41.8 (C-4 and C-6), 35.5 (C-9); IR ν (CCl_4) 2965, 1713, 1465, 1420, 1360, 1305, 1260 cm^{-1}. Exact mass calcd for $C_{10}H_{12}OBr_2$: 305.926. Found: 305.928.

Anal. Calcd for $C_{10}H_{12}OBr_2$: C, 39.00; H, 3.93. Found: C, 38.62; H, 4.00.

10-*exo*-Bromotetracyclo[5.3.0.0^{4,6}.0^{5,9}]decan-3-one (24). A solution of potassium hydroxide (15.2 mg, 0.271 mmol) in methanol (1.5 mL) was added to a stirred solution of **23** (76.0 mg, 0.247 mmol) in methanol (5 mL), and the resulting solution was refluxed for 1 h. After cooling to room temperature, water (100 mL) was added and the reaction mixture was extracted with ether (3 × 25 mL). The combined ether extracts were washed with water (2 × 25 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure afforded a yellow oil which was Kugelrohr distilled to give 28.3 mg (50% yield) of **24**. Analysis of this material by ^{13}C NMR showed that **24** and **3** were present in a ratio of ca. 4:1. The ^{13}C NMR resonances of **24** occur at δ 208.2 (C-3), 55.1 (d), 53.1 (t), 48.4 (d), 44.4 (d), 42.2 (d), 39.2 (d), 38.2 (t), 34.5 (d), 27.7 (d).

4,5,9,10-Tetradehydroadamantan-2-one (3). A solution of potassium hydroxide (10.0 mg, 0.178 mmol) in methanol (1.0 mL) was added to a solution of a 4:1 mixture of **24** and **3**, respectively, (27.0 mg, 0.119 mmol) in methanol (10 mL) and the resulting solution was refluxed for 1 h. After cooling, water (100 mL) was added and the reaction mixture was extracted with ether (3 × 25 mL). The combined ether extracts were washed with water (2 × 25 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure gave an oil which was column chromatographed on silica gel with methylene chloride–hexane–ether (45:45:10) as eluent to provide 7.2 mg of **3**: mp 92–93 °C; ^1H NMR δ 2.60–2.52 (br s, 2 H), 2.46 (s, 2 H), 2.44–2.36 (m, 4 H), 1.88 (t, J = 7 Hz, 2 H); ^{13}C NMR δ 208.0 (C-2), 69.6 (C-7), 40.6 (C-4, C-5, C-9, and C-10), 35.5 (C-1 and C-3), 34.5 (C-6 and C-8); IR ν (CCl_4) 3040, 2980, 2865, 1686, 1395, 1320, 1110, 1060 cm^{-1}. Exact mass calcd for $C_{10}H_{10}O$: 146.073. Found: 146.073.

Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.89. Found: C, 82.05; H, 6.92.

Acknowledgment. This work was supported by grants from the University of Delaware Research Foundation and the United Parkinson Foundation.

Registry No. **3**, 98652-85-8; **6**, 98652-79-0; **7**, 16282-07-8; **8**, 121-46-0; **9**, 16282-06-7; **12**, 98652-77-8; **13**, 98652-78-9; **16**, 98652-80-3; **20**, 98652-81-4; **21**, 98717-51-2; **22**, 98652-82-5; **23**, 98652-83-6; **24**, 98652-84-7; tris(methylthio)methane, 5418-86-0; tetrakis(acetonitrile)copper(I) perchlorate, 14057-91-1.

Novel Photochemical Reactions of 3(2*H*)-Furanones†

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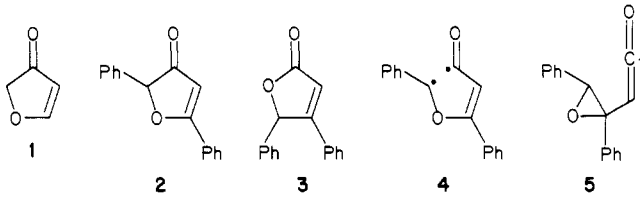
Irradiation ($\lambda \geq 280$ nm) of furanones **6–9** leads to rearrangement to enol lactones **14–17**, while the di-*tert*-butyl-substituted derivative **10** undergoes decarbonylation to form **21**. Both types of reaction are readily quenched by 2,3-dimethyl-1,3-butadiene, and a common mechanism is suggested, involving rearrangement of the furanone to an acylcyclopropanone (as **18**), followed by either reverse [1,3] shift to furnish enol lactone or alternatively decarbonylation to yield **21**. A convenient route to 3(2*H*)-furanones is provided by mercuric acetate oxidation of readily available allenic ketones.

The synthesis and reactions of simple derivatives of 3(2*H*)-furanone (**1**) have attracted considerable attention in recent years,[1-4] primarily in connection with development of routes to antitumor agents[5] that contain this ring as a central structural unit. In contrast, the intramolecular photochemistry of 3(2*H*)-furanones has received no consideration, apart from one brief study a decade ago.[6] In this earlier work Padwa[7] found that 2,5-diphenyl-3(2*H*)-furanone (**2**) rearranged on irradiation through Vycor (λ > approximately 210 nm) to form lactone **3**. The structure of **3** was confirmed by independent synthesis, and a pathway involving α-cleavage to **4**, closure to **5**, and then rearrangement to **3** was suggested to account for the observed reaction.[7] Since these proposed steps have close analogies in the photochemistry of both cyclopentenones[8] and 2-alkoxypyrrolin-5-ones,[9] rearrangement of **2** to **3** appeared reasonable, and this result may well have discouraged further photochemical exploration in this series. We now report that none of the five alkyl-substituted 3(2*H*)-furanones **6–10** behaves like **2** on irradiation; **6–9** undergo a novel isomerization, while **10** suffers two unexpected fragmentation reactions. Details are reported



† Dedicated to Professor Harold H. Warren on the occasion of his retirement.

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(5) Complete references are available in ref 1.
(6) Intermolecular [2 + 2] photocycloaddition reactions of 3(2*H*)-furanones, however, have been investigated in some detail: (a) Margaretha, P. *Chimia* **1975**, *29*, 203 and references cited therein. (b) Baldwin, S. W.; Blomquist, H. R., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 4990 and references cited therein.
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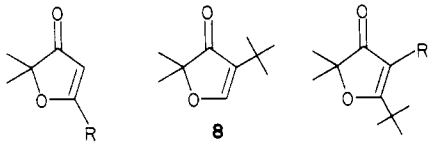
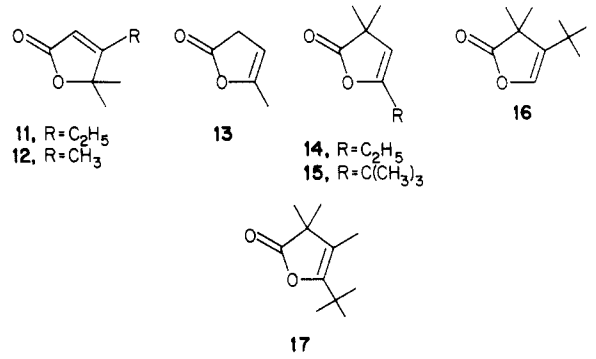
below; photochemical results are given first, followed by preparative experiments.

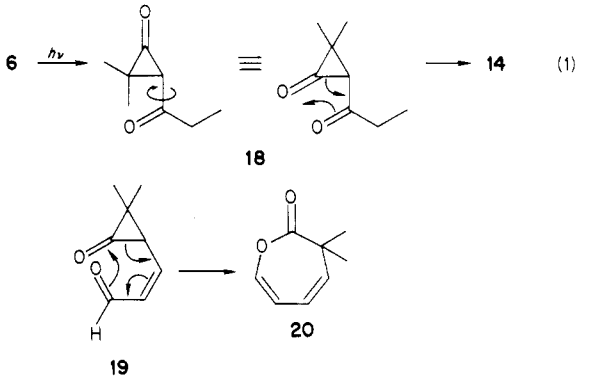


6, R=C_2H_5
7, R=$C(CH_3)_3$
8
9, R=CH_3
10, R=$C(CH_3)_3$

Photochemical Results. Irradiation of furanones **6–9** in benzene solution (~0.01 M, $\lambda \geq 280$ nm) led in each case to a single isomeric compound as the only volatile product. In each case this isomer showed a single sharp infrared (IR) carbonyl absorption in the region 1789–1800 cm^{-1}; and the nuclear magnetic resonance (NMR) spectra of the products from **6** and **7**, where C(4) is unsubstituted in the starting ketone, had an olefinic hydrogen signal at unusually high field, ~5.0 ppm. These data are not at all well in accord with previous observations for the α,β-unsaturated lactones expected as products in analogy with the isomerization of **2** to **3**. From **6** this lactone would be **11**, and such conjugated butenolides typically have either split carbonyl bands in the IR (~1750, 1785 cm^{-1}) or else a single absorption at ~1755 cm^{-1},[10] and in the NMR, a normal shift for the olefinic proton. For example, three research groups have reported spectral data for **12**: 1750–1760 cm^{-1} in the IR and 5.50–5.70 ppm for the α hydrogen.[1,11,12] Our spectroscopic results are, however, in quite good agreement with expectation for the structurally isomeric β,γ-unsaturated lactones. The relevant values for α-angelica lactone (**13**) are 1786 cm^{-1} and 5.1 ppm,[13] and in general carbonyl absorption for such lactones is in the range 1790–1800 cm^{-1}.[10] Furthermore, the ultraviolet (UV) spectra of the product from **6** had λ_{max} = 218 nm (2200), while **11** is expected[11] to absorb at ~210 nm (~10000). We thus concluded that the rearrangement products from **6–9** are the β,γ-butenolides **14–17**, respectively, and confirmed this conclusion for **14** through independent preparation of this compound as noted below. Rearrangement of **6–9** then requires formal reversal of the C(2)–C(3) unit upon irradiation, and a reasonable two-step mechanism for this is shown for **6** in eq 1. Isomerization of **6** to **18** is formally a cyclopentene–vinylcyclopropane rearrangement. While various other isomerizations of this sort are familiar, ones leading to cyclopropanones are rare; they do occur in the photochemistry of several strained bi- or polycyclic derivatives of cyclopentenone.[14] The second step, conversion



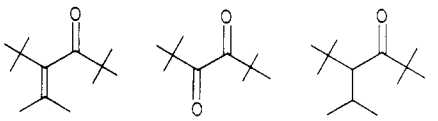
11, R=C_2H_5
12, R=CH_3
13
14, R=C_2H_5
15, R=$C(CH_3)_3$
16
17



6 → 14 (1)
18
19
20

of **18** to **14**, is merely the reverse process with involvement of the other cyclopropane center. A vinylogous example of such a process has been suggested as the final step (**19** to **20**) in two different complex photochemical reactions.[15,16]

While eq 1 is reasonable and consonant with mechanistic suggestions for these other photochemical reactions, there is no direct evidence supporting the intermediacy of acylcyclopropanones (as **18**) in the rearrangements of **6–9**. For this reason we were pleased to find that the photochemistry of the highly crowded 2,2-dimethyl-4,5-di-*tert*-butyl-3(2*H*)-furanone (**10**) diverges from that of these other furanones in a way that provides evidence in support of an intermediate acylcyclopropanone. Irradiation of **10** in benzene solution leads to formation of **21** (50%) and **8**



21 22 23

(5%). Composition and spectroscopic properties [IR 1674 cm^{-1}; ^{1}H NMR δ 1.84 (s, 3 H), 1.53 (s, 3 H), 1.18 (s, 18 H)] suggested structure **21** for the major product. Although these values are in good accord with expectation based on various models,[17] they are rather different from the spectra reported earlier for a ketone assigned this structure [IR 1692 cm^{-1}; ^{1}H NMR δ 2.16 (s, 3 H), 1.96 (s, 3 H), 1.21 (s, 9 H), 1.15 (s, 9 H)].[18] In view of this discrepancy, we oxidized our ketone with ruthenium tetraoxide to yield pivalil (**22**)[19] and converted it to the known[20] saturated ketone **23** through reduction with sodium in liquid ammonia followed by Jones oxidation.[21] These results rigorously establish structure **21** for the major photoproduct

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(11) McMorris, T. C. *J. Org. Chem.* **1970**, *35*, 458.
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(16) Another vinylogous analogy to **18** → **14**, but with a cyclopropane rather than a cyclopropanone, is available: Ishii, K.; Wolf, H. R.; Jeger, O. *Helv. Chim. Acta* **1980**, *63*, 1520.
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(19) This was identified through comparison with an authentic sample: Leonard, N. J.; Mader, P. M. *J. Am. Chem. Soc.* **1950**, *72*, 5388.
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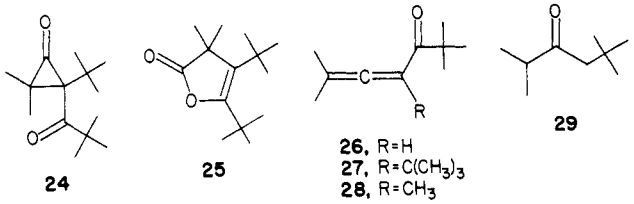
(21) Bowers, A.; Halsall, T. G.; Jones, E. R. H.; Lemin, A. *J. Chem. Soc.* **1953**, 2548. Djerassi, C.; Engle, R. R.; Bowers, A. *J. Org. Chem.* **1956**, *21*, 1547.

from **10** and require reconsideration of the structure of the substance previously described.[18] The accompanying minor product was identical with **8** prepared as indicated later.

As obvious pathway for the formation of **21** is through initial rearrangement of **10** to acylcyclopropanone **24**,



24 **25** **26**, R=H; **27**, R=C(CH$_3$)$_3$; **28**, R=CH$_3$ **29**

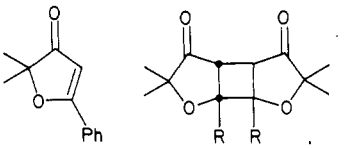
followed by decarbonylation[22] rather than isomerization to the β,γ-butenolide. The mechanism leading to 5% of **8** is less obvious, but direct γ-cleavage and disproportionation to isobutylene and **8** provides the simplest rationalization. Such cleavage would be unprecedented to our knowledge but could possibly be the effect of steric strain in **10** (see below). These pathways, as well as several more complex routes to **8**, require loss of the original carbonyl group in formation of **21** and its retention in **8**. Photolysis of **10** in which the carbonyl oxygen was enriched with ^{18}O demonstrated that these requirements are met. Treatment of **10** with ^{18}O-water in tetrahydrofuran containing hydrogen chloride for 5 days at room temperature gave **10** containing some 18% ^{18}O at the carbonyl oxygen atom in quantitative recovery. Irradiation of this labeled furanone yielded **21** with no excess ^{18}O, and both **8** and recovered **10** with no loss of the label. The excess ^{18}O in **8** and recovered **10** was washed out on treatment with unlabeled aqueous acid, indicating that the label in these furanones had remained in the carbonyl oxygen, as expected. All isotopic analyses were performed by mass spectrometry.

We suggest then that in the case of **10** decarbonylation serves to divert acylcyclopropanone **24** and thus to provide good evidence for initial formation of such intermediates from all these furanones. The unique behavior of **24** in decarbonylating rather than rearranging to a β,γ-butenolide has a straightforward explanation. As a *cis*-1,2-di-*tert*-butylethylene, **10** has 9–11 kcal/mol of nonbonded strain energy,[23] and this is relieved on conversion to **24** and rotation about the acyl–cyclopropyl bond. Subsequent isomerization of **24** to the unobserved butenolide **25** would necessarily reintroduce this strain; loss of carbon monoxide from **24**, on the other hand, can occur from a conformation that minimizes crowding of the *tert*-butyl groups.

Low concentrations of 2,3-dimethyl-1,3-butadiene efficiently quenched both of the reactions of **10** as well as the rearrangement of **9**, implying that these transformations occur from an easily quenched triplet state.

Preparative Experiments. We have previously described the preparation of **7** and **10** through oxidative cyclization of the related allenic ketones **26** and **27** with osmium tetraoxide,[3] and the synthesis of **6**, as well as a related alternative synthesis of **7**, is already on record.[1,24] Planning to reach **9** by the route used for **7** and **10**, we prepared **28** through addition[25] of the lithium derivative of trimethylallene to pivalaldehyde followed by Swern oxidation.[26] In the case of **28**, however, the osmium tetraoxide reaction failed despite the earlier success with both **26** and **27**.[3] Since mercuric acetate has been used successfully for the related cyclization of vinylallenes to cyclopentenones,[27] we tried this reagent with **28**. This proved to yield a rapid, effective route to **9**; indeed, mercuric acetate is much superior to osmium tetraoxide for this reaction.[28] Useful quantities of ketone **8** were available through α,α'-bromination of isopropyl neopentyl ketone (**29**),[29] subsequent treatment with zinc–copper couple in the presence of dimethylformamide, and elimination, all following a known procedure.[30] Finally, an authentic sample of enol lactone **14** was prepared through the reaction of dimethylketene with 1-diazo-2-butanone, first at −50 °C and then at room temperature; this procedure has been used in closely related syntheses in the past.[31]

In view of these results the behavior of the diphenylfuranone **2**[7] is puzzling. We confirmed that butenolide **3** is the major product from irradiation of **2** through Vycor as well as through Pyrex ($\lambda \geq 280$ nm), the conditions that had been used with **6–10**. We had hoped that examination of the photochemistry of bullatenone (**30**)[4] would be



30 **31**, R=H; **32**, R=Ph

helpful, since this ketone has the β-phenyl enone chromophone of **2** but, like **6–10**, cannot enolize. Irradiation of **30**, even at concentrations as low as 1.3 mM, however, gave a photodimer as the only isolable product. The factors controlling the regio- and stereochemistry of dimerization of 3(2*H*)-furanones have been analyzed in some detail, and irradiation of the related ketone 2,2-dimethyl-3(2*H*)-furanone yields a single dimer that has been assigned the head-to-head cis,anti,cis geometry shown in **31**.[6a] On this basis the photodimer of bullatenone (**30**) is tentatively assigned the analogous structure **32**. The proton NMR spectrum of **32** provides some support for this assignment. The spectrum has two methyl absorptions, one at 1.40 ppm, a normal position for such systems, and the other at 0.85 ppm. The cis,anti,cis stereochemistry places one of the methyl groups in each half of the symmetrical molecule in front of the phenyl substituent in the other half, and this nicely explains the observed upfield shift of one of these signals.

The photochemistry of bullatenone (**30**) fails to explain the unique behavior of **2**, but we can conclude that phenyl substitution plays a significant role in the photochemistry of these ketones. Beyond this observation and the interesting steric effect displayed by **10**, however, the funda-

(22) Rodriguez, H. J.; Chang, J.-C.; Thomas, T. F. *J. Am. Chem. Soc.* **1976**, *98*, 2027 and references cited therein.
(23) Wiebenga, E. H.; Bouwhuis, E. *Tetrahedron* **1969**, *25*, 453. Ermer, O.; Lifson, S. *Ibid.* **1974**, *30*, 2425. Turner, R. B.; Nettleton, D. E., Jr.; Perelman, M. *J. Am. Chem. Soc.* **1958**, *80*, 1430.
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(25) Vermeer, P.; Westmijze, H.; Kleijn, H.; van Dijck, L. A. *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 56.
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(27) Baudouy, R.; Delbecq, F.; Gore, J. *Tetrahedron* **1980**, *36*, 189.
(28) Further discussion and examples of the mercuric acetate oxidation, including an alternative preparation of **10**, appear in our preliminary report (ref 4) on this reaction.
(29) This was prepared following a known procedure: Dubois, J.-E.; Boussu, M.; Lion, C. *Tetrahedron Lett.* **1971**, 829. Spectra were in agreement with those reported: Reetz, M. T.; Maier, W. F.; Chatziiosifidis, I.; Giannis, A.; Heimbach, H.; Löwe, U. *Chem. Ber.* **1980**, *113*, 3741.
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mental factors controlling photochemical behavior in 3-(2*H*)-furanones remain to be more fully delineated.

Experimental Section

Materials and Equipment. All VPC was carried out on a Varian Aerograph Model 920 gas chromatograph with either a 10-ft 25% QF-1 column (A) or 3-ft 25% QF-1 column (B) packed in 0.25-in. aluminum tubing with 45/60 Chromosorb W. Column chromatography on silica gel was performed according to the procedure of Still et al.[32] All NMR spectra were recorded on a Varian Model T-60 (60 MHz) spectrometer. Isobutane chemical ionization mass spectrometric measurements were obtained on a VG-70250 Magnetic Sector instrument. The samples were contained in fine capillaries and introduced by using a direct insertion probe. The scans taken during the evaporation of the sample were averaged and the ratios of ^{18}O to ^{16}O ion species were calculated by using these averaged spectra. Unless otherwise noted, all pure compounds were obtained as colorless oils; melting points are corrected; boiling points are uncorrected.

Preparation of 2,4-Dibromo-2,5,5-trimethylhexan-3-one. To a mixture of **29**[29] (995 mg, 7 mmol), $CHCl_3$ (10 mL), and 48% HBr (2 drops) was added a small amount of a solution of Br_2 (2.24 g, 14 mmol) in $CHCl_3$ (10 mL). No decolorization was observed at room temperature. The mixture was heated to 60 °C at which point Br_2 began to be taken up. After two-thirds of the Br_2 solution had been added, the reaction stopped. Standard workup yielded an oil (1.830 g) which was shown by NMR to be a mixture of 62% of 2-bromo and 38% of the 2,4-dibromo ketone. This mixture was taken up in glacial acetic acid (10 mL) and was treated with Br_2 (0.700 g) in acetic acid (2 mL). Br_2 uptake began after the reaction was heated to 95 °C. Workup yielded 1.932 (92%) of an oil whose NMR spectrum showed resonances due only to the dibromide. This was used directly in the following reaction.

Preparation of 2,2-Dimethyl-4,5-dihydro-4-*tert*-butyl-5-(dimethylamino)-3(2*H*)-furanone. Following the published procedure, 2,4-dibromo-2,5,5-trimethylhexan-3-one (1.932 g, 6.44 mmol) in DMF (5 mL) was added to a suspension of Zn(Cu) couple (1.263 g, 19.3 mmol) in DMF (10 mL) at −35 °C under an Ar atmosphere.[30] The mixture was stirred at this temperature for 15 min, pentane (10 mL) was added, and the reaction mixture was allowed to warm to room temperature. Stirring was continued for 4 days. The mixture was filtered through Celite, diluted with H_2O, and extracted with Et_2O. After removal of solvent, the dihydrofuranone (1.125 g, 82%) was obtained. Further purification was achieved by preparative VPC (column B, 85 °C): IR 2975 (s), 2880 (m), 1745 (s), 1390 (w), 1362 (m), 1080 (m), 973 (m) cm^{-1}; NMR (60 MHz) δ 4.64 (d, J = 8 Hz, 1 H), 2.38 (s, 6 H), 1.23 (d, J = 8 Hz, 1 H), 1.18 (s, 3 H), 1.08 (s, 3 H), 1.03 (s, 9 H). Anal. Calcd for $C_{12}H_{23}NO_2$: C, 67.56; H, 10.87; N, 6.57. Found: C, 67.89; H, 10.75; N, 6.41.

Preparation of 4-*tert*-Butyl-2,2-dimethyl-3(2*H*)-furanone (8). A mixture of the (dimethylamino)dihydrofuranone from above (923 mg, 4.33 mmol), iodomethane (2.46 g), diisopropylethylamine (2.24 g), and benzene (15 mL) was heated to reflux. The elimination of dimethylamine was followed by VPC analysis (column B). After 4 days it was virtually complete. Standard workup yielded crude **8** (724 mg, 100%), which was further purified by flash chromatography[32] with 85:15 hexanes/Et_2O. This gave pure **8**, mp 71–73 °C: IR 2955 (s), 2860 (m), 1692 (s), 1601 (s), 1375 (w), 1360 (m), 1335 (m), 1190 (m), 1075 (s), 900 (w) cm^{-1}; NMR (60 MHz) δ 7.70 (s, 1 H), 1.26 (s, 6 H), 1.18 (s, 9 H); mass spectrum, m/z 168.1160 (M^+, calcd for $C_{10}H_{16}O_2$, 168.1150).

Preparation of 2,2,4,6-Tetramethylhepta-4,5-dien-3-one (28). To a solution of trimethylallene[33] (821 mg, 10 mmol) in THF (20 mL) cooled to −70 °C under a N_2 atmosphere was added *t*-BuLi (6.5 mL of a 1.8 M solution in pentane, 11.7 mmol). The mixture was stirred at −50 °C for 3 h. After recooling to −78 °C, trimethylacetaldehyde (1.03 g, 12 mmol) in THF (5 mL) was added dropwise. The reaction was allowed to warm to 25 °C and was worked up in the usual way. VPC analysis (column A, 140 °C) of the residue (1.843 g) remaining after removal of solvent indicated one major component. This was collected by preparative VPC and identified as 2,2,4,6-tetramethylhepta-4,5-dien-3-ol: IR 3640 (w), 3600–3300 (br), 2950 (s), 2860 (s), 1475 (m), 1360 (m), 1000 (m) cm^{-1}; NMR (60 MHz) δ 3.58 (br d, J = 5 Hz, 1 H), 1.71 (s, 9 H), 1.29 (br d, J = 5 Hz, 1 H), 0.83 (s, 9 H); mass spectrum, m/z 168.1523 (M^+, calcd for $C_{11}H_{20}O$, 168.1514).

The crude alcohol (1.843 g) was oxidized according to the procedure of Swern[3,26] to give **28** (1.61 g, 97%) after purification by bulb-to-bulb distillation (120 °C, 15 mm): IR 2985 (s), 2860 (m), 1955 (w), 1671 (s), 1367 (m), 1276 (w), 1185 (m), 1076 (m), 1010 (m), 925 (w) cm^{-1}; NMR (60 MHz) δ 1.78 (s, 6 H), 1.67 (s, 3 H), 1.17 (s, 9 H); mass spectrum, m/z 166.1370 (M^+, calcd for $C_{11}H_{18}O$, 166.1357).

Preparation of 5-*tert*-Butyl-2,2,4-trimethyl-3(2*H*)-furanone (9). Allene **28** (168 mg, 1 mmol) was added dropwise to a stirred suspension of $Hg(OAc)_2$ (350.5 mg, 1.1 mmol) in glacial acetic acid (4 mL). Mercury precipitated immediately; stirring was continued for 0.5 h. The reaction mixture was diluted with H_2O and extracted with Et_2O (2×). The combined extracts were washed with H_2O, $NaHCO_3$, and brine and were dried. Removal of solvent in vacuo yielded **9** (169 mg, 93%). VPC analysis (column A, 150 °C) indicated this material to be pure: IR 2975 (s), 2925 (m), 2865 (w), 1688 (s), 1600 (s), 1400 (m), 1360 (m), 1227 (m), 1188 (m), 1090 (s), 950 (w) cm^{-1}; NMR (60 MHz) δ 1.77 (s, 3 H), 1.33 (s, 9 H), 1.27 (s, 3 H); mass spectrum, m/z 182.1306 (M^+ calcd for $C_{11}H_{18}O_2$, 182.1307); UV λ_{max} 274 nm (ϵ 11 085).

General Procedure for Irradiation of 3(2*H*)-Furanones 6–9. A solution of the furanone (40–100 mg) in C_6H_6 (60 mL)/MeOH (5 mL) was degassed with N_2 and irradiated through Pyrex. When VPC analysis indicated no remaining starting material (2–4 days), the solvent was removed by distillation and the residue was purified by preparative VPC to afford the butenolide (20–40%) as the only volatile product.

Photolysis of **6** gave **14**: IR 2950 (s), 2940 (m), 1800 (s), 1675 (m), 1462 (m), 1242 (s), 1075 (s), 827 (s) cm^{-1}; NMR δ 4.98 (t, J = 1.5 Hz, 1 H), 2.28 (dd, J = 1.5, 7.5 Hz, 2 H), 1.25 (s, 6 H), 1.13 (t, J = 7.5 Hz, 3 H); mass spectrum, m/z 140.0835 (M^+, calcd for $C_8H_{12}O_2$, 140.0837).

Photolysis of **7** gave **15**, mp 71–73 °C: IR 2950 (m), 1798 (s), 1661 (w), 1239 (m), 1090 (m), 1055 (s), 928 (m) cm^{-1}; NMR δ 5.00 (s, 1 H), 1.26 (s, 6 H), 1.20 (s, 9 H); mass spectrum, m/z 168.1148 (M^+, calcd for $C_{10}H_{16}O_2$, 168.1150).

Photolysis of **8** gave **16**: IR 2950 (s), 2870 (w), 1797 (s), 1630 (w), 1362 (m), 1282 (m), 1105 (m), 1040 (s) cm^{-1}; NMR δ 6.53 (s, 1 H), 1.38 (s, 6 H), 1.20 (s, 9 H); mass spectrum, m/z 168.1130 (M^+, calcd for $C_{10}H_{16}O_2$, 168.1150).

Photolysis of **9** gave **17**: IR 2965 (s), 2860 (m), 1789 (s), 1252 (m), 1125 (w), 1040 (s), 1010 (m) cm^{-1}; NMR δ 1.73 (s, 3 H), 1.27 (s, 9 H), 1.17 (s, 6 H); mass spectrum, m/z 182.1332 (M^+, calcd for $C_{11}H_{18}O_2$, 182.1307).

Photolysis of 10. Furanone **10** (114 mg) in C_6H_6 (70 mL) was irradiated through Pyrex until VPC analysis (column A, 140 °C, indicated almost complete disappearance of starting material (~41 h) and the formation of two products. These were collected by preparative VPC. The first eluted component (5%) was identified as **8**, having identical IR and NMR spectra with an authentic sample (see above). The second component (50%) was further purified by flash chromatography and was identified as **21**; NMR (60 MHz) δ 1.84 (s, 3 H), 1.53 (s, 3 H), 1.18 (s, 18 H); IR 2965 (s), 2865 (m), 1675 (s), 1470 (m), 1360 (m), 1258 (m), 1120 (m), 1072 (m), 865 (m) cm^{-1}; mass spectrum, m/z 139.1124 [(M-*t*-Bu)$^+$, calcd for $C_9H_{15}O$, 13.1122]. Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.33. Found: C, 79.55; H, 12.42.

Only small amounts of **8** and **21** were produced when **1** (1.28 × 10^{-2} M) was irradiated in the presence of 2,3-dimethylbutadiene (2.56 × 10^{-2} M, 2 equiv).

Oxidation of 21 with Ruthenium Tetraoxide. To a solution of RuO_4 in CCl_4 (4 mL), prepared from RuO_2 (53.5 mg) and 0.21 M $NaIO_4$, was added **21** (~15 mg) in CCl_4 (0.5 mL). The mixture was stirred at 25 °C for 0.5 h before excess oxidant was destroyed by the addition of 2-propanol. After removal of RuO_2 by filtration, VPC analysis (column A, 140 °C) indicated the formation of one product. This was collected and identified as pivalil (**22**) on the basis of its retention time and comparison of its NMR and IR spectra with those of an authentic sample.[19]

(32) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(33) This was prepared by treating 2-methyl-3-butyn-2-yl acetate with lithium dimethylcuprate following a known method: Rona, P.; Crabbé, P. *J. Am. Chem. Soc.* **1969**, *91*, 3289.

Reduction of 21. To a solution of lithium (~20.0 mg) in liquid NH_3 (~50 mL) at reflux was added **21** (74.4 mg, 0.38 mmol) in ether (4 mL) containing *tert*-butyl alcohol (169 mg). After another small portion of lithium was added, stirring was continued at -33 °C for 0.5 h. The usual workup (addition of NH_4Cl, evaporation of NH_3, Et_2O extraction) yielded a residue which was taken up in acetone and treated with Jones reagent. After standard workup, the residue was purified by VPC (column B, 120 °C) to give **23**, having NMR and IR spectra identical with those of an authentic sample.

^{18}O Labeling of 10. A mixture of **10** (285.2 mg), 98% $H_2{}^{18}O$ (0.40 mL), and THF (5.8 mL), through which dry HCl gas had been bubbled for 0.5 min, was allowed to stand at 25 °C for 6 days. The mixture was neutralized with $NaHCO_3$, diluted with H_2O, and extracted with Et_2O. The residue after removal of solvent was combined with that from a smaller scale run (53.5 mg) and was flash chromatographed using 90:10 hexanes/Et_2O to give **10** (302 mg, 90%). Mass spectrometric analysis indicated that the value of $(M + H)^+_{227}/(M + H)^+_{225}$ was 0.218 (i.e., **10** contained 17.9% ^{18}O).

Photolysis of ^{18}O-Labeled 10. The labeled furanone (290 mg) was dissolved in anhydrous benzene (85 mL) and was irradiated as described above for 74 h at which time very little **10** remained. The benzene was removed by distillation and the residue was flash chromatographed using 92.5:7.5 hexanes/Et_2O. Enone **21** was eluted in fractions 12-17, furanones **10** and **8** in fractions 20-27. These were further purified by preparative VPC (column A, 150-160 °C) before analysis by mass spectrometry. The ratio of $(M + H)^+_{199}/(M + H)^+_{197}$ for **21** was 0.015 (1.5% ^{18}O); the ratio of these ions in the spectrum of **21** obtained from unlabeled **10** was 0.013. The value of $(M + H)^+_{171}/(M + H)^+_{169}$ found for **8** was 0.212, and the value of $(M + H)^+_{227}/(M + H)^+_{225}$ from recovered **10** was 0.216, indicating essentially no loss of label from these compounds.

A small amount of labeled furanone **8** was treated with unlabeled hydrochloric acid in THF for 3 days as described above for **10**. Mass spectrometric analysis indicated that most of the ^{18}O had been washed out.

Photolysis of 2. A solution of **2** (100 mg) in C_6H_6 (70 mL) was irradiated through Vycor. TLC analysis (silica gel plates, 98:2 CH_2Cl_2/MeOH) indicated little starting material after 1.75 h and the formation of one major and several minor products. The residue after removal of solvent was flash chromatographed using 99:1 CH_2Cl_2/MeOH to give **3**, mp 150.5-152 °C (lit.[7] mp 149-150 °C) and having a NMR spectrum identical with that reported.[7] Irradiation through Pyrex gave a slower reaction but comparable results.

Photolysis of Bullatenone (30). A solution of **30**[4] (138 mg) in C_6H_6 (90 mL) was irradiated through Pyrex for 9 h. TLC as above indicated one faster R_f product. Flash chromatography using 99.5:0.5 CH_2Cl_2/MeOH gave recovered **30** (20.5 mg) and **31** (101.6 mg, 86%), mp 189-191 °C: IR 3028 (w), 2980 (m), 1764 (s), 1378 (m), 1362 (m), 1120 (s), 1007 (m) cm^{-1}; NMR (60 Mz) δ 7.27 (s, 5 H), 3.62 (s, 1 H), 1.40 (s, 3 H), 0.85 (s, 3 H); CI mass spectrum, m/z 377.1717 [$(M + H)^+$, calcd for $C_{24}H_{25}O_4$, 377.1753].

The dimer was the only product detected when the concentration of the furanone irradiated was lowered to 0.25 mg/mL.

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Reactions of 1,2-Oxaphospholenes. 4.[1] Responses toward Oxidations, Cycloadditions, and Conjugate Additions

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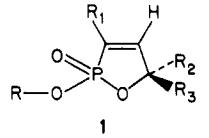
In contrast to the more normal reactivity of the carbon-carbon double bond in vinyl phosphonates, the oxaphospholene double bond in 5,5-dimethyl-2-phenyl-1,2-oxaphosphol-3-ene 2-oxide (**7**) has proven to be quite resistant to a broad spectrum of reagents including typical electrophiles, most electrophilic and nucleophilic epoxidizing reagents, and organometallic nucleophiles as well as representative Diels-Alder dienes and 1,3-dipoles. Four exceptions to this trend were *N*-bromoacetamide (NBA), ozone, lithium dimethylcuprate, and sodium naphthalene. Reaction of **7** with NBA involved formation of a bromonium ion followed by methyl migration, ring opening, and dehydrobromination to give (3-keto-2-methyl-1-butenyl)phenylphosphinic acid, characterized as its methyl ester **14**. Ozonolysis of **7** proceeded with cleavage of the double bond, affording (after a series of decarboxylations and oxidations) acetone, phenylphosphonic acid, and 1-carboxy-1-methylethyl phenylphosphonate (**21**). The latter two acids were characterized as their methyl esters. Reactions of **7** with the cuprate gave, instead of methylation, the two-electron reduction product (3-methyl-2-butenyl)phenylphosphinic acid (**24**), also characterized as its methyl ester. Reduction of **7** with naphthalene sodium also gave **24**, in support of the stepwise two-electron reduction mechanism suggested in the case of the cuprate. Finally, in a related reaction, treatment of the 4-bromo derivative of **7** with magnesium or the cuprate led via ring opening to (3-methyl-1,2-butadienyl)phenylphosphinic acid (**8**), the original precursor of **7**, and its 4-bromo derivative.

In the decade since we first discovered a general synthetic route to 1,2-oxaphosphol-3-enes from propargyl alcohols,[2] we have investigated in detail the mechanisms of the reactions involved.[3] Recently we began a systematic study of the chemistry of this novel phosphorus heterocyclic system. Our initial interest was focused on nucleophilic substitution at the phosphorus atom in **1**.[1,4]



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