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Chemistry of (2- and 3-Furyl)methylenes and (2- and 3-Thienyl)methylenes[1a]

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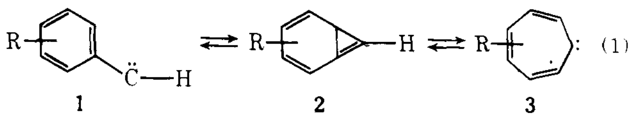
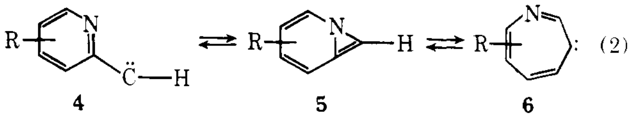
Abstract: Pyrolysis of diazo(2-furyl)methane (**16a**) and its substituted analogues (**16b–f**), as generated from the corresponding tosylhydrazone sodium salts (**15a–f**), yields γ,δ-acetylenic α,β-olefinic carbonyl products (**18a–f, 19a–e**) resulting from furan ring opening. Generation of 2-furylmethylene (**17a**) in decomposition of **16a** is indicated by its trapping with cyclooctane and styrene. There is no evidence for isomerization of **17a** to α-pyranylidene (**9a**, Z = O; R = H). Diazo(3-furyl)methane (**35**) thermolyzes to *cis*- (**37**) and *trans*- (**38**) 1,2-di(3-furyl)ethylenes; neither ring opening nor ring expansion of 3-furylmethylene (**36**) was detected. Diazo(2-thienyl)methane (**26a**) and its substituted analogues (**26b,c**) decompose thermally with ring opening to α,β-unsaturated, γ,δ-acetylenic thiocarbonyls (**28a–c**) and their subsequent derivatives (**29a–c**); conversions to the corresponding 1,2-di(2-thienyl)ethylenes (**30a–c** and **31a–c**) are the principal processes, however. The greater resistance of 2-thienylmethylenes (**27**) than 2-furylmethylenes (**17**) to ring opening is rationalized on the basis of the greater resonance energy of the thiophene ring and the lower stability of its ring-opened products. Diazo(3-thienyl)methane (**40**) converts to *cis*- (**42**) and *trans*- (**43**) 1,2-di(3-thienyl)ethylenes at 300 °C. Ring expansions of 2- (**27a–c**) and 3- (**41**) thienylmethylenes to their corresponding α- and γ-thiopyranylidines (such as **9** and **14**, Z = S) were not observed.

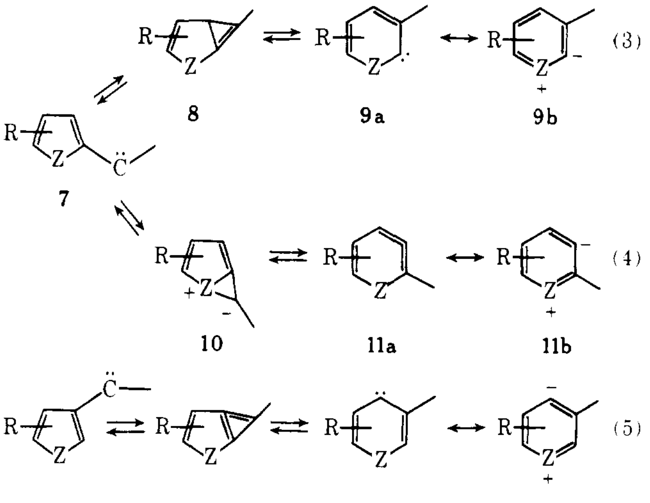
One of the most intriguing carbenic rearrangements is the interconversion (eq 1) of arylmethylenes (**1**) and cycloheptatrienylidenes (**3**).[2] These isomerizations are frequently reversible and apparently involve cyclopropene (**2**) intermediates.[2] Analogous interrelationships (eq 2) are observed for (2-pyridyl)methylenes (**4**) and azacycloheptatrienylidenes (**6**) in which an important feature is participation of heterocyclic nitrogen (**5**).[2k,l,3]





The mechanistic features of the above rearrangements (eq 1 and 2) are in principle extendable to five-membered ring, 6 π-electron heterylmethylenes. Thus (2-heteryl)methylenes such as **7** (Z = O and S) might (1) isomerize (eq 3) by carbon bridging to six-membered ring 6π-electron α-heterylidenes (**9a,b**) which are theorized to be highly stabilized[4] or (2) rearrange (eq 4) involving participation of the heteroatom to give species such as **10** and **11a,b** and products derived therefrom. Analogously, (3-heteryl)methylenes (**12**, Z = O and S) would give (1) stabilized six-membered ring, 6π-electron γ-heterylidenes (eq 5, **14a,b**) or (2) cyclic allenes analogous to **11a,b** as derived by cyclization at C-3 or products thereof.

A study is presently reported of the behavior of 1-(2- and 3-furyl)-1-alkylidenes (**7** and **12**, Z = O) and 1-(2- and 3-thienyl)-1-alkylidenes (**7** and **12**, Z = S). These systems have been found to be of interest in that the (2-heteryl)methylenes (**7**) undergo ring opening, whereas the (3-heteryl)methylenes (**12**) do not isomerize; ring expansion of **7** to **9a,b** or **11a,b** and of **12** to **14a,b** or allenic intermediates has not been detectable.



Results

Vacuum pyrolysis of diazo(2-furyl)methane (**16a**), as generated in situ from the sodium salt of furfural tosylhydrazone (**15a**) at ~300 °C,[5] gives the ring-opened products, 2-penten-4-ynals (eq 6), as cis (**18a**, 81%) and trans (**19a**, 19%) isomers[6] along with 2-furonitrile (1–4%). Similarly, the substituted diazo(2-furyl)methanes **16b,c** as derived from tosylhydrazone salts **15b,c**, decompose to their corresponding carbonyl products, *cis*- (**18b**) and *trans*- (**19b**) hexen-5-yn-2-ones and *cis*- (**18c**) and *trans*- (**19c**) 5-phenyl-2-penten-4-ynals, respectively, in which the cis isomers are predominant (Table I). Since isomerizations of (cis) **18a–c** to (trans) **19a–c**, respectively, occur at the temperatures for decomposition of

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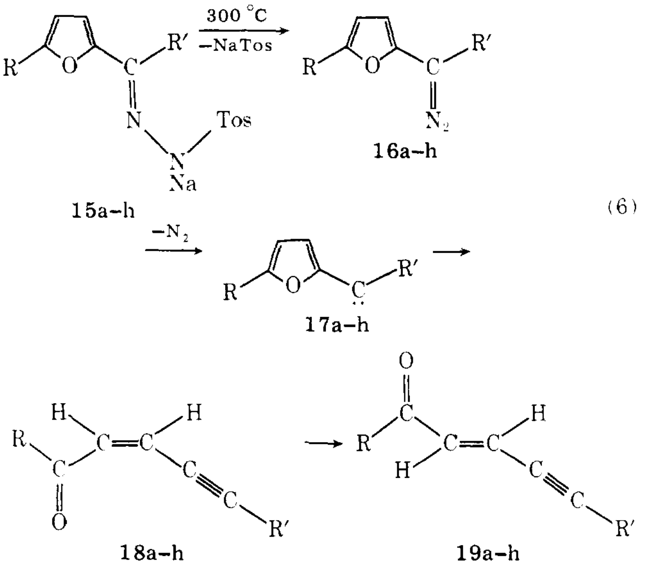
Table I. Products of Decomposition of Diazo(2-furyl)alkanes and Diazo(2-thienyl)alkanes

diazo compd	product distribution (%)	yield, %
16a	**18a** (81), **19a** (19)	60
16b	**18b** (86), **19b** (14)	43[a]
16c	**18c** (53), **19c** (47)	43[a]
16d	**18d** (70), **19d** (30)	36[a]
	20	
16e	**18e** (68), **19e** (32)	47[a]
	21	
	22	
16f	**18f** (100)	21[a]
26a	**29a**	>8[a,b]
	30a	8
	31a	21
26b	**29b**	>9[a,c]
	30b	11
	31b	21
	32	
26c	**29c**	>8
	30c	25
	31c	6

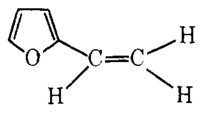
[a] The yields of products were not maximized in these pyrolyses. [b] 2-Thiophenecarboxaldehyde azine is also formed in 3% yield. [c] Methyl 2-thienyl ketone azine is also obtained (4%).

15a–c, it is likely that the ring-opening reactions are stereospecific, giving initially the cis isomers which convert to the trans products under the pyrolysis conditions. Of further interest is that 1-diazo-1-(2-furyl)ethane (**16d**) and 1-diazo-1-(2-furyl)propane (**16e**) decompose primarily with ring opening (eq 6) to give *cis*- (**18d**) and *trans*- (**19d**) 2-hexen-4-ynals and *cis*- (**18e**) and *trans*- (**19e**) 2-hepten-4-ynals, respectively. Rearrangements of α hydrogen in **17d** and in **17e** to yield 2-vinylfuran (**20**) and *cis*- (**21**) and *trans*- (**22**) 1-(2-furyl)propenes, respectively, are very minor processes (Table I).[7]



a, R = H; R′ = H b, R = CH$_3$; R′ = H c, R = H; R′ = C$_6$H$_5$
d, R = H; R′ = CH$_3$ e, R = H; R′ = C$_2$H$_5$ f, R = Cl; R′ = H
g, R = NO$_2$; R′ = H h, R = CH$_3$O$_2$C; R′ = H

As expected enynals **18a** and **19a** are highly reactive; the unusually conjugated aldehydes resinify rapidly at room temperature and during preparative gas chromatography but may be stored effectively at −78 °C. The carbonyl pyrolysates from **16b–e** are more stable than **18a** and **19a** and a major cis product (**18b–e**) could usually be separated from its trans isomer (**19b–e**) by gas chromatography. The structures of **18a–e** and **19a–e** are confirmable from their distinct spectral properties. Thus these products all exhibit infrared stretching frequencies for unsaturated carbonyl, olefin, and acetylene groups. When only a major cis isomer is isolable from a product by gas chromatography, assignments of both the cis and trans isomers in crude admixture can be made by spectral methods. The cis (**18a–e**) and trans (**19a–e**) isomers have vinyl coupling constants of $J_{\text{vic}} = 11$ and 15–16 Hz, respectively, and the chemical shifts of aldehyde and acetylenic protons of isomeric products vary distinguishingly (Table II). Thus a crude pyrolysate could be examined with an added standard and the yield and the ratio of isomeric products are determinable by NMR methods. As further proofs of structure, pure cis (**18**) or trans (**19**) aldehydes and ketones were converted to analytically pure, crystalline, 2,4-dinitrophenylhydrazones.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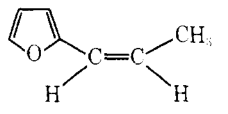
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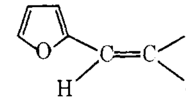
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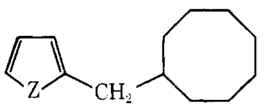
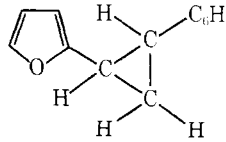
Diazo(2-furyl)methanes containing electron-withdrawing groups in the 5 positions of their furan rings decompose with loss of nitrogen; however, volatile products are produced inefficiently. Thus diazo(5-chloro-2-furyl)methane (**16f**) thermolyzes (eq 6) to *cis*-2-penten-4-ynoyl chloride (**18f**, 21%), an unstable acid chloride identified by its mass spectral, infrared, and ultraviolet properties. Diazo(5-nitro-2-furyl)methane[8] (**16g**) decomposes violently upon pyrolysis; however, 1-nitro-2-penten-4-yn-1-ones (**16g** and **17g**) could not be convincingly identified. Conversion of the sodium salt (**15h**) of 5-carbomethoxyfurfural tosylhydrazone to methyl 2-penten-4-ynoates (**18h** and **19h**) was unsuccessful; the principal pyrolysis products are methyl *p*-tolyl sulfone (40%)[9] and methyl *p*-toluenesulfinate (7%).[9]

Thermolysis of **15a** in a trapping environment was studied to determine whether furfurylidene (**17a**) is a discrete intermediate under conditions in which ring opening to **18a** occurs. Indeed decomposition of **16a** in cyclooctane at 140 °C results in furfurylcyclooctane (**23**, >7%) along with ring-opened products **18a** and **19a**. Carbon–hydrogen insertion into cyclooctane to give **23** thus indicates that **17a** is indeed generated from **16a** and supports the premise that **17a** is an intermediate in the ring-opening process to **18a**. Additionally, **15a** decomposes in neat styrene at 140 °C to yield 1-(2-furyl)-2-phenylcyclopropane (**24**, 6%) as isolated by gas chromatography.


23, Z = O
33, Z = S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Cyclopropane **24** may result from addition of carbene **17a** to styrene and/or diazomethane **15a** to styrene with evolution of nitrogen. No attempts were made to increase the yields of **23** and **24** in these studies but it is apparent that **17a** is usable carbenically without collapse of its furfurylidene moiety.

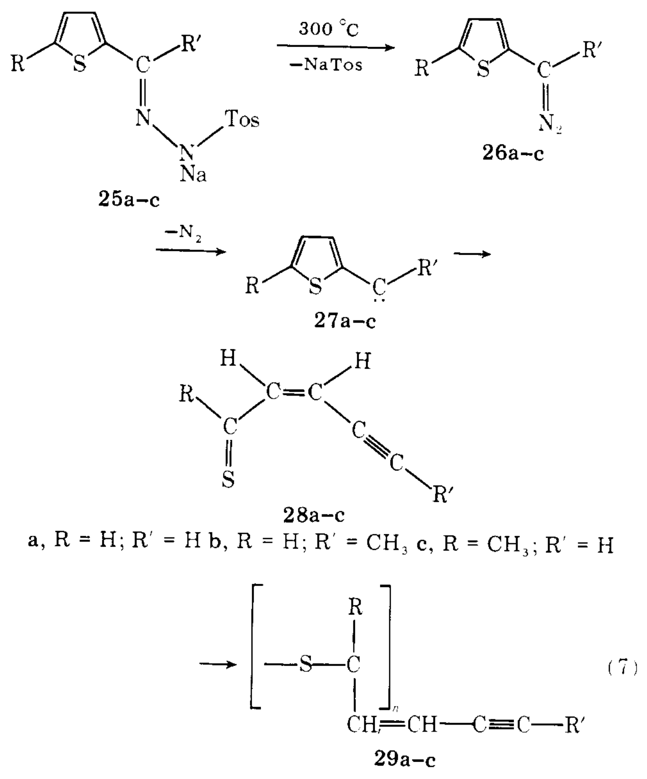
Pyrolysis of the sodium salt of 2-thiophenecarboxaldehyde tosylhydrazone (**25a**) at 300 °C was then investigated (eq 7) to determine the properties of (2-thienyl)methylene (**27a**) as derived from diazo(2-thienyl)methane (**25a**). The major volatile products are *cis*- (**30a**) and *trans*- (**31a**) 1,2-di(2-thi-

Table II. Properties of **18** and **19** and Their 2,4-Dinitrophenylhydrazones (2,4-DNPH)

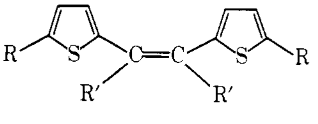
$R_1COC(H_2)=$ $C(H_3)C\equiv CR_4'$	IR, μ		¹H NMR,[b] δ 1	2	3	4	2,4-DNPH mp, °C[c]
18a[a]	5.98	4.77	10.46, $J_{1-2} = 7$	6.54, $J_{2-3} = 11$	6.92, $J_{3-4} = 2$	3.84	128–129 dec
19a[a,d,e]			9.86, $J_{1-2} = 8$			4.00	
18b[e]	6.05	4.81	2.48	6.37, $J_{2-3} = 12$	6.11, $J_{3-4} = 2$	3.72	152 dec
19b[a,e]	5.94, 6.00		2.14			3.50	
18c[a]			10.50, $J_{1-2} = 8$	6.40, $J_{2-3} = 11$	6.96	7.49	
19c	6.00	4.60	9.66, $J_{1-2} = 6$ $J_{1-3} = 1$	6.41, $J_{2-3} = 16$	6.90	7.49	123–125 dec
18d	5.95	4.55	10.34, $J_{1-2} = 8$	6.44, $J_{2-3} = 11$	6.89, $J_{3-4} = 2$	2.22	154 dec
19d[a]			9.78, $J_{1-2} = 7$			2.2	179 dec
18e	5.95	4.55	10.23, $J_{1-2} = 8$	6.16, $J_{2-3} = 11$	6.60, $J_{3-4} = 2$	2.47	123–124 dec
19e	5.95	4.52	9.53, $J_{1-2} = 6$ $J_{1-3} = 1.5$	6.28, $J_{2-3} = 15$	6.63, $J_{3-4} = 1.5$	2.47	171–172 dec
18f	5.63	4.75		6.58, $J_{2-3} = 10$	6.22, $J_{3-4} = 3$	3.88	

[a] Compound could not be isolated pure. Available data were extracted from a cis-trans mixture. [b] Where R, R′ ≠ H, chemical shift is given for methyl or methylene. *J* values in hertz. [c] Satisfactory analyses and mass spectra were obtained for all derivatives. [d] F. Bohlmann and H. Viehe, *Ber.*, **88**, 1330 (1955). [e] I. Bell, E. Jones, and M. Whiting, *J. Chem. Soc.*, 1313 (1958).

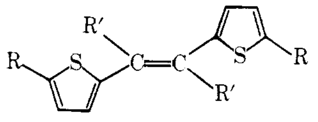
enyl)ethylenes, produced presumably by reactions of **26a** and **27a** with loss of nitrogen. Such products are not observed for diazo(2-furyl)methane systems, and it is apparent that (2-thienyl)methylene (**27a**) resists ring rupture as compared to its furan analogue (**17a**). Ethylenes **30a** and **31a** were isolated by column chromatography and identified by their analyses and their spectroscopic properties. Of particular note is that pyrolysis of **25a** gives a third product assigned as an oligomer (**29a**) of 2-penten-4-ynethial (**28a**) derived from ring opening of **27a**. The structural assignment of **29a** is based on its (1) empirical formula, C_5H_4S, as derived from elemental analyses, (2) infrared absorption for terminal acetylene (3.02 μ, $\equiv$C–H; and 4.78 μ, C$\equiv$C) and olefin (6.28 μ, C=C) groups, and (3) NMR spectrum indicating an allylically coupled acetylenic proton (δ 3.21, $J = 2$ Hz), a two-proton vinyl multiplet (δ 6.66), and a one-proton doublet (δ 5.37, $J = 10$ Hz). The pronounced ability of thioaldehydes to oligomerize[10] and the chemical shift of the thioacetal proton[11] and its coupling with the α-vinyl proton provide strong support that **29a** is an extended thioacetal.



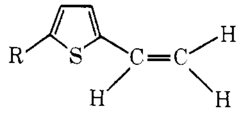
a, R = H; R′ = H b, R = H; R′ = CH_3 c, R = CH_3; R′ = H



30a, R = H; R′ = H
b, R = H; R′ = CH_3
c, R = CH_3; R′ = H



31a, R = H; R′ = H
b, R = H; R′ = CH_3
c, R = CH_3; R′ = H



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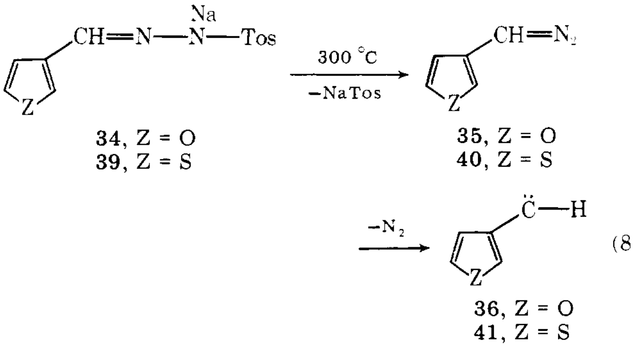
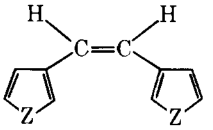
The pyrolytic reactions of sodium 2-acetylthiophene tosylhydrazone (**25b**) and of sodium 5-methyl-2-thiophene carboxaldehyde tosylhydrazone (**25c**) at 300 °C are similar (eq 7) to that of **25a**. Thus **25b** gives *cis*- (**30b**) and *trans*- (**31b**) 2,3-di(2-thienyl)-2-butenes, 2-vinylthiophene (**32**) as formed from hydrogen migration in **27b**, and oligomers (**29b**) of 2-hexen-4-yne-1-thial (**28b**) resulting from ring opening of **27b**. Tosylhydrazonate **25c** decomposes (300 °C, 0.1 mmHg) to *cis*- (**30c**) and *trans*- (**31c**) 1,2-di(5-methyl-2-thienyl)ethylenes; 2-hexen-4-yne-1-thial (**28c**) is apparently formed by collapse of **27c** and converts rapidly to oligomer **29c**. As is true for **17a**, the presence of **27a** in the pyrolysis of **25a** is demonstrable by trapping. Thus when **25a** is heated in cyclooctane at 140 °C, and after vapor phase chromatography, 2-(cyclooctylmethyl)thiophene (**33**, 23%) is obtained.

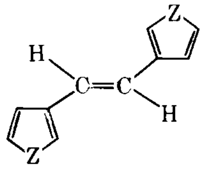
Generation of (3-heteryl)methylenes (**12**, X = O and S) was then investigated because ring opening as for **15** (eq 6) and **25** (eq 7) is impossible and perhaps isomerization to γ-heterylidenes (**14a,b**) would occur.[12] Pyrolysis of the sodium salt (**34**) of 3-furaldehyde tosylhydrazone at 300 °C (1 mmHg) gives (eq 8), however, *cis*- (**37**) and *trans*- (**38**) 1,2-di(3-furyl)eth-



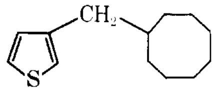
ylenes in 47:53 ratio in >29% yield. Similarly, the sodium salt (**39**) of 3-thiophenecarboxaldehyde tosylhydrazone decomposes (eq 8) at 300 °C (1 mmHg) to produce *cis*- (**42**) and *trans*- (**43**) 1,2-di(3-thienyl)ethylenes in 30:70 ratio in >24% yield. Thus ethylenes **37** and **38** are apparently formed from reactions of **35** and **36**, and **42** and **43** result from **40** and **41**.[13] There is no evidence for ring fragmentation or carbenic products arising from ring expansion to γ-heterylidenes (**14a,b**). The integrity of **41** as a carbene is indicated further by decomposition of **39** in cyclooctane to yield 3-(cyclooctylmethyl)thiophene (**44**, 60%). Thermolysis of **34** in 1,1-diphenylethylene at 160 °C also possibly involves **36** as a discrete intermediate in that 2-(3-furyl)-1,1-diphenylcyclopropane (**45**, 43%) is formed along with **37** and **38** (10%).



37, Z = O
42, Z = S



38, Z = O
43, Z = S



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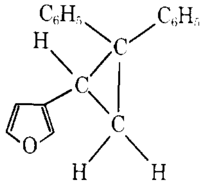

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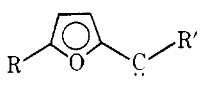
Discussion

From the yields of ring-opened products (Table I), it is apparent that furfurylidenes **17a–f** undergo ring opening much more readily than do 1-(2-thienyl)-1-alkylidenes **27a–c**. Although the mechanistic details of these isomerizations have not yet been established, these processes appear to reflect the contributions of delocalization as in **46–47** and in **48–49** to the structures of the carbenes initially generated. Thus the type and extent of delocalization within the heteroaromatic rings and the electron-acceptor abilities of the carbenic centers will affect the strengths of the heteryl bonds which are to be cleaved. The greater resonance energy of thiophene than furan[14] suggests that **48** is a major contributor in the thienyl systems relative to **46** in the furyl series. Also the greater electron-donating properties of furan than thiophene rings render **47** as an important contributor. Thus rupture of the C–O (single) bond in **46–47** will require less energy than the C–S (double) bond in **48–49**. Furthermore, formation of carbon-oxygen double bonds in ring-opened products **18** is much more favorable thermodynamically than for carbon-sulfur double bonds in **28**. These factors complement each other in the furan series so that ring fragmentation is the major carbenic process. In the thiophene series the major carbenic products result from ring maintenance and ring opening is minor. The greater resistance of (2-thienyl)methylene (**27a**) than furfurylidene (**17a**) to ring opening is also consistent with the observation that **27a** is captured more efficiently (27%) than is **17a** (7%) by cyclooctane under identical conditions.



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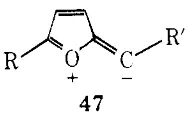

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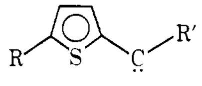

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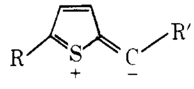

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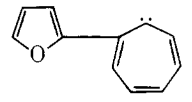
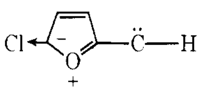
Alkyl or aryl groups on carbene carbon and/or the 5 position in the furan series **17a–e** and the thiophene series **27a–c** do not affect the efficiency of ring fragmentation significantly (Table I). A point of interest is that migrations of α hydrogen to the carbenic centers in **17d,e** and **27b** are minor processes. Since hydrogen migration is usually a very low energy carbenic pathway, ring openings of **17** and **27** must be extremely facile processes. Further, there is no evidence for phenyl ring expansion of **17c** to 2-(2-furyl)cycloheptatrienylidene (**50**); ring collapse is a more rapid process. It is emphasized that carbenic collapse of appropriate furfurylidenes is an excellent and convenient synthetic method.

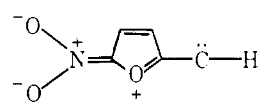


50

Electron-withdrawing groups at the 5 position of the furan rings in furfurylidenes (**17f–h**, Table I) drastically reduce ring opening. Thus (5-chloro-2-furyl)methylene (**17f**) gives **18f** in only 21% yield and ring cleavage in (5-nitro-2-furyl)methylene (**17g**) and in (5-carbomethoxy-2-furyl)methylene (**17h**) is inappreciable. The lack of ring opening (or expansion) for **17f–h** may be due to increased C–O bond strengths in their furan rings as illustrated in **51** and **52** because of electronic induction or delocalization into the electron-attracting substituents. It is expected that furfurylidenes containing various strong electron-withdrawing groups on their furan rings will maintain their structures effectively and thus be usable synthetically as carbenes.



51



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Experimental Section

Melting points were determined on a Thomas-Hoover Meltemp and are uncorrected. IR spectra were recorded on a Perkin-Elmer infrared spectrophotometer and NMR spectra were obtained on Varian A-60A or Jeolco MH-100 instruments. Liquid products were separated and analyzed on an Aerograph A-90P gas chromatograph. Elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz. In several cases decomposition of the products prevented acceptable analyses and thus exact masses of these materials freshly prepared were obtained using a MS-9 mass spectrometer.

Aldehydes and Ketones. Furfural, 5-methylfurfural, acetylfuran, ethyl 2-furyl ketone, 2-thiophenecarboxaldehyde, 5-methyl-2-thiophenecarboxaldehyde, and 2-acetylthiophene were purchased from the Aldrich Chemical Co. 5-Nitrofurfural was obtained from 5-nitro-2-furaldehyde diacetate (Aldrich Chemical Co.). 2-Furyl phenyl ketone,[15a] 5-chlorofurfural,[15b] 5-carbomethoxyfurfural,[15c] and 3-thiophenecarboxaldehyde[15d] were prepared by literature procedures.

3-Furaldehyde. A mixture of 3-furoic acid[16] (4.48 g, 0.04 mol) and *N,N′*-carbonyldiimidazole (6.68 g, 0.041 mol) in ether (250 mL) was refluxed for 12 h after which a portion of the ether was evaporated to remove remaining carbon dioxide. After the stirred mixture was cooled to −20 °C, an ether solution of lithium aluminum hydride (1.5 N, 27 mL, 0.0405 equiv) was added dropwise. The mixture was stirred for 1 h, allowed to warm to room temperature, treated sequentially with water (0.3 mL), 10% sodium hydroxide (0.6 mL), and water (1.5 mL), and then filtered. The ethereal filtrate was dried (Na_2SO_4) and then distilled to give 3-furaldehyde[17] (1.46 g, 38%), bp 64–66 °C (39 mmHg).

Furfural Tosylhydrazone. Freshly distilled furfural (20 g, 0.2 mol) was added to a solution of tosylhydrazine (37.2 g, 0.2 mol) in methanol (15 mL) maintained at 0 °C. The vigorous reaction yielded an orange solid which on recrystallization from absolute ethanol gave white crystals of furfural tosylhydrazone (24.7 g, 50%): mp 125–126 °C; IR (KBr) μ 6.19 (C=N), 3.07 (N-H) 6.26 (C=C), 7.5 and 8.6 (-SO_2-); ^{1}H NMR ($CHCl_3$) δ 11.6 (s, H, NH) 8.1 (m, 4 H, C-H, 4-furyl H, 2 aromatic protons), 7.6 (d, 2 H, aromatic H, *J* on m = 8 Hz), 7.0 (d, 1 H, 3-furyl H), 6.75 (m, 1 H, 4-furyl H), 2.50 (s, 3 H, -CH_3). Anal. Calcd for $C_{12}H_{12}N_2O_3S$: N, 10.61. Found: N, 10.62.

Various Tosylhydrazones. The tosylhydrazones prepared from their corresponding carbonyl compounds in good yields by extension of the above method, their melting points, and their analytical data follow. 5-Methylfurfural tosylhydrazone, mp 119–121 °C. Anal. Calcd for $C_{13}H_{14}N_2O_3S$: N, 10.07. Found: N, 10.27. Phenyl 2-furyl ketone tosylhydrazone, mp 131–133 °C. Anal. Calcd for $C_{18}H_{16}N_2O_3S$: N, 8.23. Found: N, 8.29. 2-Acetylfuran tosylhydrazone, mp 157–159 °C. Anal. Calcd for $C_{13}H_{14}N_2O_3S$: N, 10.07. Found: N, 10.02. Ethyl 2-furyl ketone tosylhydrazone, mp 143–144 °C. Anal. Calcd for $C_{14}H_{16}N_2O_3S$: N, 9.59. Found: N, 9.36. 5-Chlorofurfural tosylhydrazone: mp 128–130 °C; ^{1}H NMR ($CHCl_3$) δ 2.43 (s, 3 H), 6.35 (d, 1 H), 6.76 (d, 1 H), 7.18 (q, 4 H), and 7.50 (s, NH). Anal. Calcd for $C_{12}H_{11}ClN_2O_3S$: C, 48.32; H, 3.69. Found: C, 47.91; H, 3.59. 5-Nitrofurfural tosylhydrazone, mp 149–150 °C dec. Anal. Calcd for $C_{12}H_{11}N_3O_5S$: C, 46.60; H, 3.56; N, 13.59. Found: C, 46.43; H, 3.60; N, 13.33. 5-Carbomethoxyfurfural tosylhydrazone: mp 179–181 °C; ^{1}H NMR ($CHCl_3$) δ 2.42 (s, 3 H), 3.92 (s, 3 H), 7.08 (d, 1 H, *J* = 3 Hz), 7.24 (d, 1 H, *J* = 3 Hz), 7.64 (q, 4 H), and 7.97 (s, 1 H). Anal. Calcd for $C_{14}H_{14}N_2O_5S$: C, 52.17; H, 4.35; N, 8.69. Found: C, 52.09; H, 4.15; N, 8.89. 3-Furaldehyde tosylhydrazone, mp 116–119 °C. Anal. Calcd for $C_{12}H_{12}N_2O_3S$: C, 54.54; H, 4.55; N, 10.6. Found: C, 54.68; H, 4.60; N, 10.70. 2-Thiophenecarboxaldehyde tosylhydrazone, mp 142–143.5 °C. Anal. Calcd for $C_{12}H_{12}N_2O_2S_2$: N, 10.00. Found: 10.15. Methyl 2-thienyl ketone tosylhydrazone, mp 207–208 °C. Anal. Calcd for $C_{13}H_{14}N_2S_2O_2$: N, 9.52. Found: N, 9.51. 5-Methyl-2-thiophenecarboxaldehyde tosylhydrazone, mp 157–158 °C. Anal. Calcd for $C_{13}H_{14}N_2O_2S_2$: N, 9.51. Found: N, 9.60. 3-Thiophenecarboxaldehyde tosylhydrazone, mp 157.5–159 °C. Anal. Calcd for $C_{12}H_{12}N_2O_2S_2$: N, 10.00. Found: N, 10.25. The tosylhydrazones usually gave IR (KBr) absorptions at μ 3.08–3.13 (N–H), 6.15–6.30 (C=N, C=C), and 7.45–7.50 and 8.60–8.70 (-SO_2-).

Preparation of Sodium Salts of Tosylhydrazones. The same general procedure was used for the preparation of most of the sodium salts investigated. A 3% excess of sodium hydride (57% suspension in mineral oil) was added to a solution of the tosylhydrazone (1–1.5 g) in dry dichloromethane (10 mL). The mixture was stirred until gas evolution ceased (10–20 min) and ether (30 mL) was added. The precipitated sodium salt was filtered under dry nitrogen and transferred to the pyrolysis vessel, usually a 50-mL round-bottom flask, and dried under vacuum for 2 h. When a sodium salt was appreciably soluble in dichloromethane, the solvent was changed to tetrahydrofuran. Tetrahydrofuran was used in preparing the sodium salts of tosylhydrazones of 2-furyl phenyl ketone, 5-nitrofurfural, 5-chlorofurfural, and 5-carbomethoxyfurfural.

Pyrolysis of Sodium Furfural Tosylhydrazone (15a). Decomposition of **15a** (1.37 g, 4.8 mmol) was effected at 250 °C (0.3 mmHg) by immersion in a heated bath. The volatile products were collected at −78 °C and a weighed amount of dichloromethane was added to the pyrolysate. NMR analysis showed the product to be a mixture of *cis*- (**18a**) and *trans*- (**19a**) 2-penten-4-ynals in a 81:19 ratio. Gas chromatography (on 20% diisodecyl phthalate, 10 ft, 140 °C, 120 mL/min, for all separations unless noted otherwise) allowed isolation of **18a**: IR (neat) μ 3.05 (≡CH), 3.55 (-C-H), 4.77 (C≡C), 5.98 (conjugated C=O), and 6.35 (C=C). The detailed NMR of the trapped material is in Table II. Pure **19a** could not be isolated by chromatography and thus its NMR spectrum (Table II) was derived from the cis–trans mixture (**18a** and **19a**). Aldehydes **18a** and **19a** are unstable and, although they are trapped as a white solid at −78 °C, warming for short periods above their melting points at room temperature leads to black, intractable materials.

Treatment of the crude pyrolysate with 2,4-dinitrophenylhydrazine reagent gave a red-orange precipitate which was dissolved in benzene, eluted through neutral alumina, concentrated, and crystallized to give orange 2-penten-4-ynal 2,4-dinitrophenylhydrazone: mp 128–129 °C dec; IR (KBr) μ 3.05 (C≡C–H), 6.21 (>C=N), and 6.35 (C=C); ^{1}H NMR (Me_2SO-d_6) δ 9.00–8.00 (series of lines, 4 H), 6.84 (t, 1 H, *J* = 9 Hz, α-vinyl H), 6.10 (d of d, 1 H, *J* = 9, 2 Hz, β-vinyl H), and 4.00 (d, 1 H, *J* = 2 Hz, acetylene H). Anal. Calcd for $C_{11}H_8N_4O_4$: C, 50.77; H, 3.10; N, 21.53. Found: C, 50.92; H, 2.86; N, 21.66.

The described pyrolysis represents the best yield obtained. Lower or higher pyrolysis temperatures lead to decreased yields of ring-opened products. Slow decomposition of **15a** at 91 °C and passage of the gaseous product (presumably 2-furyldiazomethane) through a tube at 350 °C gave 10–15% yields of **18a** and **19a**. When **15a** was incompletely formed or not completely dry, 2-furonitrile (1–4%) was produced which was isolated by preparative gas chromatography: IR (neat), μ 4.50 (C≡N); ^{1}H NMR ($CDCl_3$) δ 6.50 (m, 1 H), 7.00 (m, 1 H), and 7.50 (m, 1 H).

Pyrolysis of Sodium 5-Methylfurfural Tosylhydrazone (15b). Pyrolysis of **15b** (1.4 g, 4.6 mmol) at 250 °C (0.3 mmHg) and condensation of the volatiles at −78 °C yielded *cis*- (**18b**) and *trans*- (**19b**) 3-hexen-5-yn-2-ones (43%) in 86:14 ratio and 5-methyl-2-furonitrile (4%).

Preparative gas chromatography gave slightly impure **18b** but which could be characterized readily: IR (neat) μ 3.05 (≡C–H), 4.81 (C≡C, weak), 6.05 (conjugated C=O), 6.35 (C=C). The ^{1}H NMR spectrum of **18b** is summarized in Table II. Pure **19b** could not be obtained by gas chromatography but its NMR spectrum (Table II) was derived from the cis/trans mixture (**18b**/**19b**).

5-Methyl-2-furonitrile was isolated by gas chromatography: IR (neat) μ 4.50 (C≡N) and 6.30 (furan C=C); ^{1}H NMR ($CDCl_3$) δ 7.01 (d, 1 H), 6.12 (d, 1 H, $J_{3,4}$ = 4 Hz), and 2.38 (s, 3 H); mass spectrum *m/e* 107 (parent).

The 2,4-dinitrophenylhydrazone of **18b**, prepared by adding 2,4-dinitrophenylhydrazine reagent to the crude pyrolysate, is a red-orange solid (from ethanol), mp 152 °C dec (lit.[18] mp 150 °C dec. Anal. Calcd for $C_{12}H_{10}N_4O_4$: C, 52.55; H, 3.68; N, 20.43. Found, C, 52.83; H, 3.65; N, 20.16.

The residue from several pyrolyses was extracted with methylene chloride and the solvent evaporated. The yellow solid (~10%) obtained upon recrystallization from methanol-water (80:20) is 5-methyl-2-furfuryl *p*-tolyl sulfone: IR (KBr) μ 6.30 (furan C=C), 7.65 and 8.70 (-SO_2-); mass spectrum *m/e* 250 (parent).

Pyrolysis of Sodium 2-Furyl Phenyl Ketone Tosylhydrazone (15c). *cis*-5-Phenyl-2-penten-4-ynal (**18c**, 22%) and *trans*-5-phenyl-2-penten-4-ynal (**19c**, 21%) are the only volatile products of pyrolysis of **15c** (1.73 g, 4.76 mmol) at 275 °C. Gas chromatography (20% SE-30, 6 ft, 200 °C, 100 mL/min) allowed isolation of **19c**: IR (neat) μ 4.60 (C≡C), 6.00 (conjugated OCH), 6.32 and 6.39 (C=C); ^{1}H NMR (see Table II). Reaction of **19c** with 2,4-dinitrophenylhydrazine gave *trans*-5-phenyl-2-penten-4-ynal 2,4-dinitrophenylhydrazone, mp 123–125 °C, mass spectrum *m/e* 336 (parent). Anal. Calcd for $C_{17}H_{12}N_4O_4$: C, 60.71; H, 3.60; N, 16.66. Found: C, 61.01; H, 3.60; N, 16.25. The ^{1}H NMR spectrum of **18c** as obtained from a mixture of **18c** and **19c** is given in Table II.

Pyrolysis of Sodium 2-Acetylfuran Tosylhydrazone (15d). Thermolysis of **15d** (1.3 g, 4.3 mmol) at 275 °C and collection of the product at −78 °C yielded 2-vinylfuran (**20**, 3.6%) and *cis*- (**18d**) and *trans*- (**19d**) 2-hexen-4-ynals (36%; 70% cis, 30% trans). Preparative gas chromatography gave **18d**: IR (neat) μ 3.05 (C≡C–H), 4.55 (C≡C), 5.95 (conjugated OCH), 6.32 (C=C); its ^{1}H NMR spectrum is in Table II. *trans*-1-Ynal **19d** could not be isolated pure but its aldehydic and acetylenic methyl ^{1}H NMR absorptions were obtained from the cis/trans mixture (Table II). 2-Vinylfuran (**20**) was identified by comparison of its gas chromatographic retention time with that of an authentic sample.

Treatment of the crude product with 2,4-dinitrophenylhydrazine reagent gave an orange-red solid which on solution in benzene and elution through neutral alumina was separated into *trans*-2-hexen-4-ynal 2,4-dinitrophenylhydrazone (mp 179 °C dec) and *cis*-2-hexen-4-ynal 2,4-dinitrophenylhydrazone (mp 154–156 °C dec). Both derivatives have essentially identical IR spectra (KBr) [μ 4.53 (C≡C, weak), 6.20 (C=N), and 6.33 (C=C)], and their mass spectra, *m/e* 274 (parent), are consistent with their assigned structures. Anal. Calcd for $C_{12}H_{10}N_4O_4$: C, 52.55; H, 3.68; N, 20.43. Found (179 °C isomer): C, 52.81; H, 3.66; N, 19.91. Found (154 °C isomer): C, 52.50; H, 3.77; N, 19.62.

Pyrolysis of Sodium Ethyl (2-Furyl) Ketone Tosylhydrazone (15e). Pyrolysis of **15e** (1.48 g, 4.37 mmol) and preparative gas chromatography of the condensate (−78 °C) gave *cis*- (**21**) and *trans*- (**22**) 1-(2-furyl)propenes (3.2%), *cis*-2-hepten-4-ynal (**18e**, 32%), and *trans*-2-hepten-4-ynal (**19e**, 15%). 1-(2-Furyl) propenes **21** and **22** were present at a 1:1 ratio and **22** was identified by its ^{1}H NMR spectrum (CCl_4): δ 7.30 (d, 1 H) and 6.15 (m, 2 H, furan ring H), 5.15 (m, 1 H), 4.50 (m, 1 H, vinyl H), and 1.87 (d, 3 H, -CH_3). *cis*-Ynal

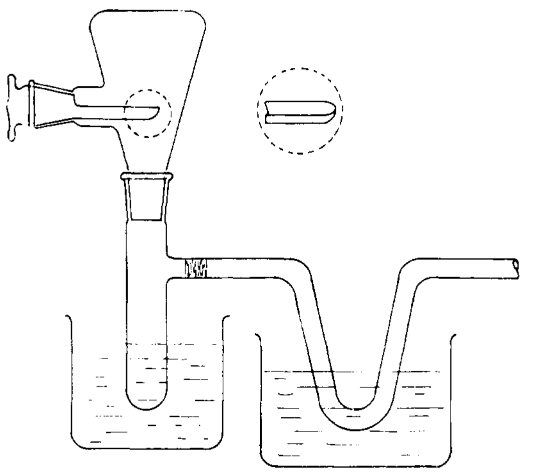

Figure 1. Apparatus for vacuum pyrolytic decomposition of salts of tosylhydrazones.

18e was converted to its 2,4-dinitrophenylhydrazone (red-orange, from 95% ethanol), mp 123–124 °C dec, mass spectrum *m/e* 288 (parent). Anal. Calcd for $C_{13}H_{12}N_4O_4$: C, 54.16; H, 4.20; N, 19.44. Found: C, 54.43; H, 4.12; N, 19.80. Identification of **19e** was based on its ^1H NMR spectrum (Table II), 2,4-dinitrophenylhydrazone, mp 171–172 °C dec, and mass spectrum, *m/e* 288 (parent). Anal. Calcd for $C_{13}H_{12}N_4O_4$: C, 54.16; H, 4.20; N, 19.44. Found: C, 54.55; H, 3.84; N, 19.38.

Pyrolysis of Sodium 5-Chlorofurfural Tosylhydrazone (15f). Small amounts of **15f** were dropped from the sample boat of Figure 1 into the pyrolysis chamber at 275 °C. In this way quantities (1.0 g, 3.1 mmol) of **15f** were decomposed without explosion. The yellow condensate darkened on warming and contained the following components in the indicated yields. (1) *cis*-Pent-2-en-4-ynoyl chloride (**18f,** 21%): IR μ 3.00 ($C\equiv C-H$), 4.75 ($-C\equiv C-$), 5.63 ($-C-Cl$), and 6.33 ($C=C$); mass spectrum *m/e* 114 (parent); ^1H NMR (Table II). (2) 5-Chloro-2-furonitrile (5%): IR μ 4.46 ($C\equiv N$); mass spectrum *m/e* 127 (parent). (3) 5-Chlorofurfural (2%): IR μ 5.90 ($C=O$); mass spectrum *m/e* 130 (parent).

Pyrolysis of Sodium 5-Carbomethoxyfurfural Tosylhydrazone (15h). Decomposition of **15h** (1.12 g, 3.2 mmol) at 280 °C (0.1 mmHg) in a cylindrical vessel provided with a side arm leading to a dry ice trap gave a brown-yellow product containing (1) methyl 3-hexen-2-one-5-ynoates (**18h, 19h**) [IR μ 3.30 ($C\equiv C-H$), 4.80 ($C\equiv C$), and 5.85 ($C=O$); mass spectrum *m/e* 138 (parent)], (2) 5-carbomethoxy-2-furonitrile [IR μ 4.5 ($C\equiv N$); mass spectrum *m/e* 151 (parent)], (3) methyl *p*-toluenesulfinate (7%), and (4) methyl *p*-tolyl sulfone (40%) [mp 86–87 °C (lit.[20] mp 88–89 °C), IR spectrum identical with that of an authentic sample].

Decomposition of Sodium Furfural Tosylhydrazone (15a) in Cyclooctane. A suspension of **15a** (1.16 g, 4.1 mmol) in cyclooctane (5.6 g, 50 mmol) was heated at 140 °C until nitrogen evolution ceased (3 min). Benzene (50 mL) was added and the mixture was filtered, evaporated, and chromatographed on silica gel with Skellysolve B to give furfurylcyclooctane (**23,** 7%): IR (neat) μ 6.25 ($C=C$) and 3.45 (strong, C-H); ^1H NMR ($CDCl_3$) δ 7.22 (m, 1 H, furan H), 6.20 (m, 1 H, furan H), 5.91 (m, 1 H, furan H), 2.45 (d, 2 H, $-CH_2-$, $J = 8$ Hz), and 1.50 (m, 15 H, cyclooctyl H). Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.36; H, 10.60.

Decomposition of Sodium Furfural Tosylhydrazone (15a) in Styrene. Dry **15a** (1.00 g, 3.50 mmol) suspended in styrene (5.5 g, 52.6 mmol) was immersed in a 140 °C bath. After nitrogen stopped being evolved (3 min), the mixture was cooled, diluted with benzene (30 mL), and filtered. The benzene was evaporated and excess styrene was removed by trap to trap (25 to 0 °C) distillation at 1 mmHg. Preparative gas chromatography of the residue on a 6-ft, 20% SE-30 column at 225 °C yielded 1-(2-furyl)-2-phenylcyclopropane (**24,** 6%): IR (neat) μ 3.25 (cyclopropyl C-H) and 6.24 ($C=C$); ^1H NMR ($CDCl_3$) δ 7.25 (m, 6 H, aromatic H and 5-furyl H), 6.27 (m, 1 H, furyl H), 6.00 (m, 1 H, furyl H), 2.25 (m, 2 H, cyclopropyl H), and 1.39 (m, 2 H, cyclopropyl H); mass spectrum *m/e* 184 (parent). Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.24; H, 6.26.

Pyrolysis of Sodium 2-Thiophenecarboxaldehyde Tosylhydrazone (25a). Column chromatography on silica gel with petroleum ether eluent of the pyrolysate of **25a** at 300 °C (0.1 mmHg) yielded *cis*- (**30a,** 8%) and *trans*- (**31a,** 20%) 1,2-di(2-thienyl)ethylenes. The properties of **30a** and **31a** follow. **30a:** IR μ 11.72, 11.92, 14.39 (broad); ^1H NMR ($CDCl_3$) δ 7.03 (m, 3 H) and 6.54 (s, 1 H); mass spectrum *m/e* (rel intensity) 192 (100) $P^{+\cdot}$. **31a:** mp 129–131 °C; IR μ 7.30, 10.58, 11.76, 12.13, 14.39 (broad); ^1H NMR (CCl_4) δ 7.20 (m) and 6.98 (s), overlapping absorption.

Further elution separated a yellow liquid (**29a,** 8% by weight, based on the crude pyrolysate). The column darkened as elution continued and it was necessary to store **29a** at −78 °C to maintain its homogeneity: IR μ 3.02 (sharp), 4.78, 6.28, 7.40, 10.23; ^1H NMR (CCl_4) δ ~6.60 (m, 2 H), 5.37 (d, 1 H, $J = 10$ Hz), 3.21 (d, 1 H, $J = 2$ Hz); mass spectrum 150 °C source and inlet, *m/e* (rel intensity) 256 (11), 224 (12), 223 (10), 192 (95), 160 (44), 128 (12), 97 (100), 96 (18), 63 (15). Anal. Calcd for $(C_5H_4S)_x$. C, 62.45; H, 4.19. Found: C, 62.31; H, 4.32.

Pyrolysis of Sodium 2-Acetylthiophene Tosylhydrazone (25b). Thermolysis of **25b** (2.0 g, 6.33 mmol) was effected at 300 °C (0.1 mmHg) and the volatiles were condensed at −78 °C. Vapor phase chromatography of the products on a 20% SE-30 Chromosorb P column (6 ft × $^1/_4$ in.) at 129 °C allowed identification of 2-vinylthiophene (**32,** 8%) by comparison of its retention time with that of an authentic sample. Column chromatography of the crude pyrolysate on silica gel-petroleum ether (200:1, adsorbent:sample) separated *cis*- (**30b**) and *trans*- (**31b**) 2,3-di(2-thienyl)-2-butenes as a mixture. Isomers **30b** and **31b** were separated by vapor phase chromatography on a 20% SE-30 Chromosorb P column (6 ft × $^1/_4$ in.). With a column temperature of 187 °C and a flow rate of 72 mL/min, the retention times of **30b** and **31b** (19%) were 5.1 and 5.8 min, respectively. The ^1H NMR of the mixture corroborated the ratio of **30b** to **31b**. Preparative vapor phase chromatography was not successful in separating **30b** and **31b**. The following properties are exhibited by **30b–31b:** IR μ 14.50 (broad); ^1H NMR (CCl_4) δ 7.00 (m, 3 H); **30b,** δ 2.20 (s, 81%); **31b,** 2.05 (s, 19%), total 1 H. Anal. Calcd for $C_{12}H_{22}S_2$: C, 65.48; H, 5.49. Found: C, 65.71; H, 5.56.

As column chromatography continued, the column darkened, presumably owing to alteration of the oligomer(s) of 2-hexen-4-yne-1-thial (**28b**). No homogeneous component was isolable. The spectral data of the crude pyrolysate provide evidence for the presence of oligomer(s) of **28b** (8% of the products based on the ^1H NMR (CCl_4): δ 1.95, 2 peaks assigned to $CH_3C\equiv C-$). Olefinic and allylic proton absorptions are camouflaged by absorptions of other components.

Pyrolysis of Sodium 5-Methyl-2-thiophenecarboxaldehyde Tosylhydrazone (25c). The crude pyrolysate of **25c** (2.0 g, 6.32 mmol, 300 °C, 1 mmHg; collected at −78 °C), on chromatography on silica gel with petroleum ether, yielded *cis*- (**30c,** 7%) and *trans*- (**31c,** 14%) 1,2-di(5-methyl-2-thienyl)ethylenes. Ethylene **30c** is a yellow oil [IR μ 12.50 (broad); ^1H NMR (CCl_4) δ 6.60 (m, 2 H), 6.37 (s, 1 H), 2.46 (s, 3 H); mass spectrum *m/e* 220 M^+] which isomerizes to **31c** in light. Ethylene **31c** is a white solid: mp 92–93 °C; IR μ 10.63, 12.50 (broad); ^1H NMR (CCl_4) δ 6.73 (s) and 6.60 (m, 3 H), 2.46 (s, 3 H). Anal. Calcd for $C_{12}H_{12}S_2$: C, 65.48; H, 5.49. Found: C, 65.69; H, 5.59.

As elution continued, the column darkened presumably owing to oligomerization (**29c**) of 3-hexen-1-yne-5-thione (**28c**). The crude pyrolysate showed evidence for the presence of **28c** and/or **29c:** IR μ 3.02 (sharp, $C\equiv C-H$ stretch), 6.25 (sharp); ^1H NMR (CCl_4) δ 3.20 (d, 1 H, $C\equiv C-H$, $J = 2$ Hz), 1.84 (s, 3 H). The olefinic protons are camouflaged by the thiophene ring protons of **30c** and **31c**. Integration of the NMR absorptions areas showed that oligomer(s) of **28c** were obtained in 8% overall yield.

Decomposition of Sodium 2-Thiophenecarboxaldehyde Tosylhydrazone (25a) in Cyclooctane. Solid **25a** (2.0 g, 6.61 mmol) was added to refluxing cyclooctane (10 g, 12.0 mmol). Decomposition was instantaneous with violent gas evolution. The mixture was cooled, filtered free of sodium *p*-toluenesulfinate, and concentrated to a brown liquid (1.05 g) which was analyzed gas chromatographically on a 20% SE-30 Chromosorb P column (6 ft × $^1/_3$ in.). With a column temperature of 222 °C and a flow rate of 50 mL/min, 2-(cyclooctylmethyl)-thiophene (**33,** retention time of 6.9 min) was collected (23% yield): IR μ 3.39, 14.39 (broad); ^1H NMR ($CDCl_3$) δ 1.53 (br s, 15 H), 2.67 (d, 2 H), 6.82 (m, 3 H). Anal. Calcd for $C_{13}H_{20}S$: C, 74.94; H, 9.68. Found: C, 75.21; H, 9.64.

Pyrolysis of Sodium 3-Furaldehyde Tosylhydrazone (34). Thermolysis of **34** (1.06 g, 3.70 mmol) at 300 °C yielded (1) brown involatiles insoluble in organic solvents, acids, and bases, and (2) a yellow pyrolysate trapped at −78 °C. Chromatography of the pyrolysate on silica gel with hexane allowed separation of *cis*- (**37**) and *trans*- (**38**) 1,2-di-(3-furyl)ethylenes (29%; **37**:**38** = 47:33).

Ethylene **37** is a yellow oil: IR (neat) μ 6.35 (weak, C=C) and 12.11 (weak, cis C=C); ^{1}H NMR ($CDCl_3$) δ 7.25 (m, 4 H, 2 and 5-furyl H), 6.29 (m, 2 H, 4-furyl H), and 6.17 (s, 2 H, vinyl H); mass spectrum *m/e* 160 (parent). Analyses were not obtained for **37** because of its slight contamination by hydrocarbon impurities.

Ethylene **38** is white: mp 136-139 °C; IR (KBr) μ 6.35 (weak, C=C) and 10.40 (strong, trans C=C); ^{1}H NMR ($CDCl_3$) δ 7.41 (m, 2 H, 2-furyl H), 7.33 (m, 2 H, 5-furyl H), 6.52 (m, 2 H, 4-furyl H), and 6.60 (s, 2 H, vinyl H); mass spectrum *m/e* 160 (parent). Anal. Calcd for $C_{10}H_8O_2$: C, 74.99; H, 5.00. Found: C, 74.87; H, 5.11.

Pyrolysis of Sodium 3-Furaldehyde Tosylhydrazone (34) in 1,1-Diphenylethylene. A suspension of **34** (0.87 g, 3.07 mmol) in 1,1-diphenylethylene (2.70 g, 15.0 mmol) was immersed in a 275 °C bath. After gas evolution ceased (1 min), the mixture was cooled, diluted with ether (50 mL), filtered to remove sodium *p*-toluenesulfinate (100%), and evaporated. Chromatography of the residue on silica gel with Skellysolve B yielded a mixture of **37** and **38** in 10% yield and then 1,1-diphenyl-2-(3-furyl)cyclopropane (**44**, 0.33 g, 43%): a clear oil; IR (neat) μ 3.29 and 3.35 (C-H), 6.24 (C=C); ^{1}H NMR ($CDCl_3$) δ 7.23 (m, 11 H), 6.96 (m, 1 H, 5-furyl H), 5.71 (m, 1 H, 4-furyl H), 2.62 (t, 1 H, J = 8 Hz, furfuryl cyclopropyl H), and 1.68 (d of d, 2 H, J = 8, J_{gem} = 1.5 Hz, geminal cyclopropyl H); mass spectrum *m/e* 260 (parent). Anal. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.15. Found: C, 87.23; H, 6.37.

Pyrolysis of Sodium 3-Thiophenecarboxaldehyde Tosylhydrazone (39). The product of pyrolysis of **39** (2.0 g, 6.60 mmol) at 300 °C (0.1 mmHg) and condensation of the volatiles at −78 °C gave *cis*- (**42**, 7%) and *trans*- (**43**, 17%), 1,2-di(3-thienyl)ethylenes upon column chromatography on silica gel with petroleum ether. Ethylene **42**, an oil which isomerizes to **43** in light, has the following properties: IR μ 11.90, 12.28, 13.32 (broad); ^{1}H NMR (CCl_4) δ 7.11 (m, 3 H), 6.43 (s, 1 H); mass spectrum *m/e* 192 $M^{+\cdot}$. Ethylene **43** is white (needles): mp 148-150 °C; IR (KBr) μ 10.41 (trans C=C), 11.05, 12.90 (broad); ^{1}H NMR (CCl_4) δ 7.28 (m, 3 H), 7.00 (s, 1 H). Anal. Calcd for $C_{10}H_8S_2$: C, 62.45; H, 4.19. Found: C, 62.65; H, 3.95.

Pyrolysis of Sodium 3-Thiophenecarboxaldehyde Tosylhydrazone (39) in Cyclooctane. Addition of **39** (2.0 g, 5.30 mmol) to refluxing cyclooctane (50 mL) results in instantaneous elution of nitrogen. The mixture was cooled, filtered, concentrated at reduced pressure, and gas chromatographically analyzed on a 20% SE-30 Chromosorb P column (6 ft × 1/4 in.). With a column temperature of 232 °C and a flow rate of 20 mL/min, 3-(cyclooctylmethyl)thiophene (**45**), a water-white liquid, was obtained (60%) with a retention time of 8.85 min: IR (neat) μ 3.39, 12.98 (broad); ^{1}H NMR (C_6D_6) δ 6.80 (m, 3 H), 2.47 (d, 2 H), 1.52 (br s, 15 H). Anal. Calcd for $C_{13}H_{20}S$: C, 74.94; H, 9.68. Found: C, 74.77; H, 9.63.

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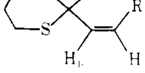

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