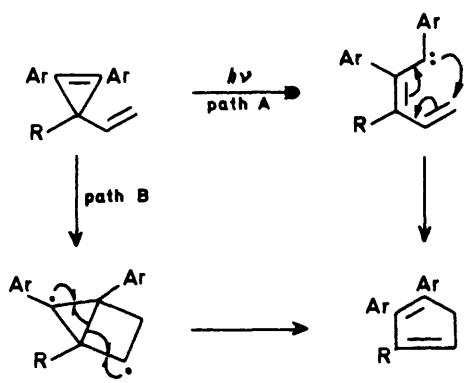
Photochemistry of Cyclopropene Derivatives. Ring-opening Reaction of 3-Heteroaryl Substituted Cyclopropenes

Ugo Chiacchio,* Anna Compagnini, Roberto Grimaldi, and Giovanni Purrello
Department of Chemistry, University of Catania, Catania, Italy
Albert Padwa *,†
Department of Chemistry, Emory University, Atlanta, Georgia 30322, U.S.A.

The photochemical rearrangement of several 3-heteroaryl substituted cyclopropenes has been studied. The rearrangements are derived from the π–π^* singlet state of the cyclopropene. Ring opening occurs to give a vinylcarbene intermediate which undergoes a subsequent electrocyclization. The transient intermediate so produced can undergo either a 1,3- or a 1,5-sigmatropic hydrogen shift to give the observed products. One strong piece of evidence for carbene intervention is the observation of a 1,3-butadiene derivative as one of the photoproducts obtained from the photolysis of a 3-pyrrolyl substituted cyclopropene. The 1,3-diene is thought to be derived by insertion of the vinylcarbene into the neighbouring methyl group. The regioselectivity of the rearrangement can be accounted for in terms of competitive 1,3- and 1,5-sigmatropic hydrogen migrations.

Small-ring hydrocarbons are particularly interesting compounds because their high energy content, relative to their acyclic isomers, often endows them with unusual reactivity patterns.[1] Cyclopropene is one of the simplest of such molecules in terms of chemical composition and at the same time perhaps the most strained of the compounds hitherto known, if strain energy is calculated per carbon atom.[2] During the past few years the chemistry of cyclopropene derivatives has attracted considerable interest, presumably as a result of the high strain energy (53 kcal/mol ‡ in the ground state[3]) associated with the unsaturated three-membered ring. The relief of ring strain combined with resonance stabilization of the corresponding ring-opened species accounts for the relatively facile ring-opening reaction of this molecule. One of the more frequently encountered photochemical reactions of 3-aryl (or 3-vinyl) substituted cyclopropenes involves rearrangement to indenes (or cyclopentadienes).[4–9] Formally analogous to the vinylcyclopropane–cyclopentene isomerization, this rearrangement can also be effected by acid,[10] transition metals,[11–13] or heat.[14] In our previous publications on the vinylcyclopropene rearrangement to cyclopentadienes, we have suggested two alternative reaction mechanisms.[6] Zimmerman and co-workers have arrived at the same two possible pathways.[7–9] These mechanisms are labelled A and B and are outlined in Scheme 1.

The carbene mechanism (path A) consists of an initial opening of the three-membered ring. Formation of the cyclopentadiene ring involves cyclization of the transient vinylcarbene. The electronically excited singlet state of the cyclopropene correlates directly with the lower lying vinylcarbene state.[15] The formation of the vinylcarbene can be viewed as the result of heterolytic cleavage and simultaneous rotation of the disubstituted methylene carbon. Both electrons occupy an in-plane σ-orbital with only two electrons in the conjugated π-orbital. The vinylcarbene species can rotate back to the diradical state[16] or undergo electrocyclization to the cyclopentadiene. The alternative ' housane ' diradical mechanism differs only in the chronology of bond formation and scission. The carbene mechanism begins with ring scission and follows with bond formation, while the ' housane ' diradical mechanism (path B) has these reversed. As had been noted earlier, gradations between these two extremes are not only possible but also likely.[6,7]



Scheme 1.

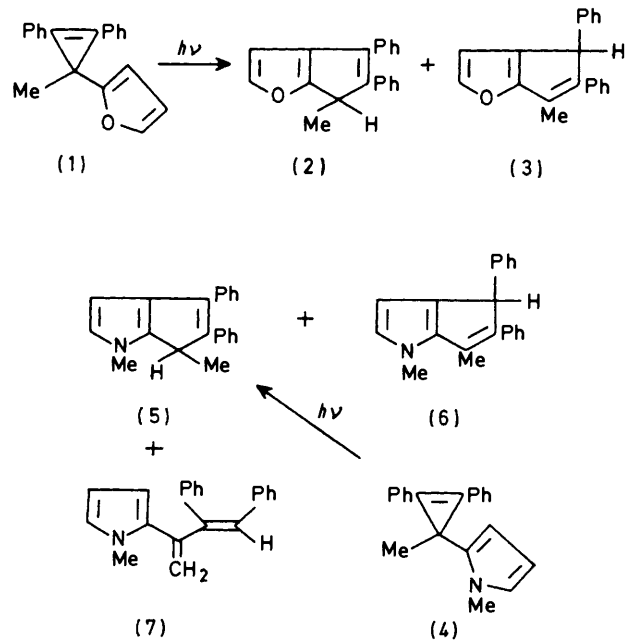
The present study began with the objective of investigating additional examples of the arylcyclopropene rearrangement where, in contrast to the previously studied cases, heterocyclic rings were attached to the 3-position of the cyclopropene ring. We report here the results of this study which show that these systems also undergo this interesting photochemical rearrangement.

Results and Discussion

Cyclopropenes possessing five-ring heteroarynes at the 3-position were prepared by treating the appropriate lithium heterocycle with 3-methyl-1,2-diphenylcyclopropenyl cation according to the general procedure of Breslow and co-workers.[17] In all cases studied, nucleophilic attack by the lithium reagent on the cyclopropenyl cation afforded the 1,2-diphenyl substituted cyclopropene as the major product. This is consistent with Breslow's previous observations in that nucleophilic attack occurs preferentially on the carbon atom of the cyclopropenyl cation which is best able to localize the positive charge.[17,18] He suggests that this is the alkyl substituted, rather than the aryl substituted, carbon. The mixture of isomers could readily be separated by silica-gel chromatography.

Direct irradiation of 3-(2-furyl)-3-methyl-1,2-diphenylcyclopropene (1) in benzene for 4 h afforded a mixture of 6-methyl-4,5-diphenyl-6*H*-cyclopenta[*b*]furan (2) (45%) and 6-methyl-4,5-diphenyl-4*H*-cyclopenta[*b*]furan (3) (40%). The

† John Simon Guggenheim Memorial Fellow, 1981—1982.
‡ 1 Cal = 4.184 J.



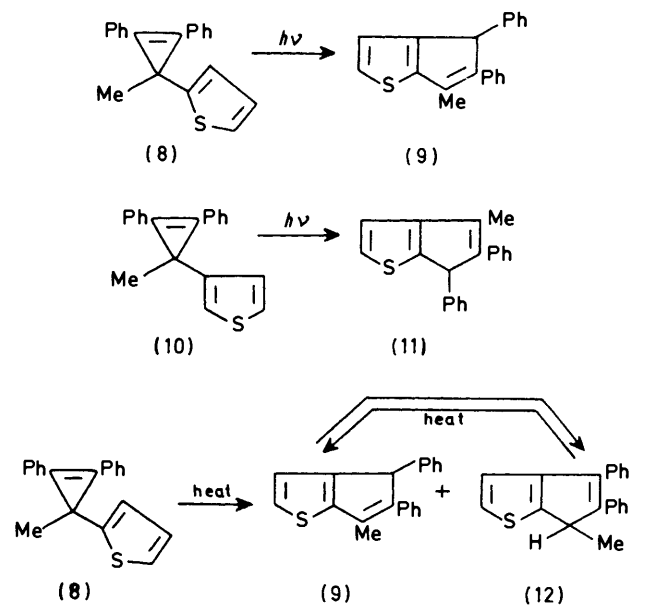
Scheme 2.

assignment of structure rests on their characteristic n.m.r., i.r., and mass spectra (see Experimental section). A study of product distribution *vs.* the extent of irradiation established that the ratio of (2) : (3) did not vary as a function of time. Appropriate control experiments established that no photoisomerization of the products was operative under the reaction conditions.

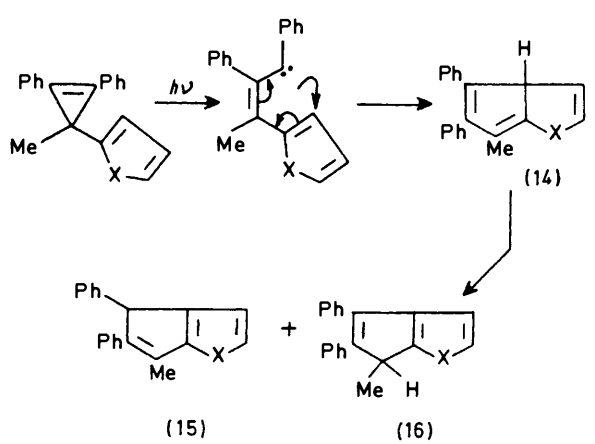
Attention was next turned to the photochemical behaviour of 3-methyl-1,2-diphenyl-3-(*N*-methylpyrrol-2-yl)cyclopropene (4). Direct irradiation in benzene led to three photoproducts. The first was 1,6-dimethyl-4,5-diphenyl-1,6-dihydrocyclopenta[*b*]pyrrole (5) (15%) [δ 1.2 (d, 3 H, *J* 8.0 Hz), 3.63 (q, 1 H, *J* 8.0 Hz), 3.7 (s, 3 H), 6.17 (d, 1 H, *J* 2.6 Hz), 6.62 (d, 1 H, *J* 2.6 Hz), and 7.1—7.5 (m, 10 H)]. The second photoproduct (6) (63%), also proved to be isomeric with the photoreactant and showed signals in the n.m.r. spectrum at δ 2.35 (d, 3 H, *J* 2.0 Hz), 3.83 (s, 3 H), 4.87 (q, 1 H, *J* 2.0 Hz), 6.02 (d, 1 H, *J* 3.0 Hz), 6.55 (d, 1 H, *J* 3.0 Hz), and 7.4—7.7 (m, 10 H). The structure of this material is assigned as 1,6-dimethyl-4,5-diphenyl-1,4-dihydrocyclopenta[*b*]pyrrole (6). A third product, (7) (10%), also proved to be isomeric with the starting material. The ^{1}H n.m.r. spectrum consisted of a methyl singlet at δ 3.66, doublets at 5.23 (1 H, *J* 1.6 Hz) and 5.48 (1 H, *J* 1.6 Hz), a set of doublets of doublets at 6.57 (1 H, *J* 2.7 and 1.8 Hz), 6.03 (1 H, *J* 3.8 and 1.8 Hz), and 6.23 (1 H, *J* 3.8 and 2.7 Hz), together with an aromatic multiplet at 6.98—7.7 (10 H). This led to the assignment of 3-(*N*-methylpyrrol-2-yl)-1,2-diphenylbuta-1,3-diene (7) as the structure of the third photoproduct. This photochemistry is summarized in Scheme 2.

We have also studied the photochemistry of the closely related 3-(2-thienyl) substituted cyclopropene system (8). Direct irradiation of (8) in benzene with Pyrex-filtered light afforded 6-methyl-4,5-diphenyl-4*H*-cyclopenta[*b*]thiophen (9) (93%), m.p. 83—84 °C, as the exclusive photoproduct.

One additional system which was also investigated involved the photochemistry of 3-methyl-1,2-diphenyl-3-(3-thienyl)-cyclopropene (10). Irradiation of (10) with Pyrex-filtered light afforded 4-methyl-5,6-diphenyl-6*H*-cyclopenta[*b*]thiophen (11) as the exclusive photoproduct (90%), m.p. 80—



Scheme 3.



Scheme 4.

81 °C; δ($CDCl_3$; 60 MHz) 2.35 (d, 3 H, *J* −2.0 Hz), 4.86 (m, 1 H), and 6.85—7.40 (m, 10 H).

We have also carried out a study on the photobehaviour of the structurally related 3-(3-furyl)-3-methyl-1,2-diphenylcyclopropene. We anticipated that this compound would rearrange in a fashion analogous to that encountered with thiophen (8). However, close examination of the crude photolysate showed that a complex mixture of products had been formed. All our efforts to isolate a characterizable

product from the crude reaction mixture failed and further work with this system was abandoned.

Attention was next turned to the thermal behaviour of these systems. In contrast to the direct photolysis, thermolysis of (8) afforded a mixture of two products which were identified as cyclopenta[*b*]thiophens (9) and (12) (Scheme 3). Similarly, heating a sample of compound (10) afforded a mixture of (11) and (13). One additional point worth noting is that thiophens (9) and (12) [as well as (11) and (13)] are readily interconverted under the reaction conditions employed.

We consider that the most economical explanation to rationalize the observed photochemical rearrangement is that illustrated in Scheme 4. The electronically excited singlet state of the cyclopropene undergoes fission of the three-membered ring to give a vinylcarbene which is subsequently converted into compound (14) by means of an electrocyclic ring closure. Intermediate (14) can either undergo a 1,3- or a 1,5-sigmatropic hydrogen shift to give the observed products. One strong piece of evidence for carbene intervention is the observation of butadiene (7) as one of the photoproducts derived from cyclopropene (4). This diene is derived by insertion of the vinylcarbene into the neighbouring methyl group.

Turning now to the matter of the regioselectivity of rearrangement, we note that the irradiation of the 3-thienyl substituted cyclopropenes (8) and (10) affords a single product, while the photolysis of the closely related oxygen (1) and nitrogen heterocycles (4) produces a mixture of products. Moreover, the resulting mixture of photoproducts is not interconverted under the photolytic conditions employed. The product-determining step involves hydrogen migration from the initially cyclized intermediate (14). Photoproduct (15) is formed from (14) by a concerted suprafacial 1,5-hydrogen migration which is symmetry-allowed when it occurs between two neighbouring carbon atoms with coefficients of the same sign in the highest occupied molecular orbital. One possible explanation to account for the difference in product distribution is that the thermal 1,5-sigmatropic hydrogen shift is extremely rapid for the case where X = S. This in turn is probably related to the greater aromaticity of thiophen when compared to furan or pyrrole.[19] It is tempting to suggest that intermediate (14) is long lived enough when X = O or NCH_3 to absorb a photon of light and undergo a photochemically allowed 1,3-hydrogen shift to give (16). This is less likely to occur with the corresponding thiophen system. Clearly, further work will be necessary to establish this point.

Experimental

Preparation of 3-(2-*Furyl*)-3-*methyl*-1,2-*diphenylcyclopropene* (1).—To a stirred suspension containing 1-methyl-2,3-diphenylcyclopropenylium perchlorate (5g) in anhydrous tetrahydrofuran (50 ml) at −78 °C under nitrogen was added a solution containing 4.8×10^{-2} mol of 2-furyl-lithium in a tetrahydrofuran–hexane solution. The reaction mixture was stirred for 1 h at −78 °C and was then allowed to warm to room temperature and was stirred for 14 h. The solution was quenched with a saturated ammonium chloride solution and the organic layer was taken up in ether, washed with water, and dried ($MgSO_4$). Removal of the solvent under reduced pressure left 3 g of a yellow oil which was chromatographed on a 1.5 × 100-cm column of silica gel, using hexane as the eluant. The first component isolated contained a white solid (2.1 g, 42%), m.p. 98—100 °C, which was identified as 3-(2-furyl)-3-methyl-1,2-diphenylcyclopropene (1) on the basis of its spectral properties: i.r. ($\lambda_{max.}$) (KBr) 3.36, 3.40, 3.48, 5.45, 6.30, 6.60, 6.66, 6.92, 7.30, 7.60, 8.60, 9.30, 9.90, 10.6, 11.20, 12.5, 13.2, 13.40, 14.05, and 14.40 μm; $\lambda_{max.}$ (95% ethanol) 236 (ε 24 900), 300sh (23 465), 313 (28 400), and 329 nm (20 900); δ($CDCl_3$; 60 MHz) 1.83 (s, 3 H), 6.13 (dd, 1 H, *J* 3.5 and 0.8 Hz), 6.4 (dd, 1 H, *J* 3.5 and 1.8 Hz), and 7.1—7.9 (m, 11 H); *m/e* 272 (M^+, base), 257, 243, 229, 228, 165, 152, 115, and 77 (Found: C, 88.2; H, 5.85. Calc. for $C_{20}H_{16}O$: C, 88.23; H, 5.88%).

Direct Irradiation of 3-(2-*Furyl*)-3-*methyl*-1,2-*diphenylcyclopropene* (1).—A solution containing (1) (200 mg) in benzene (300 ml) was irradiated under argon with a 450-W Hanovia mercury lamp equipped with a Pyrex filter sleeve for 4 h. Removal of the solvent under reduced pressure left a dark yellow oil which was subjected to preparative h.p.l.c. using a 2% chloroform–hexane mixture as the eluant. The first component isolated from the column contained a clear oil (80 mg, 40%) whose structure was assigned as 6-methyl-4,5-diphenyl-6*H*-cyclopenta[*b*]furan (2) on the basis of its spectral properties: i.r. ($\lambda_{max.}$) (neat) 3.22, 3.24, 3.26, 3.35, 3.42, 3.50, 6.3, 6.69, 6.8, 6.9, 7.3, 7.5, 7.9, 8.1, 8.80, 9.2, 9.7, 11.0, 11.1, 11.3, 12.15, 13.0, 13.50, and 14.2 μm; $\lambda_{max.}$ (95% ethanol) 320 (ε 5 600) and 254 nm (ε 21 250); δ($CDCl_3$; 60 MHz) 1.3 (d, 3 H, *J* 8.0 Hz), 3.96 (q, 1 H, *J* 8.0 Hz), 6.66 (d, 1 H, *J* 2 Hz), and 7.1—7.76 (m, 11 H); *m/e* 272 (M^+, base), 178, and 77. This material did not analyse well as a result of its rapid decomposition.

The second fraction isolated from the column contained a white solid (76 mg, 38%), m.p. 83—85 °C, whose structure was assigned as 6-methyl-4,5-diphenyl-4*H*-cyclopenta[*b*]furan (3) on the basis of its spectral properties: i.r. ($\lambda_{max.}$) (KBr) 3.3, 3.4, 3.5, 6.3, 6.88, 7.02, 7.20, 8.4, 9.10, 9.90, 11.10, 13.0, 13.4, 13.8, 14.3, and 14.5 μm; $\lambda_{max.}$ (95% ethanol) 330 (ε 14 325) and 232 nm (ε 9 870); δ($CDCl_3$; 60 MHz) 2.3 (d, 3 H, *J* 2.0 Hz), 4.72 (m, 1 H), 6.50 (d, 1 H, *J* 2.0 Hz), and 7.1—7.6 (m, 11 H); *m/e* 272 (M^+, base), 273, 178, and 77 (Found: C, 88.15; H, 5.85. Calc. for $C_{20}H_{16}O$: C, 88.23; H, 5.88%).

Preparation of 3-*Methyl*-3-(N-*methylpyrrol*-2-*yl*)-1,2-*diphenylcyclopropene* (4).—To a stirred suspension containing 1-methyl-2,3-diphenylcyclopropenylium perchlorate (5 g) in anhydrous tetrahydrofuran (100 ml) at −78 °C under nitrogen was added a solution containing 4.8×10^{-2} mol of *N*-methylpyrrol-2-yl-lithium. The reaction mixture was stirred for 1 h at −78 °C and was then allowed to warm to room temperature and was stirred for 14 h. The solution was quenched with a saturated ammonium chloride solution and the organic layer was taken up in ether, washed with water and dried ($MgSO_4$). Removal of the solvent under reduced pressure left a yellow oil (3.5 g) which was chromatographed on a 1.5 × 100-cm column of silica gel using hexane as the eluant. The principal component isolated contained a clear oil (2.66 g, 53%) which was identified as 3-methyl-3-(*N*-methylpyrrol-2-yl)-1,2-diphenylcyclopropene (4) on the basis of its spectral properties: i.r. ($\lambda_{max.}$) (KBr) 3.22, 3.24, 3.26, 3.32, 3.41, 3.52, 5.5, 6.25, 6.7, 6.9, 7.0, 7.2, 7.7, 8.2, 9.1, 9.3, 9.7, 11.0, 13.10, 14.0, and 14.25 μm; $\lambda_{max.}$ (95% ethanol) 230 (ε 32 210), 260 (ε 7 800), 301sh (ε 26 400), and 314 (ε 29 755); δ($CDCl_3$; 60 MHz) 1.80 (s, 3 H), 3.43 (s, 3 H), ABX system: part X centred at δ 6.4, AB part respectively at 6.1 and 6.22 (J_{AB} 3.8; J_{AX} 1.8; J_{BX} 2.2 Hz), and 7.2—7.8 (m, 10 H); *m/e* 285 (M^+, base), 284, 270, 208, and 77 (Found: C, 88.4; H, 6.7; N, 4.9. Calc. for $C_{21}H_{19}N$: C, 88.42; H, 6.66; N, 4.91%).

Direct Irradiation of the Cyclopropene (4).—A sample containing (4) (300 mg) in benzene (300 ml) was irradiated under argon with a 450-W Hanovia mercury lamp equipped with a Pyrex filter sleeve for 4 h. Removal of the solvent under reduced pressure left a dark yellow oil whose n.m.r. spectrum indicated the presence of three products. The mixture was subjected to preparative h.p.l.c. using 3% chloro-

form–hexane as the eluant. The first component isolated from the column contained a clear oil (30 mg, 10%) whose structure was assigned as 3-(*N*-methylpyrrol-2-yl)-1,2-diphenylbuta-1,3-diene (7) on the basis of its n.m.r. and mass spectra: δ($CDCl_3$, 60 MHz) 3.66 (s, 3 H), 5.23 (d, 1 H, *J* 1.6 Hz), 5.48 (d, 1 H, *J* 1.6 Hz), ABX system: part X centred at δ 6.57, AB part respectively at 6.03 and 6.23 (J_{AB} 3.8; J_{AX} 1.8; J_{BX} 2.7 Hz), and 6.98—7.7 (m, 10 H); *m/e* 285 (M^+, base), 208, 178, 91, 81, and 77.

The second component isolated from the chromatography column contained a clear oil (45 mg, 15%) whose structure was assigned as 1,6-dimethyl-4,5-diphenyl-1,6-dihydrocyclopenta[*b*]pyrrole (5) on the basis of its spectral properties: i.r. ($\lambda_{max.}$) (neat) 2.4, 3.26, 3.30, 3.44, 6.25, 6.65, 6.9, 7.2, 7.42, 8.02, 9.18, 9.32, 10.8, 11.6, 12.2, 13.0, 13.4, and 14.2 μm; δ($CDCl_3$; 60 MHz) 1.2 (d, 3 H, *J* 8 Hz), 3.63 (q, 1 H, *J* 8 Hz), 3.7 (s, 3 H), 6.17 (d, 1 H, *J* 2.6 Hz), 6.62 (d, 1 H, *J* 2.6 Hz), and 7.1—7.5 (m, 10 H); *m/e* 285 (M^+, base), 284, 270, 91, and 77.

The third component isolated from the chromatography column contained a clear oil (189 mg, 63%) whose structure was assigned as 1,6-dimethyl-4,5-diphenyl-1,4-dihydrocyclopenta[*b*]pyrrole (6) on the basis of its spectral properties: $\nu_{max.}$ (neat 3.22, 3.24, 3.26, 3.40, 3.48, 6.255, 6.7, 6.90, 5.94, 7.2, 7.4, 8.01, 8.6, 9.1, 9.3, 9.6, 10.8, 11.6, 12.1, 13, 13.5, and 14.0 μm; $\lambda_{max.}$ (95% ethanol) 238 (ε 16 560), 290 (ε 12 000), and 322 nm (ε 9 870); δ($CDCl_3$; 60 MHz) 2.35 (d, 3 H, *J* 2 Hz), 3.83 (s, 3 H), 4.87 (m, 1 H), 6.02 (d, 1 H, *J* 3 Hz), 6.55 (d, 1 H, *J* 3 Hz), and 7—7.4 (m, 10 H); *m/e* 285 (M^+, base), 284, 270, 91, and 77. The ready decomposition of the above compounds made it impossible to obtain an elemental analysis.

Preparation of 3-*Methyl*-1,2-*diphenyl*-3-(2-*thienyl*)*cyclopropene* (8).—To a stirred suspension containing 1-methyl-2,3-diphenylcyclopropenylium perchlorate (5 g) in anhydrous tetrahydrofuran (100 ml) at −78 °C under nitrogen was added a solution containing 4.8×10^{-2} mol of 2-thienyllithium. The reaction mixture was stirred for 1 h at −78 °C, and was then allowed to warm to room temperature and stirred for 16 h. The reaction was quenched with a saturated ammonium chloride solution and the organic layer was taken up in ether, washed with water and dried ($MgSO_4$). Removal of the solvent under reduced pressure left a yellow oil (4.5 g) which was chromatographed on a 1.5 × 100-cm column of silica gel using hexane as the eluant. The first component isolated contained a white solid, (4 g, 75%), m.p. 87—88 °C, which was identified as 3-methyl-1,2-diphenyl-3-(2-thienyl)-cyclopropene (8) on the basis of its spectral properties: i.r. ($\lambda_{max.}$) (KBr) 3.22, 3.24, 3.26, 3.3, 3.34, 3.38, 3.42, 3.51, 5.5, 6.25, 6.6, 6.7, 6.9, 6.94, 7.2, 8.0, 9.2, 9.6, 10.8, 11.02, 11.7, 11.9, 12.0, 13.2, 13.4, 13.6, 14.0, 14.02, 14.2, 14.4, and 14.6 μm; $\lambda_{max.}$ (95% ethanol) 228 (ε 24 250), 300sh (ε 24 074), 311 (ε 29 629), and 330 nm (ε 22 777); δ($CDCl_3$; 60 MHz) 1.96 (s, 3 H), 6.86—7.03 (m, 3 H), and 7.3—7.83 (m, 10 H); *m/e* 288 (M^+, base), 273, 239, 211, 197, 178, 165, and 77 (Found: C, 83.3; H, 5.5; S, 11.1. Calc. for $C_{20}H_{16}S$: C, 83.33; H, 5.55; S, 11.11%).

Direct Irradiation of the Cyclopropene (8).—A solution containing (8) (200 mg) in benzene (300 ml) was irradiated under argon with a 450-W Hanovia mercury lamp equipped with a Pyrex filter sleeve for 4 h. Removal of the solvent under reduced pressure left a pale yellow oil which was subjected to preparative h.p.l.c. using a 3% chloroform–hexane mixture as the eluant. The product isolated from the column contained a white solid (186 mg, 93%), m.p. 83—84 °C, whose structure was assigned as 6-methyl-4,5-diphenyl-4*H*-cyclopenta[*b*]-thiophen (9) on the basis of its spectral properties: i.r. ($\lambda_{max.}$) (KBr) 3.2, 3.24, 3.26, 3.38, 3.41, 3.5, 6.25, 6.6, 6.85, 6.94, 7.2, 9.18, 9.30, 10.8, 11.3, 11.65, 11.90, 12.3, 13.0, 13.2, 13.6, 14.2, 14.3, and 15.0 μm; $\lambda_{max.}$ (95% ethanol) 238 (ε 10 025) and 320 nm (ε 14 290); δ($CDCl_3$; 60 MHz) 2.38 (d, 3 H, *J* 2.0 Hz), 4.93 (m, 1 H), and 6.93—7.56 (m, 12 H); *m/e* 288 (M^+, base), 273, 271, 211, 197, and 77 (Found: C, 83.3; H, 5.55; S, 11.1. Calc. for $C_{20}H_{16}S$: C, 83.33; H, 5.55; S, 11.11%).

Thermolysis of the Cyclopropene (8).—A sample of (8) (200 mg) was placed in a Pyrex tube and degassed at 10^{-4} mmHg, sealed, and was then heated for 30 min at 190—200 °C. After cooling, the tube was opened and the pale yellow oil was subjected to preparative h.p.l.c. using 3% chloroform–hexane as the eluant. The first component isolated from the column contained a clear oil (66 mg, 33%) whose structure was assigned as 6-methyl-4,5-diphenyl-6*H*-cyclopenta[*b*]-thiophen (12) on the basis of its spectral properties: i.r. ($\lambda_{max.}$) (neat) 3.24, 3.26, 3.28, 3.3, 3.44, 3.46, 3.5, 3.58, 6.22, 6.25, 5.58, 6.9, 6.93, 7.2, 7.3, 8.5, 9.1, 9.32, 9.62, 9.3, 10.7, 11.15, 12, 12.7, 12.9, 13.4, 13.8, 14.0, 14.5, 15, and 15.75 μm; $\lambda_{max.}$ (95% ethanol) 238 (ε 20 960) and 325 nm (ε 7 410); δ($CDCl_3$; 60 MHz) 1.4 (d, 3 H, *J* 8 Hz), 4.13 (q, 1 H, *J* 8 Hz), and 6.93—7.7 (m, 12 H); *m/e* 288 (M^+, base), 273, 239, 211, 178, and 77 (Found: C, 83.35; H, 5.55; S, 11.1. Calc. for $C_{20}H_{16}S$: C, 83.33; H, 5.55; S, 11.11%).

The second fraction isolated from the column contained compound (9) (100 mg, 50%) which was identical with an authentic sample obtained from the direct irradiation of (8).

Preparation of 3-*Methyl*-1,2-*diphenyl*-3-(3-*thienyl*)*cyclopropene* (10).—To a stirred solution containing 3-thienyl-lithium (4.8×10^{-2} mol) at −78 °C under nitrogen was slowly added 1-methyl-2,3-diphenylcyclopropenylium perchlorate (5 g). The reaction mixture was stirred for 20 h at −78 °C and was then allowed to warm to room temperature and was stirred for 4 h. The solution was quenched with a saturated ammonium chloride solution and the organic layer was taken up in ether, washed with water, and dried ($MgSO_4$). Removal of the solvent under reduced pressure left a yellow oil (2.1 g) which was chromatographed on a silica-gel column using hexane as the eluant. The first component isolated contained a solid (0.95 g, 18%) which was identified as 3-methyl-1,2-diphenyl-3-(3-thienyl)cyclopropene (10), m.p. 65—67 °C, on the basis of its spectral properties: i.r. ($\lambda_{max.}$) (KBr) 3.27, 3.3, 3.38, 3.41, 5.43, 6.25, 5.55, 6.89, 7.25, 7.46, 7.81, 11.63, 12.98, and 14.29 μm; $\lambda_{max.}$ (95% ethanol) 238 (ε 15 200), 280 (ε 16 340), 312 (ε 18 190), and 328 nm (ε 14 400); δ($CDCl_3$; 60 MHz) 2.46 (s, 3 H) and 6.9—7.8 (m, 13 H); *m/e* 288 (M^+, base), 274, 211, 197, 178, 165, and 77 (Found: C, 83.3; H, 5.5; S, 11.1. Calc. for $C_{20}H_{16}S$: C, 83.33; H, 5.55; S, 11.11%).

The second component isolated from the chromatography column contained a white solid (95 mg, 29%), m.p. 77—79 °C, which was identified as 2-methyl-1,3-diphenyl-3-(3-thienyl)-cyclopropene on the basis of its spectral properties: i.r. ($\lambda_{max.}$) (KBr) 3.22, 3.25, 3.26, 3.3, 3.41, 5.40, 6.25, 6.75, 6.89, 7.87, 9.25, 10.87, 11.97, 12.98, 14.08, and 14.28 μm; $\lambda_{max.}$ (95% ethanol) 254 nm (ε 14 000); δ($CDCl_3$; 60 MHz) 2.46 (s, 3 H) and 6.9—7.8 (m, 13 H); *m/e* 288 (M^+, base), 274, 211, 197, 178, 165, 136, and 77 (Found: C, 83.3; H, 5.55; S, 11.1. Calc. for $C_{20}H_{16}S$: C, 83.33; H, 5.55; S. 11.11%).

Direct Irradiation of the 3-(3-*Thienyl*)*cyclopropene* (10).—A solution containing (10) (200 mg) in benzene (300 ml) was irradiated under argon with a 450-W Hanovia lamp equipped with a Pyrex filter sleeve for 12 h. Removal of the solvent under reduced pressure left a yellow oil which was subjected to preparative h.p.l.c. using 2% chloroform–hexane as the

eluant. The product isolated from the column contained a white solid (180 mg, 90%), m.p. 79—81 °C, whose structure was assigned as 4-methyl-5,6-diphenyl-6*H*-cyclopenta[*b*]-thiophen (11) on the basis of its spectral properties: i.r. ($\lambda_{max.}$) (KBr) 3.21, 3.25, 6.25, 6.66, 6.89, 7.24, 9.17, 10.86, 11.62, 12.34, 12.98, 13.51, 14.28, and 14.92 μm; $\lambda_{max.}$ (95% ethanol) 235 (ε 10 500) and 320 nm (ε 13 700); δ($CDCl_3$; 60 MHz) 2.35 (d, 3 H, *J* 2.0 Hz), 4.86 (m, 1 H), and 6.85—7.4 (m, 12 H); *m/e* 288 (M^+, base), 273, 239, 211, 197, 91, and 77 (Found: C, 83.3; H, 5.55; S, 11.1. Calc. for $C_{20}H_{16}S$: C, 83.33; H, 5.55; S, 11.11%).

Thermolysis of the 3-(3-*Thienyl*)*cyclopropene* (10).—A sample containing (10) (200 mg) was placed in a Pyrex tube and was degassed at 10^{-4} mmHg, sealed and then heated for 30 min at 190—200 °C. After cooling, the tube was opened and the pale yellow oil was subjected to preparative column h.p.l.c. using 2% chloroform–hexane as the eluant. The first component isolated from the column contained a white solid, m.p. 89—91 °C (66 mg), whose structure was assigned as 4-methyl-5,6-diphenyl-4*H*-cyclopenta[*b*]thiophen (13) on the basis of its spectral properties: i.r. ($\lambda_{max.}$) (KBr) 32.47, 32.68, 33.67, 33.73, 34.84, 6.25, 66.66, 68.49, 69.44, 9.29, 11.43, 12.05, 12.66, 12.85, 13.33, 14.18, 14.92, and 15.62 μm; $\lambda_{max.}$ (ethanol 95%) 233 (ε 7 900) and 325 μm (ε 20 850); δ($CDCl_3$; 60 MHz) 1.23 (d, 3 H, *J* 8 Hz), 4.13 (q, 1 H, *J* 8 Hz), and 7.1—7.65 (m, 12 H); *m/e* (M^+, base) 288, 273, 271, 212, 91, 84, and 77 (Found: C, 83.3; H, 5.55; S, 11.1. Calc. for $C_{20}H_{16}S$: C, 83.33; H, 5.55, S, 11.11%).

The second fraction isolated from the column contained (11) (89.6 mg, 45%) which was identical with an authentic sample obtained by direct irradiation of (10).

Preparation of 3-(3-*Furyl*)-3-*methyl*-1,2-*diphenylcyclopropene*.—To a stirred solution containing 3-furyl-lithium (4.8×10^{-2} mol) at −78 °C under nitrogen was slowly added 1-methyl-2,3-diphenylcyclopropenylium perchlorate (5 g). The reaction was stirred for 20 h at −78 °C and was then allowed to warm to room temperature and was stirred for 4 h. The solution was quenched with a saturated ammonium chloride solution and the organic layer was taken up in ether, washed with water and dried ($MgSO_4$). Removal of the solvent under reduced pressure left a yellow oil (3.05 g) which was chromatographed on a silica-gel column using hexane as the eluant. The first component isolated contained a solid (1.5 g, 28%), m.p. 59—61 °C, which was identified as 3-(3-furyl)-3-methyl-1,2-diphenylcyclopropene on the basis of its spectral properties: i.r. ($\lambda_{max.}$) (KBr) 3.24, 3.26, 3.3, 3.37, 3.42, 3.495, 5.49, 6.25, 6.62, 6.7, 6.89, 8.69, 9.25, 9.52, 10.31, 11.9, 13.1, 13.51, and 14.28 μm; $\lambda_{max.}$ (95% ethanol) 238 (ε 21 130), 298sh (ε 20 000), and 312 nm (ε 25 280); δ($CDCl_3$; 60 MHz) 1.86 (s, 3 H), 6.41 (d, 1 H, *J* 1.8), and 7.25—7.8 (m, 12 H); *m/e* 272 (M^+, base), 257, 243, 229, 228, 175, and 77 (Found: C, 88.2; H, 5.85. Calc. for $C_{20}H_{16}O$: C, 88.23; H, 5.88%).

The second component isolated from the chromatography column contained a white solid (0.15 g, 3%), m.p. 94—95 °C, which was identified as 3-(3-furyl)-2-methyl-1,3-diphenylcyclopropene on the basis of its spectral properties: i.r. ($\lambda_{max.}$) (KBr) 3.22, 3.24, 3.27, 3.3, 5.34, 6.23, 6.62, 6.66, 6.90, 8.4, 8.69, 9.4, 10.2, 10.92, 11.6, 13.15, and 14.28 μm; $\lambda_{max.}$ (95% ethanol) 257 nm (ε 14 200); δ($CDCl_3$; 60 MHz) 2.55 (s, 3 H), 6.48 (d, 1 H, *J* 1.8 Hz), and 7.2—7.8 (m, 12 H); *m/e* 272 (M^+, base), 257, 243, 229, 228, 165, and 77 (Found: C, 88.2; H, 5.85. Calc. for $C_{20}H_{16}O$: C, 88.23; H, 5.88%).

Direct Irradiation of 3-(3-*Furyl*)-3-*methyl*-1,2-*diphenylcyclopropene*.—A sample containing the 3-(3-furyl)cyclopropene (300 mg) in benzene (300 ml) was irradiated under argon with a 450-W Hanovia mercury lamp equipped with a Pyrex sleeve for 4 h. Removal of the solvent under reduced pressure left a yellow oil which turned black within a few seconds. No characterizable compounds could be obtained on extensive chromatography. Similar results were obtained when the same compound was heated in a degassed n.m.r. tube at 200 °C. Further work with this system was abandoned at this time.

Acknowledgements

This work was supported by the National Science Foundation (A. P.) and by the C.N.R. of Italy (grant no. CT100608.03) (G. P.).

References

1 K. C. Bishop, *Chem. Rev.*, 1976, **76**, 461.
2 K. B. Wiberg and R. A. Fenoglio, *J. Am. Chem. Soc.*, 1968, **90**, 3395.
3 S. W. Benson, ' Thermodynamic Kinetics,' Wiley Interscience, New York, 1968, p. 179.
4 H. Durr, *Justus Liebigs Ann. Chem.*, 1969, **723**, 103.
5 B. Halton, M. Kulig, M. A. Battiste, J. Perreten, D. M. Gibson, and G. W. Griffin, *J. Am. Chem. Soc.*, 1971, **93**, 2327.
6 A. Padwa, T. J. Blacklock, D. Getman, and N. Hatanaka, *J. Am. Chem. Soc.*, 1977, **99**, 2344; *J. Org. Chem.*, 1978, **43**, 1481.
7 H. E. Zimmerman and S. M. Aasen, *J. Am. Chem. Soc.*, 1977, **99**, 2342; *J. Org. Chem.*, 1978, **43**, 1493.
8 H. E. Zimmerman and M. C. Hovey, *J. Org. Chem.*, 1979, **44**, 2331.
9 H. E. Zimmerman and D. J. Kreil, *J. Org. Chem.*, 1982, **47**, 2060.
10 R. Breslow, *Mol. Rearrangements*, 1963, **1**, 257.
11 J. A. Walker and M. Orchin, *Chem. Commun.*, 1968, 1239.
12 A. S. Monahan, J. D. Freilich, and J. J. Fong, *Tetrahedron Lett.*, 1970, 1865.
13 R. Fiato, P. Mushak, and M. A. Battiste, *J. Chem. Soc., Chem. Commun.*, 1975, 869.
14 M. A. Battiste, B. Hatton, and R. H. Grubbs, *Chem. Commun.*, 1967, 907.
15 J. H. Davis, W. A. Goddard, and R. G. Bergman, *J. Am. Chem. Soc.*, 1976, **98**, 4017; 1977, **99**, 2427.
16 E. J. York, W. Dittmar, J. R. Stevenson, and R. G. Bergman, *J. Am. Chem. Soc.*, 1972, **94**, 2882; 1973, **95**, 5680.
17 R. Breslow, H. Hover, and H. W. Chang, *J. Am. Chem. Soc.*, 1962, **84**, 3168.
18 R. W. Johnson, T. Widlanski, and R. Breslow, *Tetrahedron Lett.*, 1976, 4685.
19 L. A. Paquette, ' Principles of Modern Heterocyclic Chemistry,' W. A. Benjamin, Inc., N.Y., 1968.

Received 12*th July* 1982; *Paper* 2/1168