative intensity) 436 (91), 435 (100), 364 (19), 295 (7), 281 (8); high-resolution mass spectrum calcd for $C_{30}H_{32}D_6O_2$ 436.32483, found 436.32471.

Use of 2,4,6,6-tetramethyl-3,5-dimethyl-d_6-2,4-cyclohexadienone (**4**-d_6)[9] in place of **4** gave **5**-d_{12} as white needles, mp 327 °C dec, whose ^{1}H NMR spectrum differed from that of **5** in that the peaks at δ 1.69 and 1.62 were absent and the peak at δ 1.78 sharpened to a singlet. Therefore, the peak at δ 1.62 can be assigned to the C1,C5 methyls and the peak at δ 1.67 is due to the C4,C8 methyls: mass spectrum, *m/e* (relative intensity) 442 (M^+, trace), 372 (M^+ - dimethylketene, 8), 302 (M^+ - 2 - dimethylketene, 100), 70 (29); high-resolution mass spectrum calcd for $C_{30}H_{26}D_{12}O_2$ 442.36249, found 442.36263.

Acid-Catalyzed Rearrangement of 5. A solution of **5** (500 mg, 1.16 mmol) in 50 mL of neat TFA was heated at reflux for 21 h, then cooled, and poured into ice-water. The mixture was extracted with methylene chloride (3 × 100 mL), and the combined extracts were washed with saturated aqueous $NaHCO_3$ (3 × 50 mL), dried ($MgSO_4$), and evaporated to dryness. The crude product mixture was chromatographed on a preparative silica gel plate with 4:1 chloroform-hexane (five developments) to afford 207.5 mg (41.5%) of **13**, mp 256-257 °C, 90 mg (18%) of **14**, mp 248-249 °C, 69.5 mg (14%) of **15**, mp 313-314 °C, and 38 mg (8%) of **16**, mp 335-336 °C. NMR integration of the aromatic proton region (δ 6.7-8) in the crude product before chromatography gave the yields shown in eq 5. Samples for all spectra were obtained by recrystallization from ethanol. For the ^{1}H and ^{13}C NMR spectra of **13**-**16**, see Table I. For **13**: mass spectrum, *m/e* (relative intensity) 430 (23), 415 (100), 387 (4), 360 (3), 345 (5), 237 (3), 179 (3), 165 (4); IR (KBr) 2970, 2930, 2887, 1655, 1600, 1430, 1380, 1280, 1213, 1195 cm^{-1}; UV ($CHCl_3$) λ_{max} 246 nm (ϵ 2700); high-resolution mass spectrum, calcd for $C_{30}H_{38}O_2$ 430.28716, found 430.28717. for **14**: mass spectrum, *m/e* (relative intensity) 430 (28), 415 (100), 360 (16), 330 (4), 275 (6), 149 (28); IR (KBr) 2968, 2930, 1720, 1670, 1598, 1450, 1380, 1260, 1210 cm^{-1}; high-resolution mass spectrum found 430.28701. For **15**: mass spectrum, *m/e* (relative intensity) 430 (17), 415 (100), 385 (1), 200 (22); IR (KBr) 2986, 2930, 2875, 1670, 1440, 1400, 1376, 1272, 1185, 1158 cm^{-1}; UV ($CDCl_3$) λ_{max} 239 nm (ϵ 2100); high-resolution mass spectrum found 430.28717. For **16**: mass spectrum, *m/e* (relative intensity) 430 (100), 415 (78), 387 (18), 361 (10), 265 (7), 251 (3), 97 (84); IR (KBr) 3010, 2985, 2930, 2875, 1650, 1615, 1385, 1320, 1305, 1228 cm^{-1}; UV ($CHCl_3$) λ_{max} 240 nm (ϵ 2200); high-resolution mass spectrum found 430.28749.

Deuteriation of 13 and 16. The diketone (15 mg) was dissolved in 20 mL of methanol-*d* containing 0.1 g of sodium and heated at reflux for 30 h. The cooled solution was added to 100 mL of methylene chloride and washed with water (2 × 25 mL). Any residual base was neutralized with solid CO_2. Removal of the solvent in vacuo gave 14 mg (93%) of deuteriated diketone. For the ^{1}H NMR spectra of **13**-d_3 and **16**-d_6, see the text. Neither **14** nor **15** underwent exchange under these conditions.

Irradiation of 16. A degassed solution of **16** (20 mg) in 20 mL of spectroscopic grade acetone was irradiated for 21 h by using a 450-w Hanovia lamp with a Pyrex filter. Removal of the solvent in vacuo gave essentially pure **17**, contaminated with <2% of **16**. for **17**: mp 367 °C dec; ^{1}H NMR δ 6.89 (s, 2 H), 1.48 (s, 6 H), 1.28 (s, 6 H), 1.19 (s, 6 H), 1.14 (s, 6 H), 0.96 (s, 6 H), 0.34 (s, 6 H); ^{13}C NMR δ 199.03, 136.87, 136.12, 117.59, 54.70, 45.32, 42.07, 39.96, 35.97, 23.00, 17.65, 13.13, 9.96, 7.83, 5.60; mass spectrum, *m/e* (relative intensity) 430 (100), 415 (84), 387 (16), 361 (12), 333 (11), 303 (10), 275 (8), 245 (9), 205 (3), 97 (57); IR (KBr) 2975, 2921, 1715, 1460, 1387, 1323, 1270, 1048, 985 cm^{-1}; high resolution mass spectrum calcd for $C_{30}H_{38}O_2$ 430.28716, found 430.28701.

X-ray Data for 5. Cell dimensions: a = 7.942 (3) Å, b = 16.715 (6) Å, c = 9.234 (2) Å, β = 96.38 (2)°; V = 1218.2 (6) Å^3, ρ = 1.17 g/cm^3; $C_{30}H_{38}O_2$, FW 430.64, Z = 2; monoclinic $P2_1/n$; Mo Kα (λ = 0.71073 Å; 2406 reflections total, 2153 unique; Nicolet P3F diffractometer, direct methods, full-matrix least-squares refinement, R = 0.041.

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Supplementary Material Available: Tables of positional parameters, thermal parameters, bond distances, bond angles, and torsional angles for the crystal structure of **5** (12 pages). Ordering information is given on any current masthead page.

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Benzothiet-2-ones: Synthesis, Reactions, and Comparison with Benzoxet-2-ones and Benzazetin-2-ones

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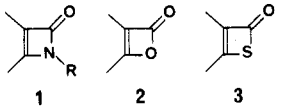
Benzothiet-2-one (**5**) is obtained as a neat solid, stable below -20 °C (-45 °C in solution), by flash vacuum pyrolysis of benzothiophene-2,3-dione (**9**). Naphtho[2,3-*b*]thiet-2-one (**21**) and naphtho[2,1-*b*]thiet-1-one (**42**) are obtained as stable crystalline solids in near-quantitative yields from the corresponding napthothiophenediones **20** and **41**. Naphtho[2,3-*b*]oxet-2-one (**31**) and naphtho[2,3-*b*]azetin-2-one (**36**) were generated and observed by IR spectroscopy to be stable below -40 °C and 0 °C, respectively. The thietones, oxetones, and azetinones undergo rapid ring-opening reactions with methanol to give the corresponding carboxylic acid esters. They undergo thermal CO elimination with concomitant Wolff-type ring contraction to thioketenes (**17**, **25**, **45**), ketenes (**30**), and nitriles (**37**), respectively. The di-, oligo-, and polymerization of the thietones has been elucidated. Naphtho[2,1-*b*]thiet-1-one (**42**) reacts with 1-thiocarbonyl-1*H*-indene (**45**) to give cycloaddition product **46**. Naphthothietones **21** and **42** react with dicyclohexylcarbodiimide to furnish 2-imino-1,3-thiazin-4-one derivatives **47** and **49**.

The four-membered unsaturated heterocycles **1**-**3** are little-known and generally highly reactive compounds.



1 **2** **3**

Unsubstituted azetinones (**1**, R = H) can only be isolated at low temperatures,[2,3] but phenyl and bulky alkyl sub-

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