VOLUME 114, NUMBER 17
AUGUST 12, 1992

JOURNAL
OF THE
AMERICAN
CHEMICAL
SOCIETY

Triplet Photochemistry of Acyl and Imino Cyclopropenes. A Rearrangement To Afford Furans and Pyrroles: Reaction and Mechanism[1]

Howard E. Zimmerman* and Charles W. Wright

Contribution from the Chemistry Department of the University of Wisconsin, Madison, Wisconsin 53706. *Received December 30, 1991. Revised Manuscript Received April 22, 1992*

Abstract: Syntheses of 3-substituted 3-acylcyclopropenes and 3-benzoylcyclopropene imines were devised. A triplet rearrangement of acylcyclopropenes having C-3 aryl substitution to afford furans has been uncovered and studied with several examples. Unlike the singlet reaction, the triplet process does not afford multiple products such as indenones and cyclopentenones. Two examples of an imino counterpart to afford a pyrrole were found. The acylcyclopropene rearrangement contrasts with the triplet dimerization encountered when there is no C-3 aryl substitution. The four reaction mechanisms considered in the rearrangement of vinylcyclopropenes to afford cyclopentadienes were a priori possibilities in the acylcyclopropene rearrangement. Mechanistic studies established that "mechanism C", involving a cyclobutenylcarbinyl diradical utilized by the vinylcyclopropenes, was not followed. Rather, "mechanism A" proceeding via an oxahousane diradical was established as leading to product from the triplet acylcyclopropenes.

Introduction

Previously we have studied the photochemistry of vinylcyclopropenes.[2] While the singlet photochemistry of these molecules gave a multiplicity of products including cyclopentadienes, the triplet rearrangements (i.e., sensitized) gave only cyclopentadienes.[2,3] It was remarkable that the literature[4] reported the closely related acylcyclopropenes as affording only dimers, no furans, and as being formed from the triplet. It was therefore of interest to investigate the triplet behavior of acylcyclopropenes with structures similar to those of the vinylcyclopropenes of our earlier studies. We hoped that a parallel rearrangement would provide a convenient route to furans. Acylcyclopropenes have been proposed as intermediates in the interconversion of furan isomers,[5] although these interconversions were studied with direct irradiation rather than with the use of a triplet sensitizer. Finally, we planned to investigate the behavior of an imine analog of the keto cyclopropenes. With this background in mind, we selected for study acylcyclopropenes **1–7** as well as the corresponding cyclopropene imines **8** and **9**.

Results

Synthesis of Photochemical Reactants. Our research began with the synthesis of the required photochemical cyclopropene reactants. The preparation of the 3-methyl-substituted cyclopropenes is outlined in Scheme I.

(1) (a) This is Part 164 of the series. (b) For a preliminary account and Part 162 of our photochemical series, see: Zimmerman, H. E.; Wright, C. W. *J. Am. Chem. Soc.* **1992**, *114*, 363–365. (c) Part 163: Zimmerman, H. E. The Di-π-Methane Rearrangement. *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker, Inc.: New York, 1991; Vol. 11.

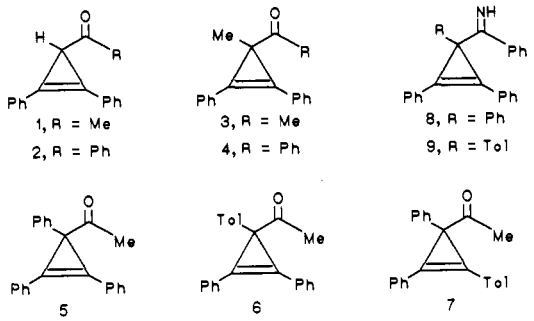
(2) (a) Zimmerman, H. E.; Aasen, S. M. *J. Org. Chem.* **1978**, *43*, 1493–1506. (b) Zimmerman, H. E.; Hovey, M. C. *J. Org. Chem.* **1979**, *44*, 2331–2345. (c) Zimmerman, H. E.; Bunce, R. A. *J. Org. Chem.* **1982**, *37*, 3377–3396. (d) Zimmerman, H. E.; Fleming, S. A. *J. Org. Chem.* **1985**, *50*, 2539–2551.

(3) (a) Note also the simultaneous discovery of the singlet rearrangement by Padwa and co-workers.[3b] (b) Padwa, A.; Blacklock, T. J.; Getman, D.; Hatanaka, N. *J. Am. Chem. Soc.* **1977**, *99*, 2344–2345.

(4) (a) Obata, N.; Moritani, I. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2250–2255. (b) For reports on dimerizations of 1-methyl-2-phenylcyclopropene-3-carboxylate and related compounds, see refs 4c,d. (c) DeBoer, C. D.; Wadsworth, D. H.; Perkins, W. C. *J. Am. Chem. Soc.* **1973**, *95*, 861–869. (d) Pincock, J. A.; Boyd, R. J. *Can. J. Chem.* **1977**, *55*, 2482–2491.

(5) For a review, see: Rendall, W. A.; Torres, M.; Lown, E. M.; Struasz, O. P. *Rev. Chem. Intermed.* **1986**, *6*, 335–364.

0002-7863/92/1514-6603$03.00/0



Of particular interest was the regioselectivity encountered in the reaction of the cyclopropenium cations with cyanide anion wherein attack of the cyanide at the methyl-substituted carbon was preferred 93:7. The source of this selectivity seems to be both steric and electronic.[6] From the synthetic standpoint, this regioselectivity provided a practical route to the keto cyclopropenes **3** and **4**. In the subsequent organolithium reaction of nitrile **12**, imine intermediates were observed, but not readily isolated; this is relevant to the more highly substituted nitriles discussed below.

Due to the regioselectivity of the cyanide attack on the methyl-substituted cyclopropenium cation, the remaining desired cyclopropenes were synthesized by an alternative approach as outlined in Scheme II. Scheme II includes the preparation of the benzoyl imines **8** and **9**. Since there was doubt[7] as to whether these structures were correct, an X-ray structure determination was utilized to confirm the identity of **8** (Figure 1). The structure of **9** was revealed by UV, NMR, IR, and MS data, which closely paralleled that of **8**. The alternative structures considered, namely, tetraarylpyrroles, had widely different spectra as shown by comparison with independently synthesized compounds.

The structures of acylcyclopropenes **1**, **3**, and **6** were also determined by X-ray analysis. A summary of the X-ray results is given in the Experimental Section. Complete details are included in the supplementary material.

Synthesis of Potential Photoproducts. Since furan and pyrrole photoproducts were anticipated and, indeed, preliminary efforts confirmed this expectation, a number of these were synthesized as depicted in Scheme III.

Exploratory Photolysis of 3-Acetyl-1,2,3-triarylcyclopropenes. The irradiation of 3-acetyl-1,2,3-triphenylcyclopropene (**5**) was carried out in benzene using two alternative triplet sensitizers, thioxanthone (E_T = 65.5 kcal/mol[8a]) and *p*-(dimethylamino)-benzophenone (E_T = 67 kcal/mol[8b]). However, thioxanthone proved more convenient since it was more readily separated from the photolysis products by chromatography. The irradiations were carried out using a sodium metavanadate filter, removing wavelengths below 360 nm in order to ensure essentially complete light absorption by the sensitizer and none by the cyclopropene reactant. Benzene and methanol were used as solvents with equivalent results, including similar yields. The photolyses were carried to ca. 90–95% conversions. A single photoproduct resulted, and lower conversions gave only the same photoproduct. The yields of furan ranged from 55 to 68% in runs made to 95% conversion, while at conversions on the order of 35% the yields based on reacted cyclopropene were on the order of 80–85%. The singlet products,[9] 2,3,4-triphenyl-2-cyclopentenone and 3-acetyl-1,2-diphenylindene, were absent. The triplet reaction is depicted in eq 1.

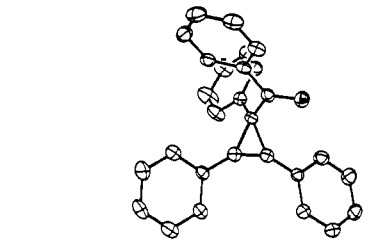
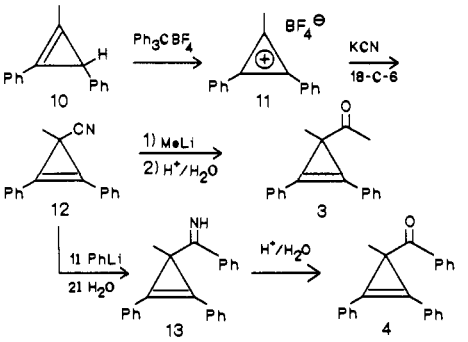
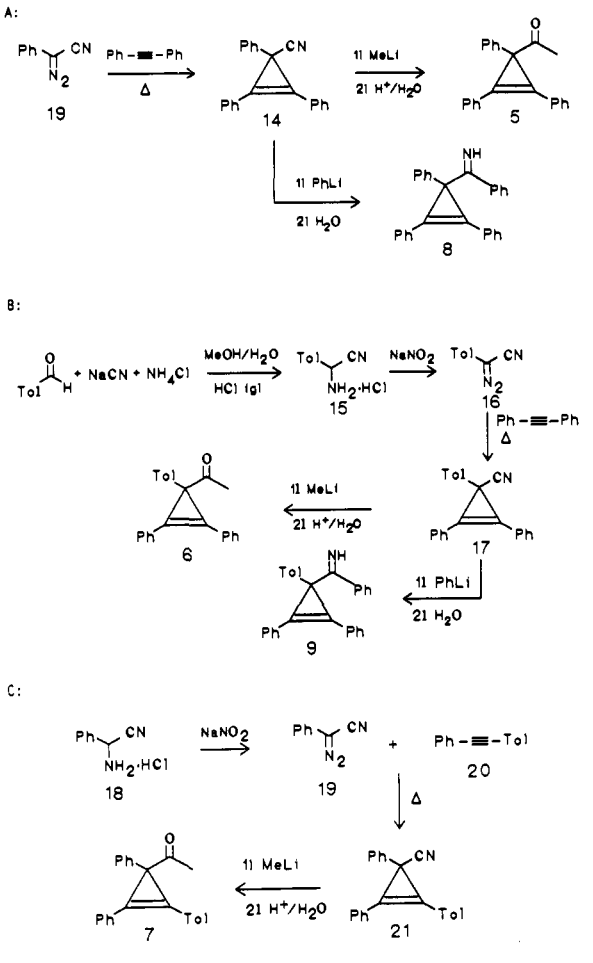


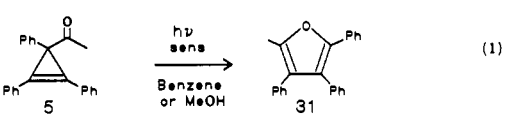
Figure 1. ORTEP drawing of cyclopropene imine **8**.

Scheme I. Syntheses of 3-Methylcyclopropenes



Scheme II. Syntheses of 3-Arylcyclopropenes and 3-Benzoylcyclopropene Imines





(1)

(6) (a) One would expect lesser steric hindrance for attack of a nucleophile at the methyl-bearing cyclopropenium carbon and greater hindrance at the phenyl-substituted carbons. (b) Simple Hückel calculations indicate a higher positive charge at the methyl carbon (electron density of 0.7059 at the methyl ring carbon versus 0.7389 at the phenyl ring carbon). Also there is NMR evidence[6c] confirming these calculations. (c) Breslow, R.; Höver, H.; Chang, H. W. *J. Am. Chem. Soc.* **1962**, *84*, 3168–3174.

(7) (a) A rearrangement of an iminocyclopropene lithium conjugate base to pyrrole has been reported.[7b] (b) Breslow, R.; Boikess, R.; Battiste, M. *Tetrahedron Lett.* **1960**, 42–44.

(8) (a) Herkstroeter, W. G.; Lamola, A. A.; Hammond, G. A. *J. Am. Chem. Soc.* **1964**, *86*, 4537–4540. (b) The triplet energy is taken as that of *p*-aminobenzophenone; see ref 8c,d. (c) Porter, G.; Suppan, P. *Trans. Faraday Soc.* **1965**, *61*, 1664–1673. (d) O'Connell, E. J. *Jr. J. Chem. Soc., Chem. Commun.* **1969**, 571–572.

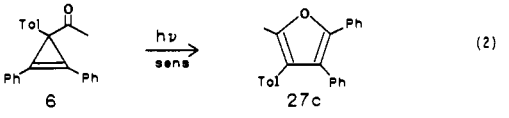
(9) Padwa, A.; Akiba, M.; Chou, C. S.; Cohen, L. *J. Org. Chem.* **1982**, *47*, 183–191.

Table I. Tabulation of Thioxanthone-Sensitized Quantum Yields

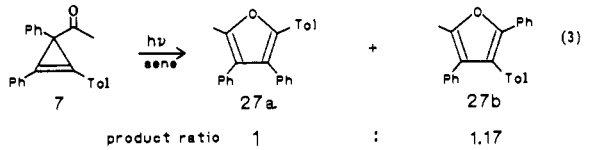
cyclopropene reactant	product	quantum yield[a]
3-acetyl-1,2,3-triphenylcyclopropene (**5**)	5-methyl-2,3,4-triphenylfuran (**31**)	0.14
3-acetyl-1,2-diphenyl-3-tolylcyclopropene (**6**)	5-methyl-2,3-diphenyl-4-tolylfuran (**27c**)	0.15
3-acetyl-2,3-diphenyl-1-tolylcyclopropene (**7**)	5-methyl-3,4-diphenyl-2-tolylfuran (**27a**)	0.066
	5-methyl-2,4-diphenyl-3-tolylfuran (**27b**)	0.068
3-benzoyl-1,2,3-triphenylcyclopropene imine (**8**)	2,3,4,5-tetraphenylpyrrole (**30a**)	0.024
3-benzoyl-1,2-diphenyl-3-tolylcyclopropene imine (**9**)	3-tolyl-2,4,5-triphenylpyrrole (**30c**)	0.025

[a] Error of ±10%.

We then proceeded to investigate the photochemical course of the reactions of 3-acetyl-1,2-diphenyl-3-tolylcyclopropene (**6**) and 3-acetyl-1-tolyl-2,3-diphenylcyclopropene (**7**). These reactants were selected because the structure of the anticipated reaction products promised to permit determination of the reaction mechanism being utilized (vide infra). Again, sensitization was with thioxanthone, and the 360-nm sodium metavanadate filter was utilized. The reactions are given in eqs 2 and 3. The yields were comparable to that obtained in the sensitized irradiation of the acetyltriphenylcyclopropene **5**.

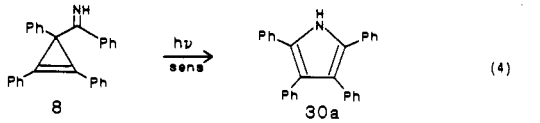


(2)

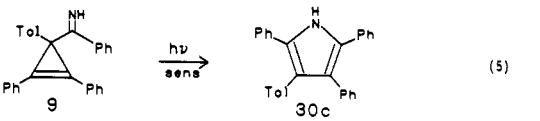


(3)

Exploratory Photolysis of 3-Acyl-1,2,3-triarylcyclopropene Imines. Two imines were photolyzed, namely, 3-benzoyl-1,2,3-triphenylcyclopropene imine (**8**) and 3-benzoyl-1,2-diphenyl-3-tolylcyclopropene imine (**9**). The photolyses were carried out in a fashion similar to that used for the acetylcyclopropenes and checked to make certain that light was not captured directly by the cyclopropenes. From each reaction one photoproduct was isolated, each a pyrrole. Interestingly, from the reaction of the benzoyltolylcyclopropene imine **9** only one *p*-tolyltriphenylpyrrole was formed. This was identified as 3-tolyl-2,4,5-triphenylpyrrole (**30c**) by its comparison with the authentic photoproduct which had been independently synthesized (note above in Scheme III). The course of these reactions is given in eqs 4 and 5. Low yields were obtained in these reactions; however, in each case, isomeric pyrroles possibly produced in the reaction were shown to be absent.



(4)

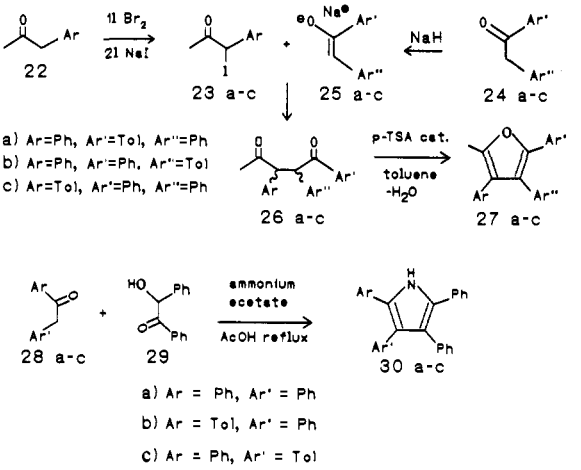


(5)

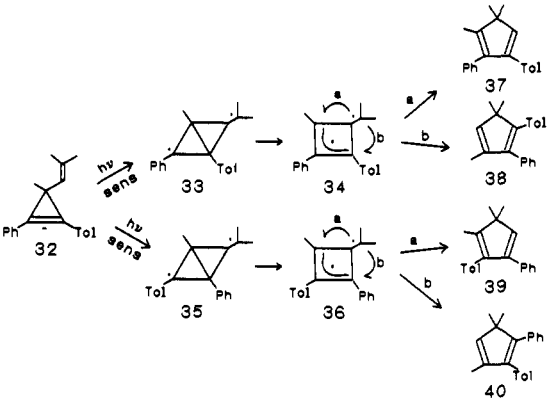
Determination of Quantum Yields. The quantum yields were determined using the black box apparatus[10] with a cobalt–copper–vanadate solution filter[2a] in conjunction with the three-compartment filter cell described earlier.[10] Concentrations were adjusted to give a 60-nm band pass of 355–415 nm to permit light absorption only by thioxanthone triplet sensitizer. Quantum yields were extrapolated to 0% conversion with runs in the range of 28 to 1%, and with most runs between 12 and 1%. The quantum yields obtained are summarized in Table I.

(10) Zimmerman, H. E. *Mol. Photochem.* **1971**, *3*, 281–292.

Scheme III. Syntheses of Potential Photoproducts



Scheme IV. Mechanism C Utilized in the Vinylcyclopropene to Cyclopentadiene Rearrangement



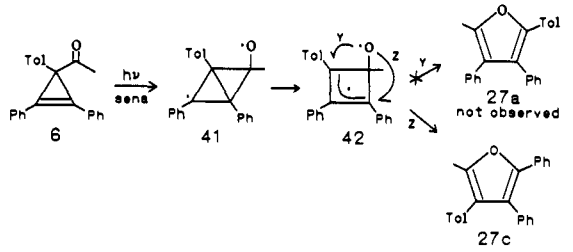
Observed Reactivity of 3-Methyl- and 3-Hydrogen-Substituted Cyclopropenes. The synthetic discussion above described the preparation of two 3-acyl-3-methylcyclopropenes. These and two 3-acylcyclopropenes unsubstituted at carbon-3 were investigated photochemically. The 3-methyl compounds **3** and **4** proved unreactive under the usual thioxanthone sensitization conditions. The unsubstituted relatives **1** and **2**, which had been previously studied by Obata and Moritani,[4a] were also investigated, and the observations of the previous investigators were confirmed, namely, the finding that only triplet dimerization products were obtained. An interpretation of the lack of rearrangements for these compounds is provided below.

Interpretative Discussion

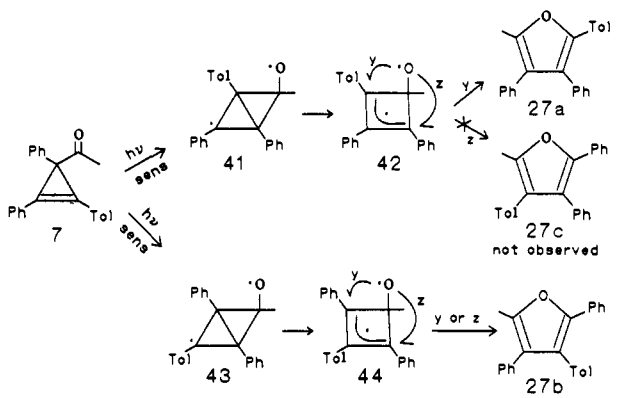
Comparison of the Triplet Vinylcyclopropene and Acylcyclopropene Reaction Mechanisms. In our previous study[2d] on the triplet rearrangement of vinylcyclopropenes, we established that of four possible reaction mechanisms mentioned earlier, "mechanism C", as outlined in Scheme IV, was operative. However, it soon became clear that the analogous acylcyclopropene rearrangement did not proceed by this mechanism. While mechanism C is capable of leading any individual acylcyclopropene reactant studied to the observed products, this mechanism possesses one fatal flaw. This is seen most clearly by inspection of Scheme

Scheme V. Mechanism C Applied to the Triplet Rearrangement of Acylcyclopropenes **6** and **7**

a. Application to Reactant **6**



b. Application to Reactant **7**



V. In this scheme, the cyclobutenyloxy diradicals **42** and **44** have the a priori option of closing in either of two ways (y and z) with net ring expansion via oxahousenes (i.e., 2-oxabicyclo[2.1.0]-pentanes) to afford furan photoproducts. In order to account for the experimentally observed products, it is seen in Scheme V that cyclobutenyloxy diradical **42** would have to proceed regioselectively with closure via path z when generated in the reaction of the 3-tolylcyclocyclopropene **6** (note Scheme Va), but **42** would have to react with opposite regioselectivity by closing via path y when generated in the reaction of the 3-phenylcyclopropene **7** (note Scheme Vb). Clearly, the relative rates of reaction of a species such as the cyclobutenyloxy diradical **42** cannot depend on the mode of its formation as long as it is thermally equilibrated.[11] We thus conclude that mechanism C is inappropriate for the acyl-cyclopropene triplet rearrangement, despite its operation in the related vinylcyclopropene reaction.

Mechanism D. A second potential reaction mechanism is one which was considered for the vinylcyclopropene rearrangement. This involves a Paterno–Büchi[12] 2 + 2 cycloaddition of the carbonyl group to the cyclopropene double bond. In our vinyl-cyclopropene efforts we termed this "mechanism D". The mechanism applied to the 3-acetyl-3-tolylcyclopropene **6** is given in Scheme VIa, while the same mechanism applied to the 3-acetyl-1-tolylcyclopropene **7** is in Scheme VIb.

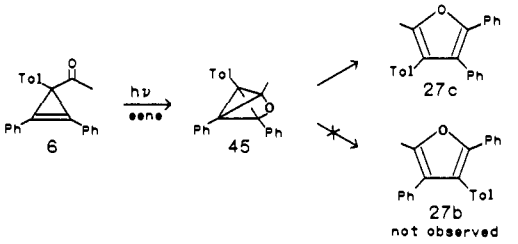
However, the same type of difficulty encountered for mechanism C again results. Thus, the tricyclic oxetane **45** is an intermediate derived from both reactants **6** and **7**. In the reaction of the 3-tolylcyclopropene **6** the mechanism leads onward regioselectively to one of the observed products, namely, the 3-tolylfuran **27c**. In the reaction of the 1-tolylcyclopropene **7**, the mechanism utilizes the same tricyclic oxetane intermediate **45**. However, in this case, the intermediate needs to be postulated as affording no 3-tolylfuran **27c** but, instead, the 3-tolylfuran **27b**. This would mean that the

(11) It is conceivable that cyclobutenyloxy diradical **42** takes on different (e.g., aryl) conformations depending on its source. However, diradical **42** arises from diradical **41** which, again, is common to both diradical sources. It seems unlikely that a different conformation would arise in this multistep mode of generation.

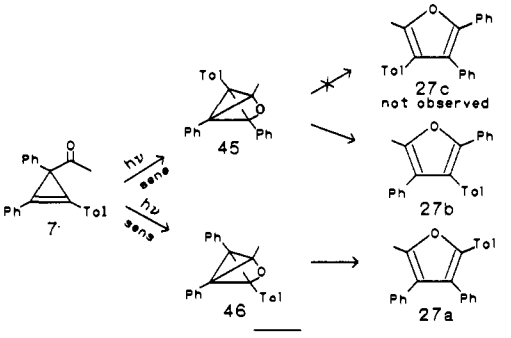
(12) (a) Paterno, E.; Chieffi, G. *Gazz. Chim. Ital.* **1909**, *39*, 341. (b) Büchi, G.; Inman, C. G.; Lipinsky, E. S. *J. Am. Chem. Soc.* **1954**, *76*, 4327–4331. (c) For a review, see: Jones, G. *Org. Photochem.* **1981**, *5*, 1–122.

Scheme VI. Mechanism D Applied to the Triplet Acylcyclopropene Rearrangement

a. Application to Reactant **6**

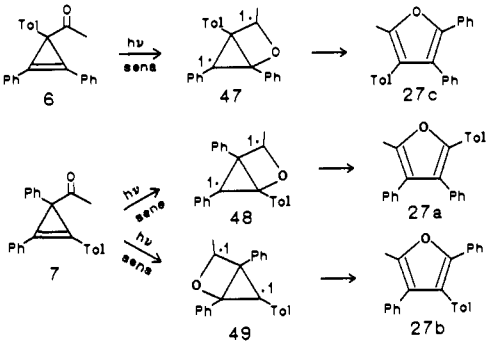


b. Application to Reactant **7**

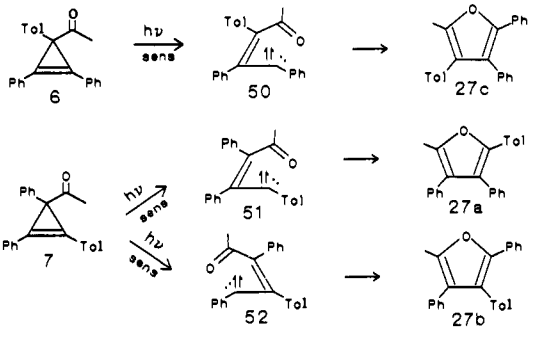


Scheme VII. Mechanisms A and B Applied to the Triplet Acylcyclopropene Rearrangement

a. Mechanism A



b. Mechanism B



partition of the tricyclic oxetane intermediate would depend on the cyclopropene forming it, which is not reasonable.

Mechanisms A and B. These mechanisms are outlined in Scheme VIIa,b. Mechanism A involves formation of an oxahousane diradical (i.e., **47**, **48**, or **49**), followed by fission of the internal C–C σ bond. In mechanism B, the chronology of these events is precisely reversed, with fission of the σ bond occurring first, to afford a triplet carbene (i.e., **50**, **51**, or **52**). Neither alternative possesses the difficulties encountered with the previous mechanisms, C and D.

Nevertheless, there are problems with mechanism B. It has been shown in elegant studies by Pincock[4d,13] that, in contrast to

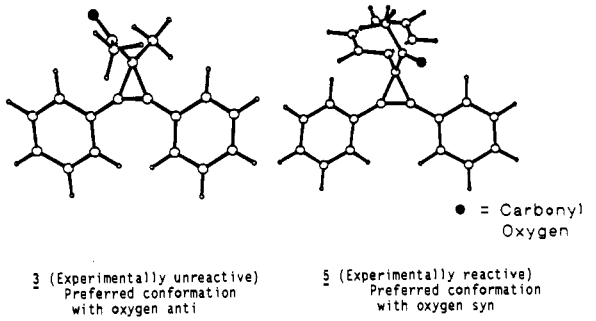


Figure 2. Preferred cyclopropene conformers.

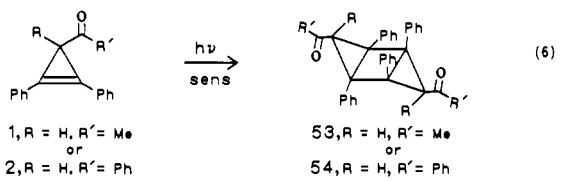
the excited singlet (i.e., the S_1) state of cyclopropenes, the triplet counterpart has a large energy barrier to three-ring opening to the triplet carbene. Similarly, our own studies[2b,c] also have demonstrated the reluctance of triplet cyclopropenes to ring open, and the same conclusion has been noted by Padwa.[14]

In contrast, mechanism A does not suffer these deficiencies. In addition, in the reaction of acetylcyclopropene **7** the, albeit small, regioselectivity favoring the 3-tolylfuran **27b** over the 2-tolylfuran **27a** can be accounted for on the basis of mechanism A. The intermediate oxahousane diradical **49** leading to the preferred ((1.17 ± 0.05):1.00) furan has a tolyl group stabilizing an odd-electron center rather than the phenyl group that stabilizes the diradical **48**, which leads to the more minor photoproduct **27a**. This is reasonable in view of the lower energy of the *p*-methylbenzyl radical relative to the benzyl radical.[15]

Nevertheless, since mechanisms A and B differ only in chronology, the actual mechanism operating may well be a composite in which the three-ring bond is in the process of opening (i.e., the process of mechanism B) while the initial carbon to oxygen bonding is occurring (i.e., the process of mechanism A). The extreme of a pure mechanism B, as noted, is unlikely, while on the contrary, a pure mechanism A is permitted by the evidence.

There is one esoteric and yet intriguing consequence of the determination that mechanism D is inapplicable while mechanism A is operative. If in mechanism A the two odd-electron centers in diradicals **47** and **49** were to intersystem cross, "touch", and bond reversibly, we would have generated the tricyclic intermediate **45** of mechanism D and provided a pathway for **47** and **49** to interconvert. Since diradicals **47** and **49** give different products, the odd-electron centers must remain at a distance. Hence, these triplet diradicals must intersystem cross to S_0 as they proceed onward to furan product, too late for any singlet diradical bonding.

Effect of C-3 Substitution on the Reaction Course. Inspection of all of the examples of the acylcyclopropene to furan rearrangement presented thus far reveals that without exception these have aryl groups at carbon-3. As stated above, cyclopropene triplets with 3-methyl or 3-hydrogen substitution did not give the rearrangement. The 3-methylcyclopropenes **3** and **4** were totally unreactive, while the 3-hydrogen-substituted compounds **1** and **2** gave rise to dimers. The dimerization of **1** and **2**, in contrast with the behavior of the 3-substituted cyclopropenes, is understandable, since the triplet dimers that would have to result from 3-substituted cyclopropenes bear R groups (note eq 6). These dimers would be badly sterically encumbered.[4c]



(6)

However, the lack of the reactivity of the 3-methylcyclopropene reactants has another source. MNDO calculations[16a,d] of the

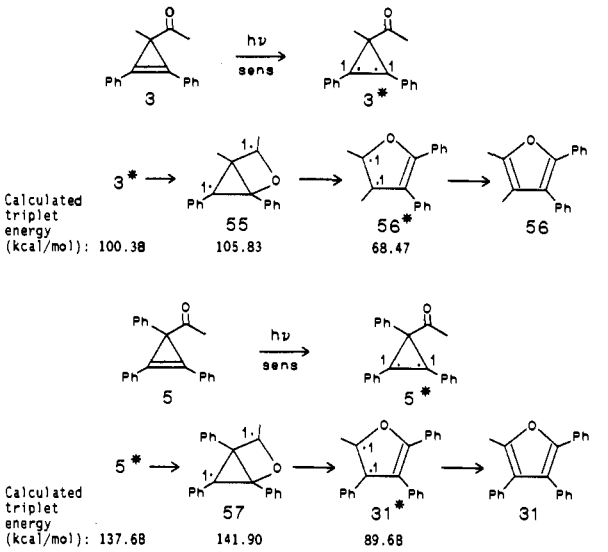


Figure 3. VAMP-MNDO computation results. The VAMP-MNDO computations afford heats of formation, including σ bond contributions, and are not to be confused with 0–0 excitation energies.

preferred conformations of the 3-phenyl- and 3-methylcyclopropenes reveal a preference for reactive and unreactive conformers, respectively, as indicated in Figure 2. The two syn and two anti conformers were obtained as local minima. However, the experimentally reactive 3-phenylcyclopropene **5** has its favored conformer with the acetyl oxygen approaching one end of the three-ring π-bond. This syn conformer is favored over its anti counterpart by 1.163 kcal/mol as determined by MNDO calculations.[16a,d] Conversely, the unreactive 3-methylcyclopropene **3** has its preferred orientation with the carbonyl oxygen anti to the three-ring π-bond. This conformer is favored by 0.663 kcal/mol over its syn counterpart. These results correspond to a 1.826 kcal/mol difference favoring reaction of the 3-phenylcyclopropene **5** over the 3-methyl analog **3**. The implicit assumption is that these differences arising from calculated ground-state steric interactions are paralleled in the reacting triplet excited state.

A second factor was determined using VAMP-MNDO computations.[16c,d] Note Figure 3. Computations afforded the triplet energies for cyclopropenes **5*** and **3***, the phenyl- and methyloxahousane diradicals **57** and **55**, and the reactive phenyl- and unreactive methylfuran triplets **31*** and **56***. The triplet energies with geometry optimization revealed closely parallel energy changes along the reaction coordinate until the triplet furans were approached. Then there was an energy drop for the reactive phenyl-substituted furan triplet **31***. This is illustrated in Figure 3. To the extent that the housane diradical formation is not rate limiting, the triplet energies of the furans would reflect the transition-state energies with a net preference for reaction leading to the phenyl-substituted furan. In this process it seems likely that intersystem crossing to the ground-state product occurs prior to the triplet furans being formed adiabatically.

Imine Reaction. While only exploratory studies were made of the rearrangement of the two imines, **8** and **9**, to afford pyrroles, it remains to be considered whether mechanism A or mechanism C, which is utilized by the vinylcyclopropene triplet rearrangement,[2d] is likely to hold for this rearrangement. Application of Schemes VIIa and V to the imine nitrogen analogs reveals that either mechanism could account for the observed photoproducts. However, mechanism C predicts that the imine analog of a diradical such as **42** (note Scheme V) should afford two photoproducts, while experimentally only one photoproduct results from the 3-tolyl imine **9**. In the corresponding vinylcyclopropene triplet

(13) Pincock, J. A.; Moutsokapas, A. A. *Can. J. Chem.* **1977**, *55*, 979–985.
(14) Padwa, A. *Org. Photochem.* **1979**, *4*, 261–326.
(15) Hayashibara, K.; Kruppa, G. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 5441–5443.

(16) (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899–4912. (b) Clark, T. Unpublished results.[16c] (c) VAMP is a vectorized semiempirical version of MOPAC (version 4.0)[d] and is available from Dr. Timothy Clark, Universität Erlangen, Nürnberg, Germany. (d) Stewart, J. J.; Seiler, F. J. *QCPE Bull.* **1985**, *5*, 133–144.

photochemistry where carbon replaced the carbonyl oxygen and imine nitrogen and where mechanism C was utilized,[2d] very little selectivity was observed in this step. In contrast, mechanism A predicts only one pyrrole product in the rearrangement. Our continuing studies will resolve this matter with more cogent information.

Conclusion. Exploratory organic photochemistry continues to provide new rearrangements, and mechanistic studies provide molecular details. In the present instance, the triplet photochemistry of cyclopropene derivatives has proven to be internally consistent within any molecular category while dramatically variable between different types.

Experimental Section[17]

1,2-Diphenyl-3-methylcyclopropenium Tetrafluoroborate (11). The general method of Breslow and co-workers was used.[6] To a solution of 6.31 g (30.6 mmol) of 1,3-diphenyl-2-methyl-1-cyclopropene[4a] (**10**) in 35.0 mL of acetonitrile was added a solution of 10.1 g (30.7 mmol) triphenylmethyl tetrafluoroborate[20] in 50.0 mL of acetonitrile. The reaction was stirred for 30 min at room temperature and was then added to cold diethyl ether. The precipitate was filtered to give 6.41 g of crude product as a bright green powder. The crude material was recrystallized twice by dissolution in the minimum amount of acetonitrile at room temperature and addition of this solution to cold ether. A total of 3.54 g (39.6%) of 1,2-diphenyl-3-methylcyclopropenium tetrafluoroborate was recovered as an off-white powder, mp 254 °C dec. The spectral data were as follows: ^{1}H NMR (CD_3CN, 200 MHz) δ 8.82–7.47 (m, 10 H, arom), 3.23 (s, 3 H, CH_3); IR (KBr) 3164, 3049, 2985, 2924, 1587, 1490, 1412, 1337, 1304, 1294, 1274, 1171, 1042, 766, 682 cm^{-1}. Anal. Calcd for $C_{16}H_{13}BF_4$: C, 65.79; H, 4.48. Found: C, 65.71; H, 4.45.

3-Cyano-1,2-diphenyl-3-methylcyclopropene (12). The method of Padwa and co-workers was used.[9] To a stirred solution of 2.26 g (7.74 mmol) of 1,2-diphenyl-3-methylcyclopropenium tetrafluoroborate (**11**) in 65 mL of acetonitrile were added 2.56 g (39.4 mmol) of potassium cyanide and 50 mg of 18-crown-6. The reaction was stirred at 0 °C for 2 h, and then the temperature was allowed to slowly rise to room temperature over 16 h. The solvent was removed in vacuo. The residue was dissolved in diethyl ether, washed with water, and dried. After filtration and removal of the solvent in vacuo, 1.80 g (100%) of a brown oil was recovered. The oil was chromatographed on a 2.8 × 63 cm silica gel column slurry packed with hexane. Elution with 1 L of hexane and then with 1% diethyl ether in hexane and collection of 50-mL fractions gave 0.467 g of a colorless oil from fractions 60–95. Upon remaining at −20 °C the oil crystallized as an off-white solid, mp 55–61 °C. The ^{1}H NMR data showed the product contained 6.7% of the isomeric 2-cyano-1,2-diphenyl-3-methylcyclopropene as a contaminant. Recrystallization from 10% benzene in hexane gave 3-cyano-1,2-diphenyl-3-methylcyclopropene, mp 67–69 °C, uncontaminated by the isomer. The spectral data were as follows: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.74–7.25 (m, 10 H, arom), 1.72 (s, 3 H, CH_3); IR (thin film) 3081, 3061, 3032, 2974, 2925, 2217, 1833, 1492, 1446, 1313, 1149, 1072, 929, 757, 688 cm^{-1}; MS *m/e* 231.1047 (calcd for $C_{17}H_{13}N$ *m/e* 231.1048). Anal. Calcd for $C_{17}H_{13}N$: C, 88.28; H, 5.66; N, 6.06. Found: C, 88.27; H, 5.63; N, 5.95.

3-Acetyl-1,2-diphenyl-3-methylcyclopropene (3). To a solution of 0.249 g (1.08 mmol) of 3-cyano-1,2-diphenyl-3-methylcyclopropene (**12**) in 5.0 mL of diethyl ether cooled to 0 °C was added 1.60 mL (2.08 mmol) of a 1.3 M MeLi solution. The resulting orange suspension was stirred at 0 °C for 3 h, and then 10 mL of saturated ammonium chloride solution was added. After the mixture was stirred for 0.5 h at room temperature, the layers were separated and the organic layer was dried. After filtration, the solvent was removed in vacuo, and the residue crystallized upon cooling to give 0.262 g of a yellow solid, mp 82–85 °C. The crude product was chromatographed using a preparative thick-layer plate. Elution with 5% acetone in hexane and removal of the R_f = 0.15 band produced 0.240 g of a pink oil which solidified upon cooling. Recrystallization twice from methanol gave 0.184 g (69.9%) of 3-acetyl-1,2-diphenyl-3-methylcyclopropene, mp 96.5–97.5 °C. The spectral data were as follows: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.66–7.41 (m, 10 H, arom), 1.84 (s, 3 H, $(CO)CH_3$), 1.58 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 212.6, 129.6, 129.4, 129.1, 126.9, 114.9, 37.0, 25.4, 16.4; IR ($CHCl_3$) 3081, 3030, 3010, 2972, 2959, 1846, 1678, 1495, 1445, 1359, 1271, 1196, 1094, 1072, 967, 913, 902, 989, 572 cm^{-1}; UV (95% EtOH) 206 (ϵ 14 850), 228 (ϵ 19 060), 298 (ϵ 19 650), λ_{max} 324 nm (ϵ 22 250); MS *m/e* 248.1214 (calcd for $C_{18}H_{16}O$ *m/e* 248.1202). Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 86.87; H, 6.46.

3-Benzoyl-1,2-diphenyl-3-methylcyclopropene Imine (13). To a solution of 0.201 g (0.87 mmol) of 3-cyano-1,2-diphenyl-3-methylcyclopropene (**12**) in 5.0 mL of diethyl ether cooled to 0 °C was added 1.6 mL (2.9 mmol) of a 1.8 M phenyllithium solution. The resulting mixture was stirred at 0 °C for 1.5 h, and then 2 mL of water was added. The layers were separated, and the ether layer was dried. After filtration, the solvent was removed in vacuo to produce 0.326 g of crude product as a soft, orange solid, mp 102–108 °C. The crude product was recrystallized from 20 mL of 25% diethyl ether in pentane to provide 0.122 g (45.3%) of 3-benzoyl-1,2-diphenyl-3-methylcyclopropene imine as a light orange solid, mp 117–119 °C. The spectral data were as follows: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.64–7.13 (m, 16 H, arom and imine H), 1.78 (s, 3 H, CH_3); IR (neat) 3078, 3055, 3040, 3029, 2962, 1837, 1594, 1574, 1492, 1444, 1374, 1369, 1193, 971, 899, 769, 699, 688 cm^{-1}; UV (cyclohexane) 208 (ϵ 20 430), λ_{max} 228 (ϵ 21 120), 320 nm (ϵ 20 200); MS *m/e* 309.1518 (calcd for $C_{23}H_{19}N$ *m/e* 309.1519). Anal. Calcd for $C_{23}H_{19}N$: C, 89.28; H, 6.19. Found: C, 89.03; H, 6.23.

3-Benzoyl-1,2-diphenyl-3-methylcyclopropene (4). To a solution of 0.195 g (0.845 mmol) of 3-cyano-1,2-diphenyl-3-methylcyclopropene (**12**) in 5.0 mL of diethyl ether cooled to 0 °C was added 1.4 mL (2.5 mmol) of a 1.8 M phenyllithium solution. The resulting suspension was stirred at 0 °C for 2 h, and then 4 mL of saturated ammonium chloride solution was added. After the mixture was stirred for 15 min, the layers were separated and the solvent was removed in vacuo. The residue was dissolved in 0.5 mL of chloroform, and 10 mL of saturated ammonium chloride solution was added. The reaction mixture was stirred for 17 h at room temperature to complete the hydrolysis. Diethyl ether was then added, and the layers were separated. The ether layer was dried and filtered, and the solvent was removed in vacuo to give 0.287 g of a brown oil. The crude product mixture was chromatographed using a deactivated 20 × 20 cm preparative thick-layer plate. Elution with 5% acetone in hexane and collection of the R_f = 0.22 band produced 0.141 g of a yellow oil which crystallized upon standing. Following recrystallization from methanol, 0.076 g (29%) of 3-benzoyl-1,2-diphenyl-3-methylcyclopropene was obtained, mp 121–122 °C. The spectral data were as follows: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.65–7.10 (m, 15 H, arom), 1.76 (s, 3 H, CH_3); IR (neat) 3078, 3058, 3028, 1654, 1493, 1445, 1283, 987, 756, 728 cm^{-1}; UV (95% EtOH) λ_{max} 202 (ϵ 2490), 232 (ϵ 1990), 304 (ϵ 1960), sh 332 nm (ϵ 988); MS *m/e* 310.1354 (calcd for $C_{23}H_{18}O$ *m/e* 310.1358). Anal. Calcd for $C_{23}H_{18}O$: C, 89.00; H, 5.84. Found: C, 88.65; H, 5.80.

3-Acetyl-1,2,3-triphenylcyclopropene (5). The method of Padwa and co-workers was used[9] employing 3-cyano-1,2,3-triphenylcyclopropene (**14**), which was made by the method of Breslow and co-workers.[7]

Attemped Oxidation of 3-Acetyl-1,2,3-triphenylcyclopropene (5).[9] Oxygen was bubbled through a solution of 0.012 g (0.037 mmol) of 3-acetyl-1,2,3-triphenylcyclopropene (**5**) in 5.0 mL of benzene for 26 h at ambient temperature. The solvent was removed in vacuo, and several

(17) Melting points were determined on a Mel-Temp heating block and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN 37921-1750. All reactions were performed under an atmosphere of anhydrous nitrogen or argon. Anhydrous magnesium sulfate was used as the drying agent unless otherwise noted. Column chromatography was performed on silica gel (J. T. Baker, Inc., 60–200 mesh) or basic alumina (Fischer Scientific, Inc., 80–200 mesh) mixed with Sylvania 2282 phosphor and slurry packed into Vycor columns permitting monitoring by hand-held UV lamps. Preparative thick-layer chromatography was carried out with MN-Kieselgel G/UV 254 silica gel. Deactivation of the thick-layer plates was accomplished where noted by pre-elution with 2% triethylamine in pentane and drying for ca. 40 min under a stream of nitrogen before use. High-pressure liquid chromatography (HPLC) was performed on a liquid chromatograph employing an LDC 254-nm detector and an LDC 6000-psi minipump, using a 0.95 × 50 cm polished stainless steel column packed with 5–15-μm porous silica beads.[18] Exploratory photolyses were conducted with a Hanovia 450-W medium-pressure mercury lamp equipped with a 2-mm Pyrex filter sleeve and used 0.4 M sodium metavanadate in 5% sodium hydroxide solution (0% T < 360 nm) as a recirculating filter solution. All photolysis solutions were thoroughly purged with purified nitrogen[19] both prior to and during photolysis. The sensitizer used in all runs was either thioxanthen-9-one or *p*-(dimethylamino)benzophenone. Photograde benzene used in photolyses was purified by successive washing with saturated potassium permanganate in 10% sulfuric acid, water, sulfuric acid until colorless, saturated aqueous sodium bicarbonate, and saturated aqueous sodium chloride, followed by drying over anhydrous calcium chloride, filtration, and distillation from calcium hydride. Tetrahydrofuran (THF) used in reactions was purified and dried by successive distillation from calcium hydride, lithium aluminum hydride, and sodium benzophenone ketyl. Diethyl ether used in reactions was distilled from sodium benzophenone ketyl. Hexane used for HPLC was washed with nitric acid and sulfuric acid (1:1), water, and saturated aqueous sodium bicarbonate, dried over calcium chloride, passed through alumina, and distilled from calcium hydride.

(18) Zimmerman, H. E.; Welter, T. R.; Tartler, D.; Bunce, R. A.; Ramsden, W. D.; King, R. K.; St. Clair, J. D.; Baker, M. R.; Mangette, J. E. Unpublished results.

(19) Meites, L.; Meites, T. *Anal. Chem.* **1948**, *20*, 984–985.

(20) Dauben, H. J., Jr.; Honnen, L. R.; Harmon, K. M. *J. Org. Chem.* **1960**, *25*, 1442–1445.

drops of methanol were added to triturate the product. The methanol was then removed in vacuo to give white solids with mp 141–142 °C which was unchanged from the starting cyclopropene. The NMR and IR spectra were also identical to the starting acetylcyclopropene.

3-Benzoyl-1,2,3-triphenylcyclopropene Imine (8). To a mixture of 0.301 g (1.03 mmol) of 3-cyano-1,2,3-triphenylcyclopropene[21] (**14**) and 10.0 mL of diethyl ether cooled to 0 °C was added 2.0 mL (4.0 mmol) of a 2.0 M phenyllithium solution. The resulting mixture was stirred for 2 h at 0 °C, and then 10 mL of water and 4.0 mL of ether were added. The ether layer was dried and filtered, and the solvent was removed in vacuo, leaving 0.451 g of a yellow semisolid residue. The residue was recrystallized from 20 mL of ether. A total of 0.275 g (72%) of 3-benzoyl-1,2,3-triphenylcyclopropene imine was obtained as off-white crystals, mp 138–139 °C. The spectral data were as follows: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.78–7.73 (m, 6 H, arom), 7.48–7.15 (m, 14 H, arom); IR ($CDCl_3$) 3079, 3059, 3024, 1599, 1572, 1493, 1445, 1351, 908, 756, 730, 688; MS *m/e* 371.1688 (calcd for $C_{28}H_{21}N$ *m/e* 371.1674). Anal. Calcd for $C_{28}H_{21}N$: C, 90.53; H, 5.70. Found: C, 90.31; H, 5.68.

2-Tolylglycinonitrile Hydrochloride (15). To a solution of 10.0 g (0.2 mol) of sodium cyanide in 40 mL of water was added 11.8 g (0.22 mol) of ammonium chloride, and the mixture was stirred until dissolution was complete. A solution of 24.0 g (0.20 mol) of *p*-tolualdehyde in 40 mL of methanol was added all at once, and the mixture was stirred for 2 h. To the mixture were added 100 mL of water and 100 mL of benzene, and the layers were separated. The aqueous layer was extracted once with 25 mL of benzene. The combined organic layers were washed once with water and then dried and filtered. Hydrogen chloride gas was bubbled through the solution until precipitation of the hydrochloride salt was complete. The solid was collected by filtration to give 17.0 g (46.5%) of 2-tolylglycinonitrile hydrochloride as a yellow solid after drying under vacuum, mp 157–160 °C dec. The spectral data were as follows: ^{1}H NMR ($CDCl_3$ and DMSO-d_6, 200 MHz) δ 9.83 (broad s, 2 H, NH_2), 7.58 (d, J = 8.0 Hz, 2 H, arom), 7.20 (d, J = 8.0 Hz, 2 H, arom), 5.44 (s, 1 H, CH), 2.31 (s, 3 H, CH_3); IR (KBr) 3426, 2840, 2603, 2363, 1587, 1516, 1281, 1188, 1125, 1103, 1004, 818 cm^{-1}; MS *m/e* 146.0843 (calcd for $C_9H_{10}N_2$ ($C_9H_{11}N_2Cl$ – HCl) *m/e* 146.0844). Anal. Calcd for $C_9H_{11}N_2Cl$: C, 59.18; H, 6.07. Found: C, 58.95; H, 6.26.

3-Cyano-1,2-diphenyl-3-tolylcyclopropene (17). The general method of Breslow and Yuan was used.[21] A solution of 7.10 g (38.9 mmol) of 2-tolylglycinonitrile hydrochloride (**15**) in 130 mL of water was washed with 65 mL of ether. A 65-mL portion of ether was then added to the aqueous layer and the mixtue was cooled to 0 °C. To the cold, two-phase mixture was added a solution of 4.0 g (58 mmol) of sodium nitrite in 33 mL of water. One milliliter of 3 N HCl solution was then added and the reaction was stirred for 5 min. The layers were separated, and the organic layer was washed with 10% sodium carbonate solution and then dried over sodium sulfate. To the water layer was added another 65 mL of ether, and the mixture was stirred for 5 min at 0 °C, at which point the layers were again separated and the organic layer was treated as above. The combined organic layers were filtered. To the ether solution was added 8.60 g (48.3 mmol) of diphenylacetylene, and the solution was warmed with a steam bath with stirring until the ether was removed. Gas evolution was vigorous and warming was continued until this had stopped. After cooling to ambient temperature, the mixture was chromatographed on a 2.8 × 30 cm alumina column slurry packed with hexane. Elution with 3 L of hexane and then with 2 L of 50% benzene in hexane and collection of 1-L fractions gave a total of 8.15 g of unreacted diphenylacetylene from fractions 1–3. A total of 0.50 g of the desired product was recovered as an oil which solidified upon cooling from fractions 3–5. The product was recrystallized using 15% benzene in hexane to produce 0.35 g (39% based upon unrecovered diphenylacetylene) of 3-cyano-1,2-diphenyl-3-tolylcyclopropene as a white solid, mp 125–126 °C. The spectral data were as follows: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.73–7.10 (m, 14 H, arom), 2.31 (s, 3 H, CH_3); IR ($CHCl_3$) 3020, 2922, 2226, 1513, 1493, 1447, 1312, 1216, 929, 826, 759 cm^{-1}; MS *m/e* 307.1356 (calcd for $C_{23}H_{17}N$ *m/e* 307.1361). Anal. Calcd for $C_{23}H_{17}N$: C, 89.86; H, 5.58; N, 4.56. Found: C, 89.45; H, 5.61; N, 4.64.

3-Acetyl-2,3-diphenyl-3-tolylcyclopropene (6). To a solution of 0.201 g (0.653 mmol) of 3-cyano-1,2-diphenyl-3-tolylcyclopropene (**17**) in 16.0 mL of ether cooled to 0 °C was added 1.3 mL (1.7 mmol) of a 1.2 M methyllithium solution. The reaction mixture was stirred at 0 °C for 3 h and then quenched by the addition of saturated ammonium chloride solution. The layers were separated, and the ether layer was concentrated in vacuo. To the remaining reside, which still contained unhydrolyzed imine by NMR and IR analysis, were added 0.20 mL of chloroform and 20 mL of saturated ammonium chloride solution, and the mixture was stirred for 18 h. The product was ether extracted and dried. The solvent was removed in vacuo to produce 0.22 g of a light-brown residue. The residue was chromatographed on a deactivated 20 × 20 cm preparative thick-layer plate. Elution with 10% acetone in hexane containing 2% triethylamine and collection of the R_f = 0.25 band produced 0.206 g (97%) of a yellow oil which was triturated with 10% benzene in hexane. The solid was collected by filtration, mp 115–116 °C. Two recrystallizations from 10% benzene in hexane produced 0.140 g (66%) of 3-acetyl-2,3-diphenyl-3-tolylcyclopropene as white crystals, mp 119–120 °C. The spectral data were as follows: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.76–7.05 (m, 14 H, arom), 2.28 (s, 3 H, CH_3-arom), 2.03 (s, 3 H, CH_3); IR ($CHCl_3$) 3057, 3023, 1686, 1512, 1495, 1446, 1353, 1193, 756, 689 cm^{-1}; MS *m/e* 324.1522 (calcd for $C_{24}H_{20}O$ *m/e* 324.1514); UV (95% EtOH) 206 (ϵ 76 250), λ_{max} 228 (ϵ 78 580), sh 286 (ϵ 42 700), 298 (ϵ 49 500), 328 nm (ϵ 50 800). Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 88.85; H, 6.40.

3-Benzoyl-1,2-diphenyl-3-tolylcyclopropene Imine (9). To a 0 °C mixture of 0.194 g (0.632 mmol) of 3-cyano-1,2-diphenyl-3-tolylcyclopropene (**17**) and 7.0 mL of ether was added 1.35 mL (2.7 mmol) of a 2.0 M phenyllithium solution. The resulting mixture was stirred for 2 h at 0 °C, and then 10 mL of water and 5.0 mL of ether were added. The layers were separated, and the aqueous layer was washed once with 10 mL of ether. The combined ether layers were dried and filtered, and the solvent was removed in vacuo to give a yellow oil which slowly crystallized upon standing but crystallized more quickly by trituration with 10% benzene in hexane. The solids were recrystallized twice from ether to give 0.193 g (94%) of 3-benzoyl-1,2-diphenyl-3-tolylcyclopropene imine as white crystals, mp 131–133 °C. The spectral data were as follows: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 9.83 (s, 1 H, NH), 7.76–6.98 (m, 19 H, arom), 2.25 (s, 3 H, CH_3-arom); IR ($CDCl_3$) 3058, 3023, 1600, 1572, 1512, 1493, 1446, 1350, 1183, 1166, 909, 756, 634, 689, 593 cm^{-1}; MS *m/e* 385.1836 (calcd for $C_{29}H_{23}N$ *m/e* 385.1830); UV (cyclohexane) 324 (ϵ 11 593), λ_{max} 232 nm (ϵ 21 437). Anal. Calcd for $C_{29}H_{23}N$: C, 90.35; H, 6.01. Found: C, 90.51; H, 6.08.

3-Cyano-2,3-diphenyl-1-tolylcyclopropene (21). A solution of 10.0 g (59.3 mmol) of phenylglycinonitrile hydrochloride (**18**) in 200 mL of water was washed with 100 mL of ether. A 100-mL portion of ether was then added to the aqueous layer, and the mixture was cooled to 0 °C. To the cold, two-phase mixture was added a solution of 6.0 g (87.0 mmol) of sodium nitrite in 40 mL of water. One milliliter of a 3 N HCl solution was then added, and the reaction was stirred for 5 min. The layers were separated, and the organic layer was washed with 10% sodium carbonate solution and then dried over sodium sulfate. To the water layer was added another 100 mL of ether, and the mixture was stirred for 5 min at 0 °C, when the layers were again separated and the organic layer was treated as above. The combined organic layers were filtered. To the ether solution was added 15.0 g (78.1 mmol) of *p*-tolylphenylacetylene[23] (**20**), and the solution was warmed on a steam bath with stirring until the ether was removed. Gas evolution was vigorous and warming was continued until this had stopped. After cooling to ambient temperature, the mixture was chromatographed on a 2.8 × 33 cm alumina column slurry packed with hexane and eluted with 4 L of hexane and then with 2 L of 50% benzene in hexane. A total of 13.8 g of unreacted tolylphenylacetylene was recovered from the hexane elutions. The desired product was recovered from the benzene in hexane fraction as 1.87 g of a yellow oil which solidified upon cooling. The product was recrystallized from 10% benzene in hexane to give 0.970 g (4% or 50% based upon unrecovered *p*-tolylphenylacetylene) of 3-cyano-2,3-diphenyl-1-tolylcyclopropene as light-yellow crystals, mp 146–147 °C. The spectral data were as follows: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.71–7.25 (m, 14 H, arom), 2.41 (s, 3 H, CH_3); IR ($CDCl_3$) 3061, 3028, 2223, 1607, 1601, 1508, 1495, 1447, 1310, 910, 817, 776, 759, 698, 689 cm^{-1}; MS *m/e* 307.1365 (calcd for $C_{23}H_{17}N$ *m/e* 307.1361). Anal. Calcd for $C_{23}H_{17}N$: C, 89.86; H, 5.58; N, 4.56. Found: C, 89.87; H, 5.80; N, 4.75.

3-Acetyl-2,3-diphenyl-1-tolylcyclopropene (7). To a mixture of 0.250 g (0.815 mmol) of 3-cyano-2,3-diphenyl-1-tolylcyclopropene (**21**) and 20.0 mL of ether cooled to 0 °C was slowed added 1.15 mL (1.72 mmol) of a 1.5 M methyllithium solution. The reaction mixture was stirred for 3 h at 0 °C. The reaction was quenched by the addition of 15.0 mL of saturated ammonium chloride solution and 3.0 mL of water. The layers were separated, and the aqueous layer was extracted three times with 10-mL portions of ether. The solvent was removed from the combined ether layers in vacuo. The residue which still contained unhydrolyzed imine by NMR and IR spectroscopy was dissolved in 0.5 mL of chloroform, 20 mL of saturated ammonium chloride solution was added, and the mixture was stirred for 16 h at ambient temperature. Ether was added to the mixture and the layers were separated. The aqueous layer was extracted three times with 10-mL portions of ether, and the combined ether layers were dried, filtered, and concentrated in vacuo to give

(21) Breslow, R.; Yuan, C. *J. Am. Chem. Soc.* **1958**, *80*, 5991–5994.
(22) Davidson, D. J. *J. Org. Chem.* **1938**, *3*, 361–364.
(23) Drefahl, G.; Ploümltner, G. *Chem. Ber.* **1958**, *91*, 1280–1285.

a brown semisolid residue. The residue was chromatographed on a deactivated 20 × 20 cm preparative thick-layer silica gel plate. Elution using 10% acetone in hexane containing 2% (by volume) of triethylamine and removal of the R_f = 0.37 band provided the desired product as a yellow oil. Trituration with 10% benzene in hexane and then recrystallization of the solids from 15% benzene in hexane gave 0.180 g (68%) of 3-acetyl-2,3-diphenyl-1-tolylcyclopropene as a white solid, mp 117–118 °C. The spectral data were as follows: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.77–7.10 (m, 14 H, arom), 2.42 (s, 3 H, CH_3-arom), 2.02 (s, 3 H, $(CO)CH_3$); IR ($CDCl_3$) 3057, 3026, 1685, 1507, 1445, 1354, 1192, 818, 761, 690 cm^{-1}; MS *m/e* 324.1513 (calcd for $C_{24}H_{20}O$ *m/e* 324.1514). Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 88.84; H, 6.25.

1,2-Diphenyl-3-tolyl-1,4-pentanedione (26c). A variation of the method of Yates and co-workers was used.[24] To a stirred suspension of 0.369 g (9.23 mmol) of sodium hydride (60% dispersion in mineral oil) and 12 mL of THF was added 1.81 g (9.22 mmol) of deoxybenzoin. When gas evolution had slowed, the mixture was warmed until a solution was obtained and gas evolution had stopped. To the sodium enolate solutions was added 2.09 g (9.21 mmol) of 2-bromo-2-tolylacetone[25a] in a rapid stream. The reaction mixture was heated at reflux for 5 h. After the reaction was cooled to ambient temperature, 5.0 mL of water and 10.0 mL of ether were added, and the resulting layers were separated. The organic layer was dried and filtered, and the solvent was removed in vacuo to give 3.47 g of a brown oil. The oil was chromatographed on a 43 × 2.8 cm silica gel column slurry packed with hexane. Elution with 1 L of hexane, 1 L of 0.5% ether in hexane, and then 5 L of 1% ether in hexane and collection of 500-mL fractions gave 0.916 g (51%) of deoxybenzoin as a yellow oil which solidified from fractions 2–7. A total of 0.223 g (7% or 14.3% based upon unrecovered deoxybenzoin) of 1,2-diphenyl-3-tolyl-1,4-pentanedione was collected as a mixture of diastereoisomers from fractions 9–12. The diastereomeric mixture was successfully used for further transformations, and attempts to separate the diastereomers were not pursued. The spectral data for the diastereomeric mixture were as follows: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.01–6.85 (m, 14 H, arom), 5.56 (d, J = 11.3 Hz, 0.7 H, CH), 5.16 (d, J = 11.0 Hz, 0.3 H, CH), 4.80 (d, J = 11.3 Hz, 0.7 H, CH), 4.56 (d, J = 11.0 Hz, 0.3 H CH), 2.23 (s, 3 H, CH_3-arom), 2.16 (s, 2 H, $(CO)CH_3$), 1.91 (s, 1 H, $(CO)CH_3$); IR ($CDCl_3$) 3060, 3028, 2923, 1714, 1678, 1598, 1447, 1352, 1284, 910, 739, 698, 541 cm^{-1}; MS *m/e* 342.1610 (calcd for $C_{24}H_{22}O_2$ *m/e* 342.1620).

2,3-Diphenyl-5-methyl-4-tolylfuran (27c). A solution of 0.223 g (0.653 mmol) of 1,2-diphenyl-3-tolyl-1,4-pentanedione (**26c**), 30.0 mL of toluene, and 0.106 g (0.56 mmol) of *p*-toluenesulfonic acid monohydrate was refluxed for 1 h with water removal via a Dean–Stark trap. The reaction was then cooled to ambient temperature, and the solvent was removed in vacuo. The residue was chromatographed using a 20 × 20 cm preparative thick-layer silica gel plate. Elution with 10% ether in hexane and collection of the R_f = 0.41 band provided 0.154 g (72.5%) of an oil which slowly crystallized upon standing, mp 105–142 °C. The solid was recrystallized twice from methanol to provide 2,3-diphenyl-5-methyl-4-tolylfuran as a white solid, mp 146–148 °C. The spectral data were as follows: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.44–7.03 (m, 14 H, arom), 2.43 (s, 3 H, CH_3-arom), 2.30 (s, 3 H, CH_3); IR ($CDCl_3$) 3058, 3051, 1600, 1512, 1501, 1443, 1246, 1070, 954, 829, 751, 700 cm^{-1}; MS *m/e* 324.1528 (calcd for $C_{24}H_{20}O$ *m/e* 324.1514). Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 88.47; H, 6.33.

2,3-Diphenyl-1-tolyl-1,4-pentanedione (26a). To a stirred suspension of 0.410 g (10.3 mmol) of sodium hydride (60% dispersion in mineral oil) and 7.0 mL of THF was added 2.10 g (10.0 mmol) of 2-phenyl-1-tolyl-1-ethanone. When gas evolution had slowed, the mixture was warmed until a solution was obtained and gas evolution had stopped. The sodium enolate solution was added to a solution of 1.75 g (8.20 mmol) of 2-iodo-2-phenylacetone prepared[26] by the addition of 2.00 g (12.0 mmol) of potassium iodide to 1.75 g (8.20 mmol) of 2-bromo-2-phenylacetone[25b] in 5.0 mL of THF. The reaction mixture was heated at reflux for 2 h. After cooling to ambient temperature, the mixture was added to 20 mL of water. Ether (15 mL) was added, and the resulting layers were separated. The aqueous layer was washed with 3 × 20 mL of ether. The combined ether layers were washed with 4 × 25 mL of 10% sodium thiosulfate solution, dried, and filtered. The solvent was removed in vacuo to give 3.87 g of a brown oil. The oil was chromatographed on a 44 × 2.8 cm silica gel column slurry packed with hexane. Elution with 1 L of hexane and then with 12 L of 0.5% ether in hexane and collection of 1-L fractions gave 0.475 g (22.6%) of the starting material, benzyl tolyl ketone, as a yellow oil which solidified from fractions 2–4. A total of 0.382 g (12% or 30% based upon unrecovered benzyl tolyl ketone) of 2,3-diphenyl-1-tolyl-1,4-pentanedione was collected as a mixture of diastereoisomers from fractions 4–13. The diastereomeric mixture was successfully used for further transformations. Attempts to separate the diastereomers were not pursued. The spectral data for the diastereomeric mixture were as follows: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.88–6.96 (m, 14 H, arom), 5.16 (d, J = 11.0 Hz, 0.8 H, CH), 4.83 (d, J = 11.3 Hz, 0.2 H, CH), 4.58 (d, J = 11.0 Hz, 0.8 H, CH), 2.31 (s, 2 H, CH_3-arom), 2.28 (s, 1 H, CH_3-arom), 2.18 (s, 2 H, $(CO)CH_3$), 1.91 (s, 1 H, $(CO)CH_3$); IR ($CDCl_3$) 3062, 3030, 1712, 1668, 1606, 1494, 1453, 1355, 1285, 908, 804, 733, 699, 548 cm^{-1}; MS *m/e* 342.1619 (calcd for $C_{24}H_{22}O_2$ 342.1620).

3,4-Diphenyl-5-methyl-2-tolylfuran (27a). A solution of 0.330 g (0.964 mmol) of 2,3-diphenyl-1-tolyl-1,4-pentanedione (**26a**), 35.0 mL of toluene, and 0.110 g (0.58 mmol) of *p*-toluenesulfonic acid monohydrate was refluxed for 1 h with water removal via a Dean–Stark trap. The reaction was then cooled to ambient temperature, and the solvent was removed in vacuo. The residue was chromatographed using a 35 × 2.8 cm silica gel column slurry packed with hexane. Elution with 500 mL of hexane, 500 mL of 0.5% ether in hexane, and 1 L of 1% ether in hexane and collection of 50-mL fractions provided 0.13 g (41%) of a white solid, mp 122–123 °C, from fractions 24–29. Recrystallization from methanol gave 3,4-diphenyl-5-methyl-2-tolylfuran as a white solid, mp 139–140 °C. The spectral data were as follows: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.33–7.02 (m, 14 H, arom), 2.43 (s, 3 H, CH_3-arom), 2.30 (s, 3 H, CH_3); IR ($CDCl_3$) 3056, 3034, 2916, 1608, 1513, 1443, 954, 908, 821, 771, 733, 701 cm^{-1}; MS *m/e* 324.1522 (calcd for $C_{24}H_{20}O$ *m/e* 324.1514). Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 88.61; H, 6.33.

1,3-Diphenyl-2-tolyl-1,4-pentanedione (26b). To a stirred suspension of 0.411 g (10.3 mmol) of sodium hydride (60% dispersion in mineral oil) and 7.0 mL of THF was added 2.10 g (10.0 mmol) of 1-phenyl-2-tolyl-1-ethanone. When hydrogen evolution had slowed, the mixture was warmed until a solution was obtained and gas evolution had stopped. The sodium enolate solution was added to a solution of 2.72 g (10.5 mmol) of 2-iodo-2-phenylacetone, which was prepared[26] by the addition of 2.10 g (12.6 mmol) of potassium iodide to 2.23 g (10.5 mmol) of 2-bromo-2-phenylacetone[25b] in 5.0 mL of THF. The reaction mixture was heated at reflux for 1.5 h. After cooling to ambient temperature, the mixture was added to 20 mL of water; 15 mL of ether was added, and the resulting layers were separated. The aqueous layer was washed with 3 × 20 mL of ether. The combined ether layers were washed with 4 × 25 mL of 10% sodium thiosulfate solution, dried, and filtered, and the solvent was removed in vacuo to give the crude product as a brown oil. The oil was chromatographed on a 61 × 2.8 cm silica gel column slurry packed with hexane. Elution with 1 L of hexane and then with 11 L of 0.5% ether in hexane and collection of 100-mL fractions gave 1.03 g (50%) of the starting 1-phenyl-2-tolyl-1-ethanone as a yellow oil which solidified from fractions 20–43. A total of 0.454 g (13.8% or 27.7% based upon unrecovered 1-phenyl-2-tolyl-1-ethanone) of 1,3-diphenyl-2-tolyl-1,4-pentanedione was collected as a mixture of diastereoisomers from fractions 43–120. The diastereomeric mixture was successfully used for further transformations; attempts to separate the diastereomers were not pursued. The spectral data for the diastereomeric mixtures were as follows: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.0–6.85 (m, 14 H, arom), 5.54 (d, J = 11.3 Hz, 0.5 H, CH), 5.16 (d, J = 11.0 Hz, 0.5 H, CH), 4.82 (d, J = 11.3 Hz, 0.5 H, CH), 4.58 (d, J = 11.0 Hz, 0.5 H, CH), 2.25 (s, 1.5 H, CH_3-arom), 2.17 (s, 1.5 H, CH_3-arom), 2.14 (s, 1.5 H, $(CO)CH_3$), 1.91 (s, 1.5 H, $(CO)CH_3$); IR ($CDCl_3$) 3059, 3027, 2923, 1711, 1678, 1597, 1512, 1447, 1355, 1284, 1249, 909, 733, 699, 690 cm^{-1}; MS *m/e* 342.1619 (calcd for $C_{24}H_{22}O_2$ *m/e* 342.1620).

2,4-Diphenyl-5-methyl-3-tolylfuran (27b). A solution of 0.493 g (1.44 mmol) of 1,3-diphenyl-2-tolyl-1,4-pentanedione (**26b**) 75 mL of toluene, and 0.149 g (0.786 mmol) of *p*-toluenesulfonic acid monohydrate was refluxed for 1 h with water removal via a Dean–Stark trap. The reaction was then cooled to ambient temperature, and the solvent was removed in vacuo. The residue was chromatographed using a 44 × 2.8 cm silica gel column slurry packed with hexane. Elution with 500 mL of hexane, 500 mL of 0.5% ether in hexane, and 1 L of 1% ether in hexane and collection of 100-mL fractions provided 0.362 g (77%) of a yellow foam from fractions 13–16. Recrystallization three times from methanol gave 0.164 g (35%) of 2,4-diphenyl-5-methyl-3-tolylfuran as white crystals, mp 108–109 °C. The spectral data were as follows: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.47–7.04 (m, 14 H, arom), 2.43 (s, 3 H, CH_3-arom), 2.33 (s, 3 H, CH_3); IR ($CDCl_3$) 3081, 3054, 2919, 1597, 1513, 1493, 1445, 955, 909, 830, 766, 733, 699 cm^{-1}; MS *m/e* 324.1515 (calcd for $C_{24}H_{20}O$ *m/e* 324.1514). Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 88.61; H, 6.41.

2-Tolyl-3,4,5-triphenylpyrrole (30b). An adaption of the method of Davidson was used for the synthesis of the pyrroles.[22] A solution of 1.99

(24) Yates, P.; Abrahams, G. D.; Betts, M. J.; Goldstein, S. *Can. J. Chem.* **1971**, *49*, 2850–2860.

(25) (a) Prepared in a manner similar to the first step in ref 25b. (b) Schultz, E.; Mickey, S. *Org. Synth.* **1949**, *29*, 38–42.

(26) Finkelstein, H. *Chem. Ber.* **1910**, *43*, 1528–1532.

g (9.47 mmol) of 2-phenyl-1-tolyl-1-ethanone, 2.00 g (9.43 mmol) of benzoin, 12.0 g (156 mmol) of ammonium acetate, and 100 mL of glacial acetic acid was heated at reflux for 1.25 h. To the hot solution was added 20 mL of hot water. The product which precipitated upon cooling was collected by filtration, washed with water, and then recrystallized from 95% ethanol. A total of 2.23 g of off-white solids, mp 181–183 °C, was recovered after reduction of the solvent volume by one-half. The solids were recrystallized from 10% benzene in hexane. After filtration and drying, 1.89 g (52%) of 2-tolyl-3,4,5-triphenylpyrrole was recovered as off-white solids, mp 185–186 °C. The spectral data were as follows: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.35 (s, 1 H, NH), 7.35–7.05 (m, 19 H, arom), 2.32 (s, 3 H, CH_3-arom); IR ($CDCl_3$) 3431, 3053, 3028, 1598, 1511, 1487, 1444, 1290, 1241, 953, 912, 820, 767, 744, 693, 554, 528 cm^{-1}; MS *m/e* 385.1843 (calcd for $C_{29}H_{23}N$ *m/e* 385.1830). Anal. Calcd for $C_{29}H_{23}N$: C, 90.35; H, 6.01. Found: C, 90,33; H, 6.21.

3-Tolyl-2,4,5-triphenylpyrrole (30c). A solution of 1.90 g (9.04 mmol) of 1-phenyl-2-tolyl-1-ethanone, 2.00 g (9.43 mmol) of benzoin, 12.0 g (156 mmol) of ammonium acetate, and 100 mL of glacial acetic acid was heated at reflux for 1 h, and then 20 mL of hot water was added. The product, which precipitated upon cooling, was collected by filtration, washed with water, and then recrystallized from 95% ethanol. A total of 1.94 g of off-white solids, mp 202–204 °C, were recovered after the volume of the recrystallization solvent was reduced by one-half and 10 mL of water was added. The solids were recrystallized from 10% benzene in hexane. The product was collected by filtration and dried to produce 1.49 g (43%) of 3-tolyl-2,4,5-triphenylpyrrole as off-white solids, mp 209–210 °C. The spectral data were as follows: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.35 (s, 1 H, NH), 7.35–6.96 (m, 19 H, arom), 2.28 (s, 3 H, CH_3-arom); IR ($CDCl_3$) 3430, 3053, 3025, 1601, 1503, 1485, 1443, 1291, 1242, 955, 908, 827, 780, 764, 697, 647 cm^{-1}; MS *m/e* 385.1843 (calcd for $C_{29}H_{23}N$ 385.1830). Anal. Calcd for $C_{29}H_{23}N$: C, 90.35; H, 6.01. Found: C, 90.48; H, 6.00.

Exploratory Sensitized Photolysis Attempt of 3-Acetyl-1,2-diphenyl-3-methylcyclopropene (3). A solution of 47.8 mg (0.192 mmol) 3-acetyl-1,2-diphenyl-3-methylcyclopropene (**3**) and 202 mg (0.953 mmol) thioxanthen-9-one in 200 mL of benzene was photolyzed for a total of 10 h. Samples of the photolysate were withdrawn periodically to check for reaction. Only the starting cyclopropene and sensitizer were observed by NMR analysis. Photolyses using (*N,N*-dimethylamino)benzophenone as the sensitizer showed only incremental photodecomposition of the sensitizer and no reaction of the cyclopropene.

Exploratory Sensitized Photolysis Attempt of 3-Benzoyl-1,2-diphenyl-3-methylcyclopropene (4). A solution of 20.0 mg (0.064 mmol) 3-benzoyl-1,2-diphenyl-3-methylcyclopropene (**4**) and 130 mg (0.615 mmol) thioxanthen-9-one in 200 mL of benzene was photolyzed for a period of 2 h. Samples of the photolysate were withdrawn at 30-min intervals to check for reaction. Only the starting cyclopropene and the sensitizer were observed by NMR analysis.

Exploratory Sensitized Photolysis of 3-Acetyl-1,2,3-triphenylcyclopropene (5). A solution of 53.2 mg (0.171 mmol) 3-acetyl-1,2,3-triphenylcyclopropene (**5**) and 84.0 mg (0.396 mmol) of thioxanthen-9-one in 200 mL of benzene was photolyzed for 30 min. NMR analysis showed that 90% of the starting cyclopropene had reacted. Concentration in vacuo and preparative thick-layer chromatographic separation of the sensitizer by elution with hexane provided 36.2 mg (68%) of a white solid, mp 144–145 °C, from the fastest moving band at R_f = 0.15, which was identified as 5-methyl-2,3,4-triphenylfuran (**31**). Sensitized photolysis in methanol proceded similarly except 95% of the starting cyclopropene had reacted in 15 min. 5-Methyl-2,3,4-triphenylfuran (55%) was isolated from the photolysate by chromatography as described above. The spectral data for the furan **31** were identical with those of the independently synthesized material.[9]

Exploratory Sensitized Photolysis of 3-Benzoyl-1,2,3-triphenylcyclopropene Imine (8). A solution of 56.5 mg (0.152 mmol) of 3-benzoyl-1,2,3-triphenylcyclopropene imine (**8**), 210 mg (0.988 mmol) of thioxanthen-9-one, and 200 mL of benzene was irradiated for 30 min. Removal of the solvent in vacuo gave a yellow solid residue. The photolysate was recrystallized from ethanol. The solvent was removed in vacuo, and the residue was chromatographed using a preparative thick-layer silica gel plate. Elution with 50% benzene in hexane and collection of the fastest moving band at R_f = 0.65 gave 12.8 mg (23%) of a yellow solid, which was identified as tetraphenylpyrrole **30a**. The spectral data for this pyrrole were identical with those of independently synthesized material.[22]

Exploratory Sensitized Photolysis of 3-Acetyl-1,2-diphenyl-3-tolylcyclopropene (6). A solution of 52.1 mg (0.161 mmol) 3-acetyl-1,2-diphenyl-3-tolylcyclopropene (**6**) and 85.4 mg (0.402 mmol) of thioxanthen-9-one in 200 mL of benzene was irradiated for 35 min. Removal of the solvent in vacuo left 143 mg of a light-yellow solid. NMR analysis showed that ca. 98% of the starting cyclopropene had reacted. The photolysate was chromatographed using a preparative thick-layer plate. Elution twice with hexane and removal of the only UV-absorbing band above the base line produced 37.8 mg (72.5%) of 2,3-diphenyl-5-methyl-4-tolylfuran (**27c**) as white solids, mp 147–148 °C. The spectral data for the furan were identical with those found for the independently synthesized material.

Exploratory Sensitized Photolysis of 3-Benzoyl-1,2-diphenyl-3-tolylcyclopropene Imine (9). A solution of 44.1 mg (0.114 mmol) of 3-benzoyl-1,2-diphenyl-3-tolylcyclopropene imine (**9**), 203 mg (0.955 mmol) of thioxanthen-9-one, and 220 mL of benzene was irradiated for 2 h. Removal of the solvent in vacuo and preparative thick-layer chromatography of the residue using 50% benzene in hexane as eluent gave 11.0 mg (25%) of a slightly yellow solid, mp 207–209 °C, from the fastest moving band at R_f = 0.323, which was identified as 3-tolyl-2,4,5-triphenylpyrrole (**30c**). The spectral data for this pyrrole were identical with those of the independently synthesized material.

Exploratory Sensitized Photolysis of 3-Acetyl-2,3-diphenyl-1-tolylcyclopropene (7). A solution of 54.2 mg (0.167 mmol) of 3-acetyl-2,3-diphenyl-1-tolylcyclopropene (**7**) and 116 mg (0.55 mmol) of thioxanthen-9-one in 200 mL of benzene was irradiated for 40 min. Removal of the solvent in vacuo left 173 mg of a light-yellow solid. The NMR spectra of this solid showed that two furans in a ratio of 1:1.17 were present. Chromatographic separation of the sensitizer by elution four times with hexane allowed the isolation of 30.7 mg (56.6% yield) of a mixture of furans as an oil from the fastest moving band. All attempts to separate the two furans by column chromatography and by HPLC were unsuccessful. The spectral data for the furans were identical with those of a 1:1.17 mixture of 3,4-diphenyl-2-tolyl-5-methylfuran (**27a**) and 2,4-diphenyl-3-tolyl-5-methylfuran (**27b**), respectively, which were independently synthesized.

Minimum Detection of Isomeric Furans and Pyrroles. To a 9.86×10^{-3} M solution of 4-tolyl-2,3-diphenyl-5-methylfuran (**27c**) in $CDCl_3$ was added 2-tolyl-3,4-diphenyl-5-methylfuran (**27a**) in a series of small portions. At a concentration of 6.41×10^{-4} M (6.5%), the 2-tolyl isomer **27a** could be detected in the presence of the 4-tolyl isomer **27c** by 200-MHz NMR spectroscopy using the same data collection parameters that were used to analyze the products from the photolyses.

To a 2.54×10^{-2} M solution of 3-tolyl-2,4,5-triphenylpyrrole (**30c**) in $CDCl_3$ was added 2-tolyl-3,4,5-triphenylpyrrole (**30b**) in a series of small portions. At a concentration of 1.55×10^{-3} M (6.1%), the 2-tolyl isomer **29b** could be detected in the presence of the 3-tolyl isomer **29c** by 200-MHz NMR spectroscopy using the same data collection parameters that were used to analyze the products from the photolyses.

Photostability of Furan and Pyrrole Photoproducts. A solution of 32.0 mg (0.0986 mmol) of 2,4-diphenyl-5-methyl-3-tolylfuran (**27b**) and 99.5 mg (0.469 mmol) of thioxanthen-9-one in 200 mL of benzene was photolyzed for 30 min using the same conditions and equipment used for the cyclopropene photolyses. NMR analysis of the photolysate showed significant decomposition of the furan had occurred. The photolysate was chromatographed using a preparative thick-layer plate. Elution with hexane and collection of the only band above the base line gave 14.3 mg (44%) of the starting 2,4-diphenyl-5-methyl-3-tolylfuran.

A solution of 51.4 mg (0.159 mmol) of 2-tolyl-3,4,5-triphenylpyrrole (**30b**) and 200 mg (0.943 mmol) of thioxanthen-9-one in 200 mL of benzene was photolyzed for 2 h. NMR analysis of the photolysate indicated almost complete decomposition of the pyrrole had occurred.

Conformations of Cyclopropenes 3 and 5. The conformational optimizations were carried out on the ground electronic states of 3-acetyl-1,2-diphenyl-3-methylcyclopropene (**3**) and 3-acetyl-1,2,3-triphenylcyclopropene (**5**) using the MNDO method[16a] incorporated in the MOPAC program package.[16b] For each compound, optimizations were carried out with two starting geometries. The first had the carbonyl group pointing away from the double bond of the cyclopropene. In this conformation, the oxygen atoms were as far from the cyclopropene double bond as possible. The second starting geometry had the carbonyl group directly over the cyclopropene double bond. In this conformation, the oxygen was as close to the cyclopropene double bond as possible. All parameters were allowed to optimize. The energy minima and the corresponding conformations were obtained and are shown in Table II.

Triplet Energy Calculations. Triplet energies for the cyclopropenes **3*** and **5***, the methyl- and phenyloxahousane diradicals **55** and **57**, and the methyl- and phenylfurans **31*** and **56*** were determined using the MNDO[16a] method incorporated into the VAMP program package.[16c] For each structue, the calculations were performed on the triplet states, and all parameters were allowed to optimize. For the furans **31*** and **56***, the calculations revealed steric congestion of the groups on the furan by producing the lowest energies when the aromatic rings were twisted out of coplanarity with the π-system of the furan. The calculation results are as given in Figure 3.

Table II. Optimized Conformations and Energies for Cyclopropanes 3 and 5

	optimized results			
cyclopropene	angle[a]	distance[b]	distance[c]	MNDO energy[d] (kcal/mol)
3	45.2059	3.4551	3.7627	64.9235
3	124.1776	2.9329	3.3110	65.5869
5	4.1663	3.6980	3.7404	102.6483
5	145.7003	2.9247	3.1657	101.4856

[a] Dihedral angle between the carbonyl oxygen and the atom attached to the 3-carbon of the cyclopropene. [b] Distance in angstroms from the oxygen atom to the closest cyclopropene double-bonded carbon. [c] Distance in angstroms from the oxygen atom to the farthest cyclopropene double-bonded carbon. [d] Heat of formation value from the calculation.

Photolysis Equipment for Quantum Yield Determinations. Quantum yields were performed on the "Wisconsin black box".[10] Light output was measured with a digital actinometer[27] calibrated by ferrioxalate actinometry.[28] The following filter solution combination was used: (a) 1.0 M copper sulfate in 5% sulfuric acid, (b) 2.0 M cobalt sulfate in 5% sulfuric acid, (c) 0.1 M sodium metavanadate in 5% sodium hydroxide solution; this combination gave a transmission maximum at 376 nm (15.6% transmission) and was opaque above 416 and below 356 nm. All runs were performed in 250 mL of benzene utilizing thioxanthen-9-one as the sensitizer and were analyzed by 200- or 270-MHz NMR spectroscopy with triphenylmethane as the internal standard or by HPLC (20% chloroform in hexane) and NMR where indicated. The photoreactions were found to be oxygen sensitive, and all runs were thoroughly purged with deoxygenated[19] nitrogen for a minimum of 2 h before and during the photolyses. In each case only photoproducts and only the original reactant cyclopropene were detected.

Extrapolated quantum yield data is given in Table I. Typical runs are summarized below. The data are listed as follows: mass (mmol) of starting cyclopropene; mass (mmol) of thioxanthen-9-one sensitizer; light absorbed; mmol of photoproduct, quantum yield; percent conversion. Analysis was by NMR integration.

3-Acetyl-1,2,3-triphenylcyclopropene (5). Run 1A: 20.6 mg (0.0664 mmol) of cyclopropene; 105.2 mg (0.495 mmol) of sensitizer; 0.0057 mE; 0.000 76 mmol of 5-methyl-2,3,4-triphenylfuran (**31**), $\phi = 0.133$; 1.1%. Run 1B: 22.0 mg of (0.0709 mmol) cyclopropene; 105.2 mg (0.495 mmol) of sensitizer; 0.036 mE; 0.0043 mmol of furan $\phi = 0.119$; 6.1%. Run 1C: 20.0 mg (0.0644 mmol) of cyclopropene; 100.6 mg (0.474 mmol) of sensitizer; 0.056 mE; 0.0058 mmol of furan, $\phi = 0.104$; 9.0%. Run 1D: 20.7 mg (0.0667 mmol) of cyclopropene; 102.3 mg (0.482 mmol) of sensitizer; 0.080 mE; 0.0081 mmol of furan, $\phi = 0.101$; 12.1%.

Sensitized Quantum Yield Results for 3-Acetyl-1,2-diphenyl-3-tolylcyclopropene (6). Run 2A: 20.3 mg (0.0626 mmol) of cyclopropene; 99.0 mg (0.466 mmol) of sensitizer; 0.030 mE; 0.0040 mmol of 5-methyl-2,3-diphenyl-4-tolylfuran (**27c**), $\phi = 0.133$; 6.4%. Run 2B: 20.7 mg (0.0638 mmol) of cyclopropene; 99.7 mg (0.470 mmol) of sensitizer; 0.037 mE; 0.0046 mmol of furan, $\phi = 0.124$; 7.2%. Run 2C: 20.7 mg (0.0638 mmol) of cyclopropene; 101.8 mg (0.479 mmol) of sensitizer; 0.041 mE; 0.0048 mmol of furan, $\phi = 0.117$; 7.5%. Run 2D: 20.5 mg (0.0632 mmol) of cyclopropene; 100.4 mg (0.473 mmol) of sensitizer; 0.203 mE; 0.0142 mmol of furan, $\phi = 0.070$; 22.5%.

Quantum Yield Results for 3-Acetyl-2,3-diphenyl-1-tolylcyclopropene (7). The data are listed as follows: mass (mmol) of starting cyclopropene; mass (mmol) of thioxanthen-9-one sensitizer; light absorbed; mmol of photoproduct 1 (5-methyl-2,4-dimethyl-3-tolylfuran (**27b**)), quantum yield; mmol of photoproduct 2 (5-methyl-3,4-dimethyl-2-tolylfuran (**27a**)), quantum yield; percent conversion. Analysis was by 270-MHz NMR integration. Run 3A: 20.5 mg (0.0632 mmol) of cyclopropene; 99.8 mg (0.470 mmol) of sensitizer; 0.035 mE; 0.0022 mmol of photoproduct 1, $\phi = 0.063$; 0.0022 mmol of photoproduct 2, $\phi = 0.063$; 7.0%. Run 3B: 20.3 mg (0.0626 mmol) of cyclopropene; 100.3 mg (0.472 mmol) of sensitizer; 0.052 mE; 0.0028 mmol of photoproduct 1, $\phi = 0.054$; 0.0026 mmol of photoproduct 2, $\phi = 0.050$; 8.6%. Run 3C: 20.3 mg (0.0626 mmol) of cyclopropene; 99.7 mg (0.470 mmol) of sensitizer; 0.079 mE; 0.0035 mmol of photoproduct 1, $\phi = 0.045$; 0.0033 mmol of photoproduct 2, $\phi = 0.042$; 11.1%. Run 3D: 20.1 mg (0.0620 mmol) of cyclopropene; 100.6 mg (0.474 mmol) of sensitizer; 0.106 mE; 0.0047 mmol of photoproduct 1, $\phi = 0.044$; 0.0047 mmol of photoproduct 2, $\phi = 0.044$; 15.2%.

Sensitized Quantum Yield Results for 3-Benzoyl-1,2,3-triphenylcyclopropene Imine (8). Analysis was by HPLC and NMR integration. Run 5A: 20.4 mg (0.0549 mmol) of cyclopropene; 102.7 mg (0.484 mmol) of sensitizer; 0.592 mE; 0.0071 mmol of tetraphenylpyrrole **30a**, $\phi = 0.012$; 12.9%. Run 5B: 19.8 mg (0.0533 mmol) of cyclopropene; 97.2 mg (0.458 mmol) of sensitizer; 0.551 mE; 0.011 mmol of pyrrole, $\phi = 0.020$; 20.6%. Run 5C: 20.8 mg (0.0560 mmol) of cyclopropene; 101.3 mg (0.477 mmol) of sensitizer; 0.797 mE; 0.0150 mmol of pyrrole, $\phi = 0.019$; 26.8%. Run 5D: 20.2 mg (0.0544 mmol) of cyclopropene; 100.1 mg (0.471 mmol) of sensitizer; 1.07 mE; 0.015 mmol of pyrrole, $\phi = 0.014$; 27.6%.

Sensitized Quantum Yield Results for 3-Benzoyl-1,2-diphenyl-3-tolylcyclopropene Imine (9). Run 4A: 21.1 mg (0.0547 mmol) of cyclopropene; 101.0 mg (0.476 mmol) of sensitizer; 0.119 mE; 0.0026 mmol of 2,4,5-triphenyl-3-tolylpyrrole (**30c**), $\phi = 0.022$; 4.7%. Run 4B: 19.5 mg (0.0506 mmol) of cyclopropene; 100.1 mg (0.471 mmol) of sensitizer; 0.347 mE; 0.0062 mmol of pyrrole, $\phi = 0.018$; 12.2%. Run 4C: 19.4 mg (0.0503 mmol) of cyclopropene; 97.7 mg (0.460 mmol) of sensitizer; 0.750 mE; 0.010 mmol of pyrrole, $\phi = 0.013$; 19.9%. Run 4D: 20.8 mg (0.0540 mmol) of cyclopropene; 95.8 mg (0.450 mmol) of sensitizer; 0.768 mE; 0.0089 mmol of pyrrole, $\phi = 0.012$; 16.5%.

Single-Crystal X-ray Structure of 3-Acetyl-1,2-diphenylcyclopropene (1). Crystals of 3-acetyl-1,2-diphenylcyclopropene were prepared by slow crystallization from methanol. X-ray data were collected with Mo Kα radiation on a Siemens P3f diffractometer at −165 °C from a colorless prism of dimensions 0.10 × 0.20 × 0.50 mm. Unit cell parameters were obtained by least-squares refinement of 24 reflections ($21.00° < 2\theta < 30.00°$). Data were collected in the (*hkl*) range (−2,0,0) to (6,9,34), with 3 reflections monitored out of every 50. A total of 1631 unique data was collected, with 1187 of $F > 3.0\sigma(F)$. Lorentz and polarization corrections were applied, and the structure was solved under $P2_12_12_1$ symmetry by direct methods using SHELXTL PLUS (VMS).[29] Hydrogen atoms were located from difference Fourier syntheses, and full-matrix least-squares refinement was carried out with anisotropic parameters for all non-hydrogen atoms and with isotropic thermal parameters for all hydrogen atoms. Refinement of 164 parameters converged to $R_1(F) = 5.90\%$ and $R_w(F) = 5.02\%$. Results and structural parameters are available as supplementary material.

Single-Crystal X-ray Structure of 3-Acetyl-1,2-diphenyl-3-methylcyclopropene (3). Crystals of 3-acetyl-1,2-diphenyl-3-methylcyclopropene were prepared by slow crystallization from ether. X-ray data were collected with Cu Kα radiation on a Siemens P3f diffractometer at −165 °C from a colorless crystal of dimensions 0.10 × 0.35 × 0.45 mm. Unit cell parameters were obtained by least-squares refinement of 25 reflections ($31.00° < 2\theta < 50.00°$). Data were collected in the (*hkl*) range (−7,0,0) to (7,13,18) with 3 reflections monitored for every 100. A total of 1959 independent reflections were collected, with 1563 of $F > 4.0\sigma(F)$. Lorentz and polarization corrections were applied, and the structure was solved under $P2_12_12_1$ symmetry by direct methods using SHELXTL PLUS (VMS).[29] Hydrogen atoms were located from difference Fourier syntheses, and full-matrix least-squares refinement was carried out with anisotropic parameters for all non-hydrogen atoms and with isotropic thermal parameters for all hydrogen atoms. Refinement of 179 parameters converged to $R_1(F) = 6.94\%$ and $R_w(F) = 8.03\%$. Results and structural parameters are available as supplementary material.

Single-Crystal X-ray Structure of 3-Acetyl-1,2-diphenyl-3-tolylcyclopropene (6). Crystals of 3-acetyl-1,2-diphenyl-3-tolylcyclopropene were prepared by slow crystallization from ether. X-ray data were collected with Mo Kα radiation on a Siemens P3f diffractometer at −165 °C from a colorless crystal of dimensions 0.20 × 0.45 × 0.60 mm. Unit cell parameters were obtained by least-squares refinement of 24 reflections ($22.00° < 2\theta < 26.00°$). Data were collected in the (*hkl*) range (−10,−10,−20) to (3,10,20) with 3 reflections monitored for every 100. A total of 4738 independent reflections were collected, with 3136 of $F > 4.00\sigma(F)$. Lorentz and polarization corrections were applied, and the structure was solved under $P\bar{1}$ symmetry by direct methods using SHELXTL PLUS (VMS).[29] Hydrogen atoms were located from difference Fourier syntheses, and full-matrix least-squares refinement was carried out with anisotropic parameters for all non-hydrogen atoms and with isotropic parameters for all hydrogen atoms. Refinement of 452 parameters converged to $R_1(F) = 8.05\%$ and $R_w(F) = 10.24\%$. Results and structural parameters are available as supplementary material.

Single-Crystal X-ray Structure of 3-Benzoyl-1,2,3-triphenylcyclopropene Imine (8). Crystals of 3-benzoyl-1,2,3-triphenylcyclopropene imine were prepared by slow crystallization from ether. X-ray data were

(27) Zimmerman, H. E.; Cutler, T. P.; Fitzgerald, V. R.; Weight, T. J. *Mol. Photochem.* **1971**, *3*, 281–292.

(28) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *23*, 518–536.

(29) Sheldrick, G. M. SHELXTL PLUS, Version 4.1, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1990.

collected with Mo Kα radiation on a Siemens P3f diffractometer at −165 °C from a colorless crystal of dimensions 0.40 × 0.40 × 0.60 mm. Unit cell parameters were obtained by least-squares refinement of 24 reflections (21.00° < 2θ < 27.00°). Data were collected in the (*hkl*) range (−11,−15,−16) to (0,15,17) with 3 reflections monitored out of every 100. A total of 5350 independent reflections were collected, with 3722 of $F > 4.00\sigma(F)$. Lorentz and polarization corrections were applied, and the structure was solved under $P\bar{1}$ symmetry by direct methods using SHELXTL PLUS (VMS).[29] Hydrogen atoms were located from difference Fourier syntheses, and full-matrix least-squares refinement was carried out with anisotropic parameters for all non-hydrogen atoms and with isotropic thermal parameters for all hydrogen atoms. Refinement of 524 parameters converged to $R_1(F) = 4.31\%$ and $R_w(F) = 4.25\%$. Results and structural parameters are available as supplementary material.

Acknowledgment. Support of this research by the National Science Foundation and NIH Grant GM07487 is gratefully acknowledged. Initial synthetic portions of the research were supported by the National Institutes of Health, while the subsequent parts and mechanistic aspects were supported by NSF.

Supplementary Material Available: Tables of molecular coordinates and geometries from single-crystal X-ray structure determinations of **1**, **3**, **6**, and **8** (28 pages). Ordering information is given on any current masthead page.

Flavin-6-carboxylic Acids as Novel and Simple Flavoenzyme Models. Nonenzymatic Stabilization of the Flavin Semiquinone Radical and the 4a-Hydroperoxyflavin by Intramolecular Hydrogen Bonding

Taishin Akiyama,[†] Fusae Simeno,[†] Morio Murakami,[‡] and Fumio Yoneda*,[†]

Contribution from the Faculty of Pharmaceutical Sciences, Kyoto University, Sakyo-ku, Kyoto, 606-01, Japan, and Chemistry Research Laboratories, Takeda Chemical Industries, Ltd., Yodogawa-ku, Osaka, 532, Japan. *Received January 2, 1992. Revised Manuscript Received April 18, 1992*

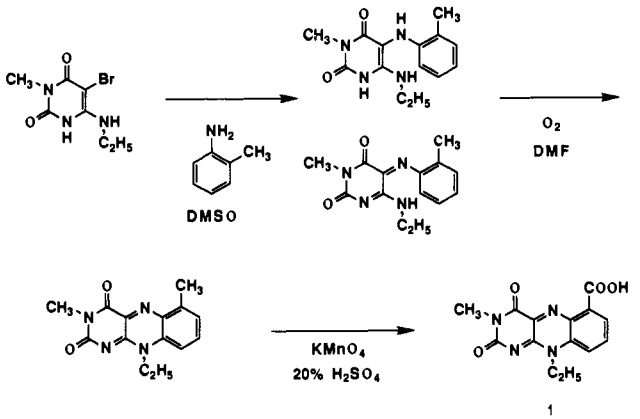
Abstract: Novel flavin derivatives, 10-ethyl-3-methylisoalloxazine-6-carboxylic acid (**1**) and 10-ethyl-3-methylisoalloxazine-6,8-dicarboxylic acid (**2**), which have a carboxyl group at C(6) position, were prepared. Even in the absence of metal cations and under aerobic condition, these flavin derivatives produced the corresponding stable semiquinone radicals by the dithionite reduction in sodium phosphate buffer (pH 6.89). Hyperfine electron spin resonance (ESR) spectra for the flavin semiquinone radicals have been obtained and were stable even after 1 day under ambient circumstances. Further characterization was obtained for these semiquinone radicals by UV–visible spectroscopy. The quantum chemical calculations have shown that the highest spin densities are located at N(5) position, and ESR experiments in D_2O established that the exchangeable protons are attached to N(5). The flavin-6-carboxylic acids **1** and **2** also activated H_2O_2 oxidizing thioanisoles to their sulfoxides. These remarkable reactivities of the flavin derivatives **1** and **2** were ascribed to the intramolecular hydrogen bonding between N(5) and carboxyl group at C(6) position of the flavin nucleus.

Introduction

Flavin coenzymes represented by FAD (flavin adenine dinucleotide) and FMN (flavin mononucleotide) play important roles in versatile redox reactions involving oxygen atom transfer and one-electron transfer as well as hydrogen transfer in many biological systems.[1] In order to catalyze the reactions in such systems, flavin coenzymes can take three readily accessible oxidation states, which include oxidized, semiquinone radical, and reduced forms.

It has been documented that, at the flavoenzymes active sites, there are many hydrogen bondings between heteroatoms of flavin coenzymes and amino acid residues of the apoproteins and that these hydrogen bondings are of importance for promotion of the reactivities of flavoenzymes including the regiospecific activation of flavin skeleton.[2] Massey and Hemmerich[3] have proposed to classify the flavoenzymes into two classes in terms of the position of hydrogen bonding with flavin skeleton; one group has a hydrogen bonding with the N(1) position which activates the C(10a) position, another has a hydrogen bonding with the N(5) position which activates the C(4a) position. Shinkai and co-workers[4] have synthesized a flavin derivative which has an ability of intramolecular hydrogen bonding between N(5) and phenolic hydroxy group. They have shown that thiols oxidation using this flavin involves C(4a) intermediates and was accelerated by activation of the C(4a) position through the above hydrogen bonding.[5]

Scheme I. Synthesis of Flavin Derivative **1**



1

[†] Kyoto University.
[‡] Takeda Chemical Industries, Ltd.

(1) (a) Chance, B.; Williams, G. R. *J. Biol. Chem.* **1955**, *217*, 383–393. (b) Pouslen, L. L.; Zeigler, D. M. *J. Biol. Chem.* **1979**, *254*, 6449–6455.
(2) Burnett, R. M.; Darling, G. D.; Kendal, D. S.; LwQuesn, M. E.; Mayhew, S. G.; Smith, W. W.; Ludwig, M. L. *J. Biol. Chem.* **1974**, *249*, 4383–4392.

0002-7863/92/1514-6613$03.00/0