Na metal and distilled under nitrogen into the reaction flask. Alkali metals were cut in small pieces and washed free of oil with diethyl ether immediately before adding to the reaction mixtures.

Materials. Acetonitrile (B.P.C., Erba) was purified and dried as described.[5] All the halobenzenes, naphthalene, anthracene, and benzophenone were analytical grade, commercially available products and were used as received. Pyridine was dried over KOH and distilled before use. Phenylacetonitrile[20] and 1,2-diphenylethane[21] were prepared as described. Cyanomethyl anion was prepared in situ as described.[5]

Photostimulated Reactions. The photostimulated reactions were carried out in a photochemical reactor equipped with two 250-W Pyrex-filtered UV lamps, Philips Model HTP, emitting maximally at ca. 350 nm, with water-jacketed refrigeration. The method used was as described.[5]

Potassium Metal Stimulated Reactions. The procedure and the preparation of cyanomethyl anion was done as usual.[5] Then the electron acceptor (sodium benzoate or naphthalene) and bromobenzene were added. After about 10–15 min, the potassium metal was added slowly in small bits. An excess of water was added, followed by 100 mL of diethyl ether, and the ammonia was allowed to evaporate. An internal standard was added and the two layers were separated. The water was twice extracted with ether. The ether extract was twice washed with water and dried over anhydrous Na_2SO_4 and then was analyzed by GLC.

Identification of Products. All products were identified and quantified by comparison of their retention times on both columns with authentic samples. Pure samples of 1,2-diphenylethane and 1,1,2,2-tetraphenylethane were isolated, and their melting points and NMR and IR spectra were identical with those of authentic materials.

4,5-Diphenyloctane was purified by column chromatography on neutral alumina. The mass spectrum has a molecular peak at m/e 266 and peaks at m/e 233, 209, 133, and 91. The NMR spectrum gave δ 0.8 (14 H), 2.7–3.2 (2 H), and 6.8–7.4 (10 H).

Acknowledgments. A.B.P. gratefully acknowledges receipt of a fellowship from the Consejo Nacional de Investigaciones Cientīficas y Tēcnicas, Argentina. We thank Professor Joseph F. Bunnett for helpful suggestions and critical reading of the manuscript.

Registry No. PhF, 462-06-6; PhCl, 108-90-7; PhBr, 108-86-1; PhI, 591-50-4; cyanomethyl anion, 21438-99-3; diphenylacetonitrile, 86-29-3; valeronitrile anion, 42117-15-7; toluene, 108-88-3; PAN, 140-29-4; DPE, 103-29-7; DPM, 101-81-5; T_3PE, 1520-42-9; T_4PE, 632-50-8; 4,5-diphenyloctane, 42117-21-5; benzene, 71-43-2; phenylacetonitrile anion, 18802-89-6.

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[20] R. Adams and A. F. Thal, "Organic Syntheses", Collect. Vol. I, Wiley, New York, N.Y., 1941, p 107.

[21] R. J. W. Cremlyn and R. H. Still, "Named and Miscellaneous Reactions in Practical Organic Chemistry", Wiley, New York, N.Y., 1967, pp 151–3.

Strained Heterocycles. Properties of Five-Membered Heterocycles Fused to Four-, Six-, and Eight-Membered Rings Prepared by Base-Catalyzed Rearrangement of 4-Heterohepta-1,6-diynes

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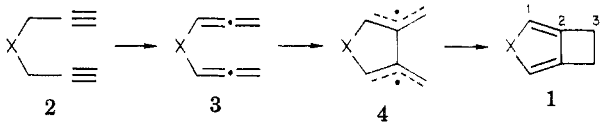
The base-catalyzed rearrangement of 4-thia-, 4-oxa-, and 4-azahepta-1,6-diynes (**2a–c**) gave the corresponding dimeric 4,5,9,10-tetrahydrocycloocta[1,2-*c*:5,6-*c*′]dithiophene, -difuran, and -dipyrrole (**5a–c**). In contrast, the base-catalyzed rearrangement of the related *tert*-butyl-substituted derivatives **6a–c** gave the monomeric 6,7-di-*tert*-butyl-3-heterobicyclo[3.2.0]hepta-1,4-dienes (**7a–c**). With the nitrogen system **6c** the dimeric cycloocta-1,5-diene **10** could also be obtained by varying the reaction conditions, and a small amount of the tricyclic dimer **9** was obtained on rearrangement of the oxygen system **6b**. Rearrangement of 1,7-diphenyl-4-heterohepta-1,6-diynes **11a–c** gave the corresponding 4,9-dihydro-4-phenylnaphtho[2,3-*c*]heterocycles **18a–c** as primary products and not the naphthalenes **14a–c** as had previously been reported. A unifying mechanism to account for all of these products is described. The ^{13}C NMR spectra of the substituted heterocycles show that annelation by small rings results in an upfield chemical shift of the α-carbon atoms, as previously observed for benzocycloalkenes. The anomalous spectrum of **10** and the chemical shifts observed on oxidizing thiophenes to thiophene 1,1-dioxides are described and discussed.

Following the synthesis of the first benzocyclopropene derivatives,[1,2] there has been a revival of interest in the preparation of aromatic systems strained by annelation of small rings.[3] Most of this work has been directed toward the synthesis of benzenoid systems, but some work has been reported on the preparation of strained heterocyclic compounds.[4,5] We have previously reported the synthesis of 3-thiabicyclo[3.2.0]hepta-1,4-diene (**1**, X = S)[5b] and we now report the preparation of *tert*-butyl derivatives of this thiophene and its pyrrole and furan analogues involving the base-catalyzed rearrangement of the corresponding 4-heterohepta-1,6-diynes.[6] We also describe other base-catalyzed rearrangements which lead to dimeric products, predominantly *syn*-bis(annelated) cyclooctadienes, and to 4,9-dihydronaphtho[2,3-*c*]thiophenes, -pyrroles, and -furans. The mechanisms of these reactions

Scheme I



2 **3** **4** **1**

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[1] R. Anet and F. A. L. Anet, *J. Am. Chem. Soc.*, **86**, 525 (1964).

[2] E. Vogel, W. Grimme, and S. Korte, *Tetrahedron Lett.*, 3625 (1965).

[3] See: B. Halton, *Chem. Rev.*, **73**, 113 (1973); R. P. Thummel and W. Nutakul, *J. Org. Chem.*, **42**, 300 (1977).

[4] B. E. Ayres, S. W. Longworth, and J. F. W. McOmie, *Tetrahedron*, **31**, 1755 (1975); K. P. C. Vollhardt and R. G. Bergman, *J. Am. Chem. Soc.*, **94**, 8950 (1972); **95**, 7538 (1973); R. G. Bergman and K. P. C. Vollhardt, *J. Chem. Soc., Chem. Commun.*, 214 (1973); H. Hauptmann, *Tetrahedron Lett.*, 3589 (1974); M. P. Cava, M. V. Lakshmikantham, and M. Behforouz, *J. Org. Chem.*, **39**, 206 (1974); P. Vogel and M. Hardy, *Helv. Chim. Acta*, **57**, 196 (1974).

[5] (a) P. J. Garratt and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, **94**, 1022, 7087 (1972); (b) P. J. Garratt and D. N. Nicolaides, *J. Org. Chem.*, **32**, 2222 (1974); (c) P. J. Garratt and S. B. Neoh, *ibid.*, **40**, 970 (1975).

[6] For a preliminary communication on part of this work, see P. J. Garratt and S. B. Neoh, *J. Am. Chem. Soc.*, **97**, 3255 (1975).

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Table I. ^{13}C NMR Chemical Shifts and J_{C-H} Coupling Constants in Thiophenes and Thiophene 1,1-Dioxides[a,b]

compd	C-1	C-2	C-3	C-4	C-5	ref
thiophene	125.0 (183.9)	126.8 (169.1)				
3,4-dimethylthiophene	120.7 (181.5)	137.2	14.4 (127.5)			
1	114.4	142.3	26.1			c
7a	114.4 (186.2)	143.9	53.6 (137.4)	32.2	27.6 (124.3)	
2,4-diphenyl-3-thiabicyclo-[3.2.0]hepta-1,4-diene	132.8	139.6	27.5 (138.8)			d
5a	121.9 (183.7)	142.0	29.9 (129.1)			
3,4-dimethylthiophene 1,1-dioxide	126.2 (191.4)	142.8	14.3 (130.6)			
2,4-diphenyl-3-thiabicyclo[3.2.0]-hepta-1,4-diene 3,3-dioxide	119.9	147.3	30.8			c
8	119.5 (199.1)	147.5	57.8 (141.9)	32.8	27.1	

[a] Spectra taken in CDCl$_3$, the chemical shifts being measured in parts per million downfield from internal Me$_4$Si; the asterisks designate shifts for which assignments could be interchanged. Numbers in parentheses are $^1J_{CH}$ constants in hertz. [b] For numbering, see formulas in text. [c] P. J. Garratt, A. J. Jones, and D. N. Nicolaides, unpublished results. [d] Reference 5c.

Table II. ^{13}C NMR Chemical Shifts and J_{C-H} Coupling Constants in Furans and Dihydrofurans[a]

compd	C-1	C-2	C-3	C-4	C-5	C-6
furan[b]	142.6 (201)	109.6 (175)				
7b	131.1 (197.7)	127.0	53.0 (136.8)	31.8	27.3 (124.9)	
5b	140.0 (199.6)	125.6	25.0 (128.7)			
9	78.5 (159.7)	135.6	126.8 (149.1)	33.2	31.1	
22	136.9	121.3	26.0	135.5	129.1	126.3
23	72.8 (146.7)	138.3	127.9*	133.2	119.1	125.8*

[a] See footnotes *a* and *b*, Table I. [b] L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra", Wiley-Interscience, New York, N.Y., 1972.

Table III. ^{13}C NMR Chemical Shifts and J_{C-H} Coupling Constants in Pyrroles[a]

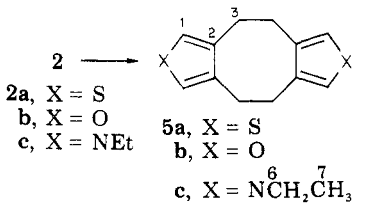
compd	C-1	C-2	C-3	C-4	C-5	C-6	C-7	solvent
pyrrole[b]	118.7 (184)	108.4 (170)						C_6D_6
7c	112.9 (183.5)	127.9	55.2 (140.0)			35.4		$(CD_3)_2CO$
5c	118.3 (179.8)	124.2	28.7 (126.1)			43.5 (137.6)	16.4	$CDCl_3$
10	113.1 (187)	128.2	55.6 (136)			35.4		$(CD_3)_2CO$
	112.7		55.7	32.4	28.0	35.0		C_6D_6

[a] Spectral solvent as indicated; otherwise see footnotes *a* and *b*, Table I. [b] J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972.

are discussed and a unifying reaction scheme is proposed.

Our original concept was that 4-heterohepta-1,6-diynes (**2**) would be expected to rearrange under base-catalyzed conditions to the corresponding 4-hetero-1,2,5,6-tetraene (**3**), which should then dimerize intramolecularly to give the diradical **4**. Among other possible reaction modes this diradical could ring close to the desired heterocycle **1** (Scheme I). Accordingly we examined the base-catalyzed rearrangement of **2** and substituted derivatives.

Base-Catalyzed Rearrangement of 4-Heterohepta-1,6-diynes. Treatment of 4-thiahepta-1,6-diyne (**2a**, X = S), prepared by reaction of propargyl bromide with Na$_2$S in methanol,[7] with KOH in methanol gave two products: 4,5,9,10-tetrahydrocycloocta[1,2-*c*:5,6-*c*′]dithiophene (**5a**), mp 138–140 °C, in 12% yield and a trimer, mp 206–212 °C, in 3% yield. The ^{1}H NMR spectrum of **5a** showed two singlets at δ 6.82 (4 H) and 2.95 (8 H), and the ^{13}C NMR spectrum (Table I) showed the presence of three types of carbon atoms. The trimer had a complex ^{1}H NMR spectrum and the ^{13}C NMR spectrum showed 14 different carbon atoms. The structure of the trimer was not investigated further.



2a, X = S
b, X = O
c, X = NEt

5a, X = S
b, X = O
c, X = $\overset{6}{N}\overset{7}{CH_2CH_3}$

Reaction of 4-oxahepta-1,6-diyne (**2b**, X = O) with KOH, even in boiling methanol, did not bring about rearrangement, but treatment with KO-*t*-Bu at room temperature gave 4,5,9,10-tetrahydrocycloocta[1,2-*c*:5,6-*c*′]difuran (**5b**), mp 164–165 °C, in 16% yield. The ^{1}H NMR spectrum showed two singlets at δ 7.20 (4 H) and 2.70 (8 H), and the ^{13}C NMR spectrum indicated the presence of three types of carbon atoms (Table II).

4-Ethyl-4-azahepta-1,6-diyne (**2c**, X = NEt) could not be rearranged with KOH in ethanol, but treatment with KO-*t*-Bu in THF at 60 °C gave di-*N*-ethyl-4,5,9,10-tetrahydrocycloocta[1,2-*c*:5,6-*c*′]dipyrrole (**5c**), mp 135–136 °C, in 9% yield. The ^{1}H and ^{13}C NMR spectra were similar to those of **5a**,**b**, except for the additional signals due to the *N*-ethyl group (Table III).

We presumed that these reactions were proceeding in the initial stages in the desired manner to give the tetraenes **3** and the diradicals **4** but that the latter undergo intermolecular rather than intramolecular reaction. Steric protection against intermolecular reaction seemed applicable for directing the reaction toward the intramolecular pathway, and we therefore examined the rearrangement of the *tert*-butyl-substituted compounds.

Base-Catalyzed Rearrangement of 2,2,10,10-Tetramethyl-6-heteroundeca-3,8-diynes. Treatment of 2,2,10,10-tetramethyl-6-thiaundeca-3,8-diyne (**6a**),[8] pre-

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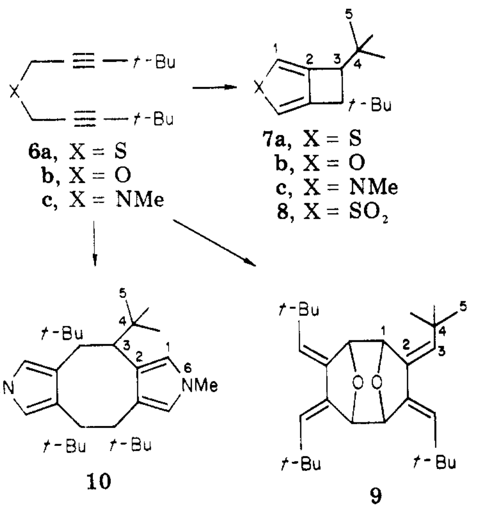
[7] See L. Brandsma, "Preparative Acetylenic Chemistry", Elsevier, Amsterdam, 1971.



6a, X = S
b, X = O
c, X = NMe

7a, X = S
b, X = O
c, X = NMe
8, X = SO_2

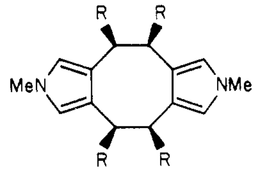
10

9

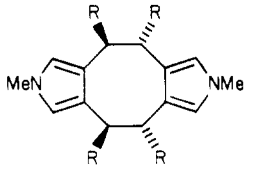
pared by the reaction of 1-bromo-4,4-dimethylpent-2-yne with sodium sulfide in methanol, with KO-*t*-Bu in *tert*-butyl alcohol gave 6,7-di-*tert*-butyl-3-thiabicyclo[3.2.0]-hepta-1,4-diene (**7a**), mp 44–45 °C, in 64% yield. The ^1H NMR spectrum showed three singlets at δ 6.75 (2 H), 2.92 (2 H), and 0.92 (18 H) assigned to the thiophene, cyclobutyl, and *tert*-butyl protons, respectively, and the ^{13}C NMR spectrum showed five types of carbon atoms (Table I). The trans stereochemistry for the *tert*-butyl groups is assumed, since models clearly indicate considerable steric congestion in the cis isomer. Compound **7a** is thermally stable, being recovered unchanged after heating at 100 °C for 3.5 h in hexachlorobutadiene. On oxidation with *m*-chloroperoxybenzoic acid in $CHCl_3$ the sulfone **8**, mp 120–121 °C, was obtained in 88% yield. Comparison of the ^1H NMR spectra of **7a** and **8** showed that in the sulfone the protons on the heterocyclic ring had moved upfield by 0.72 ppm and the cyclobutyl protons downfield by 0.3 ppm; comparable shifts are observed in the parent system and its sulfone.[5b] The downfield shift of the cyclobutyl protons is presumably due to an increase in ring strain induced by the decreased localization of the sulfone, since the methyl protons of 3,4-dimethylthiophene undergo the expected upfield shift (0.09 ppm) in the ^1H NMR spectrum on oxidation of the thiophene to the sulfone.

Treatment of 2,2,10,10-tetramethyl-6-oxaundeca-3,8-diyne (**7b**),[8] most conveniently prepared in 97% yield by the reaction of 1-bromo-4,4-dimethylpent-2-yne with 4,4-dimethylpent-2-yn-1-ol in the presence of powdered KOH, with KO-*t*-Bu in THF gave 6,7-di-*tert*-butyl-3-oxabicyclo[3.2.0]hepta-1,4-diene (**7b**) in 31% yield as a colorless oil. The spectral properties were very similar to those of the parent compound prepared by Bergman and Vollhardt.[4] A second compound was obtained in low yield (2.5%) which was identified as the tricyclic dimer **9**. Although a satisfactory microanalysis could not be obtained, the ^{13}C NMR spectrum indicated the presence of less than 1% carbon impurity. The ^1H NMR, ^{13}C NMR, and electronic spectra were all in agreement with those expected for **9**, and the NMR spectra established the symmetric nature of the molecule.

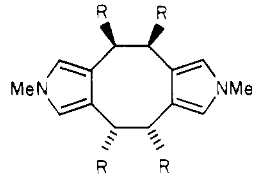
Treatment of 2,2,6,10,10-pentamethyl-6-azaundeca-3,8-diyne (**6c**)[8] with KO-*t*-Bu in boiling benzene gave *N*-methyl-6,7-di-*tert*-butyl-3-azabicyclo[3.2.0]hepta-1,4-diene (**7c**) in 14% yield. The ^1H NMR spectrum showed four singlets at δ 6.18 (2 H), 3.65 (3 H), 3.05 (2 H), and 0.95 (18 H) assigned respectively to the pyrrole, *N*-methyl, cyclobutyl, and *tert*-butyl protons. The electronic spectrum showed an absorption maximum at 233 nm (ϵ 7200), consistent with the pyrrole chromophore. When the reaction was carried out with KO-*t*-Bu in THF, the dimer di-*N*-methyl-4,5,9,10-tetra-*tert*-butyl-4,5,9,10-tetrahydrocycloocta[1,2-*c*:5,6-*c*′]dipyrrole (**10**), mp 68–69 °C, was obtained in 58% yield. The ^1H and ^{13}C NMR spectra of **10** were similar to those of **5c** (Table III), and the electronic spectrum had its maximum absorption at a position similar to that of **5c** with twice the extinction coefficient. The ^{13}C NMR spectrum of **10** shows only six types of carbon atoms, clearly indicating that **10** was either a static or dynamic symmetrical structure. Of the four possible arrangements of the *tert*-butyl substituents meeting this requirement (**10a–d**), **10d** appears, from models, to be the least sterically congested.



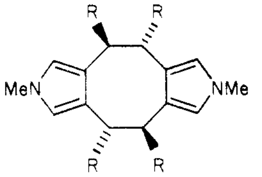
10a, R = *t*-Bu
26a, R = Ph



10b, R = *t*-Bu
26b, R = Ph



10c, R = *t*-Bu
26c, R = Ph



10d, R = *t*-Bu
26d, R = Ph

Base-Catalyzed Rearrangement of 1,7-Diphenyl-4-heterohepta-1,6-diynes. The rearrangement of 1,7-diphenyl-4-thiahepta-1,6-diyne (**11a**) and its oxygen and nitrogen analogues had been reported by Iwai and Ide.[9] These authors found that the base-catalyzed rearrangement of **11a** gave the naphthalene **14a**, which they suggested arose by rearrangement of **11a** to the enyne **12a**, which then underwent a 6π-electron cyclization to **13a** followed by a 1,5-proton shift to **14a**. This mechanism seemed unusual in that the rearrangement of propargyl systems to allenes is very rapid, and it appeared more likely that formation of the tetraene **15a** would occur before cyclization of the enyne, which requires the disruption of a benzene ring, could take place. Iwai had recognized this problem and had later included **15a** in his mechanistic

11a, X = S
b, X = O
c, X = NMe

12a–c

13a–c

14a–c

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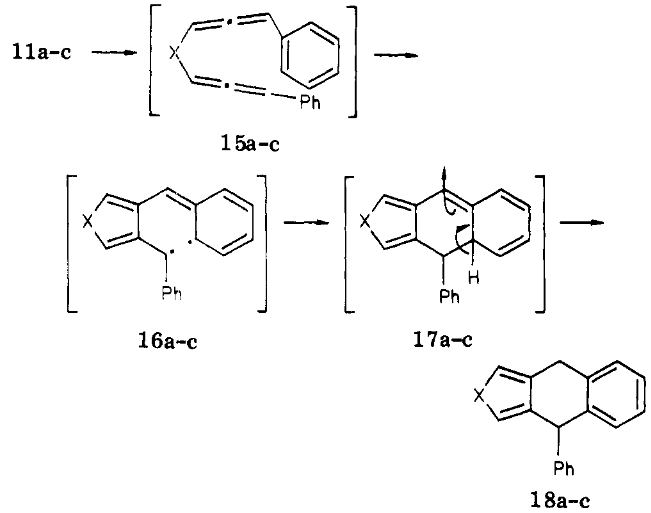
[8] Although a satisfactory microanalysis could not be obtained for this compound, probably owing to the combination of high carbon content with acetylenic functions (factors rendering compounds notoriously difficult to combust completely), the ^{13}C NMR decoupled spectrum showed no other component at concentrations above 1% carbon.

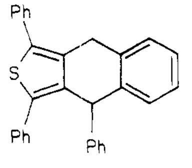
[9] I. Iwai and J. Ide, *Chem. Pharm. Bull. Jpn.*, **12**, 1094 (1964); I. Iwai in "Mechanisms of Molecular Migrations", Vol. 2, B. S. Thyagarajan, Ed., Interscience, New York, N.Y., 1969.

scheme, but he still invoked a subsequent 6π-electron cyclization. In this pathway disruption of a thiophene ring occurs, but it can be compensated by the concomitant formation of a benzene ring. From our previous investigation we considered that **15a** would be formed and that it should intramolecularly dimerize to give the diradical **16a** which could then cyclize to **17a**. Subsequent aromatization of **17a** would be expected to give **18a**, and this product might also have been expected from Iwai's modified scheme. We therefore reinvestigated the base-catalyzed rearrangement of **11a** and its analogues.

Treatment of **11a** with KO-*t*-Bu in *t*-BuOH at 20 °C gave 4,9-dihydro-4-phenylnaphtho[2,3-*c*]thiophene (**18a**), mp 46–47 °C, in 73% yield. The ^{1}H NMR spectrum showed two broad singlets at δ 3.98 (2 H) and 5.20 (1 H) due to the methylene and methine protons, respectively, and a multiplet at 7.18 (11 H) due to the aromatic and thiophene protons. The chemical shifts of the methylene and methine protons are similar to those observed by Cava et al.[4] (δ 3.98 and 5.42) for the related diphenyl derivative **19**. The electronic spectrum of **18a** showed a maximum at 246.5 nm (ϵ 8270), together with low-intensity maxima at 272 (933) and 336.5 nm (608). Reaction of **18a** with KO-*t*-Bu at 95 °C for 70 h gave the naphthalene **14a** in 95% yield, identical in its spectral properties with those reported.[9] When the rearrangement of **11a** is carried out under the conditions used by Ide and Iwai[9] (KO-*t*-Bu in *t*-BuOH at 60 °C), the thiophene **18a** is initially formed, followed (as the reaction proceeds) by the accumulation of **14a**. After 72 h, only the naphthalene **14a** is present.



The thiophene **18a** was oxidized to the corresponding sulfone **20** in 30% yield by reaction with *m*-chloroperoxybenzoic acid. The sulfone is thermally unstable, decomposing at ca. 80 °C on attempted melting point determination. The ^{1}H NMR spectrum showed two multiplets at δ 6.42 (1 H) and 6.28 (1 H), chemical shifts typical for the 2 and 5 protons of a 3,4-disubstituted thiophene 1,1-dioxide.[10]



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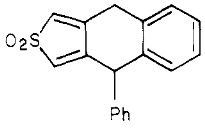
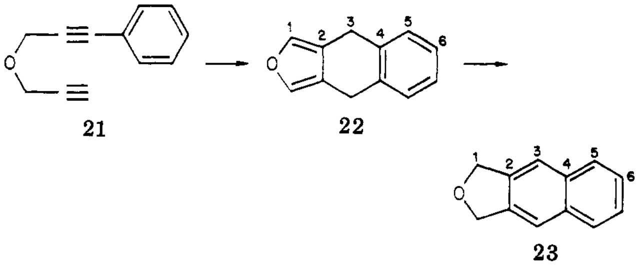


20

Reaction of 1,5-diphenyl-4-oxahepta-1,6-diyne (**11b**) with KO-*t*-Bu in THF at 0 °C gave 4,9-dihydro-4-phenylnaphtho[2,3-*c*]furan (**18b**), mp 58–59 °C, in 54% yield. If the experiment was carried out at 30 °C, a vigorous reaction ensued and only the previously observed naphthalene **14b** was obtained. The ^{1}H NMR spectrum of **18b** was similar to that of the thiophene **18a**, and the electronic spectrum showed only low-intensity maxima at 260, 264, and 271 nm. The furan **18b** could be readily converted into the naphthalene **14b** by reaction with KO-*t*-Bu in THF.

Ollis and his co-workers[11] have extended the observations of Iwai and Ide to a variety of related ethers. They adopted the mechanism of the Japanese workers and had expanded it to explain the products formed with nonsymmetric reactants. All of these products could be explained by our mechanism, but again different initial products would be expected, and we therefore reexamined the base-catalyzed rearrangement of one of these substrates. 1-Phenyl-4-oxahepta-1,6-diyne (**21**) was treated with KO-*t*-Bu in THF at 20 °C when 4,9-dihydronaphtho[2,3-*c*]furan (**22**), mp 79–80 °C, was obtained in 20% yield. The ^{1}H NMR spectrum showed a multiplet at δ 7.25 (6 H) and a singlet at 3.88 (4 H) due to the aromatic and benzylic protons, respectively, and the ^{13}C NMR spectrum showed the presence of six types of carbon atoms (Table II). The electronic spectrum had low-intensity maxima at 265.5 and 272 nm. When **22** was rearranged with KO-*t*-Bu in THF at 50 °C, the naphthalene **23**, mp 158–159 °C, was obtained in 63% yield, the spectral properties being identical with those previously reported.[11]



The rearrangement of 2,7-diphenyl-4-methyl-4-azahepta-1,6-diyne (**11c**) proved to be more complex than its sulfur and oxygen analogues. Treatment of **11c** with KO-*t*-Bu in THF at 20 °C for 3 h gave two isomeric dimers in 19.5 and 16% yields. The isomers were separated by fractional crystallization, the less soluble isomer (**24**) having a higher melting point (mp 248–252 °C) than the more soluble isomer (**25**) (mp 209–210 °C). The mass spectra of these compounds showed similar fragmentation patterns with different relative intensities for the various fragments. The ^{1}H NMR spectra were different, that of compound **24** having the signal attributed to the protons on the eight-membered ring at δ 5.30, whereas those of **25** were at δ 4.80. In the ^{13}C NMR spectra, both isomers showed only one signal attributed to the carbon atoms of the eight-membered ring, those for **24** resonating at 50.4 ppm and those for **25** at 49.6 ppm. The two isomers thus seem to differ only in the relative relationships of the phenyl substituents on the eight-membered ring, and since both have only one type of eight-membered ring hydrogen on carbon, the structures must be statically or dynamically symmetric (vide supra, **26a–d**). The formation of two isomers in this reaction, rather than one with the *tert*-butyl analogue **6c**, may reflect the greater steric demand of the

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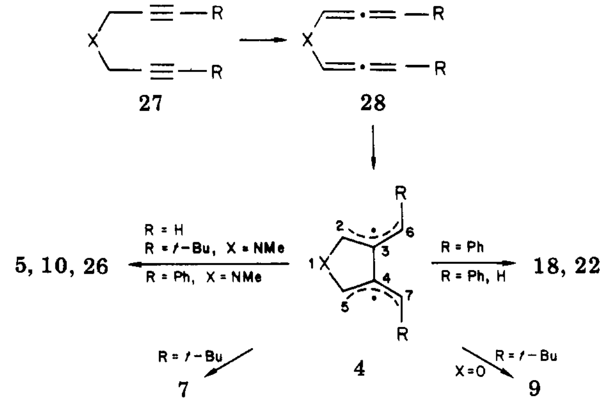
(10) The protons at the 2 and 5 positions of 3,4-dimethylthiophene 1,1-dioxide resonate at δ 6.30 in the ^{1}H NMR spectrum.

(11) T. Laird and W. D. Ollis, *J. Chem. Soc., Chem. Commun.*, 557 (1972); A. J. Bartlett, T. Laird, and W. D. Ollis, *ibid.*, 496 (1974); *J. Chem. Soc., Perkin Trans. 1*, 1315 (1975).

Scheme II



tert-butyl group. Interconversion of **24** and **25** did not occur upon heating each isomer at 180–200 °C for 2 h.

Reaction of **11c** with KO-*t*-Bu in benzene gave a 1:2 mixture of *N*-methyl-4,9-dihydro-4-phenylnaphtho[2,3-*c*]pyrrole (**18c**) and the naphthalene **14c**. The pyrrole **18c** is an unstable compound, but the ^{1}H NMR spectrum was in accord with the assigned structure, the pyrrole ring protons resonating as two multiplets at δ 6.50 (1 H) and 6.30 (1 H), with the methine and methylene protons at δ 5.20 and 4.0, respectively. Under a variety of other conditions, only **14c** or a mixture of **14c** with a small amount of **18c** was obtained. The formation of the monomer in benzene but the dimers in THF or ether duplicates the findings for the rearrangement of **6c** (vide supra).

Discussion

It is of interest that the naphthalenic systems all appear to be thermodynamically more stable than the corresponding heterocycles. A simple calculation using Dewar resonance energy data[12] on the thiophene **18a**, in which the thiophene and benzene rings were assumed to be noninteracting, gave a Dewar resonance energy (DRE) of 51.7 kcal mol^{-1}, and a similar calculation for **14a**, assuming the naphthalene and benzene rings were noninteracting, gave a DRE of 56.2 kcal mol^{-1}. Thus **14a** is more stable than **18a** by 4.5 kcal mol^{-1}. For the furan **18b** and the corresponding naphthalene **14b**, similar calculations show the naphthalene to be more stable by 6.7 kcal mol^{-1}. Conjugation between the phenyl and naphthalene rings could further increase this difference in energy.

All the compounds prepared by the rearrangement of 4-heterohepta-1,6-diynes can be accommodated by the reaction mechanism shown in Scheme II. Base-catalyzed rearrangement of the bis(propargyl) system to the bis(allene) system is followed by intramolecular allene dimerization to give the diradical **4**. This can now intramolecularly close to give a bicyclo[3.2.0]hepta-1,4-diene **7**, it can dimerize by reaction at the 6,7 positions to give a cycloocta diheterocycle (**5**, **10**, **26**) or by reaction at the 2,5 positions to give **9**, or it can cyclize by reaction with a phenyl ring to give the annelated dihydronaphthalenes (**18**, **22**).

The change from monomer to dimer on changing the solvent for the rearrangement of **27** (X = NMe, R = *t*-Bu or Ph) from benzene to THF can be explained on the basis of solvation of the diradical **4** by benzene, thus favoring intramolecular reaction. Studies on hydrogen abstraction by chlorine atoms in solution have shown that the selectivity is greater in aromatic solvents than in ethers, this difference being attributed to complexation by the aromatic solvent.[13]

Considerable evidence to support this mechanism has been advanced.[14] The postulated tetraenes **28** (X = S, R = H or *t*-Bu) have been isolated and have been shown to thermally rearrange to **5** (X = S, R = H) and **7** (X = S, R = *t*-Bu), respectively. Warming **28** (X = S, R = H or *t*-Bu) in the presence of $^3O_2$ gave the cyclic peroxides (R = H or *t*-Bu) derived from **4** by addition of oxygen across the C-6 and C-7 atoms.

^{13}C NMR Spectra

The ^{13}C NMR spectra of the thiophenes, furans, and pyrroles synthesized in this study, together with some model systems, are collected in Tables I–III. Günther and his co-workers[15] have shown that in the benzocycloalkenes, the chemical shifts and one-bond ^{13}C–H coupling constants of the benzene carbons ortho to the annelating ring are most influenced by ring strain. In the five-membered heterocycles the same effect would be expected at the α-carbon atoms, and this is indeed observed. The α-carbon atom (C-1, Table I) in both the cyclobutathiophenes **1** (X = S) and **7a** shows an upfield shift of +6.3 ppm compared to the α-carbon atom in 3,4-dimethylthiophene and +10.6 ppm compared to the α-carbon atom in thiophene. Similarly, the cyclobutafuran **7b** shows a shift of +11.3 ppm of the α-carbon atom compared to those of furan, and the cyclobutapyrrole **7c** shows a shift of +5.8 ppm of the α-carbon atom compared to those of pyrrole. By contrast, the cycloocta diheterocycles **5a–c** show much smaller shifts compared to those of the respective parent heterocycles (+3.1, +2.6, +0.4 ppm), and the cyclooctadithiophene **5a** in fact shows a downfield shift of −1.2 ppm of the α-carbon atoms compared with those of 3,4-dimethylthiophene. The upfield chemical shifts of the α carbons of the cyclobuta heterocycles compared to those of the cyclohexa heterocycles are of a very similar magnitude to the shift differences in the corresponding benzocycloalkenes. That this is a strain effect, rather than a localization effect, is revealed by the similar upfield shift in the cyclobutathiophene dioxide **8** compared to that of 3,4-dimethylthiophene 1,1-dioxide. One difference between the benzocycloalkenes and the annelated five-membered heterocycles is that in the former systems comparison of the spectra of the six- and eight-membered-ring compounds shows a small upfield shift (+0.8 ppm) for the α carbons of the eight-membered ring, whereas in the latter systems there is a continuing downfield shift (−1.7, −3.1 ppm) on going from the six- to the eight-membered-ring compounds. This difference probably reflects the preferred larger exo bond angle for the five-membered ring (126°) which is more readily accommodated in the eight- than the six-membered rings.

The tetra-*tert*-butylcyclooctadipyrrole **10** shows an anomalous shift of the α-carbon atoms, which appear at a position similar to those of the cyclobutapyrrole **7c**. This shift presumably arises from the steric interaction of the four *tert*-butyl groups, part of the strain so engendered being accommodated in the pyrrole rings.

The $^1J_{CH}$ coupling constants for the ortho carbon atoms in benzocycloalkenes increase on going from the five- to

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[12] See: M. J. S. Dewar and N. Trinajistic, *J. Am. Chem. Soc.*, **92**, 1453 (1970); *Theor. Chim. Acta*, **17**, 235 (1970); M. J. Cook, A. R. Katritzky, and P. Linda, *Adv. Heterocycl. Chem.*, **17**, 262 ff (1974).

[13] G. A. Russell, *J. Am. Chem. Soc.*, **79**, 2977 (1957); **80**, 4987 (1958).

[14] Y. S. P. Cheng, E. Dominguez, P. J. Garratt, and S. B. Neoh, *Tetrahedron Lett.*, 691 (1978).

[15] H. Günther, G. Jikeli, H. Schmickler, and J. Prestien, *Angew. Chem., Int. Ed. Engl.*, **12**, 762 (1973).

the four-membered ring and from the four- to the three-membered ring.[14] The $^1J_{CH}$ constants for the α carbons of the five-membered heterocycles show more variable behavior. In the thiophenes the changes are similar but smaller than those in benzocycloalkenes, whereas in the furans the coupling constant is smaller in the cyclobutafuran **7b** than in the cyclooctadifuran **5b**. In the case of pyrrole, the coupling constant of the cyclobutapyrrole **7c** is larger than that of the cyclooctadipyrrole **5c** but less than that of **10**. The larger coupling constant in **10** probably again reflects the strain induced by the *tert*-butyl substituents.

The coupling constants in thiophene 1,1-dioxides are larger than those in the corresponding thiophenes, which is probably due to the different bond angle requirements of the sulfur atom in the reduced and oxidized state. The bond angle in thiophenes and sulfides is near 92°, whereas in acyclic sulfones it is about 105°.[16] In the oxidation of thiophene to thiophene 1,1-dioxide the bond angles at carbon should change from 112 to 109°, and this would involve an increase in the p character of the ring bonds and in s character of the C–H bonds, which is detected by the $^1J_{CH}$ coupling constant.

Clearly the cyclobuta[*c*]thiophenes, -furans, and -pyrroles are strained systems, and although there is some chemical evidence for bond localization in cyclobuta[*c*]thiophene,[5b] the thiophene ring largely maintains its aromatic character. We are currently attempting to prepare both cyclobuta[*c*]heterocycles and heterocycles fused to three-membered rings in order to further identify the consequences of ring strain in these systems.

Experimental Section

^{1}H NMR spectra were obtained on either a Varian T-60 or HA-100 spectrometer and are reported in δ units, using Me_4Si as an internal standard. ^{13}C NMR spectra were obtained on a Varian CFT-20 spectrometer in $CDCl_3$ and are reported in parts per million from Me_4Si as the internal standard. Mass spectra were taken on an AEI MS-12 or MS-9 spectrometer. Infrared spectra were recorded on a Unicam SP200 or Perkin-Elmer PE257 recording spectrometer, and only strong and medium bands are reported. Melting points were taken on a Kofler hot stage and are uncorrected. Silica for TLC was Merck Kieselgel GF_{254} and for preparative TLC was PF_{254}. Woehlm neutral alumina (activity III) and Hopkins and Williams silica gel were used for column chromatography. Solvents were purified by standard methods. Unless otherwise stated, reactions were worked up by addition to water followed by extraction with ether. The ethereal layer was dried ($MgSO_4$) and the solvent was removed under reduced pressure.

Reaction of 4-Thiahepta-1,6-diyne (2a, X = S) with Potassium Hydroxide in Methanol. 4-Thiahepta-1,6-diyne (**2a**, X = S) (2 g, 18.2 mmol) in dry MeOH (25 mL) was added rapidly to a magnetically stirred solution of KOH (2 g) in MeOH (20 mL) at 35–38 °C under dry N_2. The reaction mixture turned orange and was stirred for a further 3 h. After workup, the etheral extracts were cooled (ca. −10 °C) and then filtered to remove a pale yellow precipitate (80 mg), which was chromatographed on silica by eluting with benzene to give a trimer (53 mg, 2.7%): mp 206–212 °C; MS *m/e* 330.0587 ($C_{18}H_{18}S_3$ requires *m/e* 330.0571), 332 (M^+ + 2, 20%), 331 (M^+ + 1, 28%), 330 (M^+, 100%), 232, 219, 205, 111, 110; ^{1}H NMR ($CDCl_3$) δ 6.99 (d, 1 H), 6.84 (m, 3 H), 5.23 (s, 1 H), 4.89 (s, 1 H), 4.08 (t, 1 H), 3.09 (d, 2 H), 2.67 (m, 6 H), 1.48 (m, 3 H); ^{13}C NMR ($CDCl_3$) 160.7, 141.8, 138.1, 130.5, 124.8, 120.9, 118.5, 106.4, 54.5, 52.1, 44.7, 39.6, 39.3, 30.5 ppm; IR (KBr) 3050, 2900, 2850, 1635, 1440, 1410, 1370, 1330 cm^{-1}; λ_{max} (EtOH) 243.5 nm (ϵ 12 400). Anal. Calcd for $C_{18}H_{18}S_3$: C, 65.40; H, 5.50. Found: C, 65.06; H, 5.45.

Workup of the filtrate gave a yellow, crystalline residue which on preparative TLC eluting with CH_2Cl_2/pentane (1:9) gave **5a** (250 mg, 12.5%): mp 138–140 °C; MS *m/e* 220.0380 ($C_{12}H_{12}S_2$ requires *m/e* 220.0381), 222 (M^+ + 2, 11%), 221 (M^+ + 1, 17%), 220 (M^+, 100%), 219, 205, 186, 172, 171, 147, 123, 110; ^{1}H NMR, see Discussion; ^{13}C NMR, see Table I; IR (KBr) 3100, 2950, 2850, 1460, 1440 cm^{-1}; λ_{max} (EtOH) 237 (sh) (ϵ 10 620), 243 (11 380), 249 (sh) nm (8950). Anal. Calcd for $C_{12}H_{12}S_2$: C, 65.39; H, 5.49; S, 29.10. Found: C, 65.63; H, 5.62; S, 28.71.

Reaction of 4-Oxahepta-1,6-diyne (2b, X = O) with Potassium *tert*-Butoxide in THF. A solution of **2b** (1.0 g, 10.64 mmol) in THF (5 mL) was added rapidly to a magnetically stirred solution of KO-*t*-Bu (1.1 g) in THF (15 mL). After 2 min the reaction mixture turned yellow and a vigorous reaction caused the solvent to boil. The mixture was allowed to stir for a further 5 min and then was poured into water. Workup gave a yellow crystalline solid which was recrystallized from ethanol as **5b** (160 mg, 16%): mp 164–165 °C; MS *m/e* 188 (M^+, 100%), 159, 119, 91; ^{1}H NMR, see Discussion; ^{13}C NMR, see Table II; IR (KBr) 3110, 3080, 2900, 2850, 1590, 1560, 1540, 1450, 1440, 1380 cm^{-1}. Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.41; H, 6.29.

Reaction of 4-Ethyl-4-azahepta-1,6-diyne (2c) with Potassium *tert*-Butoxide in THF. A solution of **2c** (10 g, 82.6 mmol) in THF (20 mL) was added to a stirred solution of KO-*t*-Bu (15 g) in THF (150 mL), under N_2. The temperature of the reaction mixture was raised to 60 °C when a reaction occurred which caused the solvent to boil vigorously. The reaction flask was removed from the heating bath and stirred for a further 5 min, after which water (100 mL) was added. Workup furnished yellow crystals, recrystallized from ether as **5c** (860 mg, 8.6%): mp 135–136 °C; MS *m/e* 243 (M^+ + 1, 20%), 242 (M^+, 91%), 241 (M^+ − 1, 100%), 273, 134, 121; ^{1}H NMR ($CDCl_3$) δ 6.35 (s, 4 H), 3.80 (q, 4 H, J = 7 Hz), 2.70 (s, 4 H), 1.35 (t, 6 H, J = 7 Hz); ^{13}C NMR, see Table III; IR (KBr) 2880, 1530, 1450, 1400, 1380, 1360, 1300 cm^{-1}; λ_{max} (EtOH) 227 nm (ϵ 10 900). Anal. Calcd for $C_{16}H_{22}N_2$: C, 79.29; H, 9.15; N, 11.56. Found: C, 78.89; H, 9.10; N, 11.63.

Preparation of 2,2,10,10-Tetramethyl-6-thiaundeca-3,8-diyne (6a). A solution of $Na_2S{\cdot}9H_2O$ (4.8 g, 20 mmol) in methanol (70 mL) was added to a magnetically stirred solution of 1-bromo-4,4-dimethylpent-2-yne (7 g, 40 mmol) in methanol (10 mL) under N_2. After the addition the mixture was stirred for a further 30 min. The temperature was then raised to 42 °C and stirring was continued for 18 h. Workup provided an oil which was purified by bulb-to-bulb distillation (bath temperature 40–50 °C, 10^{-4} mmHg) as **6a** (4.1 g, 93%): ^{1}H NMR ($CDCl_3$) δ 3.37 (s, 4 H), 1.20 (s, 18 H); IR (KBr) 2960, 2920, 2900, 2860, 1470, 1450, 1420, 1360 cm^{-1}. Anal. Calcd for $C_{14}H_{22}S$: C, 75.60; H, 9.99. Found: C, 74.72; H, 9.78.

Reaction of 6a with Potassium *tert*-Butoxide in *tert*-Butyl Alcohol. A solution of **6a** (1.30 g, 5.9 mmol) in *t*-BuOH (20 mL) was added to a magnetically stirred solution of KO-*t*-Bu (3.5 g) in *t*-BuOH (50 mL) at 45 °C under N_2. After addition, stirring and heating of the mixture was continued for 15 h. Workup gave a yellow oil which, after chromatography on silica eluting with petroleum ether, furnished colorless crystals of **7a** (830 mg, 64%): mp 44–45 °C; MS *m/e* 222.1468 ($C_{14}H_{22}S$ requires *m/e* 222.1443), 222 (M^+, 17%), 166, 165 (100%), 137, 123; ^{1}H NMR, see Discussion; ^{13}C NMR, see Table I; IR (KBr) 2950, 2920, 2890, 1500, 1475, 1400, 1370 cm^{-1}; λ_{max} (EtOH) 248 nm (ϵ 8930). Anal. Calcd for $C_{14}H_{22}S$: C, 75.60; H, 9.99. Found: C, 75.75; H, 9.95.

Oxidation of 7a. A solution of **7a** (111 mg, 0.5 mmol) in $CHCl_3$ (5 mL) was added to a solution of *m*-chloroperoxybenzoic acid (210 mg, 1.22 mmol) in $CHCl_3$ (10 mL) at 0 °C. The mixture was kept in a refrigerator for 18 h, when no starting material was present (TLC), and it was then poured onto saturated $NaHCO_3$ solution (25 mL). The $CHCl_3$ layer was separated, the aqueous layer was extracted with $CHCl_3$ (10 mL), and the combined $CHCl_3$ layers were washed with saturated $NaHCO_3$ solution (3 × 20 mL) and water (20 mL) and then dried ($MgSO_4$). Removal of the solvent under reduced pressure afforded pale yellow crystals which on recrystallization from hexane gave the sulfone **8** (112 mg, 88%): mp 120–121 °C; MS *m/e* 254 (M^+, 1.6%), 197 (100%), 196, 183, 141; ^{1}H NMR ($CDCl_3$) δ 6.03 (s, 2 H), 3.22 (s, 2 H), 1.00 (s, 18

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[16] See: C. C. Price and S. Oae, "Sulfur Bonding", Ronald Press, New York, N.Y., 1962; *Chem. Soc., Spec. Publ.*, **No. 18** (1965); "Molecular Structure and Dimensions", Vol. 1A, O. Kennard et al., Eds., IUC, London, 1972.

H); ^{13}C NMR, see Table I; IR (KBr) 2950, 2850, 1480, 1400, 1370 cm^{-1}; λ_{max} (EtOH) 255 (ϵ 4800), 297 nm (1040). Anal. Calcd for $C_{14}H_{22}SO_2$: C, 66.10; H, 8.72. Found: C, 65.99; H, 8.70.

Preparation of 2,2,10,10-Tetramethyl-6-oxaundeca-3,8-diyne (6b). Powdered KOH (2.8 g, 50 mmol) was added over a 30-min period to a vigorously stirred mixture of 1-bromo-4,4-dimethylpent-2-yne (6.52 g, 37.3 mmol) and 4,4-dimethylpent-2-yn-1-ol (4.60 g, 41.1 mmol). A vigorous reaction occurred and the temperature of the reaction mixture was maintained below 70 °C by external cooling. After addition was complete, the mixture was heated to 68 °C for 1.5 h and then allowed to cool to room temperature. Workup provided **6b** as a colorless oil (7.48 g, 97%): ^{1}H NMR (CDCl$_3$) δ 4.17 (s, 4 H), 1.20 (s, 18 H); ^{13}C NMR (CDCl$_3$) 95.5 (C≡*C*-*t*-Bu), 74.0 (*C*≡C-*t*-Bu), 57.0 (OCH$_2$), 31.1 (C(CH$_3$)), 27.5 (*C*Me$_3$); IR (NaCl) 2970, 2930, 2900, 2860, 2240, 1475, 1450, 1380, 1360, 1350 cm^{-1}. Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 78.79; H, 10.51.

Reaction of 6b with Potassium *tert*-Butoxide in THF. A solution of **6b** (2 g, 9.7 mmol) in dry THF (30 mL) was added dropwise to a magnetically stirred solution of KO-*t*-Bu (3.0 g) in dry THF (30 mL) at 55 °C under N$_2$. After completion of addition, the mixture was stirred for a further 24 h at 48 °C. Workup gave a yellow oil which on trituration with petroleum spirit at low temperature furnished a white amorphous precipitate of the dimer **9** (50 mg, 2.5%): mp 282–284 °C dec; MS *m/e* 412.3369 ($C_{28}H_{44}O_2$ requires *m/e* 412.3341), 412 (M$^+$, 31%), 355, 299, 298 (100%), 242; ^{1}H NMR (CDCl$_3$) δ 5.90 (s, 4 H), 4.90 (s, 4 H), 1.17 (36 H); ^{13}C NMR, see Table II; IR (KBr) 2940, 2900, 2860, 1475, 1460, 1355 cm^{-1}; λ_{max} (Et$_2$O) 251.5 nm (ϵ 23 000). Anal. Calcd for $C_{28}H_{44}O_2$: C, 81.48; H, 10.77. Found: C, 78.88; H, 10.37.

The filtrate separated from the above precipitate was chromatographed on silica, eluting with pentane to give **7b** (615 mg, 31%): mp ca. 10 °C; MS *m/e* 206.1673 ($C_{14}H_{22}O$ requires *m/e* 206.1671), 206 (M$^+$, 41%), 191, 163, 150, 149 (100%), 135, 121, 109, 107, 105, 91; ^{1}H NMR (CDCl$_3$) δ 7.00 (s, 2 H), 3.08 (s, 2 H), 0.95 (s, 18 H); ^{13}C NMR, see Table II; IR (KBr) 2920, 2900, 2850, 1560, 1470, 1400, 1370 cm^{-1}. Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.60; H, 10.21.

Preparation of 2,2,6,10,10-Pentamethyl-6-azaundeca-3,8-diyne (6c). 3,3-Dimethylbut-1-yne (9.72 g, 118.5 mmol) was added in five portions to a stirred solution of ethylmagnesium bromide (Mg, 2.38 g, 99.2 mmol; ethyl bromide, 12.4 g, 113.8 mmol) in THF (130 mL) at 0 °C under N$_2$. After completion of addition the mixture was allowed to warm to room temperature and was then heated at 55 °C for 1 h. A solution of *N*,*N*-bis(butoxymethyl)methylamine (11.5 g, 56.7 mmol) in THF (20 mL) was added dropwise and the mixture stirred at 55 °C for 48 h. The reaction mixture was cooled, 10% HCl solution (50 mL) was added and the mixture extracted with ether (2 × 50 mL), and the aqueous solution was made alkaline with 10% K$_2$CO$_3$ and the precipitate removed by filtration. The filtrate was extracted with ether (3 × 70 mL) and the combined ethereal extracts were dried (K$_2$CO$_3$). The solvent was removed under reduced pressure to give a pale yellow oil. Distillation (68–72 °C (0.4–0.5 mmHg)) afforded **6c** (5.0 g, 46%): MS *m/e* 219.1997 ($C_{15}H_{25}N$ requires *m/e* 219.1987), 219 (M$^+$, 38%), 218, 204, 171, 162 (100%); ^{1}H NMR (CDCl$_3$) δ 3.14 (s, 4 H), 2.21 (s, 3 H), 1.18 (s, 18 H); IR (NaCl) 2950, 2850, 2800, 1470, 1370, 1330, 1310 cm^{-1}.

Reaction of 6c with Potassium *tert*-Butoxide in Benzene. A solution of **6c** (250 mg, 1.14 mmol) in dry benzene (15 mL) was added dropwise to a magnetically stirred solution of KO-*t*-Bu in dry benzene (30 mL) under N$_2$. The mixture was heated to reflux for 24 h and then allowed to cool, water (30 mL) was added, the organic layer was removed by separation, and the aqueous layer was washed with benzene (25 mL). The combined benzene fractions were extracted with water (3 × 25 mL) and dried (MgSO$_4$), and the solvent was removed under reduced pressure to give a yellow oil. Chromatography on alumina, eluting with pentane gave, in the first 200 mL of eluant, a colorless oil which (after preparative TLC on silica eluting with pentane) furnished partially crystalline **7c** (35 mg, 14%): MS *m/e* 219.1980 ($C_{15}H_{25}N$ requires *m/e* 219.1987), 219 (M$^+$, 37%), 204, 162 (100%), 146, 132; ^{1}H NMR (CDCl$_3$) δ 6.18 (s, 2 H), 3.65 (s, 3 H), 3.05 (s, 2 H), 0.95 (s, 18 H); ^{13}C NMR, see Table III; IR (NaCl) 2950, 2890, 2860, 1510, 1470, 1460, 1410, 1385, 1370, 1360, 1330, 1315 cm^{-1}; λ_{max} (EtOH) 233 nm (ϵ 7200).

Reaction of 6c with Potassium *tert*-Butoxide in THF. A solution of **6c** (330 mg, 1.51 mmol) in THF (15 mL) was added to a magnetically stirred mixture of KO-*t*-Bu (1.0 g) in THF (25 mL) under N$_2$. The mixture was heated to reflux for 16 h and then cooled, and water (30 mL) was added. Workup provided a yellow oil which was chromatographed on alumina eluting with benzene to give pale yellow crystals, purified by sublimation to furnish colorless crystals of **10** (190 mg, 57.5%): mp 68–69 °C; MS *m/e* 438.3990 ($C_{30}H_{50}N_2$ requires *m/e* 438.3974), 438 (M$^+$, 19%), 381 (100%), 380, 374, 220, 219, 218, 163; ^{1}H NMR, see Discussion; ^{13}C NMR, see Table III; IR (KBr) 2950, 2900, 2880, 2860, 1510, 1470, 1460, 1410, 1390, 1360, 1335, 1320 cm^{-1}; electronic spectrum, see Discussion. Anal. Calcd for $C_{30}H_{50}N_2$: C, 82.13; H, 11.49; N, 6.38. Found: C, 81.98; H, 11.39; N, 6.36.

Reaction of 1,7-Diphenyl-4-thiahepta-1,6-diyne (11a) with Potassium *tert*-Butoxide in *tert*-Butyl Alcohol. A solution of **11a** (655 mg, 2.5 mmol) in *t*-BuOH (15 mL) was added dropwise to a magnetically stirred solution of KO-*t*-Bu (2 g) in *t*-BuOH (35 mL) at 20 °C under dry N$_2$. The reaction was monitored by TLC on silica, eluting with pentane. After 1.5 h, TLC of the reaction mixture showed only one compound, which was not the starting material, was present. Workup provided an oil which was chromatographed on silica, eluting with pentane to give **18a** as pale yellow crystals (EtOH) (480 mg, 73%): mp 46–47 °C; MS *m/e* 262.0798 ($C_{18}H_{14}S$ requires *m/e* 262.0816), 262 (M$^+$, 100%), 261, 215, 185, 184; ^{1}H NMR, see Discussion; ^{13}C NMR, see Table I; IR (KBr) 3020, 1600, 1500, 1460, 1430, 1410 cm^{-1}; electronic spectrum, see Discussion. Anal. Calcd for $C_{18}H_{14}S$: C, 82.41; H, 5.38. Found: C, 82.28; H, 5.40.

When the reaction was carried out at 55–60 °C, compound **18a** was initially formed (TLC) but after 30 min a second compound was also observed. After 72 h only the second compound was present. The reaction was worked up and the resulting oil chromatographed on alumina, eluting with CH$_2$Cl$_2$/pentane (1:9), to give **14a** (170 mg, 31%), mp 135–137 °C (lit.[9] mp 131–132 °C), which was identical in all observed respects with an authentic sample.

Reaction of 18a with Potassium *tert*-Butoxide in *tert*-Butyl Alcohol. A solution of **18a** (70 mg, 0.27 mmol) in *t*-BuOH (3 mL) was added to a magnetically stirred solution of KO-*t*-Bu (121 mg) in *t*-BuOH (5 mL) under N$_2$. The reaction mixture was heated to 95 °C with stirring and was monitored by TLC. After 70 h no starting material was detected and the reaction mixture was worked up to give **14a** (64 mg, 91%).

Oxidation of 18a. A solution of **18a** (2.0 g, 7.6 mmol) in CHCl$_3$ (5 mL) was added to a solution of *m*-chloroperoxybenzoic acid (2.62 g, 15.28 mmol) in CHCl$_3$ (20 mL) at 0 °C. After addition, the mixture was kept in a refrigerator at 5 °C for 22 h and then was poured into a saturated NaHCO$_3$ solution (50 mL). The organic layer was separated, washed with saturated NaHCO$_3$ solution (3 × 50 mL), and dried (MgSO$_4$). The solvent was removed under reduced pressure to afford a pale yellow solid recrystallized from CCl$_4$/hexane as **20** (600 mg, 30%): mp 82 °C dec; MS *m/e* 294 (M$^+$, 5.5%), 293, 261, 246, 229 (100), 228, 214; ^{1}H NMR, see Discussion; IR (KBr) 3500, 1720, 1590, 1560, 1420, 1395, 1300 cm^{-1}; λ_{max} (EtOH) 230 (sh) (ϵ 11 000), 275 nm (sh) (2300).

Reaction of 1,7-Diphenyl-4-oxahepta-1,6-diyne (11b) with Potassium *tert*-Butoxide in THF. A solution of **11b** (400 mg, 16.3 mmol) in dry THF (7 mL) was added dropwise to a magnetically stirred solution of KO-*t*-Bu (1.0 g) in dry THF at 0 °C. The reaction was monitored by TLC and after 15 min no starting material could be detected. Workup provided an oil which was chromatographed on alumina, eluting with CH$_2$Cl$_2$/petroleum spirit (1:9; below 40 °C), to give **18b** (215 mg, 54%): mp 58–59 °C (MeOH); MS *m/e* 246.1047 ($C_{18}H_{14}O$ requires *m/e* 246.1045), 246 (M$^+$, 100%), 245, 218, 215, 202, 169, 168; ^{1}H NMR (CDCl$_3$) δ 3.87 (s, 2 H), 5.12 (s, 1 H), 7.17 (m, 11 H); ^{13}C NMR, see Table II; IR (KBr) 3080, 3000, 1500, 1460, 1440, 1400 cm^{-1}; electronic spectrum, see Discussion. Anal. Calcd for $C_{18}H_{14}O$: C, 87.77; H, 5.73. Found: C, 87.67; H, 5.75.

When the reaction was carried out at 60 °C, naphthalene **14b** (47%), mp 121.5–123 °C (lit.[9] mp 121.5–122.5 °C), identical in all observed respects to an authentic sample, was isolated.

Reaction of 18b with Potassium *tert*-Butoxide in THF. A solution of **18b** (35 mg, 0.14 mmol) in THF (10 mL) was added to a stirred solution of KO-*t*-Bu (200 mg) in THF (10 mL) at 25 °C under N_2. After 15 min water (25 mL) was added and the reaction mixture worked up as described above to furnish **14b** (31 mg, 89%).

Reaction of 1-Phenyl-4-oxahepta-1,6-diyne (21) with Potassium *tert*-Butoxide in THF. A solution of **21** (500 mg, 2.94 mmol) in dry THF (15 mL) was added dropwise to a stirred solution of KO-*t*-Bu (500 mg, 4.5 mmol) in dry THF (20 mL) at room temperature under N_2. The mixture was stirred for 4 h. Workup provided an oil which was chromatographed on silica eluting with CH_2Cl_3/pentane (1:4) to give **22** (100 mg, 20%): mp 79–80 °C; MS *m/e* 170.0741 ($C_{12}H_{10}O$ requires *m/e* 170.0732), 170 (M^+, 20%), 142, 141, 139, 115 (100%), 89; ^1H NMR, see Discussion; ^{13}C NMR, see Table II; IR (KBr) 1490, 1450, 1420, 1380 cm^{-1}; electronic spectrum, see Discussion. Anal. Calcd for $C_{12}H_{10}O$: C, 84.68; H, 5.92. Found: C, 84.57; H, 5.85.

When the reaction was carried out at 60–62 °C for 15 h, **23** (28%), mp 158–159 °C (lit.[11] mp 153–155 °C), identical in all observed respects to an authentic sample, was isolated.

Reaction of 22 with Potassium *tert*-Butoxide in THF. A solution of **22** (20 mg, 0.12 mmol) in THF (15 mL) was added to a stirred solution of KO-*t*-Bu (150 mg) in THF (10 mL) at 50 °C under N_2. After workup, preparative TLC on silica afforded, in addition to 4 mg of **22**, **23** (10 mg, 63%).

Reaction of 1,7-Diphenyl-4-methyl-4-azahepta-1,6-diyne (11c) with Potassium *tert*-Butoxide in THF. A solution of **11c** (1.20 g, 4.6 mmol) in THF (15 mL) was added dropwise over 2 min to a stirred solution of KO-*t*-Bu (1.0 g) in THF (10 mL) at 20 °C under N_2. After addition was complete, the mixture was stirred for a further 1 min and water (30 mL) was then added. Workup provided an oily semisolid which was recrystallized from ether as the dimer **24** (230 mg, 19.5%): mp 248–252 °C; MS *m/e* 518.2740 ($C_{38}H_{34}N$ requires *m/e* 518.2722), 518 (M^+, 100%), 422, 355, 257, 256; ^1H NMR ($CDCl_3$) δ 7.20 (m, 20 H), 5.90 (s, 4 H), 5.30 (s, 4 H), 3.35 (s, 6 H); ^{13}C NMR, see Table III; IR (KBr) 3500, 3050, 2950, 1600, 1540, 1500, 1460, 1400 cm^{-1}. Anal. Calcd for $C_{38}H_{34}N_2$: C, 87.99; H, 6.66; N, 5.40. Found: C, 87.62; H, 6.50; N, 5.23.

The ethereal mother liquor was treated with methanol when a yellow precipitate formed which was recrystallized from methanol to afford pale yellow crystals of **25** (190 mg, 16%): mp 209–210 °C; MS *m/e* 518 (M^+, 92%), 422, 355, 257, 256 (100%); ^1H NMR ($CDCl_3$) δ 7.18 (bs, 20 H), 6.08 (s, 4 H), 4.80 (s, 4 H), 3.40 (s, 6 H); ^{13}C NMR, see Table III; IR (KBr) 3500, 3050, 2950, 1600, 1540, 1500, 1460, 1400 cm^{-1}. Anal. Calcd for $C_{38}H_{34}N_2$: C, 87.99; H, 6.66; N, 5.40. Found: C, 87.26; H, 6.58; N, 5.29.

Reaction of 11c with Potassium *tert*-Butoxide in Benzene. A solution of **11c** (450 mg, 1.75 mmol) in benzene (25 mL) was added to a stirred solution of KO-*t*-Bu (1.0 g) in benzene (25 mL) at 20 °C under N_2. The mixture was stirred for 6 h, water (50 mL) was added, the organic layer was separated, and the aqueous layer was extracted with benzene (2 × 20 mL). The combined benzene fractions were washed with water (2 × 25 mL) and then dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue was chromatographed on alumina, eluting with ether/pentane (1:9), to give the following two products (in order). **18c** (55 mg, 12%, yellow oil): MS *m/e* 259.1345 ($C_{19}H_{17}N$ requires *m/e* 259.1361), 259 (M^+, 18%), 258, 257, 173 (100%), 172; ^1H NMR, see Discussion; IR (KBr) 3020, 2920, 1600, 1545, 1500, 1460, 1400, 1380 cm^{-1}; λ_{max} (EtOH) 263 (ϵ 2850), 272 (1970), 348 nm (1120). **14c** (110 mg, 24%): mp 141–142 °C (lit.[9] mp 141–143 °C); identical in all observed respects to an authentic sample.

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Registry No. 2a, 13702-09-5; **2a** trimer, 70446-04-7; **2b**, 6921-27-3; **2c**, 13002-92-1; **5a**, 56146-99-7; **5b**, 56147-00-3; **5c**, 70445-95-3; **6a**, 56147-05-8; **6b**, 56147-06-9; **6c**, 56147-07-0; **7a**, 70445-96-4; **7b**, 70445-97-5; **7c**, 70445-98-6; **8**, 70445-99-7; **9**, 70446-00-3; **10d**, 70492-70-5; **11a**, 13225-60-0; **11b**, 13225-61-1; **11c**, 2568-62-9; **14a**, 14208-74-3; **14b**, 13225-65-5; **14c**, 13225-64-4; **18a**, 56146-95-3; **18b**, 56146-96-4; **18c**, 70446-01-4; **20**, 70446-02-5; **21**, 53877-63-7; **22**, 56146-97-5; **23**, 7193-16-0; **26**, 56146-98-6; 1-bromo-4,4-dimethylpent-2-yne, 52323-99-6; 4,4-dimethylpent-2-yn-1-ol, 52323-98-5; 3,3-dimethylbut-1-yne, 917-92-0; *N*,*N*-bis(butoxymethyl)methylamine, 70446-03-6.

Nucleophilic Character of Alkyl Radicals. 18.[1] Absolute Rate Constants for the Addition of Primary Alkyl Radicals to Conjugated Olefins and 1,4-Benzoquinone

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The rate constants for the addition of the 5-hexenyl radical to styrene, α-methylstyrene, butadiene, acrylic monomers, methyl vinyl ketone, and 1,4-benzoquinone were measured from 16 to 69 °C. The importance of polar effects, due to the nucleophilic character of the alkyl radical in olefin addition, is emphasized. The inhibition of chain processes by quinone is discussed in terms of the high rate constant (2.0×10^7 L mol^{-1} s^{-1} at 69 °C) of the alkyl radical addition to 1,4-benzoquinone.

The concept of polar effects in free-radical reactions shows ambiguous points being derived from the ionic reactions. Ionic electrophilic and nucleophilic species are formally well defined, but the electrophilic or nucleophilic character of free radicals cannot always be deduced from their formal structures, not even for radical ions (i.e., the radical anion $SO_4^{-}\cdot$ has a clear-cut electrophilic character) or for borderline cases such as carbon-centered free radicals. The phenomenon is kinetic in nature and the terms of electrophilicity and nucleophilicity cannot be mechanically transferred from ionic to radical reactions. For a given reaction the rate constant sequence cannot measure the relative electrophilicity and nucleophilicity of free radicals, as it occurs for ionic reactions. Moreover, fixing an electrophilic or nucleophilic character for a given

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(1) Part 17: A. Citterio, F. Minisci, A. Arnoldi, R. Pagano, A. Parravicini, and O. Porta, *J. Chem. Soc., Perkin Trans. 2*, 519 (1978).