at the lowest possible temperature was performed on the product. A mixture of 1 ml of distilled water, 2 ml of absolute methyl alcohol, and 500 mg (3.07 mmol) of sodium diazodicarboxylate in a 5-ml round-bottomed flask equipped with magnetic stirrer was degassed by bubbling argon through it, then cooled to a barely stirrable paste by means of an acetone–Dry Ice bath. A solution of 370 mg (6.15 mmol) of acetic acid in 1 ml of absolute methyl alcohol was similarly degassed and cooled. While several milligrams of *trans*-9,10-dihydronaphthalene was irradiated for 2 min at −190° a small portion of the methanolic acetic acid (~$^1/_5$th) was added to the stirring diimide reduction paste. After photolysis the EPA solution of photoproduct was poured into the stirring diimide reduction mixture by melting the frozen EPA glass with the warmth of the fingers; this addition was followed by rapid addition of the remaining methanolic acetic acid. The reaction mixture was allowed to warm up to room temperature over 15–20 min, and then extracted with three 3-ml portions of pentane. The combined pentane extracts were washed with two 3-ml portions of distilled water, dried briefly over magnesium sulfate, filtered, and concentrated to ~50 ml on a rotary evaporator. Analysis by glpc on both STAP and DC550 columns (see below) showed the presence of cyclodecane as an approximately 40% component of the hydrocarbon products. This compound was identified by comparison of retention time and coinjection with authentic material prepared by Wolf–Kishner reduction of commercial cyclodecanone. The product of four such photolyses and low-temperature diimide reductions, when combined and purified by glpc, afforded sufficient material for substantiation of the identity of cyclodecane by comparison of its mass spectral fragmentation pattern with that of authentic material.

In approximate repetitions of the above procedures (RHG), similar results were observed. Irradiations were carried out on appropriate amounts of **3** in 6 ml of EPA, contained in a quartz reaction vessel thoroughly degassed with nitrogen. The sample, cooled to −190° in liquid nitrogen, was irradiated for 45-sec periods each of seven times, with 2537-Å light from a Rayonet reactor fitted out with a new lamp.

A slurry of 1.0 g of potassium diazodicarboxylate in 4 ml of methanol and 2 ml of water which had been thoroughly degassed with argon was treated with a few drops of a solution of 0.7 ml of acetic acid in 2 ml of methanol, and was then cooled to −78° with a Dry Ice–isopropyl alcohol bath. The photoproduct was raised to this temperature with a similar bath and transferred by syringe to the diimide reduction flask. The remainder of the acetic acid solution was then added, and the reduction system was allowed to come to room temperature over 30 min and then stirred an additional 30 min. The crude product was then isolated by pentane–water extraction and carefully concentrated under low vacuum. The crude product was then reduced again with hydrogen over 5% palladium on charcoal.[14] After isolation and analysis, the results in Table IV were obtained. In two of the above irradiation experiments, the cyclodecane was isolated by glpc and identified by its characteristic nmr peak (singlet at τ 1.50).

Table IV. Per Cent Yields of Products in Diimide Reduction of [10]Annulene

Concn	*trans*-Decalin	*cis*-Decalin[b]	Cyclodecane[b]
2.5×10^{-2}	97		
$1.5\text{–}4.0 \times 10^{-3}$ [a]	92	88	12
$1.5\text{–}4.0 \times 10^{-3}$ [a]	85	67	33
6×10^{-4}	78	86	14

[a] Estimated. [b] Based on starting material consumed.

Acknowledgment. The authors express appreciation to ARO(D) for grant support (Project No. CRD-AA-5227-C).

Valence Tautomers of Heterocyclic Aromatic Species[1a]

E. E. van Tamelen* and Thomas H. Whitesides[1b]

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. Received September 30, 1970

Abstract: The photorearrangement of 2,5-di-*tert*-butylfuran (**1**) to 2,4-di-*tert*-butylfuran (**17**) and 2,2,7,7-tetramethylocta-4,5-dien-3-one (**18**) has been shown to proceed *via* the di-*tert*-butyl cyclopropenyl ketone (**16**). Independent photolysis of the furan **17** gave no cyclopropenyl ketone **16**. These results and the formation of 1,5-di-*tert*-butyl-3,3-dimethylbicyclo[3.1.0]hexan-2-one (**3**) and the cyclopropenyl ketone (**4**) from 2,3,5-tri-*tert*-butylfuran (**2**) are rationalized in terms of a proposed general mechanism for the photochemical rearrangement of five-membered aromatic heterocyclic compounds.

The photochemistry of five-membered aromatic heterocycles has been the object of a considerable amount of study since the first irradiation-induced conversion of a benzenoid to a valence bond isomer (Dewar benzene) was reported in 1962.[2a] However, there has so far been no attempt to arrive at a systematic view of the reactions and rearrangements which these molecules undergo on irradiation. As part of a broader study of valence tautomers of aromatic systems,[2b] we have examined the photochemistry of some derivatives of furan.[3] These results, together with related work carried out in these laboratories and the rearrangements reported in the literature, have allowed us to arrive at a general mechanistic description of the photochemical behavior of these compounds.

The furan derivatives chosen for study were 2,5-di-*tert*-butylfuran[4] (**1**) and 2,3,4-tri-*tert*-butylfuran[5] (**2**). The tri-*tert*-butyl derivative in particular seemed a likely candidate for conversion to valence tautomers, especially the Dewar isomer, because the nonplanarity of the latter structure would offer relief of the considerable strain involved in the presence of two (cis) *tert*-butyl

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[1] (a) Abstracted from the Ph.D. Thesis of T. H. Whitesides (Stanford University, 1969); (b) National Science Foundation Graduate Fellow, 1964–1968.

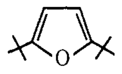
[2] (a) E. E. van Tamelen and S. P. Pappas, *J. Amer. Chem. Soc.*, **84**, 3789 (1962); (b) E. E. van Tamelen, *Angew. Chem., Int. Ed. Engl.*, **4**, 738 (1965).

[3] A portion of these results has been communicated previously: E. E. van Tamelen and T. H. Whitesides, *J. Amer. Chem. Soc.*, **90**, 3894 (1968).

[4] R. Ramasseul and A. Rassat, *Bull. Soc. Chim. Fr.*, **30**, 2214 (1963).

[5] H. Wynberg and U. E. Wiersum, *Chem. Commun.*, 1 (1965).

groups. Introduction of these bulky substituents has the added advantage that their presence might discourage polymerization reactions by preventing the close approach of the reactive centers of two molecules.



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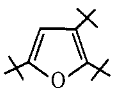
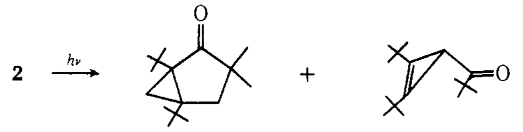


2

Results

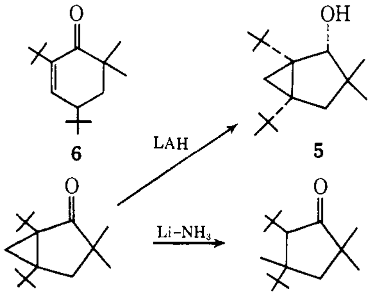
In the event, furan **2** rearranged smoothly under irradiation in pentane in almost quantitative yield to a mixture of two products in the approximate ratio of 20:1. The major product, isolated by preparative glpc, was a ketone (ν_{CO} 1716 cm^{-1}). Bands at 3060 and 1001 cm^{-1} marked the presence of a cyclopropane ring, and this assignment was supported by the appearance in the nmr spectrum of a one-proton doublet at τ 9.34. Surprisingly, however, the nmr also showed that only two *tert*-butyl groups remained in the structure (two nine-proton singlets at τ 8.88 and 8.82). Two magnetically equivalent methyl groups, apparently the remains of the third *tert*-butyl group, appeared as a six-proton singlet at τ 9.00. The rest of the spectrum consisted of a resonance at τ 8.61 coupled (J = 5.5 Hz) with the upfield cyclopropyl proton and also with one other proton (J' = 2 Hz). Finally, resonances at τ 8.37 (H_a) and 8.06 (H_b) formed an ABX pattern with J_{ab} = 13.1 Hz, J_{ax} = 0 Hz, and J_{bx} = 2 Hz. The uv spectrum (λ_{max} 206.5 mμ) suggested that the cyclopropane ring and the carbonyl group were conjugated. Since the photoproduct (molecular ion at m/e 236) was an isomer of the starting furan, these data led to the proposal that the structure of the photoketone was 1,4-di-*tert*-butyl-3,3-dimethylbicyclo[3.1.0]hexan-2-one (**3**).



3 (90%) 4 (5%)

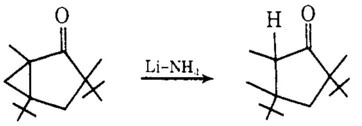
Chemical confirmation of this structure was provided by three separate reactions (Scheme I). Reduction of the photoketone with lithium aluminum hydride gave an 80% yield of the alcohol **5**. The nmr spectrum of this compound was very similar to that of **3** except that the resonance at τ 8.61 was shifted upfield to 9.18, and a singlet at 6.32 appeared (C*H*OH). That this proton is a singlet indicates that there are no protons α to the carbonyl group in the photoketone. The stereochemistry shown is the result of hydride addition from the least-hindered side, and is consistent with the lack of long-range coupling between H_2 and the exo proton at C-6.

Scheme I



6 5 3 6

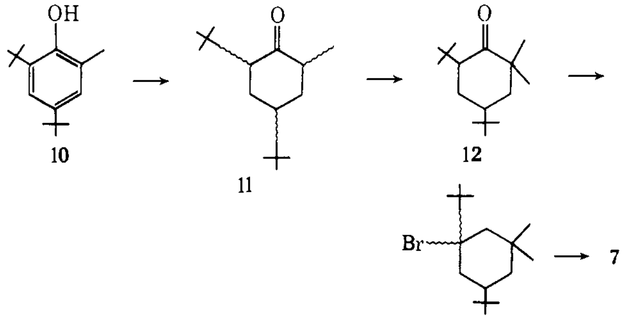
Reduction of the photoketone with lithium in liquid ammonia[6] gave (82%) a cyclopentanone (**6**, ν_{CO} 1719 cm^{-1}), the nmr spectrum of which showed *singlets* for each of three nonequivalent methyl groups. The absence of any secondary methyl group eliminates the mechanistically less likely structure **8** for the photoketone, since this compound on reduction should give cyclopentanone **9**, a structure incorporating a secondary methyl group at C-5.



8 9

Finally, the reaction of the photoketone with acid afforded a 70% yield of the cyclohexenone **7** (ν_{CO} 1683, ν_{CC} 1668 cm^{-1}). This compound (λ_{max} 237 mμ (calcd[7] 235 mμ) showed one vinyl proton (τ 3.33) and two distinct methyl groups as singlets at τ 8.94 and 8.90 in the nmr. Further, this cyclohexenone was identical with an authentic sample synthesized by the route shown in Scheme II.

Scheme II



10 11 12 13

In the first step of the synthesis, *o*-cresol was alkylated with isobutylene and sulfuric acid to give 2,4-di-*tert*-butyl-6-methylphenol (**10**),[8] which was reduced with hydrogen and Raney nickel according to Whitaker.[9] This treatment gave a mixture of the ketone **11** and the corresponding alcohol. Oxidation of the mixture with sodium dichromate in acetic acid–sulfuric acid–benzene,[10] followed by fractional distillation, gave the pure ketone as a mixture of stereoisomers. The alkylation of **11** proceeded without difficulty under the conditions of Vanderwerf and Lemmermann.[11] The dimethyl di-*tert*-butyl ketone **12** was obtained in reasonable yield as estimated by glpc, but considerable loss on recrystallization of the product reduced the isolated yield of material with a fairly sharp melting point (80–82°) to only 12%. Bromination of this ketone with bromine in acetic acid containing a trace of hydrogen bromide gave a quantitative yield of the bromo ketone **13**, a mixture of

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(6) T. Norin, *Acta Chem. Scand.*, **19**, 1289 (1965).

(7) C. N. R. Rao, "Ultraviolet and Visible Spectroscopy," 2nd ed, Butterworths, London, 1967.

(8) G. H. Stillson, D. W. Sawyer, and C. K. Hunt, *J. Amer. Chem. Soc.*, **67**, 303 (1945).

(9) A. C. Whitacker, *ibid.*, **69**, 2415 (1947).

(10) E. W. Warnhof, D. G. Martin, and W. S. Johnson, "Organic Syntheses," Collect. Vol. 4, Wiley, New York, N. Y., 1963, p 164, note 1.

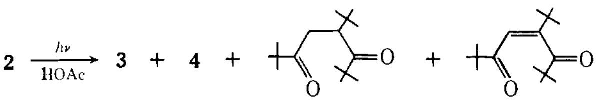
(11) C. A. Vanderwerf and L. V. Lemmermann, "Organic Syntheses," Collect. Vol. 3, Wiley, New York, N. Y., 1955, p 44.

C-2 stereoisomers. Without purification or separation of these isomers, the bromo ketone was treated with lithium carbonate in dimethylformamide,[12] affording in 87% yield the desired enone **7**, identical in all respects with the sample prepared by acid rearrangement of the photoketone.

The structure of the minor product from the photolysis of the furan **2** was inferred by comparison of the glpc trace of the product mixture from the pentane photolysis with that of the product mixture from the photolysis of the same compound in acetic acid. This comparison showed that the minor product has the same retention time as a peak identified as being due to the cyclopropenyl ketone **4** (see below).

When a solution of the furan **2** was irradiated in glacial acetic acid, a much more complicated product mixture resulted (Scheme III). Some of the major components of this mixture were identified as 1,2-di-*tert*-butyl-3-pivaloylcyclopropene (**4**, 6%), starting material (**2**, 19%), 4-*tert*-butyl-2,2,7,7-tetramethyloctane-3,6-dione (**14**, 5%), the corresponding enedione (**15**, 14%), and the photoketone (**4**, 6%). The most interesting of these products, cyclopropenyl ketone **4**, was identified by its spectral properties as follows. In the ir spectrum, bands at 1891 and 1684 cm^{-1} indicated that the compound was a cyclopropenyl ketone.[13] The nmr spectrum showed only three singlets at τ 8.89, 8.83, and 7.41 in the approximate ratio of 18:9:1. The mass spectrum was very simple, having, in addition to the peak for the molecular ion at m/e 236, principal fragment ions at m/e 221 (M − CH_3), 151 (base peak, di-*tert*-butylcyclopropenium ion), and 57 (*tert*-butyl cation). The strength of the m/e 151 peak is strong evidence for the proposed structure. The other two new compounds were identified principally by their spectral characteristics, which were consistent with the structures shown. In addition, the enedione **15** was identical with a persistent contaminant of the furan **2** which appeared when samples of the furan were allowed to stand in the presence of air for extended periods of time.

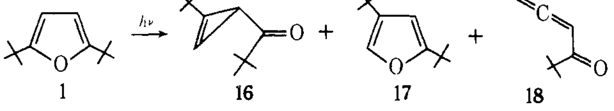
Scheme III



14 15

In the interests of understanding the rearrangement involved in the formation of the photoketone **3** more fully, the photolytic behavior of 2,5-di-*tert*-butylfuran was investigated. When this photolysis was carried out under the conditions used for the first photolysis of **3** (pentane solvent) a complex mixture of products was formed. From this mixture, a number of interesting compounds could be isolated (Scheme IV; Figure 1).

Scheme IV



1 16 17 18

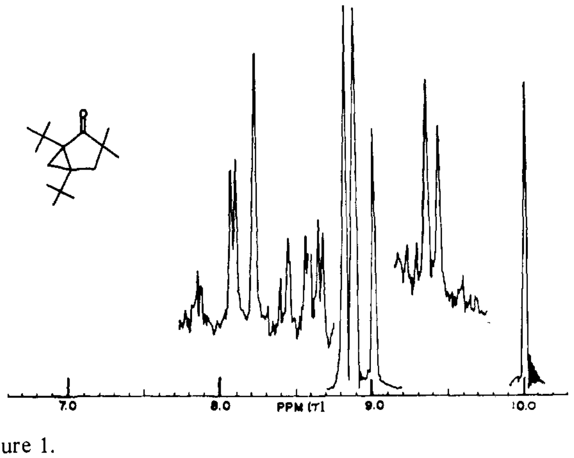


Figure 1.

The cyclopropenyl ketone **16**, isolated in about 4% yield (based on recovered starting material), had bands in the ir spectrum at 1693 (ν_{CO}) and 3150, 1790, and 1775 cm^{-1} (cyclopropene with one vinyl substituent[13]). The nmr spectrum showed two singlets for nonequivalent *tert*-butyl groups at τ 8.87 and 8.83, in addition to two one-proton doublets (J = 1.8 Hz) at 7.35 and 4.09 for the methine and vinyl protons, respectively. These data, together with peaks in the mass spectrum at m/e 180 (molecular ion) and 95 (*tert*-butylcyclopropenium ion, base peak at 12 eV), place structure **16** on firm ground.

The other two products were both formed in about 9% yield (based on recovered starting material). One, at shorter retention time on glpc, was identified as 2,4-di-*tert*-butylfuran (**17**) by comparison of its properties with those of an authentic sample (see below) and with the properties reported for this furan in the literature.[14] The other major product was identified as the allenyl ketone **18**. This unusual compound[15–17] was identified on the basis of its strong absorptions in the ir spectrum at 1950 (ν_{allene}) and 1690 cm^{-1} (ν_{CO}), its uv spectrum (λ_{max} 228 mμ), and its nmr spectrum, which showed two nonequivalent *tert*-butyl resonances at τ 8.88 and 8.84, together with two doublets in the olefinic region (τ 4.55 and 4.00) with a coupling constant of 6.2 Hz. Since the compound is isomeric with the starting material (molecular ion at m/e 180), these data require structure **18**.

Chemical evidence for the structure of the cyclopropenyl ketone was obtained by reduction to a cyclopropyl ketone by means of hydrogen over platinum. Preparative glpc of the products resulting from the hydrogenation of a small sample of **16** allowed the separation of a compound which had properties corresponding to the cyclopropyl ketone **19**: ir ν_{CO} 1695, ν_{Δ} 1070 cm^{-1}; nmr *tert*-butyl resonances at τ 9.08 and 8.82, plus multiplet; mass spectrum m/e 182 (M^+). As might have been anticipated, this compound was *not* identical with an authentic sample of *trans*-pivaloyl-2-*tert*-butylcyclopropane (**21**) synthesized by the reaction of dimethyloxosulfonium methylide[18] with the unsaturated ketone **20**.[19,20] Since cyclopropenes are known to hydro-

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(12) P. Pelc, S. Hermanek, and J. Holubek, *Collect. Czech. Chem. Commun.*, **26**, 1852 (1961).

(13) G. L. Closs, *Advan. Alicyclic Chem.*, **1**, 53 (1966).

(14) J. A. Miller, Milt Durand, and J. E. Dubois, *Tetrahedron Lett.*, 2831 (1965).

(15) To our knowledge, only two allenyl ketones have been described in the literature.[16,17] Both are natural products.

(16) J. Meinwald, K. Ericson, M. Hartshorn, Y. C. Meinwald, and T. Eisner, *Tetrahedron Lett.*, 2959 (1968).

(17) T. Mibi and Y. Hara, *Pharm. Bull.*, **4**, 89 (1956).

(18) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1353 (1965).

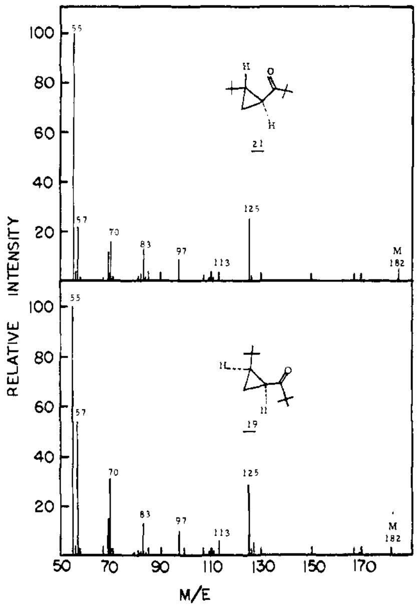
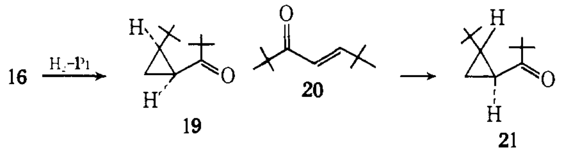


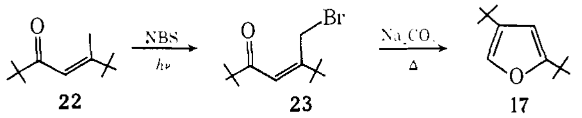
Figure 2. Mass spectra of *cis*- and *trans*-pivaloyl-*tert*-butylcyclopropane.

genate to cis-substituted cyclopropanes,[13] **19** probably has the stereostructure shown, while the method of synthesis of the authentic sample should give the more stable trans isomer, **21**. This hypothesis is supported by the very close similarity of the mass spectra of the two compounds (see Figure 2).



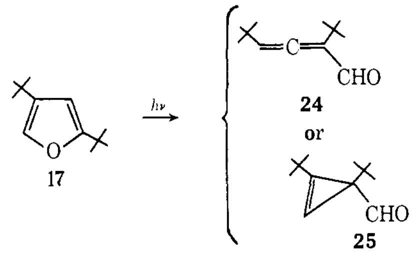
Further evidence for the intermediacy of three-membered ring compounds in the photolysis of **1** comes from the isolation of the *trans*-cyclopropyl ketone **21** (in addition to **16**, **17**, and **18**) from an irradiation carried out in ether. This product was identified by comparison of ir and nmr spectra with those of the authentic sample.

Because a sample of 2,4-di-*tert*-butylfuran (**17**) was desired for photolysis studies and comparison with the photoproduct isolated above, a synthesis was carried out as shown. The unsaturated ketone **22**[21] was



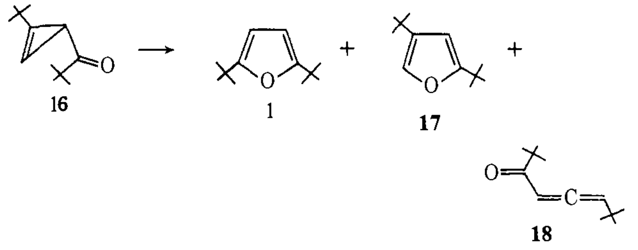
treated with *N*-bromosuccinimide in refluxing carbon tetrachloride with simultaneous irradiation by means of a GE sunlamp. The bromide obtained, **23**, was difficult to purify on a preparative scale, so that the crude bromination mixture was usually heated with solid sodium carbonate (the major contaminant was **23**), and the furan was isolated by preparative glpc after distillation of this reaction mixture at reduced pressure. The furan prepared in this manner was identical in all respects with the aromatic photoproduct from furan **1**.

Irradiation of **17** in pentane gave a very complex mixture of products, none of which was the same (glpc comparison) as any of the products obtained from the photolysis of **1**. Only one product could be isolated in nearly pure form, and it was identified as either **24** or **25** by means of ir and nmr data. In the nmr, peaks at τ 8.87, 8.86, 5.66, and 0.60 (singlets, ratio 9:9:1:1) are probably consistent with either structure, though the fact that both *tert*-butyl resonances are well below τ 9 and the olefinic proton is at such high field favors the allenyl aldehyde structure **24**. A band at 1938 cm^{-1} in the ir spectrum also supports structure **24**; but this spectrum also showed a weak band at 1770 cm^{-1}, in the position expected for the cyclopropenyl structure **25**. On the basis of the available data, a decision cannot be made unequivocally as to which structure is correct. From a mechanistic standpoint, this question is not, fortunately, a crucial one.



Several lines of evidence lend support to the contention that the cyclopropenyl ketone **16** is an intermediate photorearrangement of the furan **1**. First, irradiation of this ketone under the same conditions used for 2,5-di-*tert*-butylfuran gave, in addition to the aforementioned heterocycle, both 2,4-di-*tert*-butylfuran (**17**) and the allene **18**. Ketone **16** *can* therefore serve as an intermediate.

Scheme V



If there is no direct route from **1** to **17** and **18**, and if **16** is an intermediate in this transformation, then

$$[d(\mathbf{17})/dt]_{t=0} = [d(\mathbf{18})/dt]_{t=0} = 0$$

and $[d(\mathbf{16})/dt]_{t=0} > 0$. Therefore, plots of **17**/**16** ($\approx$ [d**17**/d*t*]/[d**16**/d*t*]) and **18**/**16** ($\approx$[d**18**/d*t*]/[d**16**/d*t*]) should both extrapolate to zero at zero time. Such a plot is shown in Figure 3, which is based on values shown in Table I. The ratio **17**/**18** clearly shows an intercept of 0.4 ± 0.1, in contrast to the zero intercepts of the other two lines.

Further support for this conclusion comes from the results of a similar study of the photolysis of **1** using the same light source, but including a filter of chlorine gas. The use of this filter cuts out some of the light emitted by the source in the 300-mμ region, that wavelength most strongly absorbed by the carbonyl group of the

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(19) J. Colonge and J. Grenet, *Bull. Soc. Chim. Fr.*, 1304 (1954).

(20) K. Wilberg and T. W. Hutton, *J. Amer. Chem. Soc.*, 76, 5367 (1954).

(21) J. Colonge, *Bull. Soc. Chim. Fr.*, 1, 1107 (1934); 2, 61 (1935).

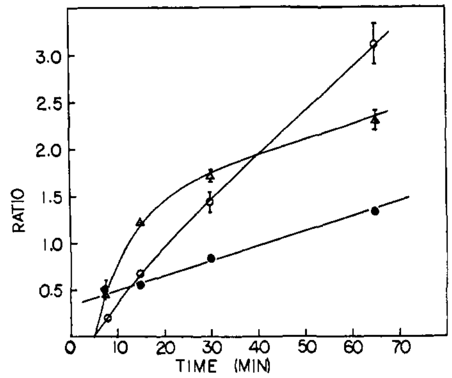

Figure 3. Plot of the ratios of products from the photolysis of 2,5-di-*tert*-butylfuran; no filter: △, **18/16**; ⊙, **17/16**; ●, **17/18**.

cyclopropene **16**. Under these conditions, the cyclopropene is not destroyed as rapidly by secondary photoreactions and so it is present in higher relative concentration during the photolysis. The results are shown in Table II and Figure 4.

Table I. Ratios of Amounts of Products Formed on Photolysis of 2,5-Di-*tert*-butylfuran as a Function of Time

Time, min	17/16	18/16	17/18
0			
4	0	0	
8	0.20 ± 0.05	0.45 ± 0.05	0.5 ± 0.1
15	0.67 ± 0.04	1.22 ± 0.04	0.55 ± 0.04
30	1.42 ± 0.08	1.71 ± 0.07	0.83
65	3.1 ± 0.2	2.3 ± 0.1	1.33
170	9.6 ± 1	3.7 ± 0.4	2.62

Table II. Ratios of Amounts of Products Formed on Photolysis of 2,5-Di-*tert*-butylfuran as a Function of Time (Chlorine Filter)

Time, min	17/16	18/16	17/18
0			
45	0.152 ± 0.003	0.28 ± 0.01	0.52 ± 0.02
90	0.274 ± 0.005	0.440 ± 0.008	0.62 ± 0.03
180	0.49 ± 0.02	0.65 ± 0.05	0.76 ± 0.05
300	0.6 ± 0.1	0.66 ± 0.05	0.91 ± 0.09

The ratios **17/16** and **18/16** both extrapolate to zero, whereas the ratio **17/18** extrapolates to the same value (0.40 ± 0.05) as before. Therefore, even though the rate of formation of **16** was increased considerably (by a factor of 3 or 4) relative to its rate of destruction by the use of the chlorine filter, the initial relative rates of formation of **17** and **18** remained the same. This fact could be true only coincidentally if there were a direct route from the starting furan to **17** and **18**. That **17** and **18** come from **16** and not some other intermediate is strongly suggested by the fact that the ratio **17/18** (0.5 ± 0.1) observed in the photolysis of the cyclopropenyl ketone is the same, within experimental error, as the extrapolated values of Figures 3 and 4.

Thus cyclopropene **16** seems certain to be an intermediate in the conversion of **1** to the other products. Can the same statement be made concerning the cyclopropene **4** obtained in the photolysis of tri-*tert*-butylfuran **2**? Examination of Table III and Figure 5 suggests that the answer is probably no, the initial relative rate of formation of photoketone **3** and **4** being 0.6 ± 0.1 and not zero. Further, as shown in Figure 6, the cyclopropene builds up to a small equilibrium concentration, which then remains essentially unchanged after 10 min of photolysis. This fact, coupled with the observation of a good material balance in this reaction, prabably means that the cyclopropene **4** can revert photochemically to the furan. The information concerning the stoichiometric[22] mechanism of these reactions thus obtained is summarized in Scheme VI.

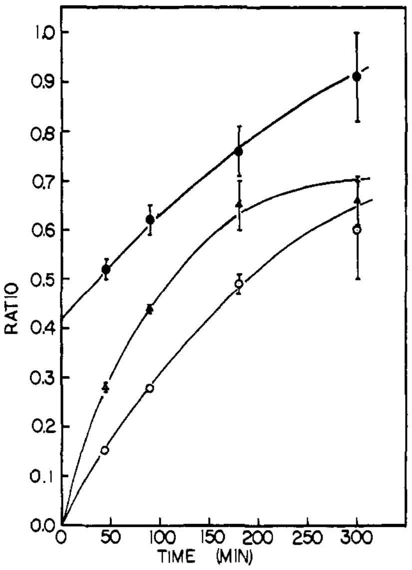

Figure 4. Plot of the ratios of products from the photolysis of 2,5-di-*tert*-butylfuran; chlorine filter: △, **18/16**; ⊙, **17/16**; ●, **17/18**.

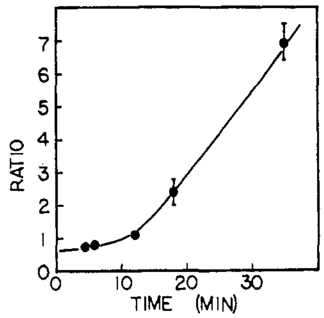

Figure 5. Ratio of products (**3**/**4**) in the photolysis of 2,3,5-tri-*tert*-butylfuran.

Table III. Ratio of Products in the Photolysis of 2,3,5-Tri-*tert*-butylfuran

Time, min	Ratio 3/4
0	
2	
4.5	0.74 ± 0.05
6	0.81 ± 0.05
12	2.1 ± 0.1
18	3.4 ± 0.4
35	6.9 ± 0.6
65	11 ± 1

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[22] For a definition of this usage, see: C. H. Langford and H. B. Gray, "Ligand Substitution Reactions," W. A. Benjamin, New York, N. Y., 1966.

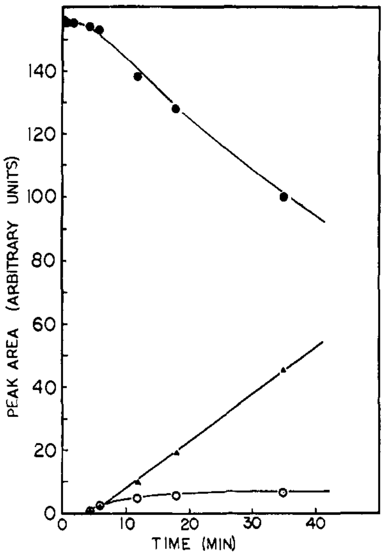
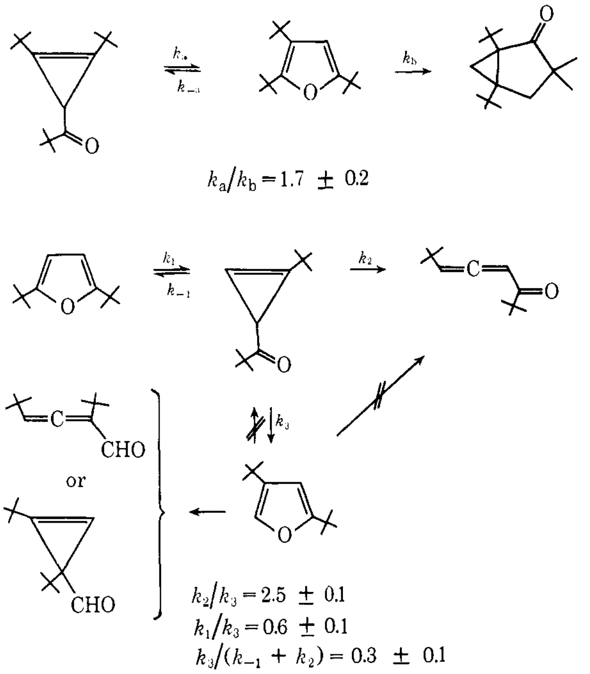


Figure 6. Relative concentrations of products as a function of time in the photolysis of 2,3,5-tri-*tert*-butylfuran: ●, **2**; ⊙, **4**; ▲, **3**.

Scheme VI. Stoichiometric Mechanism of Poly(*tert*-butylfuran) Photolysis

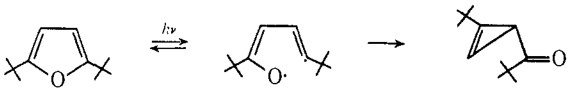


$k_a/k_b = 1.7 \pm 0.2$

$k_2/k_3 = 2.5 \pm 0.1$
$k_1/k_3 = 0.6 \pm 0.1$
$k_3/(k_{-1} + k_2) = 0.3 \pm 0.1$

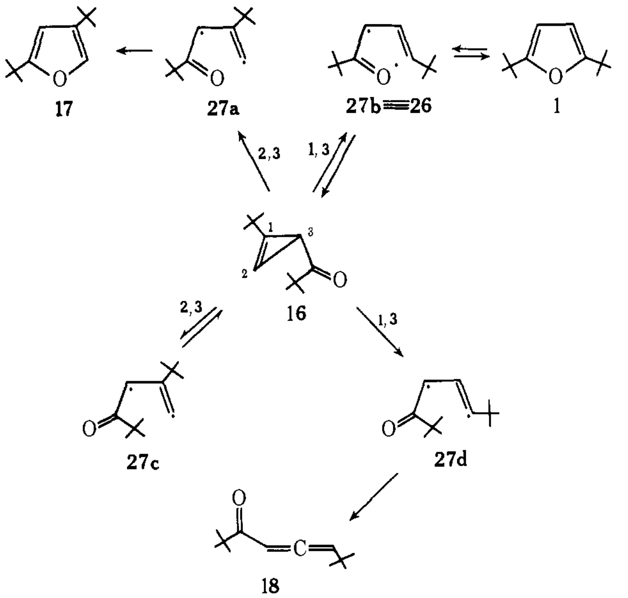
Discussion

These data can be rationalized in terms of a mechanism involving C–O bond cleavage as the immediate result of the excitation. Thus, 2,5-dibutylfuran **1** undergoes cleavage to give diradical **26**, which can close to give either the cyclopropene **16** or the starting furan.



1 26 16

The absorption of a second quantum of light by **16** again results in cleavage. In this case, however, several different intermediates are possible, depending on which bond in the three-membered ring breaks, and on which conformation the oxygen atom assumes in the intermediate. The diradicals **27a** and **27b** have the proper cisoid conformation of the oxygen atom and the vinyl radical center to close to furans: **27a**, resulting

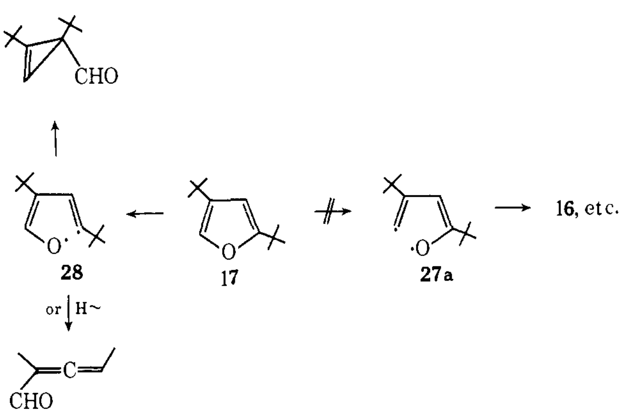


17 **27a** **27b**═**26** **1** **16** **27c** **27d** **18**

from cleavage of the 2,3 bond in the cyclopropene, leads to the rearranged furan **1**; while **27b**, resulting from cleavage of the 1,3 bond, is the same as **26**, and gives back the starting furan.

If the oxygen atom is trans to the vinyl radical center, closure to a furan is unlikely for steric reasons. In structure **27d**, stabilization of the diradical is achieved by migration of a hydrogen atom to give the allenyl ketone **18**. The alternative cleavage, resulting in the formation of **27c**, probably does not give any net reaction, since *tert*-butyl migration does not compete effectively with reclosure to give the cyclopropene.

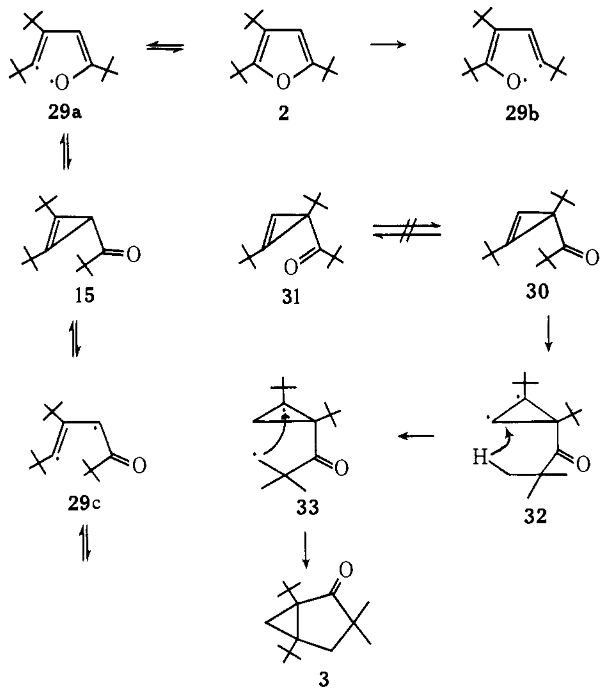
The results obtained on photolysis of 2,4-di-*tert*-butylfuran reveal that the reaction is highly selective, cleavage of the furan ring occurring on the side of the ring with the greater substitution at the α position. Thus, **17** does not give **1**, **17**, or **18**. Instead, it gives an aldehyde, which clearly results from cleavage of the C_2–O bond, presumably through diradical **28**.



28 **17** **27a** **25**

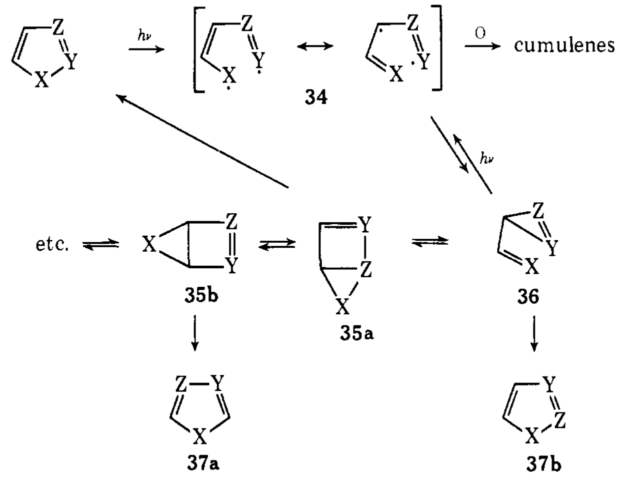
The photochemistry of 2,3,5-tri-*tert*-butylfuran (**2**) can be easily explained in terms of the same mechanism. The two cleavage reactions lead through the intermediates **29a** and **29b** to the cyclopropenyl ketones **15** and

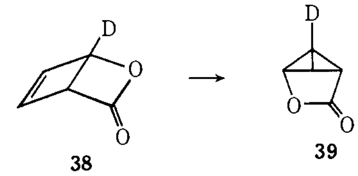
30, respectively. If **15** opens to **29c** on further excitation no obvious low-energy pathway is open to stabilize this intermediate other than reclosure to **15**. Thus, the only cleavage that results in destruction of this cyclopropene is that which leads back to the starting furan. Cyclopropene **30**, on the other hand, undergoes a completely different type of reaction. Excitation of this molecule leads to an intermediate written as **32**. Because of the strain involved in eclipsing two *tert*-butyl groups, as in **31**, **32** probably has the *tert*-butyl on the carbonyl group in close proximity to the excited double bond. Hydrogen abstraction then occurs, giving **33**, with one tertiary radical. Finally, recombination of the two radical centers gives **3**. This type of hydrogen abstraction reaction is also available to other cyclopropenyl ketones, as is shown by the fact that the cyclopropyl ketone **21** is formed during the photolysis of 2,-4-di-*tert*-butylfuran in ether. In this solvent, a better source of hydrogen atoms than pentane, hydrogen abstraction becomes relatively more favorable.

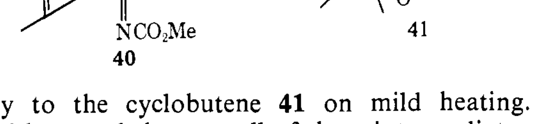


Work in other laboratories on the photochemical rearrangements of five-membered aromatic heterocycles indicates that these reactions fall into three general classes. First, there are those cases which behave similarly to furans,[23] in that the reactions involve three-membered rings as intermediates.[24-27] The second category includes those reactions which are best explained by the intermediacy of Dewar structures[28,29] (imidazoles, pyridazoles). Finally, there are a set of compounds (principally thiophene derivatives),[30] whose photoreactions are readily explained in terms of neither intermediate. In several of these examples[23,25,28a] the formation of cumulenes suggests the development of considerable free valence during the reaction in a manner analogous to the behavior of furans. These facts, taken together, suggest the following general mechanism for the rearrangement of five-membered aromatic heterocycles (Scheme VII). Absorption of light leads to cleavage of the weakest of the single bonds in the ring. The intermediate so formed then closes to a cyclopropene or a heterocyclic analog thereof (**36**), which apparently is in equilibrium with a Dewar form (see below). Alternatively, a substituent can migrate with the formation of a cumulene or triple bond. The two intermediates **35a** and **35b** and **36** are then the precursors of the rearranged heterocycles observed (**37a**, **37b**). Chemical evidence for the equilibration of three- and four-membered rings comes from the work of (1) Corey and Pirkle,[31] who observed the rearrangement of **38** to **39**, and (2) Meinwald and Aue,[32] who found that cyclopropene **40** would rearrange efficiently to the cyclobutene **41** on mild heating. It should be noted that not all of these intermediates will be necessary to explain the photochemistry of each molecule. In fact, when a strong bond can be formed

Scheme VII







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(23) (a) R. Srinivasan, *J. Amer. Chem. Soc.*, **89**, 1758 (1967); (b) R. Srinivasan, *ibid.*, **89**, 4812 (1967); (c) H. Hiroaka and R. Srinivasan, *ibid.*, **90**, 2720 (1968).

(24) F. Ullman and B. Singh, *ibid.*, **88**, 9844 (1966); **89**, 6911 (1967).

(25) H. Goth and H. Schmid, *Chimia*, **20**, 148 (1966).

(26) D. W. Kurtz and H. Schechter, *Chem. Commun.*, 689 (1966).

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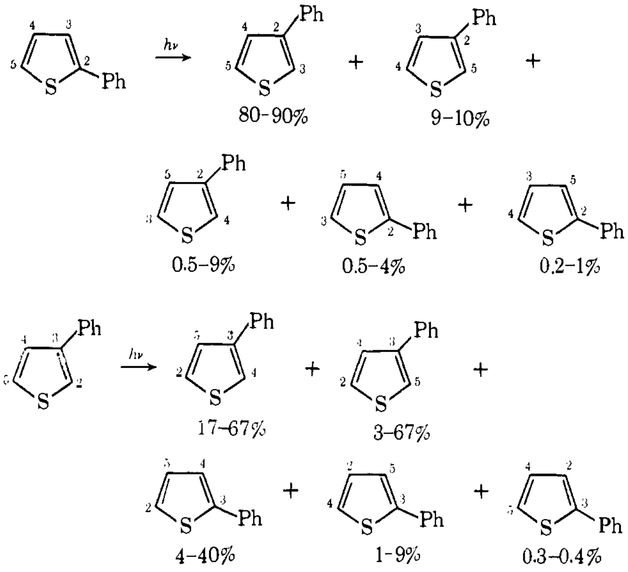
(30) (a) H. Wynberg and H. van Driel, *J. Amer. Chem. Soc.*, **87**, 3998 (1965); (b) H. Wynberg and H. van Driel, *Chem. Commun.*, 203 (1966); (c) H. Wynberg, R. Kellogg, H. van Driel, and G. E. Beekhuis, *J. Amer. Chem. Soc.*, **88**, 5047 (1966); (d) H. Wynberg, H. van Driel, R. M. Kellogg, and T. Buter, *ibid.*, **89**, 3487 (1967); (e) R. M. Kellogg and H. Wynberg, *ibid.*, **89**, 3495 (1967); (f) H. Wynberg, G. E. Beekhuis, H. van Direl, and R. M. Kellogg, *ibid.*, **89**, 3498 (1967); (g) H. Wynberg, R. M. Kellogg, H. van Driel, and G. E. Beekhuis, *ibid.*, **89**, 3501 (1967).

(31) E. J. Corey and W. H. Pirkle, *Tetrahedron Lett.*, 5255 (1967).

(32) J. Meinwald and D. H. Aue, *J. Amer. Chem. Soc.*, **88**, 2849 (1966).

(*e.g.*, a carbonyl group), the reaction proceeds essentially entirely by way of the intermediate containing this bond. Further, these reactions seem in most cases to be multiphoton processes, and the intermediates frequently are sufficiently thermally stable to be isolated.

This mechanism is most fruitful in explaining the very complex rearrangements of the thiophene ring system, extensively studied by Wynberg and coworkers.[30] In this system, as determined principally by examination of the photoproducts formed on irradiation of the isomers of methylphenylthiophene, the following rearrangements take place:



Wynberg suggests an intermediate involving sulfur with an expanded valence shell, which unfortunately accounts only for those rearrangements which interchange an α and β carbon atom in the ring. Thus, the major parts of the 3-phenylthiophene rearrangements are unexplained in terms of this intermediate. Inspection of Scheme VII shows that the proposed mechanism rationalizes the formation of all products of photolysis of the methylphenylthiophenes if the following assumptions are made: (a) Dewar structures and cyclopropenyl thiocarbonyls are in equilibrium; (b) in the formation of a given cyclopropene, the ring contraction takes place in such a fashion as to place the phenyl group on the double bond of the cyclopropene. The second assumption is not always strictly adhered to, but accounts always for the *major* products of the photoreaction. Further experimental work must be done to clarify the applicability of the suggested mechanism.

Experimental Section

Preparation of 2,5-Di-*tert*-butylfuran (1). This preparation was carried out according to the direction of Ramasseul and Rassat[4] or, more conveniently, by the following abbreviated procedure. Pinacolone (91.8 g, 0.918 mol) was dissolved in 800 ml of ether in a three-necked flask fitted with a mechanical stirrer, and 71.6 ml (220 g, 1.38 mol) of bromine in 1000 ml of chloroform was added dropwise over a period of 2.3 hr with continuous vigorous stirring. At the end of this time, the reaction mixture was poured into a mixture of 1000 g of ice and 1000 ml of saturated sodium bicarbonate solution. The aqueous layer was washed twice with ether, and the organic layers were combined and washed twice with water and then with saturated salt solution. Drying over magnesium sulfate and evaporation gave a yellow lachrymatory oil, presumably an equimolar mixture of mono- and dibromopinacolone.

The yellow oil was dissolved in 2.0 l. of ether, and 260 g of potassium hydroxide pellets was added with vigorous mechanical stirring. An ice bath was required to control the exothermic reaction. After 2 hr, the reaction mixture, containing a heavy precipitate of potassium bromide, was poured into 1.0 l. of ice-water. The ethereal layer was washed twice with water and once with a saturated salt solution, dried over magnesium sulfate, and evaporated. The yellow semisolid (2,2,7,7-tetramethyl-4,5-epoxy-3,6-octanedione) was used directly without further purification.

The crude epoxide, dissolved in 1.0 l. of glacial acetic acid, was treated with 190 g of potassium iodide, and the mixture was heated under reflux for 3 hr. At the end of this period, the dark product was cooled and poured into 5.0 l. of water. Decolorization was accomplished by the addition of a saturated solution of sodium bisulfite. Filtration gave a 60-g (67%) crude yield of 2,2,7,7-tetramethyloct-4-ene-3,6-dione. Recrystallization of this product from ethanol-water gave 38 g (42%) of glistening yellow plates, which were used in the next reaction without further purification. The literature[4] yield to this point is 57% overall.

The enedione isolated above (38 g, 0.194 mol) was refluxed in a mixture of 750 ml of glacial acetic acid and 150 ml of water with 25 g of zinc dust. Reflux was continued for 12.5 hr, at which time the reaction mixture was cooled and extracted twice with about 500 ml of 30-60° petroleum ether. The organic layers were washed three times with water, once with saturated sodium bicarbonate, and once with saturated salt solution. Drying ($MgSO_4$) and evaporation gave 2,2,7,7-tetramethyloctane-3,6-dione as a pale yellow oil.

This dione, without purification, was dissolved in 700 ml of benzene containing 4 g of *p*-toluenesulfonic acid monohydrate. With the acid of a Dean-Stark trap, water was azeotroped from the reaction mixture for 3 hr. The mixture was cooled and extracted with 10% aqueous sodium bicarbonate. The aqueous layer was washed twice wih ether. The combined organic layers were washed with saturated salt solution, dried over magnesium sulfate, and evaporated, affording 24 g (68% from the enedione; lit.[4] 70%) of 2,5-di-*tert*-butylfuran (1) as a yellow oil. Distillation gave 20.2 g (60%) of white oil, bp 72-75° (23 mm); lit.[4] bp 174-176° (760 mm). The spectral properties of this material were the same as those reported,[4] and no impurities could be detected in the freshly prepared material by glpc.

Photolysis of 2,5-Di-*tert*-butylfuran. A. In Pentane. The furan (600 mg, 3.33 mol) was dissolved in 280 ml of pentane[33] containing 500 μl of *n*-nonane as an internal standard. The solution was 1.19 × 10^{-3} *M* in the furan. A stream of nitrogen was passed through the solution for 1.5 hr, and it was then irradiated in the Hanovia immersion well apparatus with a Vycor filter for a total of 170 min. Aliquots were withdrawn and analyzed by glpc. The results obtained are shown in Table IV. After evaporation

Table IV. Analysis of Aliquots from Photolysis of 2,5-Di-*tert*-butylfuran

Time, min	2,5-Di-*tert*-butylfuran	2,4-Di-*tert*-butylfuran	Cyclopropene	Allene
0	134 ± 3[a]			
1	135	0[a]	0[a]	0[a]
4	134	0	1.0 ± 0.1	1.1 ± 0.1
8	131	0.5 ± 0.1	2.45 ± 0.05	1.1 ± 0.1
15	121	1.8	2.70	3.3
30	98	3.4	2.40 ± 0.07	4.1
65	66	6.8	2.2 ± 0.1	5.1
170	15	10.5	1.1	4.0

[a] Areas in arbitrary units relative to nonane = 100.

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(33) The pentane used in the first experiments was stirred with several portions of concentrated sulfuric acid until no color developed in the acid layer after several hours. It was then washed with water, refluxed with calcium hydride overnight, and distilled. In later experiments, commercial isopentane was used without purification. Equivalent results were obtained in either case.

of the pentane under reduced pressure, the reaction mixture was flash distilled at 0.005 mm, and the distillate was subjected to preparative glpc. The products, in order of their retention time on the Apiezon L column, are as follows. Fraction 1 was recovered 2,5-di-*tert*-butylfuran (10%). Fraction 2 was 2,4-di-*tert*-butylfuran (**17**) (9% based on recovered starting material): ir (CCl_4) 1603 (m), 1267 (s), 1111 (s), 938 (s), 863 (m), and 652 cm^{-1} (s); nmr (CCl_4) τ 8.81 (s, 9 H), 8.76 (s, 9 H), 4.23 (d, J = 1.3 Hz, 1 H), and 3.08 (d, J = 1.3 Hz, 1 H); uv max (ethanol) 215 nm (ϵ 6000); mass spectrum (70 eV) *m/e* (relative intensity) 180 (M$^+$, 15), 166 (12), 165 (100), 57 (16), 55 (10), 43 (19), 41 (23); lit.[32] ir 1600, 1265, 1108, and 934 cm^{-1}; nmr τ 8.82 (s), 8.75 (s), 4.22 (d, J = 1.1 Hz), and 3.08 (d, J = 1.1 Hz); uv max (95% ethanol) 2.15 nm (ϵ 6300). Fraction 3 was 1-*tert*-butyl-3-pivaloylcyclopropene (**16**): ir (CCl_4) 3150 (w), 1970 (m), 1775 (m), 1693 (s), 1098 (s), and 707 cm^{-1} (s); nmr (CCl_4) τ 8.87 (s, 9 H), 8.83 (s, 9 H), 7.35 (d, J = 1.8 Hz, 1 H), and 4.09 (d, J = 1.8 Hz, 1 H); uv max (pentane) 293 (ϵ *ca.* 50); mass spectrum (70 eV) *m/e* (relative intensity) 180 (M$^+$, 3), 165 (17), 95 (55), 67 (17), 57 (11), 55 (15), 44 (100), 41 (16) (12 eV), 180 (23), 165 (23), 95 (100). Fraction 4 was 2,2,7,7-tetramethylocta-4,5-dien-3-one (**15**) (9%): ir (CCl_4) 3070 (w), 1950 (s), and 1690 cm^{-1} (s); uv max (ethanol) 228 nm (ϵ 7000); nmr (CCl_4) τ 8.88 (s, 9 H), 8.84 (s, 9 H), 4.55 (d, J = 6.2 Hz, 1 H), and 4.00 (d, J = 6.2 Hz, 1 H); mass spectrum (70 eV) *m/e* (relative intensity) 180 (M$^+$, 7), 165 (11), 123 (11), 95 (10), 69 (17), 58 (21), 57 (81), 55 (18), 43 (100), 41 (38).

B. In Pentane with Chlorine Filter. The furan (124 mg, 0.69 mmol) and 100 μl of nonane were dissolved in 50 ml of pentane. This solution was placed in a long, thin quartz tube equipped with a reflux condenser and a nitrogen delivery tube. The tube was suspended *ca.* 5 cm from a quartz bottle which held the water-cooled jacket for the Hanovia 450-W lamp. Through two side arms on this bottle, one extending to the bottom, was passed a slow stream of chlorine gas. This arrangement guaranteed that the light from the lamp would pass through about 1 cm of chlorine at atmospheric pressure on its way to the sample, and thus filter out at least some of the ultraviolet light in the carbonyl region. The solution containing the furan was purged with nitrogen for 30 min before photolysis. Aliquots were removed periodically and analyzed as before; these results are shown in Table V. The same products were obtained as before, except that the cyclopropene **16** was now the major volatile product. The yields, based on recovered starting material, after 5 hr of photolysis, were: cyclopropene (**16**), 14%; 2,4-di-*tert*-butylfuran (**17**), 7%; allene (**18**), 9%. The products were isolated as before, or, somewhat more conveniently, by preliminary purification by means of chromatography on silica gel–15% water. The latter procedure allowed the easy separation of the furans from the carbonyl-containing compounds, and these separate fractions were then subjected to preparative glpc.

Table V. Analysis of Aliquots from Photolysis of 2,5-Di-*tert*-butylfuran (Cl_2 filter)

Time, min	2,5-Di-*tert*-butylfuran	2,4-Di-*tert*-butylfuran	Cyclopropene	Allene
0	161 ± 3 (av)	0	0	0
45	136 ± 5	0.78 ± 0.03[a]	5.1 ± 0.2[a]	1.5 ± 0.1[a]
90	122 ± 6 (av)	1.61 ± 0.03	5.9 ± 0.1	2.58 ± 0.04
180	111 ± 2	3.4 ± 0.1	7.0 ± 0.4	4.5 ± 0.1
300	91 ± 2	4.1 ± 0.2	6.9 ± 0.2	4.5 ± 0.1

[a] Areas in arbitrary units relative to nonane = 100.

In a similar experiment carried out in ether solvent, the cyclopropyl ketone (**21**) was isolated in a yield similar to that of the cyclopropenyl ketone. It was identified by comparison of its ir and nmr spectra to those of an authentic sample (see below).

C. Photolysis at Low Temperature. An unknown, small quantity of 2,5-di-*tert*-butylfuran was deposited on the KBr window of an ir machine designed for matrix isolation work. This material was photolyzed through a chlorine filter for a total of 22 hr at 65°K. No well-defined new maxima in the ir region were observed. There was a general decrease in absorbance of about 20–25%, and a small, broad increase in absorbance in the carbonyl region. No evidence could be obtained for unstable intermediates of any kind.

Preparation of 2,2,5,6,6-Pentamethylhept-4-en-3-one (22). This compound was prepared according to Colonge.[21]

Preparation of 2,2,6,6-Tetramethyl-5-(bromomethyl)hept-4-en-3-one (23). The unsaturated ketone **22** (182 mg, 1.00 mmol) and 180 mg (1.00 mmol) of *N*-bromosuccinimide were mixed in 3 ml of carbon tetrachloride. The solution was heated to reflux under irradiation by a GE sunlamp for 30 min, after which time examination by tlc showed no further change in the solution. The reaction mixture was cooled, diluted with an equal volume of hexane, and filtered. The filtrate was evaporated and titurated with hexane, and the hexane-soluble portion was separated by filtration. The hexane-insoluble portion weighed 105 mg, which represents 95% of the expected succinimide. Evaporation of the hexane from the filtrate gave an orange oil (260 mg, 100%), which was subjected to preparative tlc on two 20 × 20 cm plates (1-mm layer of silica gel GF, benzene–3% ether developer). Two bands were collected, the upper of which (115 mg, 44%) had spectral properties consistent with the structure 2,2,6,6-tetramethyl-5-(bromomethyl)-hept-4-en-3-one (**23**): ir (CCl_4) 3055 (w), 1685 (s), and 1604 cm^{-1} (s); nmr τ 8.85 (s, 9 H), 8.77 (s, 9 H), 5.55 (s, 2 H), and 3.58 (s, 1 H).

Preparation of 2,4-Di-*tert*-butylfuran. The unsaturated bromo ketone (1.30 g, 5.00 mmol) was heated in a sealed tube with 1.00 g of sodium carbonate for 3 hr at 150°. The tube was cooled and opened, and the product was washed with ether, filtered, and evaporated. The residue weighed 970 mg. Distillation under reduced pressure, followed by preparative glpc, led to the isolation of 2,4-di-*tert*-butylfuran[14] (416 mg, 46%), identical with the product isolated from the photolysis of 2,5-di-*tert*-butylfuran in R_f on tlc, glpc retention time, and in nmr, ir, and uv spectra.

Preparation of 2,2,6,6-Tetramethylhept-4-en-3-one (20). In a 25-ml three-necked round-bottomed flask fitted with a reflux condenser, nitrogen inlet, and pressure-equalizing dropping funnel was placed 250 mg (10.7 mg-atoms) of Mg and 10 ml of ether. With magnetic stirring, a few drops of a solution of 1.69 g (10 mmol) of bromopinacolone and 0.950 g (11.1 mmol) of pivaldehyde in 7 ml of benzene were added. After the reaction started, the rest of the benzene solution was added at such a rate as to maintain a slow reflux. After the addition was complete, the solution was stirred about 30 min, and then 5 ml of water was added dropwise, followed by enough 4 *N* hydrochloric acid to dissolve the precipitated inorganic salts. The phases were separated and the aqueous layer was washed with ether. The organic layers were then combined, and washed with water, sodium bicarbonate solution, water, and saturated salt solution. Drying over magnesium sulfate and evaporation gave an orange oil which was distilled at atmospheric pressure from a few crystals of iodine. The cloudy distillate was taken up in ether, shaken with concentrated sodium thiosulfate solution, washed with aqueous sodium bicarbonate and salt water, and then dried over magnesium sulfate and evaporated. Distillation under reduced pressure gave 1.02 g (58%) of oil crystals: bp 83–90° (30 mm), lit.[20] bp 87° (29 mm); ir (film) 3065 (w), 3015 (sh, w), 1688 (s), 1621 (s), and 830 cm^{-1} (s); nmr (CCl_4) τ 8.92 (s, 9 H), 8.89 (s, 9 H), 3.70 (d, J = 17.4 Hz, 1 H), and 3.17 (d, J = 15.4 Hz, 1 H); 2,4-dinitrophenylhydrazone mp 146–150° dec; uv max (ethanol) 365 nm (ϵ 22,600); lit.[20] mp 145–146°; uv max 365 nm (ϵ 29,000).

Preparation of *trans*-1-Pivaloyl-2-*tert*-butylcyclopropane (21). In a 50-ml three-necked round-bottomed flask fitted with a nitrogen inlet, vacuum connection, and magnetic stirrer was placed 236 mg (1.1 mmol) of trimethyloxosulfonium iodide.[18] The flask was then alternately evacuated and filled with nitrogen three times. Potassium *tert*-butylate (135 mg, 1.20 mmol) was added under positive nitrogen pressure, and the flask was flushed once more. Then 10 ml of dry dimethyl sulfoxide (DMSO) was added through a serum cap by means of a syringe. After 20 min of stirring, 178 mg (1.00 mmol) of enone **20** dissolved in 3 ml of DMSO and 1 ml of benzene was added by syringe, and the solution was stirred for 2 hr more at room temperature. The mixture was then diluted with water and extracted three times with ether. The combined ether layers were washed three times with water and then with saturated sodium chloride solution, dried over magnesium sulfate, and evaporated. The one new peak on glpc was collected (*ca.* 80% yield). Its properties were consistent with the cyclopropyl ketone structure **21**: ir (CCl_4) 3078 (w), 3058 (w), 1689 (s), 1073 (s), 1009 (m), 911 (m), and 862 cm^{-1} (m); nmr (CCl_4) τ 9.13 (s, 9 H), 8.85 (s, 9 H), 8.7–9.5 (m, 3 H), and 8.07 (doublet, J = 7.5 Hz, of triplets, J = 4.2 Hz, 1 H); uv max (ethanol) 278 and 207 nm (ϵ 103 and 2800); mass spectrum (70 eV) *m/e* (relative intensity) 182 (M$^+$, 4), 125 (23), 113 (3), 97 (8), 83 (12), 70 (15), 69 (12), 57 (21), 55 (100), 43 (11), and 41 (12).

Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.17. Found: C, 79.48, 79.32; H, 12.23, 12.32.

Hydrogenation of the Cyclopropenyl Ketone 16. The cyclopropenyl ketone (5.17 mg, 0.0287 mmol) was dissolved in 3 ml of 95% ethanol and hydrogenated over platinum (from *in situ* reduction of PtO_2). The sample absorbed 94% of 1 equiv of hydrogen. The resulting suspension was filtered through a Celite pad and diluted with water. Extraction twice with pentane gave a clear solution, which was dried ($MgSO_4$). Most of the pentane was removed on a rotary evaporator, and the resulting solution examined by glpc, which showed two peaks of approximately equal area. Preparative glpc gave two fractions.

Fraction 1 was *cis*-1-pivaloyl-2-*tert*-butylcyclopropane **19** on the basis of the following data: ir (CCl_4) 3090 (w), 3015 (sh, w), 1695 (s), 1070 (s), 1010 (m), and 862 cm^{-1} (m); nmr (CCl_4) τ 9.08 (s, 9 H), 8.82 (s, 9 H), and 8.7–9.4 (m); mass spectrum (70 eV) *m/e* (relative intensity) 182 (M^+, 3), 125 (28), 113 (6), 97 (10), 83 (13), 70 (31), 69 (15), 57 (54), 55 (100), 43 (30), and 41 (20). It was not identical with the compound prepared above in spectra or retention time on glpc.

Fraction 2 was a ketone of unknown structure: ir (CCl_4) 1708 cm^{-1}; nmr (CCl_4) τ 9.15 (s), 9.13 (s), 8.95 (s), 8.65–9.05 (m), 7.74 (d, J = 4 Hz) (integration of this spectrum was not attempted because it was taken with the acid of the computer of average transients (CAT)). This compound was shown not to be 2,2,5,6,6-pentamethylheptan-3-one by comparison with a sample prepared by lithium–ammonia reduction of the corresponding enone **22**.

The Preparation of 2,3,5-Tri-*tert*-butylfuran (2). This preparation was carried out by the alkylation of 2,5-di-*tert*-butylfuran with *tert*-butyl chloride and aluminum chloride according to Wynberg and Wiersum.[5] The product was distilled through a 36-in. spinning band column, and the fraction bp 108° (12 mm) was collected. Examination by glpc showed no detectable impurities in freshly distilled samples. On standing in air, the material developed a yellow color and a small peak on glpc corresponding to material believed to be 2,2,7,7-tetramethyl-4-*tert*-butyloct-4-ene-3,6-dione (**15**) (see below). As a result, the furan was stored under nitrogen in the freezer, where it appeared to be indefinitely stable.

Irradiation of 2,3,5-Tri-*tert*-butylfuran. A. In Pentane. A solution of 1.00 g (4.24 mmol) of the furan and 500 mg of undecane as an internal standard in 300 ml of pentane[35] was placed in a Hanovia photolysis well. After degrassing with a stream of nitrogen for 1.5 hr the lamp was turned on. At various times, aliquots were removed and analyzed by glpc. The results obtained are shown in Table VI. After 65 min of photolysis, the solvent was removed under reduced pressure, leaving 1.53 g of an orange oil. After standing overnight the minor product was no longer visible, and it was not isolated or characterized in these experiments. By comparison of the glpc traces with the product mixture resulting from photolysis in acetic acid (see below), the minor product was identified as 1,2-di-*tert*-butyl-3-cyclopropenyl *tert*-butyl ketone (**4**).

Table VI. Analysis of Aliquots from Photolysis of 2,3,5-Tri-*tert*-butylfuran

Time, min	Furan	Photoketone, **3**	Cyclopropenyl ketone **4**
0	156 ± 2[a]	0	0
0.5	156	0	0
1.0	155	0	0
2.0	155	0	0
4.5	154	0.7[a]	0.95[a]
6.0	153	2.1	2.6
12	138	9.7	4.6
18	128	19	5.8
35	100	45	6.5
65	60	76	6.8

[a] Values are peak areas in arbitrary units relative to undecane = 100.

After standing overnight, the reaction mixture was subjected to preparative glpc, and two components were isolated. Fraction 1, a very minor constituent (≤1%) of the reaction mixture, was characterized as the enedione (**15**) on the basis of the following data: ir (CCl_4) 3070 (w), 1684 (s), 1589 (s), and 868 cm^{-1} (s); nmr (CCl_4) τ 8.87, 8.83, 8.81 (singlets, 27 H), 3.48 (s, 1 H); uv (EtOH) λ_{max} (ϵ) 300 sh (172), 237.5 nm (5200); mass spectrum (70 eV) *m/e* (relative intensity) 252 (2), 196 (25), 195 (100), 181 (31), 180 (87), 165 (13), 138 (18), 111 (11), 109 (13), 95 (30), 67 (33), 57 (73), 55 (18), 43 (27), 42 (13), 41 (62), and 39 (25). Fraction 2, the major product (*ca.* 90% yield based on recovered starting material), was 1,5-di-*tert*-butyl-3,3-dimethylbicyclo[3.1.0]hexanone-2 (**3** photoketone): ir (film) 3060 (w), 1716 (s), 1001 (s), and 969 cm^{-1} (m); nmr ($CDCl_3$) τ 9.34 (d, J = 5.5 Hz, 1 H), 9.00 (s, 6 H), 8.88 (s, 9 H), 8.82 (s, 9 H), 8.61 (doublet of doublets, J = 5.5 Hz, $J' \approx$ 2 Hz, 1 H), 8.37 (d, J'' = 13.1 Hz, 1 H), and 8.06 (doublet of doublets, J'' = 2 Hz, $J' \approx$ 2 Hz, 1 H); (C_6H_6) τ 9.39 (d, J = 5.5 Hz, 1 H), 8.86 (broad singlet, $W_{1/2}$ = 0.5 Hz, 6 H), 8.82 (s, $W_{1/2}$ = 0.6 Hz, 9 H), 8.63 (doublet of doublets, J = 5.5 Hz, J' = 2 Hz, 1 H), 8.55 (s, $W_{1/2}$ = 9.5 Hz, 9 H), 8.35 (d, J'' = 13.1 Hz, 1 H), and 8.06 (doublet of doublets, J'' = 13.1 Hz, J' = 2 Hz, 1 H); uv max (EtOH) 291 nm (ϵ 143) and 206.5 (ϵ 6540); mass spectrum (70 eV) *m/e* (relative intensity) 236 (M^+, 0.4), 180 (77), 165 (50), 137 (20), 109 (10), 57 (100), 55 (13), 43 (11), and 41 (32).

Anal. Calcd for $C_{16}H_{28}O$: C, 81.29; H, 11.94. Found: C, 81.17; H, 11.82.

B. In Acetic Acid. A solution of 1.00 g (4.24 mol) of the furan in 300 ml of glacial acetic acid was placed in the Hanovia photolysis apparatus, and deoxygenated by passing a slow stream of nitrogen through it overnight. It was then irradiated under nitrogen for 1 hr. The resulting solution was poured into 500 ml of water, saturated with sodium chloride, and extracted three times with 100 ml of ether. The ether layers were combined and washed three times with 200 ml of water, twice with 100 ml of 10% aqueous potassium hydroxide, twice with water, and finally with saturated salt solution. Drying over magnesium sulfate and evaporation of the ether gave 0.775 g of sweet-smelling yellow oil. This oil was subjected to preparative glpc, and five fractions were collected.

Fraction 1 (6%) was identified as 1,2-di-*tert*-butyl-3-cyclopropenyl *tert*-butyl ketone (**4**) on the basis of the following data: ir (CCl_4) 1891 (w) and 1684 cm^{-1} (s); uv max 288 nm and strong end absorption; nmr (CCl_4) τ 8.89 (s, 18 H), 8.83 (s, 9 H), and 7.41 (s, 1 H); mass spectrum (70 eV) *m/e* (relative intensity) 236 (M^+, 1%), 221 (15%), 151 (100), 108 (9), 95 (7), 67 (6), 57 (31), 55 (5), 43 (5), and 41 (14). Fraction 2 (19%) was recovered starting material by comparison of the ir spectrum of a collected sample with that of authentic material. Fraction 3 (5%) was 4-*tert*-butyl-2,2,7,7-tetramethyloctane-3,6-dione (**14**) as identified by the following data: ir (CCl_4) 1704 (s) and 1685 cm^{-1} (s); uv max (ether) 282 nm and end absorption; nmr (CCl_4) τ 9.07 (s, 9 H), 8.90 (s, 9 H), 8.86 (s, 9 H), *ca.* 7.3 (m, 2 H), and *ca.* 6.5 (m, 1 H); mass spectrum (70 eV) *m/e* (relative intensity) 239 (M − 15, 1%), 197 (49), 113 (10), 85 (12), 83 (14), 57 (100), 43 (11), and 41 (19). Fraction 4 (14%) was 4-*tert*-butyl-2,2,7,7-tetramethyloct-4-ene-3,6-dione (**15**) by comparison of ir, nmr, and mass spectra with those of the sample isolated from the photolysis in pentane. Fraction 5 (6%) was the photoketone **3**, identified by comparison of ir spectrum of a collected sample with that of authentic material from the pentane photolysis.

The rest of the material (about 50%) was composed of a large number of compounds with high boiling points, and was not further investigated. A control experiment, which consisted of allowing a sample of the furan to stand in acetic acid under nitrogen overnight, showed that the furan was stable under these conditions in the absence of ultraviolet light.

The apparatus used to study the products formed on low-temperature photolysis was a low-temperature uv cell designed to fit in the sample compartment of the Cary 14 spectrophotometer. It consisted of an insulated metal box in which could be placed a metal cell with quartz windows. The box was provided with a reservoir for coolant (liquid nitrogen or Dry Ice–acetone) and the sample was cooled by conduction. There was no way to degas the samples using this apparatus. The light source was the Hanovia 450-W medium-pressure mercury arc. When the sample was to be photolyzed, the box, containing the cell, was removed from the Cary, and placed next to the window of the light box. To start the photolysis, the shutter of the light box was opened.

A 5 × 10^{-4} *M* solution of the furan in isopentane was placed in the cell. Photolysis at room temperature for 5 min led to the destruction of at least 71% of the starting furan, as measured by the absorbance at the wavelength of maximum extinction, and the development of shoulders at about 230 and 210 nm, attributed, respectively, to enedione **15** and photoketone **3**.

Photolysis at −78° for 8 min led to the destruction of at least 82% of the starting material. No well-defined maxima could be seen at the low temperature, but there was an increase in absorbance at around 250 nm. The solution was allowed to stand at low temperature for 1 hr, but no change in the uv absorption was seen. It was then allowed to warm to about 0°, at which temperature a maximum at 234 nm was detected, which presumably accounts for the increased absorbance at 250 nm, since recooling to −78° regenerated, within experimental error, the spectrum observed before warming.

Treatment of the Photoketone 3 with Acid. The acid-catalyzed rearrangement of the photoketone was carried out by dissolving 40 mg (0.17 mmol) of the ketone in 0.5 ml of ethyl acetate and adding 1 drop of 70% perchloric acid. The mixture was stirred for 1 hr at room temperature, and then diluted with ether, extracted with saturated aqueous sodium bicarbonate, washed with water and saturated salt solution, and dried over magnesium sulfate. Evaporation yielded 36 mg (90%) of a yellow oil, with one principal component (80%) by glpc. Preparative glpc gave pure 2,4-di-*tert*-butyl-6,6-dimethylcyclohexen-2-one (**7**): ir (CCl_4) 3060 (w), 1683 (s), 1668 (s), and 880 cm^{-1} (m); uv max (ethanol) 237 nm (ϵ 9160) and 335 (54); nmr ($CDCl_3$) τ 9.05 (s, 9 H), 8.94 (s, 3 H), 8.90 (s, 3 H), 8.83 (s, 9 H), *ca.* 8.4 (m, 2 H), *ca.* 7.9 (m, 1 H), and 3.33 (narrow multiplet, 1 H).

Anal. Calcd for $C_{16}H_{28}O$: C, 81.30; H, 11.93; O, 6.77. Found: C, 81.54; H, 11.93.

Reduction of the Photoketone 3 with Lithium in Liquid Ammonia.[6] The photoketone (52 mg, 0.22 mmol) was dissolved in a mixture of 2 ml of ether and 20 ml of liquid ammonia in a 50-ml round-bottomed flask containing a magnetic stirrer and fitted with a Dry Ice condenser. A small cube of lithium metal (a large excess) was added and the blue solution was stirred for 2 hr under reflux. The excess lithium was removed with a pair of forceps, and the blue color of the solution was discharged by the addition of ammonium chloride. Evaporation of the ammonia and ether gave a white residue, which was dissolved in a mixture of ether and water. The aqueous layer was washed once with ether, and the combined organic layers were washed with saturated salt solution, dried over magnesium sulfate, and evaporated, giving 43 mg (82%) of crude 1,1,3-trimethyl-3,4-di-*tert*-butylcyclopentanone (**6**). Pure material was obtained by preparative glpc: ir (CCl_4) 1719 cm^{-1} (s), no absorption attributable to unsaturation; nmr ($CDCl_3$) τ 9.07 (s, 9 H), 8.94 (s, 3 H), 8.87 (s, 3 H), 8.82 (s, 9 H), 8.75 (s, 3 H), 8.57 (d, J = 14.5 Hz, 1 H), 7.97 (d, J = 14.5 Hz, 1 H), and 7.65 (s, 1 H).

Anal. Calcd for $C_{16}H_{30}O$: C, 80.60; H, 12.68; O, 6.71. Found: C, 80.58; H, 12.7.

Reduction of the Photoketone 3 with Lithium Aluminum Hydride (LAH). The photoketone (121 mg, 0.513 mmol) was dissolved in 10 ml of ether, and 50 mg (large excess) of LAH was added. The mixture was stirred at room temperature for 1 hr. Ethyl acetate was then added dropwise to destroy the excess hydride. After the violent reaction subsided, 10 ml of water was added. The layers were separated, and the aqueous layer was washed twice with ether. The combined organic phases were washed with water and saturated with salt solution, dried ($MgSO_4$), and evaporated, yielding 130 mg (>100%) of a white oil which crystallized on rubbing. Recrystallization from ethanol–water gave white prisms: mp 67.2–68.5°; ir (CCl_4) 3625 (m), 3605 (m), 3085 (m), 3035 (s), 1197 (s), and 999 cm^{-1} (s); nmr (CCl_4, 100 MHz) τ 9.40 (d, J = 5.7 Hz, 1 H), 9.18 (doublet of doublets, J = 5.7 Hz, J' = 2.0 Hz, 1 H), 9.08 (borad singlet, 1 H), 9.06 (s, 6 H), 8.96 (s, 9 H), 8.83 (s, 9 H), 8.49 (d, J'' = 13 Hz, 1 H), 8.00 (doublet of doublets, J'' = 13 Hz, J' = 2.0 Hz 1 H), and 6.32 (broad singlet, 1 H); uv (ethanol) no max >200 nm; mass spectrum (70 eV) *m/e* (relative intensity) 238 (M^+, 0.1), 142 (5), 128 (6), 57 (100), 43 (9), 41 (20), and 40 (6).

Anal. Calcd for $C_{16}H_{30}O$: C, 80.60; H, 12.68; O, 6.71. Found: C, 80.37; H, 12.46.

Preparation of 2,4-Di-*tert*-butyl-6-methylphenol (10).[8] *o*-Cresol (75.6 g, 0.7 mol) was dissolved in 35 ml of benzene and 3.3 g of concentrated sulfuric acid was added. This mixture, in a cylindrical vessel equipped with a delivery tube and a Vibromixer, was heated in a water bath at 40–50°, while isobutylene was passed through the solution. The reaction was allowed to proceed for 6.5 hr and then the reaction mixture was diluted with 300 ml of benzene, and washed three times with 150-ml portions of 2% sodium sodium hydroxide solution, three times with water, and once with saturated sodium chloride solution. Drying ($MgSO_4$) and evaporation gave 149 g (97%) of yellow oil. Tlc showed that most of the cresol was gone, and replaced by less polar material. Distillation under high vacuum gave four fractions. Fraction 1 (bp 36–53° (0.04–0.05 mm)) contained solvent and some residual *o*-cresol. Fraction 2 (bp 52° (0.035 mm)) was essentially pure 2-*tert*-butyl-6-methylphenol: ir (film) 3570 (s), 1912 (w), 1848 (w), (1790 (w), 1670 (w), 1590 (m), 778, and 744 cm^{-1}; nmr (CCl_4) τ 8.58 (s, 9 H), 7.79 (s, 3 H), 5.27 (s, 1 H), and 3.0 (m, 3 H). Fraction 3 (bp 52 (0.02 mm)–71.5° (0.008 mm)) was a mixture of 2-*tert*-butylmethylphenol and **10**. Fraction 4 (bp 71.5–72° (0.008 mm)) was pure, 2,4-di-*tert*-butyl-6-methylphenol (**10**): lit.[8] bp 113° (8 mm); ir (film) 3610 (m), 3585 (m, OH), 1910 (vw), 870 (s), and 1598 cm^{-1}; nmr ($CDCl_3$) τ 8.71 (s, 9 H), 8.58 (s, 9 H), 7.78 (s, 3 H), 5.30 (s, 1 H), 2.96 (d, J = 2.3 Hz, 1 H), and 2.78 (d, J = 2.3 Hz, 1 H).

Preparation of 2,4-Di-*tert*-butyl-6-methylcyclohexanone (11).[8] The phenol **10** (*ca.* 30 g, 0.12 mol) and 3 g of Raney nickel catalyst were charged into a 90-ml bomb and pressured with hydrogen to 1480 psi. The bomb was then heated to 185 ± 3°. Over a period of 2 days, 2360 psi of hydrogen were taken up (90% of theory). After cooling and venting, the bomb was washed out with ethanol, the resulting suspension was filtered through a Celite pad, and the filtrate was evaporated. Ether was added and the solution was evaporated again, giving about 29 g (95%) of white, thick oil. Examination of this product by glpc indicated that it was a mixture of at least four compounds, and the ir spectrum showed the presence of both ketone and alcohol in the mixture. After distillation *in vacuo* (bp 60–70° (0.007 mm), 28 g), the hydrogenation product was dissolved in 120 ml of benzene and a solution of 11.4 g (0.0383 mol) of sodium dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$), 15 ml of concentrated sulfuric acid, and 5 ml of glacial acetic acid in 100 ml of water was added.[10] This mixture was stirred for 12 hr at room temperature, and then worked up by adding water and ether. The aqueous layer was washed well with ether and the combined organic layers were washed three times with water, once with 10% aqueous potassium hydroxide, once with water, and then with saturated salt solution. Drying over magnesium sulfate and evaporation, followed by distillation under reduced pressure, gave 27 g (89%) white oil: bp 121–133° (13 mm); lit.[9] for 2,4-di-*tert*-butyl-6-methylcyclohexanone, 139–140.5° (20 mm). Examination of this material by glpc showed it to be a mixture of at least three compounds. The most volatile of these could easily be completely separated by distillation on a spinning band column, and had spectral properties consistent with 2-methyl-4- or -6-*tert*-butylcyclohexanone: ir (film) 1715 cm^{-1} (s); nmr (CCl_4) 9.07 (s, 9 H), 9.05 (d, partially obscured by singlet at 9.07, $J \approx$ 6.5 Hz, 3 H), 7.5–9.0 (envelope, 8 H). The remainder of the material was not cleanly separated into pure compounds, but had spectral properties consistent with the desired ketone **11**, as a mixture of stereoisomers: ir (film) 1710 cm^{-1} (s); nmr (CCl_4) series of sharp peaks, τ 9.00–9.12 (21 H), envelope, 7.3–8.9 (7 H). The individual peaks in the 9.0–9.1 region changed in intensity as the distillation proceeded, but the ratio of the area under the methyl peaks to that under the remainder of the spectrum stayed constant at 3.0 ± 0.1. Furthermore, the pattern of peaks in the methyl region could be considerably simplified by base treatment (potassium *tert*-butylate in *tert*-butyl alcohol) such that only two peaks could be observed in this region (singlets at τ 9.02 and 9.10; apparently these peaks obscure the methyl resonance). The ratio of these singlets to the rest of the spectrum was 3.0:1.

Anal. Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58; O, 7.13. Found: C, 80.34; H, 12.53.

Preparation of 2,4-Di-*tert*-butyl-6,6-dimethylcyclohexanone (12). The monomethyl ketone **11** (12.25 g, 54.8 mmol) was dissolved in 50 ml of tetrahydrofuran (THF) which had been freshly distilled from lithium aluminum hydride. Sodium hydride, washed free of Nujol with petroleum ether and finely powdered (2.0–2.1 g, 51–54 mmol), was added, and the mixture was refluxed under a slow stream of nitrogen for 2.3 hr. The resulting solution was cooled in an ice bath under nitrogen, and 6.9 ml (15.6 g, 110 mmol) of methyl iodide in 10 ml of freshly distilled THF was added all at once. An immediate white precipitate was observed. The reaction was allowed to stir at room temperature for 2.5 hr and then poured into water (100 ml). The product was extracted with ether, and the ether layers were washed well with water, 4 *N* hydrochloric acid, saturated sodium bicarbonate solution, and saturated salt solution. Drying over magnesium sulfate and evaporation of the solvent gave 12.2 g (93%) of oily crystals. Recrystallization several times from methanol gave 1.52 g (12%) of white crystals: mp 80–82; ir (CCl_4) 1711 cm^{-1}; nmr (CCl_4) τ 9.09 (s, 9 H), 9.05 (s, 12 H), 8.85 (s, 3 H), and 7.6–8.7 (H, 6 H).

Anal. Calcd for $C_{16}H_{30}O$: C, 80.61; H, 12.68; O, 6.71. Found: C, 81.27, 81.02; H, 12.72, 12.68.

Bromination–Dehydrobromination of 2,4-Di-*tert*-butyl-6,6-dimethylcyclohexanone. Preparation of 2,4-Di-*tert*-butyl-6,6-dimethylcyclohex-2-en-1-one (7). A solution of bromine (0.90 ml of a solution of 1.0 g of bromine in 10 ml of acetic acid, 0.090 g, 0.56 mmol) was added to a solution of the dimethyl ketone (121 mg, 0.51 mmol) in 5 ml of acetic acid. One drop of 48% aqueous hydrobromic acid was added and the solution was stirred at room temperature for 14 hr. The reaction mixture was then poured into 20 ml of water, and extracted twice with ether. The ether layers were washed twice with water, once with saturated aqueous sodium bicarbonate, and once with saturated salt solution. Drying ($MgSO_4$) and evaporation gave 161 mg (100%) of white oil, which had ir (CCl_4) 1708 cm^{-1} and nmr (CCl_4) τ 8.96 (s, 3 H), 8.82 (s, 9 H), 8.61 (s, 3 H), and 7.4–8.5 (m, 5 H). There were in addition a pair of singlets at τ 9.07 and 9.10, in about 1:1 ratio, together integrating for 9 H. These data are consistent with 2-bromo-2,4-di-*tert*-butyl-6,6-dimethylcyclohexanone (**13**) as a mixture of stereoisomers at C-2.

The bromo ketone **13** prepared above (139 mg, 0.438 mmol), without further purification, was dissolved in 5 ml of dimethylformamide containing 65 mg (0.88 mmol) of lithium carbonate and refluxed under nitrogen for 3 hr.[12] The reaction mixture was cooled after this period, diluted with water, and extracted with ether twice. The combined ether layers were washed with water, 2 *N* hydrochloric acid, saturated sodium bicarbonate solution, and saturated salt solution. Drying over magnesium sulfate and evaporation give 90 mg (87%) of 2,4-di-*tert*-butyl-6,6-dimethylcyclohex-2-en-1-one, identical in glpc retention time on an Apiezon L column, thin layer R_f, and nmr and ir spectra with the same compound derived from acid-catalyzed rearrangement of the photoketone **3**.

Irradiation of 2,4-Di-*tert*-butylfuran. A solution of 416 mg (2.31 mmol) of 2,4-di-*tert*-butylfuran (**17**) and 400 μl of *n*-nonane in 280 ml of pentane (8.3×10^{-3} *M* in furan) was purged with a stream of nitrogen for 45 min. Irradiation was carried out with the medium-pressure mercury arc (Hanovia immersion well apparatus). After the light was turned on, aliquots were removed periodically at times up to 115 min (73% reaction). At no time were any of the products observed in the photolysis of 2,5-di-*tert*-butylfuran visible in the reaction mixture. After evaporation of the solvent, the major product (6.8% yield based on recovered starting material) was isolated by preparative glpc. The properties of the isolated material are as follows: ir (CCl_4) 3030 (w), 2775 (w), 2715 (w), 1938 (m), 1770 (w), and 1685 cm^{-1} (s); nmr (CCl_4) τ 8.87, 8.86, 5.66, and 0.60, all singlets, in the ratio 9:9:1:1. These data are consistent with either allenyl aldehyde **24** or cyclopropenyl aldehyde **25**, with the more probable structure being the allene **24**.

Irradiation of 1-*tert*-Butyl-3-pivaloylcyclopropene (16). A. In Pentane. A solution of 2.3 mg (0.013 mmol) of the cyclopropene and 1.0 μl of *n*-nonane in 3.5 ml of pentane was placed in a quartz cuvette equipped with a serum cap pierced by two needles, one extending to the bottom of the cuvette and serving as a nitrogen inlet, and the other extending just through the cap and serving as a vent. A slow stream of prepurified nitrogen was passed through the solution for 45 min, and then the cuvette, still under a nitrogen atmosphere, was placed as close as possible to the wall of the Hanovia immersion well apparatus. It was then irradiated for 10 min through a Vycor filter, an aliquot was removed, and the products were examined by glpc. All of the peaks in the product mixture corresponded in retention time to products found in the irradiation of 2,5-di-*tert*-butylfuran. The results obtained are shown in Table VII.

Table VII. Glpc Comparison of the Products from the Photolysis of Furan **1** and Cyclopropene **16**

Starting material	Retention times[a] 1	17	16	Unknown	18
1	1.50	2.32	2.85	3.56	4.51
16	1.49	2.32	2.84	3.56	4.50
	8%[b]	13%[b]	16%[b]	7%[b]	19%[b]

[a] The values of the retention times are quoted relative to the nonane peak on a 6 ft × 1/4 in. column packed with 5% Apiezon L on Chromosorb W. [b] These values are the yields from **16** of the indicated products at the end of 10 min of photolysis.

B. At Low Temperature. In the cell designed to fit in the Cary 14 uv spectrophotometer, a solution of about 2 mg of the cyclopropene dissolved in 10 ml of isopentane was photolyzed with the Hanovia 450-W medium-pressure arc for 33 min at room temperature. This treatment led to the development of maxima at 234, 228, and 217 nm attributed, respectively, to 2,2,7,7-tetramethyloct-4-ene-3,6-dione (λ_{max} 233 nm), allene **17** (λ_{max} 228), and furans **1** and **17** (λ_{max} 215 and 217 nm, respectively).

The same experiment was repeated with the cell cooled to −78°. Approximately the same conversion as in the room temperature experiment was obtained only after 90 min of photolysis. At the end of this period, a general increase in the absorbance was observed in the 230–260-nm region with moderately well-defined maxima at 222, 247, and about 232 nm. The solution was then allowed to warm slowly to about −8°, at which temperature it was allowed to stand for about 1 hr. The uv spectrum taken at this temperature had maxima at 226 and 235 nm, with a shoulder at 246 nm. The peaks at 226 and 235 nm are assigned as they were above. The source of the shoulder at 246 nm is not clear, but it is probably not due to an unstable compound, since the absorbance did not change on standing, and recooling the sample to −78° led to regeneration of the spectrum as it was before warming.

Acknowledgment. Financial support was provided in part by the U. S. Army Research Office, Durham (Grant No. DA-31-124-ARO-D-285).