Photorearrangement Studies of 3-Heteroaryl-substituted Cyclopropenes

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The photochemical rearrangement of several 3-heteroaryl-substituted cyclopropenes containing a methyl group on the heterocyclic ring 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 resulting product was found to undergo a sigmatropic 1,5-methyl shift on being heated in mesitylene at 200 °C to give a cyclopenta[b]furan or thiophene. Yet another reaction resulting from the vinylcarbene is insertion into the adjacent methyl group to give a buta-1,3-diene derivative. The product distribution is dependent on the stereochemistry of the vinylcarbene. Irradiation of 1,2-diphenyl-3-heteroaryl-substituted cyclopropenes also give products corresponding to a 1,2-heteroaryl substituent shift. A mechanism involving π-π^* bridging of the excited cyclopropene with the heteroaromatic ring followed by diradical cleavage is proposed to account for the formation of the rearranged cyclopropenes.

Small-ring organic molecules have interested organic chemists since 1883, when Perkin synthesized the first known cyclobutane and cyclopropane derivatives.[1] During the next 100 years, the experimental and theoretical study of strained ring hydrocarbons has burgeoned.[2,3] Cyclopropene represents one of the more intriguing small-ring polycycles.

The photochemical reactions of cyclopropenes has been studied in some detail.[4] In the singlet state, ring cleavage is the dominant process, leading to a carbene which undergoes a facile recyclization or to further reactions such as insertion into a CH bond[5] or alkyl group migration.[6] Usually, low quantum yields of transformed products are observed owing to the easy reclosure of the system, regenerating the starting molecule.[4] Triplet cyclopropenes do not undergo ring cleavage, and sensitized irradiations lead to the formation of dimers via a classical [2 + 2] addition.[7] In some cases, intramolecular cycloaddition[8] or capture of hydrogen on the γ-position of the side chain occurs.[9]

One of the more frequently encountered photochemical reactions of 3-aryl (or 3-vinyl) substituted cyclopropenes involves rearrangement to indenes (or cyclopentadienes).[10-16] Formally analogous to the vinylcyclopropane–cyclopentene isomerization, this rearrangement can also be effected by acid,[17]

transition metals,[18-20] or heat.[21] The present study began with the objective of investigating additional examples of the vinylcyclopropene 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 heteroarenes 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-
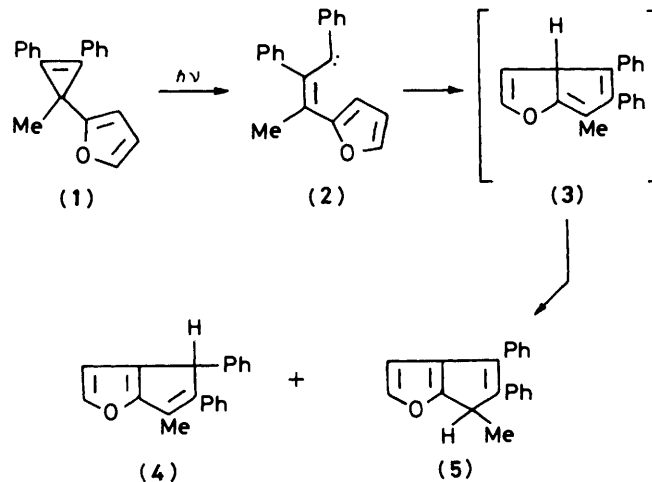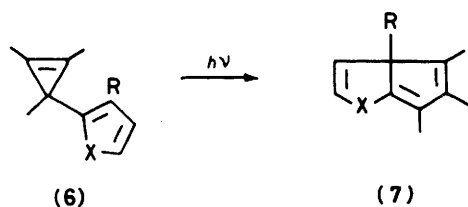

Scheme 1.

workers.[22] In an earlier study we showed that the irradiation of 3-(2-furyl)-3-methyl-1,2-diphenylcyclopropene (1) (Scheme 1) produced a 1:1 mixture of two photoproducts [i.e. (4) and (5)].[13] The electronically excited singlet state of the cyclopropene was proposed to undergo fission of the three-membered ring to give a vinylcarbene (2) which was converted into compound (3) by means of an electrocyclic ring closure. Intermediate (3) can undergo either a 1,3- or a 1,5-sigmatropic hydrogen shift to give the observed photoproducts.
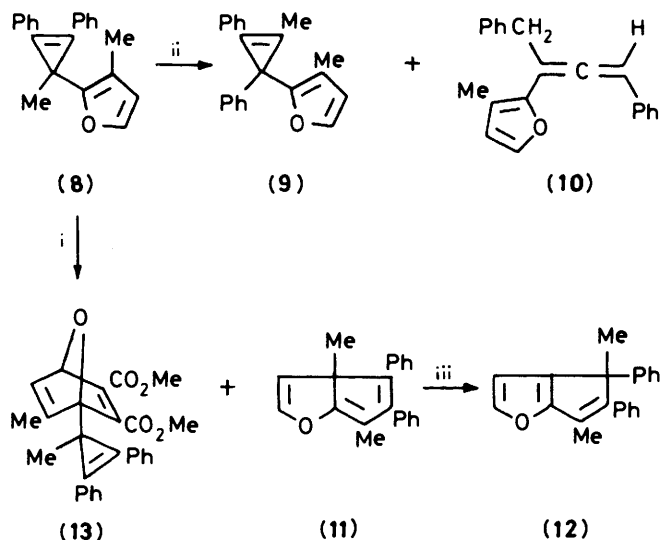
It is obvious from our earlier observations that the ready sigmatropic hydrogen shift of the intermediate (3) precludes its isolation. We decided to attempt the preparation of a derivative of (3) with a group other than hydrogen at the ring junction. Our approach was to prepare a number of compounds in which the 3-position of the heterocyclic ring was blocked by an alkyl group [i.e. (6)]; thus, the initially cyclized intermediate [i.e. (7)] would be less likely to rearomatize and could, in principle, be isolated (Scheme 2). A system such as the bicycle (7) not only offers an opportunity for investigating sigmatropic group migrations but could also undergo Diels–Alder cycloaddition. Bicyclic conjugated polyenes related to (7), where the peripheral unsaturation is interrupted by a tetrahedral carbon at the ring junction, have not been extensively studied.[23]

We first investigated the photochemical behaviour of

Scheme 2.

Scheme 4

Scheme 3. *Reagents:* i, MeO$_2$CC≡CCO$_2$Me, heat; ii, *hv*; iii, 200 °C

Scheme 5. *Reagents:* i, Bu^{n}Li; ii, 3-methyl-1,2-diphenylcyclopropenyl cation

3-methyl-2-(3-methyl-1,2-diphenylcyclopropenyl)furan (8) (Scheme 3). Direct irradiation of compound (8) in benzene produced a mixture of three compounds whose structures were assigned as (9) (20%), (10) (10%), and (11) (40%). Compounds (9) and (10) could be isolated in pure form and completely characterized (see Experimental section). The structure of the cyclopropene (9) was established by comparison with an independently synthesized sample. The identity of the bicycle (10) was deduced on the basis of its characteristic n.m.r. spectrum which showed the methyl group as a singlet at δ 1.93, a two-proton doublet at 4.94 (*J* 3.0 Hz), a triplet for the allenic proton at δ 5.25 (*J* 3.0 Hz), a doublet for the furyl 3-H at δ 6.15 (*J* 1.8 Hz), and a multiplet for the remaining hydrogens at δ 7.1—7.4 (11 H). The mass spectrum of compound (10) shows the facile loss of the benzyl group while the u.v. spectrum has absorptions at 282 and 250 nm which are consistent with the styryl chromophore. The other compound present in the crude photolysate was assigned as the cyclopentafuran (11) [δ 1.36 (3 H, s), 1.80 (3 H, s), 5.70 (1 H, d, *J* 3.5 Hz), 6.63 (1 H, d, *J* 3.5 Hz) and 7.1—7.4 (10 H, m)]. This material is readily hydrolysed on chromatographic separation and could not be obtained in pure form. We attempted to provide additional support for the structure of compound (11) by treating the crude photolysate with dimethyl acetylenedicarboxylate. However, all attempts to isolate a Diels–Alder adduct derived from (11) were unsuccessful. The only [4 + 2] cycloadduct present was identified as having structure (13). This same material could also be obtained by heating the cyclopropene (8) with dimethyl acetylenedicarboxylate in benzene at 80 °C. We did observe that thermolysis of the crude reaction mixture converted compound (11) into the thermodynamically more stable cyclopenta[*b*]furan (12). This rearrangement can be rationalized by postulating a 1,5-methyl migration. Although 1,5-sigmatropic
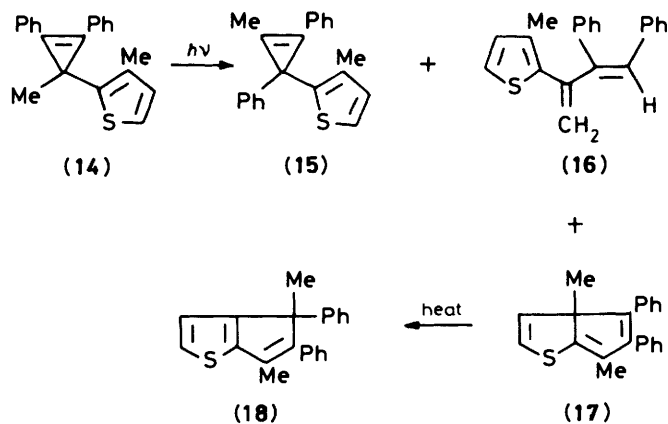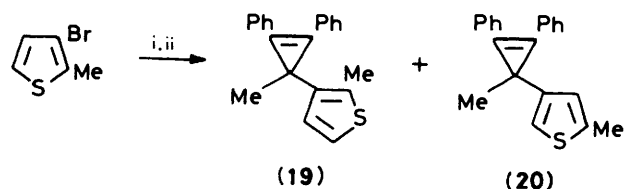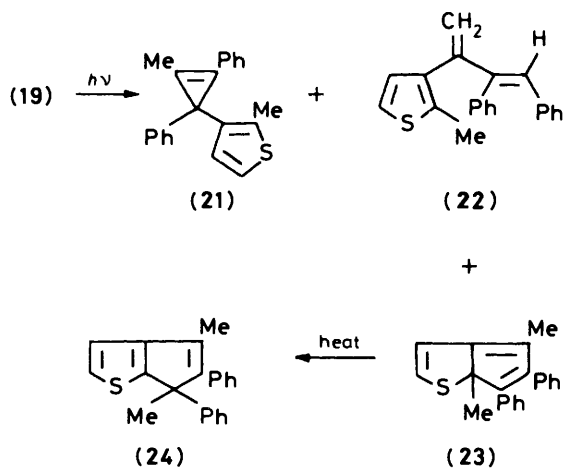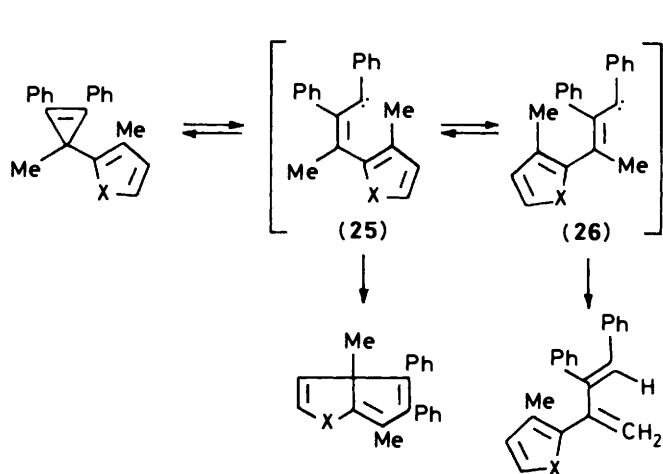
methyl shifts are rare, an analogous rearrangement has been reported in the 3a*H*-benzimidazole system.[24] In contrast to the photochemical results, thermolysis of a sample of the cyclopropene (8) resulted in the formation of the cyclopenta[*b*]furan (12) in quantitative yield.

Further examples which would support the generality of the photorearrangement of these 3-heteroaryl-substituted cyclopropenes were sought. With this in mind, we investigated the photochemistry of the closely related 2-cyclopropenyl-3-methyl-substituted thiophene system (14). Direct irradiation of compound (14) in benzene led to three photoproducts (Scheme 4). The first product (20%) was the unsymmetrically rearranged cyclopropene (15). The structure of this material was established by comparison with an independently synthesized sample. The second photoproduct (16) (10%) was also isomeric with the starting material. Its n.m.r. spectrum consisted of a methyl singlet at δ 2.31, doublets at 5.26 (*J* 1.6 Hz), 5.58 (*J* 1.6 Hz), and 6.71 (*J* 5.0 Hz) together with an aromatic multiplet at 6.91—7.60 (12 H). This led to the assignment of 1,2-diphenyl-3-(3-methyl-2-thienyl)buta-1,3-diene (16). A third product (17) (40%) was also present in the crude reaction mixture [δ 1.46 (3 H, s), 1.98 (3 H, s), 6.11 (1 H, d, *J* 6.0 Hz), 6.35 (1 H, d, *J* 6.0 Hz), and 6.80—7.80 (10 H, m)] but could not be isolated from the chromatographic separation. This material was found to undergo rearrangement on heating at 200 °C to give the cyclopenta[*b*]thiophene (18). The spectral properties and thermal rearrangement are most consistent with structure (17). Cyclopropene (14) was subjected to similar thermolysis conditions and gave (18) as the exclusive product.

We have also studied the photochemistry of the isomeric 3-cyclopropenyl-2-methyl-substituted thiophene (19). This material was prepared in 25% yield by treating 3-bromo-2-methylthiophene with n-butyl-lithium and then with 3-methyl-1,2-diphenylcyclopropenyl cation (Scheme 5). Interestingly, the major product isolated from the reaction (40%) corresponded to the 4-cyclopropenyl-2-methyl substituted isomer (20). Undoubtedly, the formation of the isomer (20) involves a proton

(19) $\xrightarrow{h\nu}$ (21) + (22)

+

(24) $\xleftarrow{heat}$ (23)

Scheme 6.

(27)

Scheme 8.

(28) (29) (30)

(25) (26)

Scheme 7.

(8) $\xrightarrow{h\nu}$ (31) (32) $\xrightarrow{h\nu}$ (10)

Scheme 9.

exchange reaction of the initially generated lithiate. The photolysis of the thiophene (19) proceeded in a manner analogous to that observed with the cyclopropene (14) and gave rise to photoproducts (21)—(23) (Scheme 6). Further evidence supporting structure (23) was obtained by its conversion into (24) on heating at 200 °C. In the case of the cyclopropene (20), the major product isolated from the photolysis corresponded to 2,4-dimethyl-5,6-diphenyl-6H-cyclopenta[b]-thiophene.

Singlet states of diaryl-substituted cyclopropenes generally react by σ-bond cleavage to give products which are explicable in terms of the chemistry of vinylcarbenes.[4] Thus, the formation of the butadienes (16) and (22) can be readily accounted for in terms of a transient vinylcarbene which undergoes a 1,4-hydrogen transfer from the adjacent methyl group.[5] Yet another reaction resulting from the vinylcarbene intermediate is the formation of the cyclopentadienyl-substituted hetero-cycles (11), (17), and (23) via an electrocyclic ring-closure reaction.[12] The product distribution will depend on the stereo-chemistry of the vinylcarbene. The intermediate (25) has the necessary geometry to undergo 1,5-electrocyclization. If the heterocyclic ring is located trans to the carbene centre [i.e. (26)], cyclization is unlikely for steric reasons. Instead, insertion into the neighbouring methyl group will occur and produce the buta-1,3-diene system (Scheme 7). It should be pointed out that cyclopropene into vinylcarbene conversions are known to be reversible both thermally[25] and photochemically.[26] This means that the product distribution may reflect the different rates of
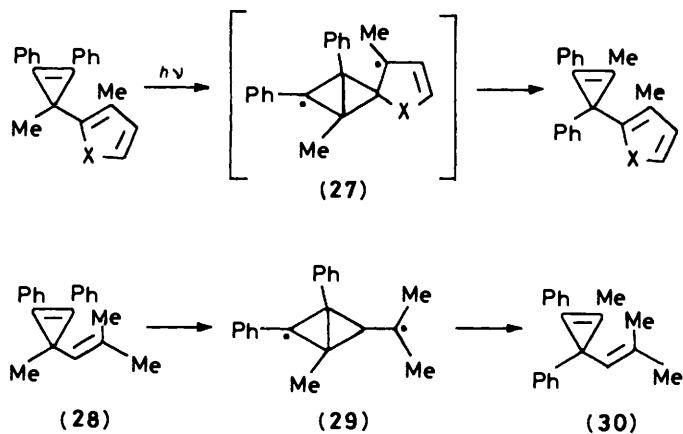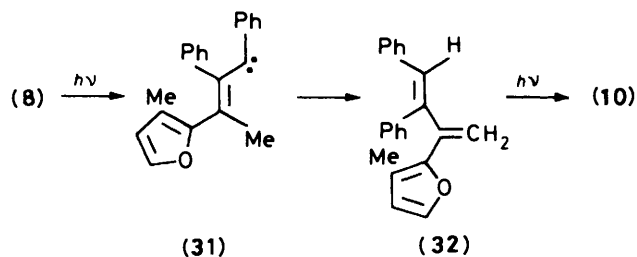
return to cyclopropene for the two possible carbenes rather than the selectivity of ring opening.

The mechanism by which the symmetrically substituted cyclopropene system [i.e. (8), (14), and (19)] rearranges to the corresponding unsymmetrically substituted isomer [i.e. (9), (15), and (21)] requires some comment. A limited number of examples exist where the electronically excited singlet state of the cyclopropene retains the three-membered ring.[27] In these special cases, the photoreaction observed corresponds to a 1,2-substituent shift. We propose a mechanism for this conversion which involves π-π* bridging of the excited cyclopropene to give the diradical (27) (Scheme 8) which subsequently cleaves to produce the rearranged cyclopropene. The bridging and cleavage steps are closely related to those suggested by Zimmerman and Hovey to rationalize the rearrangement of (28) into (30).[15]

One final point worth mentioning deals with the formation of the allene (10) from the irradiation of the furan (8). A reasonable route to account for the formation of compound (10) involves a sequence consisting of ring opening to a vinylcarbene followed by a 1,4-hydrogen transfer from the adjacent methyl group to give the butadiene (32) (Scheme 9). It is tempting to suggest that the diene (32) absorbs a photon of light and undergoes a photochemically allowed 1,3-phenyl shift to give the allene (10). Further work is necessary before this mechanism can be unequivocally established.

Additional studies dealing with the rearrangement and intra-molecular cycloaddition reactions of cyclopropene derivatives are in progress and will be reported in due course.

Experimental

All m.p.s were determined with a Kofler apparatus and are uncorrected. The i.r. absorption spectra were determined on a Perkin-Elmer 684 infrared spectrophotometer. The u.v. absorption spectra were measured with a Perkin-Elmer 330 recording

spectrophotometer, using 1-cm matched cells. The ^1H n.m.r. spectra were determined at 80 Hz, using a Bruker-FT spectrometer. Mass spectra were determined with a KLB mass spectrometer at an ionizing voltage of 70 eV. The chromatographic separations were carried out using a preparative Miniprep LC Jobin-Yvon apparatus. Ether refers to diethyl ether.

Preparation of 3-Methyl-2-(3-methyl-1,2-diphenylcyclopropen-3-yl)furan (**8**).—To a stirred suspension containing 1-methyl-2,3-diphenylcyclopropenylium perchlorate (5.0 g) in 100 ml of anhydrous tetrahydrofuran at $-78\,°C$ under nitrogen was added a solution containing 2-lithio-3-methylfuran (4.8 × 10^{-2} mol). The reaction mixture was allowed to warm to room temperature and stirred for 14 h. The solution was quenched with saturated ammonium chloride solution and the organic layer was taken up in ether, washed with water, and dried (MgSO₄). Removal of the solvent under reduced pressure left a yellow oil (3.5 g) which was chromatographed on a silica gel column using 2% chloroform–cyclohexane as the eluant. The first component isolated contained a white solid (2.3 g), m.p. 54—55 °C, which was identified as 3-methyl-2-(3-methyl-1,2-diphenylcyclopropen-3-yl)furan (**8**) on the basis of its spectral properties: i.r. ($\lambda_{max.}$) (KBr) 3.24, 3.27, 3.3, 3.42, 3.49, 5.43, 6.25, 6.66, 6.89, 7.27, 8.62, 9.13, 9.26, 9.70, 11.20, 11.76, 13.15, 13.40, and 14.41 µm; $\lambda_{max.}$ (95% ethanol) 330 (ε 18 040), 313 (29 800), 305sh (23 930), 325sh (25 000), and 228 nm (27 680); δ (CDCl₃; 60 MHz) 1.83 (3 H, s), 1.86 (3 H, s), 6.16 (1 H, d, *J* 1.8 Hz), 7.28 (1 H, d, *J* 1.8 Hz), and 7.42—7.90 (10 H, m); *m/z* 286 (*M*⁺, base), 271, 256, 243, 228, 215, 270, 178, 165, 115, 91, 85, and 77 (Found: C, 88.1; H, 6.3. Calc. for C₂₁H₁₈O: C, 88.11; H, 6.29%).

The second fraction isolated from the column contained a white solid (0.85 g), m.p. 83—84 °C, which was identified as 3-methyl-2-(2-methyl-1,3-diphenylcyclopropen-3-yl)furan (**9**) on the basis of its spectral properties: i.r. ($\lambda_{max.}$) (KBr) 3.27, 3.29, 3.31, 3.41, 3.50, 5.37, 6.25, 6.72, 6.89, 8.62, 9.09, 9.26, 10.87, 11.36, 12.50. 13.07, 13.42, and 14.28 µm; $\lambda_{max.}$ (ethanol) 262 nm (ε 24 940); δ (CDCl₃; 60 MHz) 1.96 (3 H, s), 2.43 (3 H, s), 6.10 (1 H, d, *J* 1.8 Hz), and 7.2—7.8 (11 H, m); *m/z* 286 (*M*⁺, base), 271, 228, 178, 165, 91, 85, and 7 (Found: C, 88.1; H, 6.3. Calc. for C₂₁H₁₈O: C, 88.11; H, 6.29%).

Direct Irradiation of 2-(3-methyl-1,2-diphenylcyclopropen-3-yl)furan (**8**).—A solution containing cyclopropene (**8**) (200 mg) in benzene (300 ml) was irradiated under Argon with a 450-W Hanovia lamp equipped with a Pyrex filter sleeve for 16 h. Removal of the solvent under reduced pressure left behind a dark yellow oil whose n.m.r. spectrum indicated the presence of three products. The mixture was subjected to silica gel chromatography using 2% chloroform–hexane as the eluant. The first component isolated from the column contained a clear oil (20 mg, 10%) whose structure was assigned 3-(3-methyl-2-furyl)-1,4-diphenylbuta-1,2-diene (**10**) on the basis of its spectral properties: i.r. ($\lambda_{max.}$) (neat) 3.27, 3.29, 3.31, 3.37, 3.42, 3.52, 5.15, 6.25, 6.37, 6.71, 6.89, 7.93, 8.69, 9.17, 9.75, 11.23, 11.76, 12.50, 13.15, 13.92, and 14.28 µm; $\lambda_{max.}$ (95% ethanol) 250 nm (ε 7 660) and 282sh (1 150); δ (CDCl₃; 80 MHz) 1.93 (3 H, s), 4.94 (2 H, d, *J* 3 Hz), 5.25 (1 H, t, *J* 3 Hz), 6.15 (1 H, d, *J* 1.8 Hz), and 7.1—7.37 (11 H, m); *m/z* 286 (*M*⁺), 271, 257, 215, 202, 195, 171 (base), 165, 152, 141, 128, 115, 95, 91, and 77 (Found: C, 88.1; H, 6.3. Calc. for C₂₁H₁₈O: C, 88.11; H, 6.29%).

The second component isolated from the chromatography column contained a white solid (40 mg, 20%), m.p. 83—84 °C, whose structure was assigned as 3-methyl-2-(2-methyl-1,3-diphenylcyclopropen-3-yl)furan (**9**) by comparison with an authentic sample.

The thermolysis of the crude photolysate was also carried out and was found to produce a rearranged furan. Thus, a

solution containing cyclopropene (200 mg) in benzene (300 ml) was irradiated under Argon with a 450-W Hanovia lamp equipped with a Pyrex filter sleeve for 16 h. Removal of the solvent under reduced pressure left a yellow oil. The n.m.r. spectrum of this material showed peaks attributable to compounds (**9**) and (**10**). In addition, the n.m.r. spectrum contained signals at δ 1.36 (3 H, s), 1.80 (3 H, s), 5.70 (1 H, d, *J* 3.5 Hz), 6.63 (1 H, d, *J* 3.5 Hz), and 7.1—7.4 (10 H, m). These peaks disappeared when the crude photolysate was heated under reflux in mesitylene for 2 h. Removal of the solvent left a dark oil which was subjected to silica gel chromatography using 2% chloroform–cyclohexane as the eluant. In addition to compounds (**9**) and (**10**), a clear oil (30 mg) was obtained whose structure was assigned as 4,6-dimethyl-4,5-diphenyl-4*H*-cyclopenta[*b*]furan (**12**) on the basis of its spectral properties: i.r. ($\lambda_{max.}$) (neat) 3.25, 3.27, 3.31, 3.37, 3.40, 3.51, 6.25, 6.66, 8.62, 9.09, 11.11, 12.65, 12.98, 13.13, and 14.28 µm; $\lambda_{max.}$ (95% ethanol) 310 nm (ε 10 200) and 232 (12 080); δ (CDCl₃; 60 MHz) 1.55 (3 H, s), 2.07 (3 H, s), 6.22 (1 H, d, *J* 2 Hz), and 7.1—7.32 (11 H, m); *m/z* 286 (*M*⁺, base), 271, 257, 227, 165, 115, 91, and 77. This material was somewhat sensitive and it was not possible to obtain a satisfactory analysis. The same compound was also formed in 98% yield by heating a sample of cyclopropene (**8**) in mesitylene for 2 h. However, no detectable quantities of compounds (**9**) and (**10**) were present in the crude reaction mixture derived from the thermolysis.

Cycloaddition of 3-Methyl-2-(3-methyl-1,2-diphenylcyclopropen-3-yl)furan (**8**) *with Dimethylacetylene Dicarboxylate.*—A sample containing dimethylacetylene dicarboxylate (142 mg) and cyclopropene (2.86 g) in benzene (5 ml) was heated at reflux for 30 min. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using 10% ethyl acetate–benzene as the eluant. The major product isolated from the column contained a pale yellow oil (2.5 g) whose structure was assigned as 1-(3-methyl-1,2-diphenylcyclopropen-3-yl)-2,3-bis(methoxycarbonyl)-6-methyl-7-oxabicyclo[2.2.1]hepta-2,5-diene (**13**) on the basis of its spectral properties: i.r. ($\lambda_{max.}$) (neat) 3.25, 3.37, 3.40, 5.51, 5.70, 6.09, 6.25, 6.66, 6.89, 6.94, 7.24, 7.57, 8.02, 8.54, 8.81, 12.98, and 14.28 µm; *m/z* 428 (*M*⁺), 400, 369, 341, 340, 286 (base), 271, 265, 249, 209, 178, 165, 110, 105, and 77; δ (CDCl₃; 60 MHz) 1.53 (3 H, s), 2.16 (3 H, d, *J* 2 Hz), 3.33 (3 H, s), 3.46 (3 H, s), 5.60 (1 H, d, *J* 2 Hz), 6.70 (1 H, m), and 7.2—8.01 (10 H, m) (Found: C, 75.65; H, 5.6. Calc. for C₂₇H₂₄O₅: C, 75.70; H, 5.60%).

We also carried out an experiment in which the photolysis of cyclopropene (**8**) was carried out for 32 h so that all the starting material was consumed. The crude reaction mixture was then heated with dimethyl acetylenedicarboxylate. Under these conditions, no detectable quantities of the Diels–Alder cycloadduct (**13**) could be detected. This observation indicates that structure (**11**) does not thermally re-equilibrate with cyclopropene (**8**) under the cycloaddition conditions.

Preparation of 3-Methyl-2-(3-methyl-1,2-diphenylcyclopropen-3-yl)thiophene (**14**).—This material was prepared in a fashion similar to that described for the furan (**8**). After the reaction of the cyclopropenylium perchlorate salt with 3-methyl-2-thienylmagnesium bromide, the reaction mixture was chromatographed on a silica gel chromatography column using 3% chloroform–hexane as the eluant. The first component isolated contained a yellow solid (2.5 g), m.p. 79—80 °C, whose structure was assigned as 3-methyl-3-(3-methyl-2-thienyl)-1,2-diphenylcyclopropene (**14**) on the basis of its spectral properties: i.r. ($\lambda_{max.}$) (KBr) 3.30, 3.36, 3.42, 5.52, 6.25, 6.66, 6.89, 7.29, 8.33, 9.25, 9.71, 10.98, 11.91, 13.20, 13.91, and 14.25 µm; $\lambda_{max.}$ (95% ethanol) 302 (ε 8 550), 314 (10 350), and 333 nm (7 500); *m/z* 302 (*M*⁺, base), 272, 254, 225, 211, 167, and 77; δ (CDCl₃; 60 MHz)

1.90 (3 H, s), 2.13 (3 H, s), 6.71 (1 H, d, J 5 Hz), 6.93 (1 H, d, J 5 Hz), and 7.2—7.8 (10 H, m) (Found: C, 83.4; H, 5.95; S, 10.6. Calc. for $C_{21}H_{18}S$: C, 83.44; H, 5.94; S, 10.58%).

The second component isolated from the column contained a pale yellow solid (0.45 g), m.p. 84—85 °C, whose structure was assigned as 3-methyl-2-(2-methyl-1,3-diphenylcyclopropen-3-yl)thiophene (15); i.r. $(\lambda_{max.})$ (KBr) 3.32, 3.35, 3.41, 3.45, 5.35, 6.25, 6.60, 6.91, 7.30, 8.35, 9.26, 9.74, 11.02, 11.89, 13.21, 13.88, and 14.31 µm; $\lambda_{max.}$ (95% ethanol) 262 nm (ϵ 10 650); δ (CDCl$_3$; 60 MHz) 2.16 (3 H, s), 2.46 (3 H, s), 6.83 (1 H, d, J 5 Hz), and 7.01—7.48 (11 H, m); m/z 302 (M^+, base), 271, 253, 225, 211, 209, 187, 165, 115, and 77 (Found: C, 83.45; H, 5.9; S, 10.6. Calc. for $C_{21}H_{18}S$: C, 83.44; H, 5.96; S, 10.59%).

Direct Irradiation of 3-Methyl-2-(3-methyl-1,2-diphenylcyclopropen-3-yl)thiophene (14).—A solution containing cyclopropene (14) (200 mg) in benzene (300 ml) was irradiated under similar conditions to those described for compound (8). The reaction mixture was subjected to silica gel chromatography using 2% chloroform–hexane as the eluant. The first fraction isolated from the column contained a clear oil (20 mg) whose structure was assigned as 3-(3-methyl-2-thienyl)-1,2-diphenyl-buta-1,3-diene (16) on the basis of its spectral properties: i.r. $(\lambda_{max.})$ (neat) 3.26, 3.31, 3.49, 6.25, 6.66, 6.89, 7.24, 8.19, 9.25, 9.66, 11.76, 12.98, and 14.08 µm; δ (CDCl$_3$; 60 MHz) 2.31 (3 H, s), 5.26 (1 H, d, J 1.6 Hz), 5.58 (1 H, d, J 1.6 Hz), 6.71 (1 H, d, J 5 Hz), and 6.91—7.60 (12 H, m); m/z 302 (M^+, base), 287, 272, 253, 225, 211, 178, 165, 110, 91, and 77. This material was very labile and it was not possible to obtain a satisfactory analysis. The second component isolated from the column contained a pale yellow solid (40 mg, 20%), m.p. 84—85 °C, whose structure was identical with an authentic sample of 3-methyl-2-(2-methyl-1,3-diphenylcyclopropen-3-yl)thiophene (15).

The thermolysis of the crude photolysate was also carried out and was found to produce yet another rearranged product. Thus, a solution containing cyclopropene (14) (200 mg) in benzene (300 ml) was irradiated under Argon with a 450-W Hanovia lamp equipped with a Pyrex filter sleeve for 16 h. Removal of the solvent under reduced pressure left a yellow oil whose n.m.r. spectrum showed the presence of compounds (15) and (16). In addition, the n.m.r. spectrum contained signals at δ 1.46 (3 H, s), 1.98 (3 H, s), 6.11 (1 H, d, J 6.0 Hz), 6.35 (1 H, d, 6.0 Hz), and 6.8—7.8 (10 H, m). These signals disappeared when the crude photolysate was heated in mesitylene for 2 h. Removal of the mesitylene under reduced pressure left a dark oil which was subjected to silica gel chromatography using 2% chloroform–hexane as the eluant. In addition to compounds (15) and (16), a new compound was isolated whose structure was assigned as 4,6-dimethyl-4,5-diphenylcyclopenta[b]thiophene (18) on the basis of its spectral properties: i.r. $(\lambda_{max.})$ (KBr) 3.23, 3.31, 3.36, 3.41, 3.47, 6.25, 6.71, 6.90, 7.19, 7.49, 8.12, 9.26, 9.70, 10.63, 11.76, 12.34, 12.98, 13.69, 14.28, 15.38, and 16.00 µm; δ (CDCl$_3$; 60 MHz) 1.60 (3 H, s), 2.15 (3 H, s), 6.81 (1 H, d, J 5 Hz), and 7.0—7.3 (11 H, m); m/z 302 (M^+, base), 287, 272, 254, 225, 136, and 77; $\lambda_{max.}$ (95% ethanol) 308 nm (ϵ 11 000) (Found: C, 83.4; H, 5.95; S, 10.6. Calc. for $C_{21}H_{18}S$: C, 83.44; H, 5.96; S, 10.59%). This same compound was also produced in 90% yield when a sample of cyclopropene (14) was heated at 200 °C for 3 min. Under these conditions, no detectable quantities of compound (15) or (16) could be detected in the crude reaction mixture.

Preparation of 2-Methyl-3-(3-methyl-1,2-diphenylcyclopropen-3-yl)thiophene (19).—This material was prepared analogously to the furan (14). After reaction of the cyclopropenylium perchlorate salt with 2-methyl-3-thienyl-lithium, the reaction mixture was chromatographed on a silica gel chromatography column using 2% chloroform–pentane as the eluant. The first component isolated from the column contained

a pale yellow solid (1.30 g), m.p. 124—125 °C, whose structure was assigned as 2-methyl-4-(3-methyl-1,2-diphenylcyclopropen-3-yl)thiophene (20) on the basis of its spectral properties: i.r. $(\lambda_{max.})$ (KBr) 3.23, 3.25, 3.31, 3.36, 3.40, 3.43, 3.51, 5.50, 6.51, 6.69, 6.92, 7.25, 7.64, 8.20, 9.34, 9.71, 10.10, 10.75, 11.23, 11.46, 13.20, and 14.53 µm; $\lambda_{max.}$ (cyclohexane) 326 (ϵ 16 600), 310 (23 800), 294sh (19 200), 232sh (18 900), and 226 nm (21 100); δ (CDCl$_3$; 60 MHz) 1.9 (3 H, s), 2.8 (3 H, s), 6.8 (1 H, s), and 7.2—7.8 (11 H, m); m/z 302 (M^+, base), 287, 272, 254, 225, 216, 178, 165, and 77 (Found: C, 83.4; H, 5.9; S, 10.6. Calc. for $C_{21}H_{18}S$: C, 83.44; H, 5.94; S, 10.58%).

The structure of the thiophene (20) was further verified by an independent synthesis. To a stirred suspension containing 1-methyl-2,3-diphenylcyclopropenylium perchlorate (5.0 g) in tetrahydrofuran (100 ml) at −78 °C was added a solution containing 2-methyl-4-thienyl-lithium (4.8 × 10⁻² mol). Standard work-up procedure afforded a pale yellow solid (1.8 g), m.p. 124—125 °C, which was identical with a sample of compound (20) isolated from the reaction of 2-methyl-3-thienyl-lithium with the perchlorate salt. In addition to structure (18), the thiophene (19) (980 mg) was also isolated, and was identical in all respects with the second component isolated from chromatography of the crude reaction mixture derived from the reaction of 2-methyl-3-thienyl-lithium with the perchlorate salt. The second fraction contained a pale yellow solid (950 mg), m.p. 69—70 °C, whose structure was assigned as 2-methyl-3-(3-methyl-1,2-diphenylcyclopropen-3-yl)thiophene (19) on the basis of its spectral properties: i.r. $(\lambda_{max.})$ (KBr) 3.24, 3.26, 3.31, 3.37, 3.42, 3.47, 3.51, 5.46, 6.25, 6.61, 6.89, 7.31, 8.06, 8.33, 8.54, 9.34, 9.52, 9.70, 10.98, 11.21, 12.51, 12.82, 13.10, and 14.51 µm; $\lambda_{max.}$ (cyclohexane) 328 (ϵ 13 450), 298sh (16 630), 250 (8 500), 235sh (15 000), and 227 nm (17 500); δ (CDCl$_3$; 60 MHz) 1.98 (3 H, s), 2.35 (3 H, s), 6.80 (1 H, d, J 5 Hz), and 7.1—7.8 (11 H, m); m/z 302 (M^+, base), 287, 272, 254, 225, 216, 178, 165, and 77 (Found: C, 83.4; H, 6.0; S, 10.6. Calc. for $C_{21}H_{18}S$: C, 83.44; H, 5.94; S, 10.58%).

The third fraction isolated from the chromatography column contained a pale yellow solid (150 mg), m.p. 81—82 °C, whose structure was assigned as 2-methyl-3-(2-methyl-1,3-diphenyl-cyclopropen-3-yl)thiophene (21) on the basis of its spectral properties: i.r. $(\lambda_{max.})$ (KBr) 3.25, 3.27, 3.31, 3.43, 3.51, 5.37, 6.25, 6.71, 6.90, 9.35, 11.01, 11.83, 12.65, 13.15, 14.28, 14.49, and 15.15 µm; $\lambda_{max.}$ (cyclohexane) 258 (ϵ 20 500) and 300sh nm (3 400); m/z 302 (M^+, base), 287, 271, 254, 225, 211, 178, 165, 91, and 77; δ (CDCl$_3$; 60 MHz) 2.35 (3 H, s), 2.45 (3 H, s), 6.80 (1 H, d, J 5 Hz), and 7.5—7.9 (11 H, m) (Found: C, 83.5; H, 5.9; S, 10.6. Calc. for $C_{21}H_{18}S$: C, 83.44; H, 5.94; S, 10.58%).

Direction Irradiation of 2-Methyl-3-(3-methyl-1,2-diphenylcyclopropen-3-yl)thiophene (19).—A solution containing the cyclopropene (19) (200 mg) in benzene (300 ml) was irradiated under similar conditions to those described for compound (14). The mixture was subjected to silica gel chromatography using 3% chloroform–hexane as the eluant. The first product isolated from the column contained a clear oil whose structure was assigned as 3-(2-methyl-3-thienyl)-1,2-diphenylbuta-1,3-diene (22) on the basis of its spectral properties: i.r. $(\lambda_{max.})$ (neat) 3.23, 3.32, 3.41, 6.25, 6.65, 6.88, 7.22, 8.19, 9.25, 9.66, 11.78, 12.96, and 14.06 µm; δ (CDCl$_3$; 60 MHz) 2.45 (3 H, s), 5.50 (1 H, d, J 1.6 Hz), 5.70 (1 H, d, J 1.6 Hz), 6.71 (1 H, d, J 5 Hz), and 6.9—7.6 (12 H, m); m/z 302 (M^+, base), 287, 272, 253, 225, 211, 178, 165, 10, 91, and 77. The second fraction isolated from the column contained a pale yellow solid (20 mg), m.p. 81—82 °C, whose structure was identified as 2-methyl-3-(2-methyl-1,3-diphenylcyclopropen-3-yl)thiopene (21) by comparison with an authentic sample.

The crude thermolysate was also thermolysed and gave yet another rearranged product. Thus, a solution containing the cyclopropene (19) (200 mg) in benzene (300 ml) was irradiated

with a 450-W Hanovia lamp equipped with a Pyrex filter sleeve for 16 h. Removal of the solvent under reduced pressure left a yellow oil whose n.m.r. spectrum showed the presence of compounds (21) and (22). In addition, a set of signals also appeared at δ 1.41 (3 H, s), 2.08 (3 H, s), 6.10 (1 H, d, J 6.0 Hz), 6.36 (1 H, J 6.0 Hz), and 6.9—7.8 (10 H, m). These signals disappeared when the crude photolysate was heated in mesitylene for 2 h. Removal of the solvent under reduced pressure left a dark oil which was subjected to silica gel chromatography using 2% chloroform–cyclohexane as the eluant. In addition to compounds (21) and (22), a pale yellow solid, m.p. 78—79 °C, was isolated whose structure was assigned as 4,6-dimethyl-5,6-diphenylcyclopenta[b]thiophene (23) on the basis of its spectral properties: i.r. ($\lambda_{max.}$) (KBr) 3.20, 3.25, 3.60, 6.25, 6.71, 6.92, 7.21, 7.47, 8.21, 9.70, 10.65, 11.74, 12.32, 13.01, 13.68, 14.26, and 15.38 μm; $\lambda_{max.}$ (cyclohexane) 312 nm (ϵ 11 400); δ (CDCl₃; 60 MHz) 1.41 (3 H, s), 2.30 (3 H, s), 6.81 (1 H, d, J 5 Hz), and 7.0—7.3 (11 H, m); m/z 302 (M^+, base), 287, 272, 254, 225, 136, 116, and 77 (Found: C, 83.9; H, 5.95; S, 10.55. Calc. for $C_{21}H_{18}S$: C, 83.44; H, 5.94; S, 10.58%). This same compound was also produced in 80% yield when a sample of the cyclopropene (19) was heated at 200 °C for 30 min. Under these conditions no detectable quantities of compound (21) or (22) could be detected in the crude reaction mixture.

Direct Irradiation of 2-Methyl-4-(3-methyl-1,2-diphenylcyclopropen-3-yl)thiophene (20).—A solution containing cyclopropene (20) (200 mg) in benzene (300 ml) was irradiated with a Pyrex filter sleeve for 4 h. Removal of the solvent under reduced pressure left a yellow oil which was subjected to silica gel chromatography using 2% chloroform–pentane as the eluant. The major product isolated from the column contained a white solid (184 mg, 92%), m.p. 103—104 °C, whose structure was assigned as 2,4-dimethyl-5,6-diphenyl-6H-cyclopenta[b]thiophene on the basis of its spectral properties: i.r. ($\lambda_{max.}$) (KBr) 3.27, 3.31, 3.37, 3.41, 3.50, 6.25, 6.71, 6.87, 6.94, 7.29, 7.93, 9.52, 9.81, 10.89, 11.70, 11.91, 12.98, 13.50, 13.88, and 14.67 μm; $\lambda_{max.}$ (cyclohexane) 320 (ϵ 7 220) and 225 nm (6 880); m/z 302 (M^+, base), 287, 272, 254, 225, 216, 165, 116, and 77; δ (CDCl₃; 60 MHz) 2.21 (3 H, d, J 1.5 Hz), 2.24 (3 H, s), 4.75 (1 H, m), and 7.01—7.2 (11 H, m) (Found: C, 83.4; H, 6.0; S, 10.6. Calc. for $C_{21}H_{18}S$: C, 83.44; H, 5.96; S, 10.59%). This same compound was also formed in 93% yield by heating a sample of the cyclopropene (20) at 200 °C for 30 min.

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