(3) A. Weller, *Z. Phys. Chem. (Frankfurt am Main)*, **17**, 224 (1958).
(4) J. N. Brønsted, *Z. Phys. Chem. (Leipzig)*, **102**, 169 (1922).
(5) J. N. Brønsted, *Z. Phys. Chem. (Leipzig)*, **115**, 337 (1925).
(6) C. W. Davies, *J. Chem. Soc.* 2093 (1938).
(7) E. A. Guggenheim, *Philos. Mag.*, **19**, 588 (1935).
(8) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London, 1955, Chapter 15.
(9) A. Weller, *Prog. React. Kinet.*, **1**, 187 (1961).

Formation of Isomeric Benzylidenecyclobutenones and 5-Phenylpent-2-en-4-ynals by the Gas-Phase Pyrolysis of α-Phenylfurfuryl Acetate[1]

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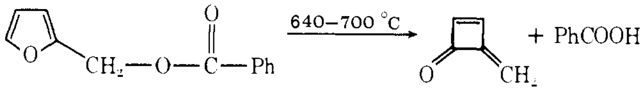
Abstract: Products of low-pressure (~10^{-4} Torr) gas-phase pyrolysis of α-phenylfurfuryl acetate at various temperatures are reported. The major oxygen-containing products, each produced in ca. 10% yield, are (*E*)- and (*Z*)-benzylidenecyclobutenones and (*E*)- and (*Z*)-5-phenylpent-2-en-4-ynals. Evidence for production of the hydrocarbons (*E*)- and (*Z*)-1-phenylbuten-3-ynes, naphthalene, and azulene is also presented. Under the pyrolysis conditions the stereoisomeric enynals are converted to the stereoisomeric cyclobutenones. The deuterium content of the four major oxygen-containing products obtained from the pyrolysis of α-phenylfurfuryl-α-d_1 acetate are reported. The d_1 species make up 54 ± 4% of the enynals and 75% of the cyclobutenones. Deuterium scrambling in the d_1-furfuryl acetate is shown to be unimportant. To account for these results a mechanistic scheme is presented which consists of both a route that involves formation of a carbene by α-elimination and a route that involves migration of the acetate group. A reversible 1,5-hydrogen shift between 5-phenylallenylketene and the (*Z*)-enynal permits species to cross from one route to the other and both sets of stereoisomeric products arise from each pathway.

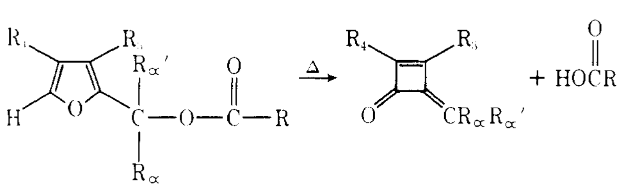
A few years ago we reported that methylenecyclobutenone (**1**) can be obtained in fair yield by the low-pressure gas-phase pyrolysis of furfuryl benzoate (**2**).[2] This is a truly remarkable transformation which makes available the previously unknown parent compound of a class of compounds that is difficult to synthesize. The only other simple member of this class of compounds that has been reported is isopropylidenecyclobutenone,[3] which was also obtained by a flash pyrolysis route, one which involved a retro-Diels–Alder reaction.



2

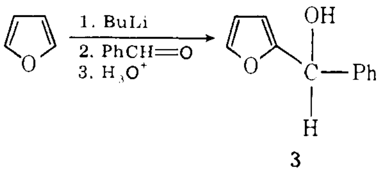
1 (40%)

The parent compound (**1**) was one of the few missing cyclobutadiene derivatives[4] and is a potentially useful synthetic intermediate since it is a cyclobutane derivative and is highly functionalized. We proposed a mechanism for the conversion of **2** to **1** based on the results of a deuterium-labeling experiment and a study of the products obtained from the pyrolysis of 5-methylfurfuryl benzoate.[2] If our mechanism is correct, the reaction should have some limitations but should be fairly general and thus allow the synthesis of a number of substituted methylenecyclobutenones. In an effort to determine the scope of this reaction and to define better its mechanism, we initiated a study of the pyrolysis of appropriately substituted furfuryl esters. α-Phenylfurfuryl acetate was selected as one of the first substituted esters to be studied because inductively the phenyl group is neither strongly electron withdrawing or electron donating and cannot lead to β-elimination reactions since it has no appropriate hydrogen atoms. Thus it was anticipated that the phenyl group should be an innocuous substituent unless it could perturb the conversion by resonance or steric interactions. The acetate was used instead of the benzoate since apparently increased steric congestion of the benzoate group resulted in a labile ester that could not be prepared and handled easily.



Results

α-Phenylfurfuryl alcohol (**3**) was prepared in high yield and purity from benzaldehyde and furfuryllithium as described by Ramanathan and Levine.[5] Alcohol **3** was converted to the benzoate by the method used for the preparation of **2**,[2] but rapid discoloration proved the ester to be labile and repeated attempts at purification were unsuccessful. The acetate (**4**) was much less reactive and could be obtained in high yield and purity by treating **3** with acetyl chloride and triethylamine in benzene.



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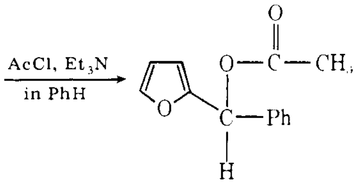

4

The low-pressure (~10^{-4} Torr) gas-phase pyrolysis of **4** at various temperatures[6] produced a yellow band of products in the cold trap at 77 K. Polymerization was observed when the amorphous solid was allowed to warm to room temperature

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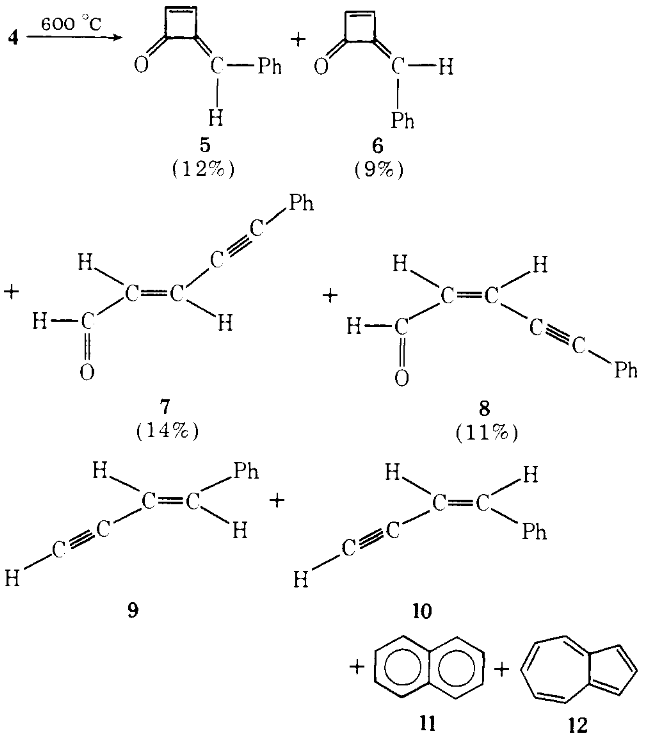
as indicated by a white, plastic-like formation on the sides of the trap. The products could only be collected by dissolving the solid in solvent. This was accomplished by solidifying the solvent at 77 K over the product band and then allowing the trap to gradually warm to room temperature. A yellow, homogenous solution resulted but polymer precipitation occurred when the solution was left at room temperature for periods greater than 0.5 h. Nonpolar solvents (i.e., benzene, carbon tetrachloride, hexane) enhanced polymer formation. Relatively polar solvents such as acetone, ethyl acetate, and chloroform retarded this phenomenon. In all cases, however, refrigeration (ca. −10°C) was required to maintain homogeneity.

Analysis of this product mixture as described below showed that the major oxygen-containing products were (*E*)- and (*Z*)-benzylidenecyclobutenones (**5** and **6**) and (*E*)- and (*Z*)-5-phenylpent-2-en-4-ynals (**7** and **8**). There were a number of other products, mostly minor ones, and evidence for the hydrocarbons (*E*)- and (*Z*)-1-phenylbuten-3-ynes (**9** and **10**), naphthalene (**11**), and azulene (**12**) was obtained. The ratio **9**:**10**:**11** is ca. 2:1:3 with the total yield being no more than 30%. Less than 1% of **12** was detected.



5 (12%) **6** (9%) **7** (14%) **8** (11%) **9** **10** **11** **12**

Initially, the product mixture was submitted to preparative thick layer chromatography (PLC) using silica gel plates. Two repetitive elutions of the pyrolysis product mixture with carbon tetrachloride afforded two bands in addition to brownish-colored deposits at the original spotting area. The IR spectrum of the upper bluish-colored band showed an intense absorption at 3320 cm^{-1} but no carbonyl absorptions. NMR analysis of this band suggested that it was a mixture and GLC analysis showed that it was composed of three major components. These three major components were collected and shown to be the three $C_{10}H_8$ isomers **9**, **10**, and **11** by NMR and IR analysis. The high-resolution mass spectrum of the PLC band showed an intense peak which corresponded to the formula of $C_{10}H_8$. It was proposed that the blue color of this mixture resulted from the presence of azulene, another $C_{10}H_8$ isomer, and this was confirmed by the visible spectrum of the mixture.

Analysis of the lower yellow PLC band showed it to be composed of **5**, **6**, **7**, and **8**. The 100-MHz NMR ($CDCl_3$) spectrum of this band showed the main features of that of the original product mixture: doublets at δ 10.02 (J = 8.0 Hz), 9.37 (J = 7.0 Hz), 8.84 (J = 3.0 Hz), and 8.47 (J = 3.0 Hz) in addition to complex upfield signals from δ 7.0 to 5.0.[7]

Separation of **5** and **6** was observed, but with substantial product loss, when the product mixture was analyzed by PLC using benzene as the eluent. When **4** was pyrolyzed at 540 °C the yields of the aldehydes **7** and **8** decreased relative to the yields of the cyclobutenones **5** and **6**, and thus the intensity of the NMR signals of **5** and **6** was increased. The assignments of these resonances to the respective protons of **5** and **6** are presented in Table I. The coupling constants and chemical shifts for the signals of the H_a and H_b protons are consistent with those reported for **1**[2] and isopropylidenecyclobutenone.[3] Double irradiation experiments enabled a pair of H_a and H_b signals to be assigned to each isomer. The lower field H_b signal was assigned to the *E* isomer on the basis that the diamagnetic anisotropy of the phenyl ring should result in a downfield shift of the H_b signal. The slightly greater yield of this isomer offers further support for this assignment since steric interactions between the phenyl group and the oxygen atom should favor formation of the *E* isomer. Assignments of the singlets at δ 6.31 and 6.00 were based on the expected lower field absorption of H_c of the *E* isomer due to the closer proximity of this proton to the deshielding region of the carbonyl group. Reports for analogous systems, including stereoisomeric alkylidenecyclobutanones, support these assignments.[2,8]

The IR spectrum of **5** and **6** showed strong absorptions at 1789 and 1774 cm^{-1}. These carbonyl bands agree well with those reported for cyclobutenone (1790 cm^{-1})[9] and 2-methylenecyclobutanone (1765 cm^{-1})[10] but are somewhat higher than those reported for isopropylidenecyclobutenone (1730 cm^{-1}, neat)[3] and 2-benzylidenecyclobutanone (1735 cm^{-1}).[11]

The aldehydes **7** and **8** were easily collected by GLC after the cyclobutenones **5** and **6** were removed by treatment of the mixture with an aqueous sodium hydroxide solution. The assignments of the NMR resonances of **7** and **8** were based upon coupling constants, decoupling experiments, and previously obtained data[12] and are presented in Table I. The IR spectra (strong absorptions at 2200[13] and 1694 cm^{-1}) and exact mass determinations were also consistent with our structural assignments. The isomer with the larger J_{bc} coupling constant was assigned the *E* stereochemistry.

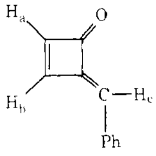
Further evidence for the production of **5**–**8** was obtained by the low-pressure (ca. 1 atm) hydrogenation of the product mixture in ethyl acetate over 5% Pd/C. The IR spectrum of the hydrogenation products showed bands at 1734 and 1788 cm^{-1} with complete disappearance of the absorptions at 3320, 2200, 1789, 1774, 1719 (acetic acid), and 1694 cm^{-1}, which were observed in the IR spectrum of the pyrolysis product mixture. The 100-MHz NMR (CCl_4) spectrum of the hydrogenated mixture exhibited only one low-field resonance at δ 9.65 (t, J = 1.5 Hz). GLC analysis showed two major products along with other minor products. These two products were collected and the compound which was eluted first gave rise to the IR band at 1734 cm^{-1} and NMR triplet at δ 9.65 while the other major product gave rise to the IR absorptions at 1788 cm^{-1}. The NMR specta and mass determinations confirmed that these compounds were 5-phenylpentanal (**13**) and 2-benzylcyclobutanone (**14**), respectively.

Yields of products **5**–**8** at various temperatures were determined by NMR analysis using an added standard and are presented in Table II.

α-Phenylfurfuryl-α-d_1 acetate (**4**-d_1) was prepared by the lithium aluminum deuteride reduction of furyl phenyl ketone[14] followed by esterification of the alcohol with acetyl chloride. Mass spectral analysis of **4**-d_1 showed a 99.7% d_1 incorporation.

Low-pressure (ca. 1 atm) hydrogenation of the pyrolysis product mixture of **4**-d_1 over 5% Pd/C in ethyl acetate afforded

Table I. NMR Spectral Data for (*E*)- and (*Z*)-Benzylidenecyclobutenones (**5**, **6**) and (*E*)- and (*Z*)-5-Phenylpent-2-en-4-ynals (**7**, **8**)[a]



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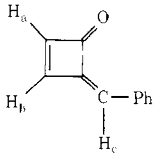

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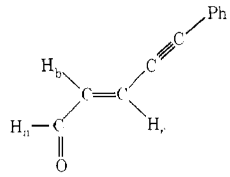

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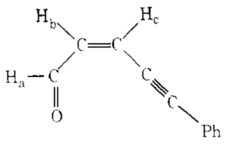


8

compd	proton	chemical shifts, δ, and coupling constants, Hz	
5			
	a	7.02	(d, 1 H, J = 3.0)
	b	8.92	(d, 1 H, J = 3.0)
	c	6.31	(s, 1 H)
	Ph	7.3	(m, 5 H)
5 (decoupled)			
	a	7.02	(irradiated)
	b	8.92	(s, 1 H)
	c	6.31	(s, 1 H)
	Ph	7.3	(m, 5 H)
6			
	a	6.81	(d, 1 H, J = 3.0)
	b	8.55	(d, 1 H, J = 3.0)
	c	6.00	(s, 1 H)
	Ph	7.3	(m, 5 H)
6 (decoupled)			
	a	6.81	(irradiated)
	b	8.55	(s, 1 H)
	c	6.00	(s, 1 H)
	Ph	7.3	(m, 5 H)
7			
	a	9.57	(d, 1 H, J_{ab} = 7.0)
	b	6.45	(d of d, 1 H, J_{bc} = 16, J_{ab} = 7.0)
	c	6.74	(d, 1 H, J_{bc} = 16)
	Ph	7.4	(m, 5 H)
7 (decoupled)			
	a	9.57	(irradiated)
	b	6.45	(d, 1 H, J_{bc} = 16)
	c	6.74	(d, 1 H, J_{bc} = 16)
	Ph	7.4	(m, 5 H)
8			
	a	10.21	(d, 1 H, J_{ab} = 8.0)
	b	6.23	(d of d, 1 H, J_{bc} = 11, J_{ab} = 8.0)
	c	6.76	(d, 1 H, J_{bc} = 11)
	Ph	7.4	(m, 5 H)
8 (decoupled)			
	a	10.21	(irradiated)
	b	6.23	(d, 1 H, J_{bc} = 11)
	c	6.76	(d, 1 H, J_{bc} = 11)
	Ph	7.4	(m, 5 H)

[a] From HA-100 NMR spectra in CCl_4.

13 and **14**, which were separated and collected by GLC. Mass spectral analysis indicated that the deuterium content of **13** was 37% d_0, 59% d_1, and 4% d_2 and that the deuterium content of **14** was 22% d_0, 75% d_1, and 3% d_2.

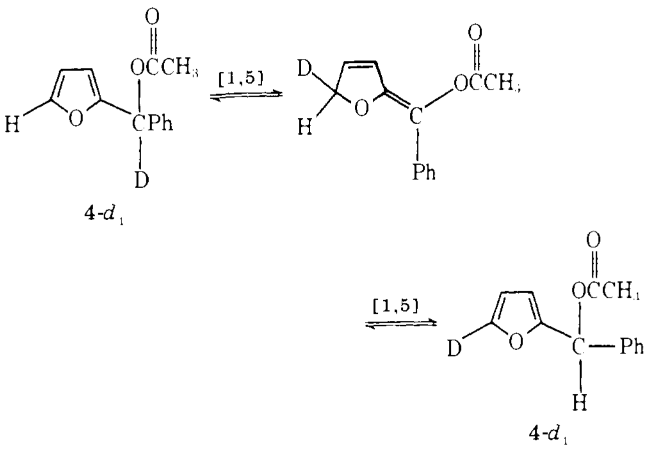
Table II. Yields of (*E*)- and (*Z*)-Benzylidenecyclobutenones (**5** and **6**) and (*E*)- and (*Z*)-5-Phenylpent-2-en-4-ynals (**7** and **8**) at Various Temperatures

compd	yields, %							
	580 °C		600 °C		620 °C		640 °C	
5	7.1	7.2	11.7	11.5	11.0	11.2	9.7	9.1
6	6.6	6.5	9.4	8.6	9.1	9.2	8.3	8.6
7	11.3	11.9	14.4	13.7	17.6	16.9	18.3	17.9
8	9.3	9.9	11.1	11.5	11.4	11.1	12.0	12.2
total yield	34.3	35.5	46.6	45.3	49.1	48.4	48.3	47.8

In another pyrolysis run of **4**-d_1, the pyrolysis products were treated with 10% sodium hydroxide solution and the aldehydes **7** and **8** were collected by GLC. Relative integration of the NMR signals of this mixture of **7** and **8** indicated that 51% deuterium had been incorporated in the aldehyde position. Analysis by mass spectrometry showed 44% d_0, 53% d_1, and 3% d_2. Thus the results of both methods of analysis are in good agreement and compare favorably with the deuterium content of **7** and **8** determined via the hydrogenated product, **13**. A similar comparison between the deuterium content of **14** and that of the benzylidenecyclobutenone isomers **5** and **6** determined directly was not made owing to the labile nature of **5** and **6** and the inability to effect a complete separation from the aldehyde isomers **7** and **8**.

Isomerization of **7** and **8** to **5** and **6** was observed by pyrolyzing a mixture of **7** and **8** under conditions similar to those used in the pyrolysis of α-phenylfurfuryl acetate (**4**). The NMR spectrum of the mixture before pyrolysis showed only two low-field resonances at δ 10.02 and 9.37. The low-field portion of the NMR spectrum of the pyrolysis products showed, in addition to the above signals, doublets at δ 8.84 (J = 3.0 Hz) and 8.47 (J = 3.0 Hz). These signals in addition to IR (CCl_4) bands at 1789 and 1774 cm^{-1} confirmed the formation of **5** and **6**. No attempt was made to perform the reverse conversion (pyrolysis of **5** and **6**) since these isomers could not be obtained in a pure state.

In order to show that no deuterium-hydrogen scrambling in **4**-d_1 was taking place during the pyrolysis, possibly by the following sequence, **4**-d_1 was pyrolyzed at 500 °C. In addition to the cyclobutenone isomers **5** and **6** and the aldehyde isomers **7** and **8**, approximately one-half of the starting ester was recovered. The product mixture was analyzed by NMR spectroscopy and no signal for a methine proton for **4** was observed. This was tested by addition of small quantities of **4** which gave rise to a singlet at δ 7.03



4-d_1

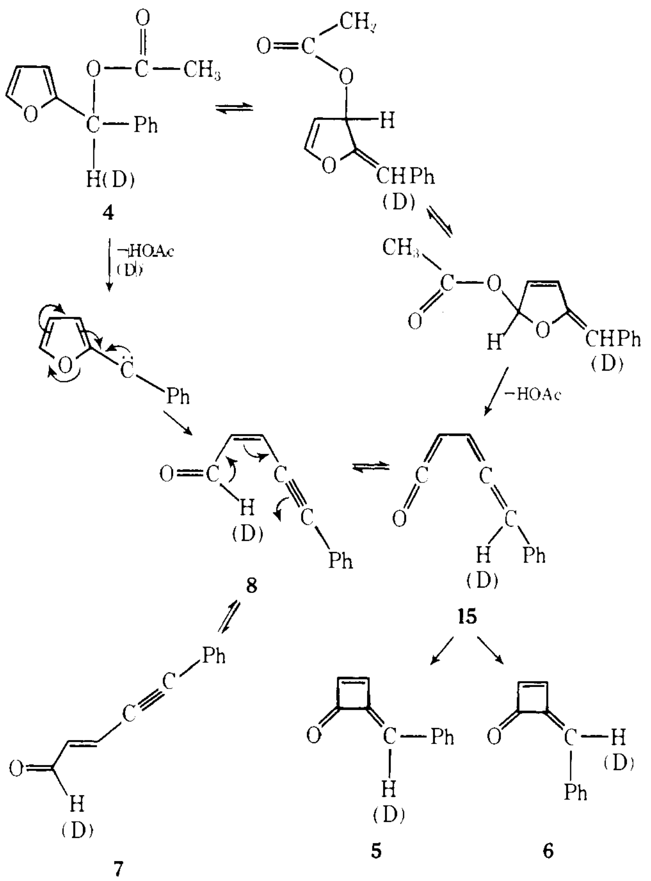
4-d_1

In order to determine if azulene (**12**) could be obtained from isomerization of naphthalene (**11**), **11** was pyrolyzed at 600 °C. Only **11** was recovered.

Discussion

Hoffman and Shechter[12] invoked a carbene mechanism to account for formation of **7** and **8** from the decomposition of diazo(2-furyl)phenylmethane at 100 °C and results which support production of carbenes from carboxylates by α-elimination have been reported.[15] We, on the basis of very good

Scheme I



evidence, advanced a migration mechanism to explain the formation of methylenecyclobutenone (**1**) from **2**.[2a] In Scheme I both of these pathways are presented for the formation of the four major products from **4**. Moreover, we established that under the pyrolysis conditions a mixture of **7** and **8** was converted to a mixture of **5**, **6**, **7**, and **8**. The thermally allowed 1,5-hydrogen shift of **8** to form the intermediate allenylketene **15**, indicated in Scheme I, reasonably accounts for this isomerization. Although we did not establish that **5** and **6** can be isomerized to **7** and **8**, if **8** undergoes a 1,5-hydrogen shift to give **15**, one would expect this process to be reversible.

This reversible 1,5-hydrogen shift opens up the possibilities that some or all of **5** and **6** could come from the carbene route and that some or all of **7** and **8** could come from the migration pathway. In order to resolve this point, the pyrolysis of the α-deuterium compound, **4**-d_1, was studied. In Scheme I the possible positions of the deuterium atom are indicated. Of major importance is that the deuterium atom is eliminated in the carbene mechanism but retained in the migration mechanism.

Both methods of analysis, direct and indirect via the hydrogenated aldehyde, of the deuterium content of **7** and **8** obtained from **4**-d_1 showed that monodeuterated species made up 54 ± 4% of the mixture. The agreement between both methods of analysis means that no deuterium-hydrogen exchange occurred during the catalytic hydrogenation. Only the indirect method of analysis could be used for **5** and **6** obtained from **4**-d_1 and this analysis showed that 75% of the mixture was composed of monodeuterated species.

Production of both d_0 and d_1 species of both sets of stereoisomeric products indicates that each set arises via both mechanistic pathways. It is conceivable that only monodeuterated **5** and **6** was produced via the migration route, and that the method of analysis resulted in deuterium-hydrogen exchange, but the lack of deuterium-hydrogen exchange during the reduction of the aldehydes **7** and **8** and the observed isomerization of **7** and **8** to **5** and **6** suggest that during the pyrolysis **8** produced from the carbene does isomerize to **15**.

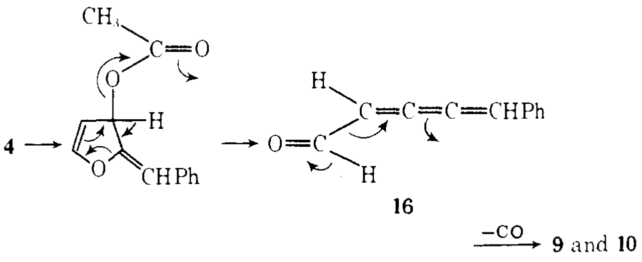
Production of both d_0 and d_1 species of both sets of stereoisomeric products would be consistent with a single mechanistic pathway if deuterium scrambling in the starting material, **4**-d_1, occurred. This possibility is untenable since it was shown that deuterium scrambling in **4**-d_1 does not occur under the pyrolysis conditions.

The aldehydes **7** and **8** constituted the major share of products produced in the pyrolysis of **4**. Although the relatively high deuterium content of **14** indicated that the migration process accounted for a major share of **5** and **6** produced, the carbene route was still operative. This is in contrast to that observed in the formation of methylenecyclobutenone (**1**) from the gas-phase pyrolysis of furfuryl benzoate (**2**) where only minor amounts of products attributable to a carbene precursor were observed.[2]

Enhancement of the carbene process over the migration process observed in this system is ascribed to the introduction of the α-phenyl substituent. It would be expected that the ground-state energy for the furfuryl acetate would be raised through steric congestion but this should increase both the rate of the first step of the migration process and that of the carbene route. However, we believe that the phenyl group would stabilize the product of the first step of the carbene process more than that of the migration pathway and thus favor the former route. The first intermediate of the migration process could be stabilized by the phenyl group as a result of conjugation of the phenyl group with the exocyclic double bond, but this conjugation would require coplanarity of the phenyl and furan rings. At best this would most likely result in a smaller energy gain than would result from interaction of the phenyl group with the carbenic center of the high-energy carbene.

The two systems also differ in that the starting ester is a benzoate in one case and an acetate in the other. The degree to which this factor is important in the mechanistic aspects of the two systems is not known and was not studied in our system owing to the inability to prepare α-phenylfurfuryl benzoate. Generally, the thermal reactions of acetates and benzoates do not differ much.[16]

No effort was made to define the pathways to the $C_{10}H_8$ isomers. A possible route to (*E*)- and (*Z*)-1-phenylbuten-3-ynes (**9** and **10**) might involve the intermediate formation of **16**. Cyclization of **10** could give rise to the naphthalene and azulene. Azulene is known to readily isomerize to naphthalene[17] and therefore could be a precursor of it, but naphthalene (**11**) is not a precursor of azulene (**12**) since only **11** was recovered when it was submitted to the pyrolysis conditions at 600 °C.



Experimental Section

Methods and Materials. Most equipment and methods,[18] including the pyrolysis apparatus[19] and generalized procedure for the gas-phase pyrolyses,[20] have been described previously. Some of the ^{1}H NMR spectra were obtained with a Bruker HX-90 spectrometer with a Nicolet 1089 computer using the Fourier Transform Mode. Infrared spectra were recorded with a Beckman 4850 high resolution spectrophotometer. Ultraviolet-visible spectra were recorded with a Cary

14 spectrophotometer. EM brand P-254 (0766) silica gel plates (20 × 20 × 0.2 cm, glass) were obtained from Brinkmann Instruments, Inc., and used for preparative thin layer chromatography (PLC). *n*-Butyllithium was obtained from Foote Chemical Co. Furoyl chloride was obtained from Aldrich Chemical Co. Lithium aluminum deuteride was obtained from Ventron Alfa Products.

α-Phenylfurfuryl alcohol (3) was prepared by the method of Ramanathan and Levine[5] in 91% yield: bp 90-94 °C (0.5 mm) [lit.[21] bp 122-125 °C (2 mm)]; IR (CCl_4) 3400 (br), 1435, 1008, 732 cm^{-1}; NMR (CCl_4) δ 7.19 (m, 6 H), 6.13 (m, 1 H), 5.88 (m, 1 H), 5.55 (s, 1 H), 3.42 (broad s, 1 H).

α-Phenylfurfuryl Acetate (4). A solution of 1.54 g (19.6 mmol) of acetyl chloride in 5.0 mL of benzene was added over a 15-min period to a stirred solution, cooled to ~5 °C, of 3.05 g (17.9 mmol) of **3** and 1.93 g (19.1 mmol) of triethylamine in 10 mL of benzene. The solution was allowed to warm to room temperature and stirred for 16 h. To the mixture was added 15 mL of water. The organic layer was separated and washed successively with one 15-mL portion of 10% hydrochloric acid, two 15-mL portions of 10% sodium hydroxide solution, and two 15-mL portions of water, dried ($MgSO_4$), and concentrated. A pale yellow liquid was obtained (3.60 g, 93% yield) which later crystallized. Recrystallization from pentane yielded pale yellow crystals: mp 64-65 °C; IR (CCl_4) 1748, 1230 cm^{-1}; NMR (CCl_4) δ 7.22 (m, 6 H), 6.80 (s, 1 H), 6.27-5.97 (m, 2 H), 1.96 (s, 3 H); exact mass 216.0782 (calcd for $C_{13}H_{12}O_3$, 216.0787).

α-Phenylfurfuryl-α-d_1-Acetate (4-d_1). To a stirred slurry of 1.05 g (0.025 mol) of lithium aluminum deuteride in 25 mL of anhydrous ether was slowly added a solution of 7.37 g (0.043 mol) of furyl phenyl ketone, prepared according to the procedure of Gilman and Hewlett,[14] in 25 mL of anhydrous ether. The mixture was heated to reflux for 4 h and a standard workup gave 7.00 g (94% yield) of a pale yellow liquid: IR (CCl_4) 3400 (br) cm^{-1}; NMR (CCl_4) δ 7.20 (m, 6 H), 6.14 (m, 1 H), 5.93 (m, 1 H), 3.93 (broad s, 1 H). Without further purification the alcohol was converted to **4**-d_1 as described previously. The pale yellow liquid which was obtained was filtered through 20 g of alumina (basic) and the alumina was washed with 50 mL of benzene. Some solvent was removed and upon refrigeration crystals formed. Recrystallization from pentane afforded 8.02 g (89% yield) of pale yellow crystals: mp 64.0-65.5 °C; IR (CCl_4) 1750, 1240 cm^{-1}; NMR (CCl_4) δ 7.28 (m, 6 H), 6.10 (m, 2 H), 2.00 (s, 3 H); exact mass 217.0846 (calcd for $C_{13}H_{11}O_3D$, 217.0849); 99.7% d_1.

Pyrolysis Procedure. Ester amounts pyrolyzed ranged from ca. 100 to 500 mg. Pyrolyses were run at temperatures from 500 to 650 °C. The sample compartment was washed with concentrated ammonium hydroxide, rinsed with distilled water, and dried at 110 °C prior to use. The pyrolysis tube and cold trap were washed with concentrated sulfuric acid, rinsed with distilled water, and dried at 110 °C prior to use. The sample compartment was heated to ca. 60 °C by the jacketed heating mantle during the pyrolysis and a pressure of ca. 1×10^{-4} Torr was maintained throughout the pyrolysis. Upon completion of the pyrolysis, nitrogen was admitted to the system. The trap was removed from the apparatus and a constant stream of nitrogen was passed through the trap while keeping it immersed in the liquid nitrogen bath. The sides of the cold trap were washed with ca. 5 mL of solvent. Upon solidification of the solvent over the product band the trap was removed from the liquid nitrogen and allowed to warm to room temperature. Upon liquefication of the solid the trap was washed with an additional 5 mL of solvent and the resulting yellow solution was transferred to a storage flask. To the solution was added ca. 1 g of sodium carbonate and after 10 min the solution was filtered and concentrated.

Product Analysis. *PLC Analysis.* The product mixture was applied to the chromatographic plate and development of the plate two times with carbon tetrachloride afforded two bands. The upper, bluish-colored band was analyzed: IR (CCl_4) 3320 cm^{-1}; 100-MHz NMR (CCl_4) δ 7.56 (signals resembling an AA′BB′ pattern), 7.25 (m), 6.95 (d, J = 16 Hz), 6.60 (d, J = 12 Hz), 6.03 (d of d, J_1 = 16, J_2 = 2.0 Hz), 5.58 (d of d, J_1 = 12, J_2 = 2.0 Hz), 3.20 (d, J = 2.0 Hz), 2.87 (d, J = 2.0 Hz). Decoupling: δ 6.95 (s, when irradiated at δ 6.03), 6.03 (d, J = 16 Hz, when irradiated at δ 2.87), 6.60 (s, when irradiated at δ 5.58), 5.58 (d, J = 12 Hz, when irradiated at δ 3.20). Integration: δ 6.95, 6.03, 2.87 (1:1:1); 6.60, 5.58, 3.20 (1:1:1). The relative intensity of the former set (δ 6.95, 6.03, 2.87) to the latter set (δ 6.60, 5.58, 3.20) was approximately 2:1. Exact mass 128.0628 (calcd for $C_{10}H_8$, 128.0626).

GLC analysis (3.7 m × 6.35 mm Al column, 5% Bentone 34, 5% diisodecyl phthalate on 60/80 Chromosorb W at 160 °C; flow rate 100 mL/min) gave three major components which were collected. **E-1-Phenylbuten-3-yne (9):** IR (CCl_4) 3320, 2110 cm^{-1} [lit.[22] IR (neat) 3279, 2105 cm^{-1}]; 100-MHz NMR (CCl_4) δ 7.26 (m, 5 H), 6.95 (d, J = 16 Hz, 1 H), 6.03 (d of d, J_1 = 16, J_2 = 2.0 Hz, 1 H), 2.87 (d, J = 2.0 Hz, 1 H) [lit.[23] 60-MHz NMR (CCl_4) δ 7.2 (m, 5 H), 6.94 (d, J = 17 Hz, 1 H), 6.00 (d of d, J_1 = 17, J_2 = 1.8 Hz, 1 H), 2.83 (d, J = 1.8 Hz, 1 H)]. **(Z)-1-Phenylbuten-3-yne (10):** IR (CCl_4) 3320, 2110 cm^{-1}; 100-MHz NMR (CCl_4) δ 7.26 (m, 5 H), 6.60 (d, J = 12 Hz, 1 H), 5.58 (d of d, J_1 = 12, J_2 = 2.0 Hz, 1 H), 3.20 (d, J = 2.0 Hz, 1 H). **Naphthalene (11):** IR (CCl_4) 3020, 1600, 865 cm^{-1}; 100-MHz NMR (CCl_4) δ 7.56 (AA′BB′ pattern). The IR and NMR spectra and GLC retention time were identical with those of an authentic sample.

In an additional experiment 300 mg of **4** was pyrolyzed at 600 °C and the products were collected in the normal manner. The product mixture was spotted to a thick layer plate and developed with benzene. The upper (R_f 0.83) band, which weighed 63 mg, was dissolved in methanol and the visible spectrum was recorded: vis (MeOH) 687, 619, 574 nm [lit.[17] vis (MeOH) azulene 697 (95), 632 (257), 579 (316)]. From the intensity of the spectrum it was calculated that ca. 0.1% azulene (**12**) was produced. By GLC analysis, the upper PLC band was shown to be composed of (E)- and (Z)-1-phenylbuten-3-ynes (**9** and **10**) and naphthalene (**11**) in the ratio of 2:1:3. This corresponds to yields of 10, 5, and 15% of **9**, **10**, and **11**, respectively.

Analysis of the lower broad yellow band gave IR (CCl_4) 2200, 1789, 1774, 1694 cm^{-1}; 100-MHz NMR ($CDCl_3$) δ 10.02 (d, J = 8.0 Hz), 9.37 (d, J = 7.0 Hz), 8.84 (d, J = 3.0 Hz), 8.47 (d, J = 3.0 Hz), 7.0-5.0 (complex m). The broad yellow band was collected, concentrated, respotted, and further developed by repetitive elutions of 10, 20, 30, 40, and 50% benzene in hexane solutions. This gave rise to a broad, yellow band and immobile, brown-colored residues. (Elution two times with either 50% benzene in hexane or 100% benzene gave similar chromatographic results for analysis of the pyrolysis products.) Analysis of the yellow band showed it to be composed of (E)- and (Z)-5-phenylpent-2-en-4-ynals (**7**, **8**): IR (CCl_4) 2820, 2735, 2200, 1694, 1612, 957, 687 cm^{-1} (lit.[13] IR 2195 cm^{-1}); 100-MHz NMR (CCl_4) δ 10.21 (d, J = 8.0 Hz), 9.57 (d, J = 7.0 Hz), 7.4 (m), 6.76 (d, J = 11 Hz), 6.74 (d, J = 16 Hz), 6.45 (d of d, J = 16, 7.0 Hz) (d, J = 16 Hz when irradiated at δ 10.21), 6.23 (d of d, J = 11, 8.0 Hz) (d, J = 11 Hz when irradiated at δ 9.57); exact mass 156.0567 (calcd for $C_{11}H_8O$, 156.0575).

GLC Analysis. A quantity of 324 mg of **4** was pyrolyzed at 600 °C in the normal manner. The products were collected in 10 mL of ethyl acetate and concentrated to ca. 0.5 mL. To the solution was added 3 mL of 10% sodium hydroxide solution. The mixture was extracted twice with 10 mL of ethyl acetate, and the organic layers were combined, dried ($MgSO_4$), and concentrated. GLC analysis (2 m × 6.35 mm Al column, 20% SE-30 on 60/80 Chromosorb P at 200 °C, flow rate 100 mL/min) showed one major component which was collected. Spectral analysis of this component was identical with that reported above for **7** and **8**.

Product Analysis of Run at 540 °C. A quantity of 200 mg of **4** was pyrolyzed at 540 °C in the normal manner and the products were collected in carbon tetrachloride. The solution was concentrated to ca. 0.5 mL and the 100-MHz NMR spectrum recorded. In addition to low-intensity signals for minor amounts of **4**, **7**, and **8** the spectrum gave rise to the following signals: δ 8.92 (d, J = 3.0 Hz) (s when irradiated at δ 7.02), 8.55 (d, J = 3.0 Hz) (s when irradiated at δ 6.81), 7.02 (d, J = 3.0 Hz), 6.81 (d, J = 3.0 Hz), 6.31 (s), 6.00 (s).

Yield Determinations. Quantities of 300 mg of **4** were pyrolyzed in duplicate runs at 580, 600, 620, and 640 °C. The products of each run were collected in ethyl acetate and the resulting solution was concentrated to ca. 0.5 mL. This solution was transferred to an NMR tube and a known mass of p-methylbenzaldehyde was added. Yields were determined by integration of the aldehydic resonance for p-methylbenzaldehyde relative to the low-field resonances for **5**, **6**, **7**, and **8**.

Catalytic Hydrogenation of the Pyrolysis Products. A 535-mg quantity of **4** was pyrolyzed at 590 °C in the normal manner. The products were collected in 10 mL of ethyl acetate. The yellow solution was hydrogenated over 5% Pd/C (10 mg) until hydrogen uptake ceased. The resulting solution was filtered and concentrated and the products were collected by GLC (2 m × 6.35 mm Al column, 20% Carbowax 20M on 60/80 Chromosorb P at 200 °C; flow rate 60 mL/min). **5-Phenylpentanal (13)** [lit.[24]] IR (CCl_4) 2820, 2720, 1734 cm^{-1}; 100-MHz NMR (CCl_4) δ 9.65 (t, J = 1.5 Hz, 1 H), 7.05 (m, 5 H), 2.7–2.2 (overlapping m, 4 H), 1.9–1.5 (m, 4 H); exact mass 162.1043 (calcd for $C_{11}H_{14}O$, 162.1045). **2-Benzylcyclobutanone (14):** IR (CCl_4) 1788 cm^{-1}; 100-MHz NMR (CCl_4) δ 7.13 (m, 5 H), 3.7–3.3 (m, 1 H), 3.2–2.5 (m, 4 H), 2.4–1.5 (m, 2 H); exact mass 160.0884 (calcd for $C_{11}H_{12}O$, 160.0888).

Pyrolysis of α-Phenylfurfuryl-α-d_1 Acetate (4-d_1). A quantity of 500 mg of 4-d_1 was pyrolyzed at 600 °C in the normal manner. The products were collected in 10 mL of ethyl acetate, catalytically hydrogenated as described above, and the reduction products were collected by GLC as described above. **5-Phenylpentanal (13):** IR (CCl_4) 1734 cm^{-1}; exact mass 162.1038 (calcd for $C_{11}H_{14}O$, 162.1045); 37% d_0; exact mass 163.1085 (calcd for $C_{11}H_{13}OD$, 163.1108); 59% d_1 (remaining, 4% d_2). Comparison of the integration of signals in the 100-MHz NMR (CCl_4) spectrum of this product showed a relative decrease in intensity at δ 9.65 (t, J = 1.5 Hz) for the aldehydic proton. **2-Benzylcyclobutanone (14):** IR (CCl_4) 1788 cm^{-1}; exact mass 160.0875 (calcd for $C_{11}H_{12}O$, 160.0888); 22% d_0; exact mass 161.0928 (calcd for $C_{11}H_{11}OD$, 161.0951); 75% d_1 (remaining, 3% d_2). Comparison of the integration of signals in the 100-MHz NMR (CCl_4) spectrum of this product showed a relative decrease in the intensity at δ 3.2–2.5 (multiplet) for the benzylic protons.

In another run 300 mg of **4**-d_1 was pyrolyzed at 600 °C in the normal manner and collected in 10 mL of ethyl acetate. The solution was treated with a 10% sodium hydroxide solution and **7** and **8** were collected by GLC as previously described. Relative integration of resonances in the 100-MHz NMR (CCl_4) spectrum indicated 51% deuterium incorporation in this product mixture. Analysis by high-resolution mass spectrometry showed 44% d_0, 53% d_1, 3.0% d_2.

Pyrolysis of (*E*)- and (*Z*)-5-Phenylpent-2-en-4-ynals 7, 8. Approximately 50 mg of a mixture of **7** and **8** was pyrolyzed at 600 °C in the normal manner. The products were collected in ca. 10 mL of acetone and the solution was concentrated: IR (CCl_4) 2200, 1789, 1774, 1694 cm^{-1}; 100-MHz NMR ($CDCl_3$) δ 10.02 (d, J = 8.0 Hz), 9.37 (d, J = 6.0 Hz), 8.84 (d, J = 3.0 Hz), 8.47 (d, J = 3.0 Hz). (Only the low-field region of the NMR spectrum was recorded).

Deuterium–Hydrogen Exchange in α-Phenylfurfuryl-α-d_1 Acetate (4-d_1). A quantity of **4**-d_1 was pyrolyzed at 500 °C in the normal manner. The products were collected in 10 mL of carbon tetrachloride. The solution was concentrated and the 100-MHz NMR spectrum recorded. The production of **5–8** was evidenced by the appearance of the previously described low-field doublets. Multiplets at δ 6.15 and 6.03 indicated the presence of **4**-d_1. The twofold expansion of the region from δ 7.15 to 5.93 gave no signal at δ 6.73 for the methine proton of α-phenylfurfuryl acetate (**4**). Upon addition of **4** a singlet appeared at δ 6.73.

Pyrolysis of Naphthalene. A quantity of 200 mg of naphthalene was pyrolyzed at 600 °C. The IR and NMR spectra of the material in the trap were identical with those of naphthalene.

Acknowledgment. We thank Professor Charles P. Casey for the suggestion that scrambling of the deuterium atom of **4**-d_1 by 1,5-hydrogen shifts might be significant under our pyrolysis conditions.

References and Notes

(1) (a) We thank the Mobil Foundation for partial support of this work. (b) Based on work by D.L.A. in partial fulfillment of the requirements for the M.S. degree at I.S.U.
(2) (a) W. S. Trahanovsky and M.-G. Park, *J. Am. Chem. Soc.*, **95**, 5412 (1973); (b) *J. Org. Chem.*, **39**, 1448 (1974).
(3) R. C. DeSelms and F. Delay, *J. Am. Chem. Soc.*, **95**, 274 (1973).
(4) M. P. Cava, "Cyclobutadiene and Related Compounds," Academic Press, New York, N.Y., 1967, pp 157–158.
(5) V. Ramanathan and R. Levine, *J. Org. Chem.*, **27**, 1216 (1961).
(6) Pyrolyses were run at temperatures ranging from 580 to 650 °C. In this range no starting ester was recovered. Incomplete conversion of the starting ester was observed at temperatures below 540 °C. At 480 °C only starting ester was recovered.
(7) Acetone, ethyl acetate, and carbon tetrachloride were also employed in the recording of NMR spectra. These solvents gave rise to slightly different chemical shifts.
(8) (a) H. A. Bampfield, P. R. Brook, and W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 132 (1975); (b) W. G. Duncan, W. Weyler, Jr., and H. W. Moore, *Tetrahedron Lett.*, 4391 (1973).
(9) J. B. Sieja, *J. Am. Chem. Soc.*, **93**, 2481 (1971).
(10) M. Mühlstädt and H. Meinhold, *J. Prakt. Chem., Ser. 4*, **37**, 162 (1968).
(11) J.-M. Conia and J.-P. Sandre, *Bull. Soc. Chim. Fr.*, **4**, 744 (1963).
(12) (a) H. Schechter private communication; (b) R. V. Hoffman and H. Schechter, *J. Am. Chem. Soc.*, **93**, 5940 (1971).
(13) T. L. Jacobs, D. Dankner, and A. R. Dankner, *J. Am. Chem. Soc.*, **80**, 864 (1958).
(14) H. Gilman and A. P. Hewlett, *Iowa State Coll. J. Sci.*, **4**, 27 (1929).
(15) R. E. Lehr and J. M. Wilson, *Chem. Commum.*, 666 (1971).
(16) G. G. Smith and F. W. Kelly, *Prog. Phys. Org. Chem.*, **8**, 75–234 (1971).
(17) M. Gordon, *Chem. Rev.*, **50**, 127 (1952).
(18) W. S. Trahanovsky and N. S. Fox, *J. Am. Chem. Soc.*, **96**, 7968 (1974).
(19) W. S. Trahanovsky, C. C. Ong, J. G. Pataky, F. L. Weitl, P. W. Mullen, J. C. Clardy, and R. S. Hansen, *J. Org. Chem.*, **36**, 3575 (1971).
(20) W. S. Trahanovsky, C. C. Ong, and J. A. Lawson, *J. Am. Chem. Soc.*, **90**, 2839 (1968).
(21) F. N. Peters, Jr., and R. Fischer, *J. Am. Chem. Soc.*, **52**, 2079 (1930).
(22) J. Lötzbeyer and K. Bodendorf, *Chem. Ber.*, **100**, 2620 (1967).
(23) J. Igeta, T. Tsuchiya, and T. Nakai, *Tetrahedron Lett.*, 2667 (1969).
(24) J. V. Braun and O. Kruber, *Chem. Ber.*, **45**, 399 (1912).

Syntheses of Trans Doubly Bridged Ethylenes.[1] (±)-C_2-Bicyclo[10.8.0]eicos-1(12)-ene and (±)-D_2-Bicyclo[8.8.0]octadec-1(10)-ene

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Abstract: Ultraviolet irradiation converted C_{2v}-bicyclo[10.8.0]eicos-1(12)-ene (**18**) and D_{2h}-bicyclo[8.8.0]octadec-1(10)-ene (**16**) into (±)-C_2-bicyclo[10.8.0]eicos-1(12)-ene (**23**) and (±)-D_2-bicyclo[8.8.0]octadec-1(10)-ene (**21**), respectively. Their chemistry was found to reflect the unusually buried and strained nature of their double bonds sandwiched between two polymethylene bridges.

On replacing two of its equivalent hydrogen atoms by a polymethylene bridge, D_{2h} symmetry inherent to ethylene molecule **1** permits the formation of three types of monocyclic compounds, **2, 3,** and **4**, each possessing approximately C_{2v}, C_{2v}, and C_s symmetry, respectively.

When the spanning carbon chain becomes smaller, the trans cycloalkene **4**[2] cannot have the achiral planar conformation **4** and is forced to have the nonplanar chiral conformations **5** or **8**, both with C_2 symmetry.[3,4] In *trans*-cyclooctene (**7**) the energy barrier between two enantiomeric conformers **7** and **10** is high enough to make its optical resolution[5,6] feasible at room temperature. Further replacing the remaining equivalent two hydrogen atoms in **2, 3,** and **6** by the second carbon chain affords the bicyclic olefins **11, 14,** and **19** illustrated in Chart III; each exhibits characteristic symmetry depending upon the relationship between *n* and *m*. Among them, the "trans"

0002-7863/79/1501-0147$01.00/0