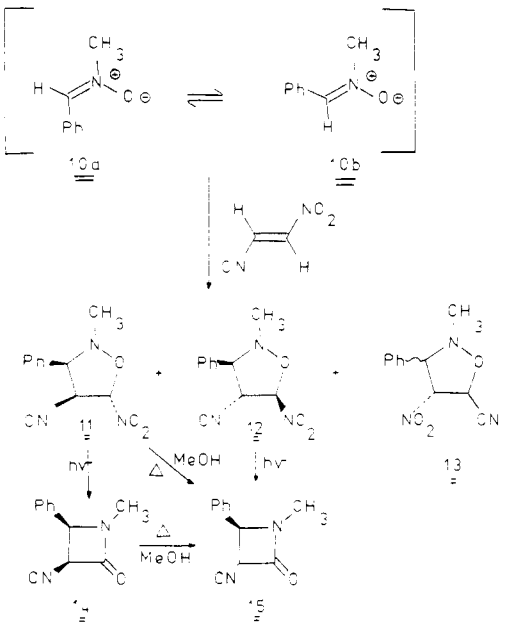
Scheme III



The ready conversion of the 5-nitroisoxazolidine regioisomer (i.e., **3**) to the β-lactam ring is most easily rationalized by the mechanism outlined in Scheme II. The nitrogen–oxygen bond of **3** is expected to be cleaved readily, since such heteroatom–heteroatom bonds are known to be relatively weak.[14,15] Thus, removal of the acidic proton adjacent to the nitro group followed by N–O bond cleavage and subsequent cyclization of the transient acyl nitro intermediate **9** nicely accommodates the formation of the β-lactam system.[16] The formation of *cis*-lactam **5** from the thermolysis of **3** in methanol reflects thermodynamic rather than kinetic factors. We have demonstrated this by heating a pure sample of **6** in methanol and recovering only the cis isomer. In this case, steric crowding about the β-lactam ring is minimized by having both the cyano and phenyl groups trans to the very large *tert*-butyl group. This would account for the greater thermodynamic stability of the *cis* isomer.[17] Photolysis of isoxazolidine **3** results in N–O bond scission which is followed by internal hydrogen transfer and subsequent cyclization of intermediate **9**.[18] It should be noted that the exclusive formation of lactam **6** from the irradiation of **3** fixes the stereochemistry of the phenyl and cyano groups as being trans in the cycloadduct.

In an effort to further establish the generality and scope of the nitrone-based synthesis of β-lactams, the cycloaddition of *C*-phenyl-*N*-methylnitrone (**10**) with *trans*-1-cyano-2-nitroethylene was investigated. In this case, a mixture of three isomeric cycloadducts was produced with properties similar to those observed for the *N*-*tert*-butylisoxazolidines. Two of these (i.e., **11** and **12**) derive from one regiochemical mode of cycloaddition of **10** to the π bond, while the other (i.e., **13**) derives from the alternate mode of addition (vide infra, Scheme III). To account for the formation of the two diastereomeric cycloadducts **11** and **12**, we assume that the trans isomer (**10a**) of phenyl-*N*-methylnitrone is in equilibrium with a small amount of the cis form (**10b**) and that the two transition states leading to **11** and **12** are of comparable energy. This is not the case with the corresponding *tert*-butylnitrone **1**, presumably as a consequence of steric factors.

The major 5-nitro substituted regioisomer **11** (mp 125–126 °C, 60%) was converted to *cis*-β-lactam **14** on photolysis with 2537-Å light [NMR ($CDCl_3$, 90 MHz) δ 2.85 (s, 3 H), 4.45 (d, 1 H, J = 6.0 Hz), 4.90 (d, 1 H, J = 6.0 Hz), 7.3–7.6 (m, 5 H)]. In marked contrast, heating a sample of **11** in methanol produced the isomeric *trans*-lactam **15**, mp 87–88 °C [NMR ($CDCl_3$, 90 MHz) 2.80 (s, 3 H), 3.80 (d, 1 H, J = 3.0 Hz), 4.75 (d, 1 H, J = 3.0 Hz), and 7.3–7.6 (m, 5 H)]. The structural assignment for β-lactams **14** and **15** was confirmed by comparison with independently synthesized samples.[19] *cis*-Lactam **14** was converted into the thermodynamically more stable trans isomer **15** on refluxing in methanol. The irradiation of the minor regioisomer **12** was also studied and was found to produce *trans*-β-lactam **15** as the exclusive ring contracted product. It should be noted that the distribution of β-lactams in the methyl series differs significantly from the encountered with the *tert*-butyl system. It is our belief that the difference in thermodynamic stability of the two lactam systems is chiefly controlled by the size of the substituent group on nitrogen.

In conclusion, we have shown that the 1,3-dipolar cycloaddition of nitrones with a nitroethylene derivative results in the production of regioisomeric adducts, one of which undergoes ready ring contraction to the β-lactam ring. We are continuing to explore the scope and mechanistic features of the reaction and will report additional findings at a later date.

Acknowledgment. We gratefully acknowledge support of this work by the National Institutes of Health. We also wish to thank Professor Charles Liotta for providing a sample of *trans*-1-cyano-2-nitroethylene.

(12) H. W. Moore, *Acc. Chem. Res.*, **12**, 125 (1979).
(13) We thank Professor H. W. Moore for providing us with a sample of furanone **7** as well as experimental details for the zwittazido cleavage reaction.
(14) J. E. Baldwin, R. G. Pudussery, A. K. Qureshi, and B. B. Sklarz, *J. Am. Chem. Soc.*, **90**, 5326 (1968).
(15) J. A. Kerr, *Chem. Rev.*, **66**, 496 (1966); T. I. Cottrell, "The Strengths of Chemical Bonds", 2nd ed., Butterworths, London, 1958.
(16) The rate of reorganization of the isoxazolidine ring to the β-lactam system is markedly enhanced in the presence of added base (i.e., sodium methoxide or sodium carbonate).
(17) A similar effect has been noted with the related arylaroylaziridine system; see R. E. Lutz and A. B. Turner, *J. Org. Chem.*, **33**, 516 (1968).
(18) For a related hydrogen atom transfer reaction in the photolysis of an isoxazolidine, see N. A. LeBel, T. A. Lajiness, and B. D. Ledlie, *J. Am. Chem. Soc.*, **89**, 3076 (1967).
(19) H. Bohme, S. Ebel, and K. Hartke, *Chem. Ber.*, **98**, 1463 (1965).

Regiocontrolled Hydration of 2-Butyne-1,4-diol Derivatives To Give 4,5-Dihydro-3(2*H*)-furanones. Practical Synthesis of Bullatenone and Geiparvarin

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Although the transformation of symmetrically substituted 2-butyne-1,4-diol derivatives into dihydro-3(2*H*)-furanones is well established and most promising in a practical sense,[1] this process has not been used for the synthesis of furanone derivatives,[2] in general, due mainly to the lack of regiocontrol in the hydration of the carbon–carbon triple bond.[3] Herewith we report a solution

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(1) (a) Richet, H. *Ann. Chim.* **1948**, *3*, 317. (b) Leonard, F.; Wajngurt, A.; Horn, H. *J. Org. Chem.* **1956**, *21*, 1402. (c) Hagens, G.; Wasacz, J. P.; Joullie, M.; Yates, P. *Ibid.* **1970**, *35*, 3682. (d) Newman, M. S.; Reichle, W. R. *Org. Synth. Coll. Vol. V.* **1973**, 1024.
(2) (a) Medvedeva, A. S.; Safronova, L. P.; Kalikhman, I. D.; Vlasov, V. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1975**, 1175. (b) Colonge, J.; Falcotet, R.; Gaumont, R. *Bull. Soc. Chim. Fr.* **1958**, 211. (c) Vartanyan, S. A.; Chukhadzhyan, G. A.; Melikyan, R. A.; Babanyan, Sh. A. *Izv. Akad. Nauk Arm. SSR., Khim. Nauki* **1962**, *15*, 45. (d) Medvedeva, A. S.; Shostakoviskii, M. F.; Chichkareva, G. G.; Favorskaya, T. A.; Voronov, V. K. *Zh. Org. Khim.* **1971**, *7*, 641. (e) Bohlmann, F. *Chem. Ber.* **1961**, *94*, 1104. (f) Chemische Werke Huels A.-G. German Patent 1 1150685; *Chem. Abstr.* **1964**, *60*, 2895e.

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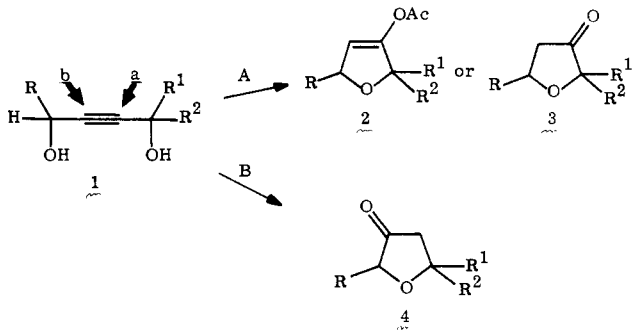
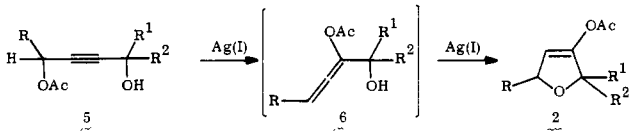
for this problem, namely, selective hydration at the position a or b in **1**.



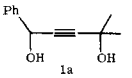
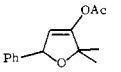
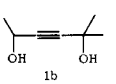
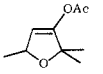
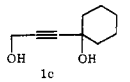
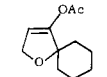
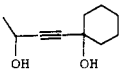
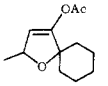
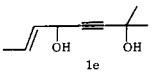
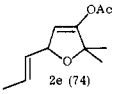
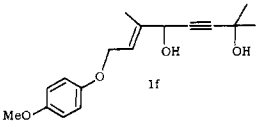
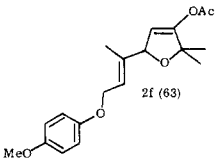
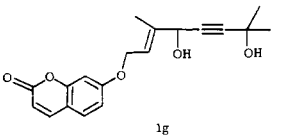
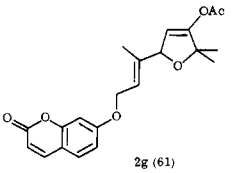
In order to introduce the oxygen function at the a position of the triple bond of **1** to give **3** with complete regioselectivity, method A is applied which involves selective monoacetylation of unsymmetrical 2-butyne-1,4-diols **1**, Ag(I)-catalyzed cyclization under acetoxyl migration to give **2**, and finally hydrolysis. In contrast, the opposite regioisomers **4** are produced directly from **1** by the catalysis of a polymer reagent Hg/Nafion-H.[4]

Treatment of **1** with acetic anhydride and pyridine at room temperature resulted in acetylation of the less hindered hydroxyl group. The monoacetate was then treated with 5 mol % of silver perchlorate in refluxing benzene in the dark, thereby giving rise to the enol acetate of type **2** in good yield. Results are summarized in Table I. On the basis of recent studies, the transformation can be explained by Ag(I)-catalyzed isomerization[5] of the monoacetate **5** to an allenyl acetate **6** followed by Ag(I)-assisted cyclization.[6] It is worthy to note that, firstly, the C=C bond in



the substituent is not affected at all and the olefinic configuration is completely retained throughout the reaction; secondly, oxidation of the resulting enol acetates **2a** and **2e–g** with dichlorodicyano-*p*-benzoquinone (DDQ) in benzene at room temperature affords 3(2*H*)-furanones[7] in quantitative yield.[8] Thus, the combined process allowed us to synthesize bullatenone (**7**)[9] in 81% overall

Table I. Ag(I)-Catalyzed Synthesis of Dihydro-3(2*H*)-furanone Enol Acetate (**2**)[a]

2-butyne-1,4-diol (**1**)	monoacetate yield,[b] %	dihydro-3(2*H*)-furanone enol acetate (**2**) (yield, %)
 **1a**	99	 **2a** (84)
 **1b**	>99	 **2b** (99)
 **1c**	>99	 **2c** (63)[c]
 **1d**	>99	 **2d** (80)
 **1e**	81[d]	 **2e** (74)
 **1f**	81[d]	 **2f** (63)
 **1g**	86[d]	 **2g** (61)

[a] The monoacetate was treated with 5 mol % of silver perchlorate. [b] Yields refer to the material purified by column chromatography (Wacogel C-100, 4 g per 0.1 g of the product, 10:1 hexane–ethyl acetate elution) for **2a–g** except **2c** which was isolated by preparative TLC (2:1 hexane–ethyl acetate, R_f 0.68–0.78). All the new compounds **2a–g** were characterized analytically and spectrometrically. Bp's and characteristic spectral properties of these follow. **2a**: see footnote 10. **2b**: bp 101–102 °C (bath temperature) (18 torr); IR (neat) 1782, 1760, 1660 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.22 (s, 3 H), 1.23 (d, J = 6.0 Hz, 3 H), 1.27 (s, 3 H), 2.14 (s, 3 H), 4.83 (dq, J = 1.7, 6.0 Hz, 1 H), 5.66 (d, J = 1.7 Hz, 1 H). **2c**: bp 122–125 °C (bath temperature) (0.04 torr); IR (neat) 1780, 1757 (sh), 1658 cm^{-1}; ^{1}H NMR (CCl_4) δ 2.13 (s, 3 H), 4.54 (d, J = 1.7 Hz, 2 H), 5.73 (t, J = 1.7 Hz, 1 H). **2d**: bp 92 °C (bath temperature) (0.05 torr); IR (neat) 1781, 1758, 1659 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.22 (d, J = 6.3 Hz, 3 H), 2.10 (s, 3 H), 4.73 (dq, J = 1.5, 6.3 Hz, 1 H), 5.60 (d, J = 1.5 Hz, 1 H). **2e**: bp 117–118 °C (bath temperature) (0.04 torr); IR (neat) 1781, 1761 (sh), 1656 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.25 (s, 3 H), 1.28 (s, 3 H), 1.69 (d, J = 5.3 Hz, 3 H), 2.14 (s, 3 H), 5.02 (dd, J = 1.5, 5.9 Hz, 1 H), 5.52 (dd, J = 5.9, 15.0 Hz, 1 H), 5.61 (d, J = 1.5 Hz), 5.62 (dq, J = 15.0, 5.3 Hz, 1 H). **2f**: bp 160–162 °C (bath temperature) (0.05 torr); IR (neat) 1778, 1657 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.27 (s, 3 H), 1.30 (s, 3 H), 1.67 (s, 3 H), 2.15 (s, 3 H), 3.71 (s, 3 H), 4.49 (d, J = 6.0 Hz, 2 H), 5.11 (br s, 1 H), 5.63 (d, J = 1.5 Hz, 1 H), 5.70 (t, J = 6.0 Hz, 1 H), 6.73 (s, 4 H). **2g**: bp 180–183 °C (bath temperature) (0.05 torr); IR (CCl_4)1780, 1745, 1615 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 3 H), 1.38 (s, 3 H), 1.74 (s, 3 H), 2.21 (s, 3 H), 4.66 (d, J = 6.0 Hz, 2 H), 5.23 (br s, 1 H), 5.69 (d, J = 1.5 Hz, 1 H), 5.83 (t, J = 6.0 Hz, 1 H), 6.25 (d, J = 4.8 Hz, 1 H), 6.8–7.0 (m, 2 H), 7.3–7.5 (m, 1 H), 7.68 (d, J = 4.8 Hz, 1 H). [c] Silver tetrafluoroborate (10 mol %) was employed. [d] Overall yield for the addition of the dilithium salt of 2-methyl-3-butyn-2-ol to an aldehyde and monoacetylation.

(3) Other methods for the synthesis of furanones: (a) Smith, A. B., III; Jerris, P. J. *Tetrahedron Lett.* **1980**, *21*, 711. (b) Semple, J. E.; Guthrie, A. E.; Joullié, M. M. *Ibid.* **1980**, *21*, 4561. (c) Smith, A. B. III; Guaciaro, M. A.; Schow, S. R.; Wovkulich, P. M.; Toder, B. H.; Hall, T. W. *J. Am. Chem. Soc.* **1981**, *103*, 219. (d) Gange, D.; Magnus, P. *Ibid.* **1978**, *100*, 7746 and references cited therein. (e) Gavrilov, L. D.; Klopotova, M. I.; Vereshchagin, L. I. *Zh. Org. Khim.* **1974**, *10*, 2064. (f) Lysenko, Z.; Ricciardi, F.; Semple, J. E.; Wang, P. C.; Joullie, M. M. *Tetrahedron Lett.* **1978**, 2679. (g) Nicolaou, K. C.; Magolda, R. L.; Sipio, W. J.; Barnette, W. E.; Lysenko, Z.; Joullie, M. M. *J. Am. Chem. Soc.* **1980**, *102*, 3784. (h) Yoshimura, J.; Kondo, S.; Ihara, M.; Hashimoto, H. *Chem. Lett.* **1979**, 819. (i) Semple, J. E.; Joullié, M. M. *Heterocycles* **1980**, *14*, 1825. (j) Smith, A. B., III Levenberg, P. A.; Jerris, P. J.; Scarborough, Jr., R. M.; Wovkulich, P. M. *J. Am. Chem. Soc.*, **1981**, *103*, 1501.

(4) The polymer reagent Hg/Nafion-H was prepared by stirring Nafion-H in aqueous saturated mercury(II) acetate, filtering, washing with water, and finally drying (room temperature, 1 torr, 1 day). The resin thus prepared contained 0.38 mmol of Hg(II) per 1 g. See: Olah, G. A.; Meidar, D. *Synthesis* **1978**, 671. We are indebted to E. I. du Pont de Nemours & Co. and Mitsui Fluorochemical Co. for a generous gift of Nafion-H.

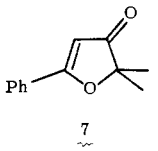
(5) (a) Oelberg, D. G.; Schiavelli, M. D. *J. Org. Chem.* **1977**, *42*, 1804. (b) Landor, P. D.; Lanodr, S. R. *J. Chem. Soc.* **1956**, 1015. (c) Saucy, G.; Marbet, R.; Lindlar, H.; Isler, O. *Helv. Chim. Acta* **1959**, *42*, 1945. (d) F. Hoffmann-La Roche & Co. A.-G. Belgian Patent 617 174; *Chm. Abstr.* **1963**, *59*, 1540f. (e) Day, A. C.; Whiting, M. C. *J. Chem. Soc. C* **1966**, 464. (f) Benn, W. R. *J. Org. Chem.* **1968**, *33*, 3113. (g) Schlossarczyk, H.; Sieber, W.; Hesse, M.; Hansen, H.-J.; Schmid, H. *Helv. Chim. Acta* **1973**, *56*, 875.

(6) (a) Olsson, L.-I.; Claesson, A. *Synthesis* **1979**, 743. (b) Leandri, G.; Monti, H.; Bertrand, M. *Tetrahedron* **1974**, *30*, 289.

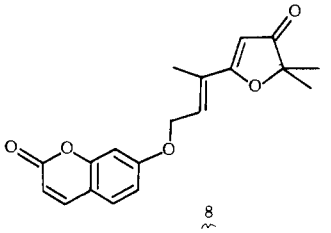
(7) Other approaches to 3(2*H*)-furanones: Hiyama, T.; Shinoda, M.; Saimoto, H.; Nozaki, H. *Heterocycles* **1981**, *15*, 263 and references cited therein.

(8) This oxidation reaction was alternatively effected by bromination of **2** followed by dehydrobromination (LiCl, Li_2CO_3, DMF) in somewhat lower yields.

yield from benzaldehyde.[10] Similarly, an antitumor furanone, geiparvarin (**8**),[11] was prepared with stereospecificity from 4-(coumarin-7-yloxy)-2-methyl-2(*E*)-butenal[12] in 52% yield and the spectral data (IR, NMR)[13] as well as the melting point were identical with those of the recorded ones on the natural material.



7

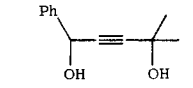
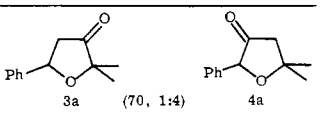
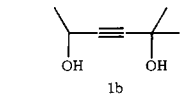
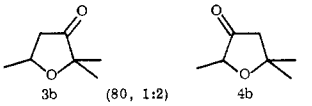
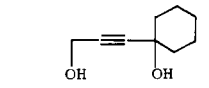
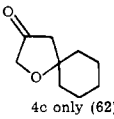
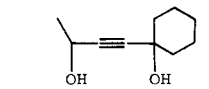
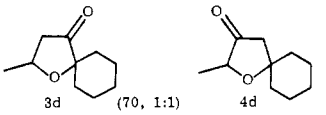
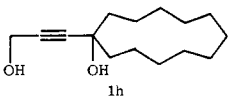
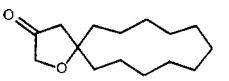


8

For access to the opposite regioisomer **4** of the dihydrofuranones an ethanol solution of the acetylenic diol **1** was stirred with Hg/Nafion-H (0.5 g/mmol of **1**)[4] in the presence of 5 equiv of water at room temperature for 1–7 h. Filtration of the catalyst, concentration, and preparative TLC purification gave **4** as a major product, as listed in Table II. Although the selectivity in **1a**, **1b**, and **1d** (secondary vs. tertiary hydroxyl) was moderate (4:1 to 1:1), the discrimination of the primary hydroxyl group from the tertiary one was excellent as exemplified in the reaction of **1c** and **1h**.

Salient features of the Hg/Nafion-H reagent follow: (1) Workup operation involves only filtration and concentration. (2)

Table II. Hg/Nafion-H Catalyzed Dihydro-3(2*H*)-furanone Synthesis[a]

2-butyne-1,4-diol derivative	dihydro-3(2*H*)-furanone (% yield, product ratio)
 1a	 3a (70, 1:4) 4a
 1b	 3b (80, 1:2) 4b
 1c	 4c only (62)
 1d	 3d (70, 1:1) 4d
 1h	 4h only (68)[b]

[a] A mixture of **1** and water (5 equiv) dissolved in ethanol was stirred at room temperature in the presence of Hg/Nafion-H catalyst (0.5 g/mmol of **1**) for 1–7 h. Product was isolated by preparative TLC. [b] A byproduct, 1-cyclododecylidene-3-hydroxy-2-propanone, was formed in 10% yield.

The catalyst is recovered easily and reused without loss of Hg(II) ion. For example, 2,5-dimethyl-3-hexyne-2,5-diol was converted into 2,2,5,5-tetramethyl-4,5-dihydro-3(2*H*)-furanone repeatedly (first run, 90% yield, and second run with the recovered reagent, 82%). (3) The reaction proceeds under mild conditions (room temperature) with high selectivity compared with the conventional catalyst HgO (or $HgSO_4$).[2]

Applications of these new methods to the synthesis of other natural products are in progress in our laboratories.

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(10) The following procedures for bullatenone synthesis are typical. Butyllithium (1.53 M hexane solution, 19.6 mL, 30 mmol) was added to a THF (150 mL) solution of 2-methyl-3-butyn-2-ol (1.26 g, 15 mmol) at −78 °C under an argon atmosphere, and the reaction mixture was stirred for 2 h between −78 and −65 °C. Benzaldehyde (1.06 g, 10.0 mmol) dissolved in THF (4 mL) was added over 10 min at −65 °C, and the resulting solution was stirred for 6 h and allowed to warm to room temperature. Workup followed by column chromatography (silica gel, dichloromethane, then 1:1 hexane–ethyl acetate elution) gave 4-methyl-1-phenyl-2-pentyne-1,4-diol (**1a**) (1.87 g, 98% yield). The adduct **1a** (0.21 g, 1.09 mmol) dissolved in dichloromethane (0.25 mL) was treated with acetic anhydride (0.5 mL) and pyridine (0.05 mL) at room temperature for 2 h. Purification of the concentrated residue by column chromatography (silica gel, hexane–ethyl acetate, from 10:1 to 2:1) gave the corresponding monoacetate (0.25 g, 99% yield). ^{1}H NMR (CCl_4) δ 1.51 (s, 6 H), 2.03 (s, 3 H), 2.96 (br s, 1 H), 6.41 (s, 1 H), 7.2–7.6 (m, 5 H); IR (neat) 3400, 1740 cm^{-1}. The monoacetate (77 mg, 0.33 mmol) dissolved in benzene (1 mL) was heated at 80 °C in the presence of silver perchlorate (4 mg) for 10 h in the dark under an argon atmosphere. Then the reaction mixture was diluted with dichloromethane (10 mL) and washed with 10% aqueous ammonia (3 mL) and saturated sodium chloride aqueous solution (3 mL). Column chromatography (silica gel, 10:1 hexane-ethyl acetate) of the concentrated crude product gave the enol acetate **2a** (65 mg, 84% yield), bp 122–124 °C (bath temperature) (0.04 torr); IR (neat) 1781, 1698, 1658 cm^{-1}; MS, *m/e* 232 (M^+); ^{1}H NMR (CCl_4) δ 1.36 (s, 3 H), 1.38 (s, 3 H), 2.17 (s, 3 H), 5.70 (d, J = 1.5 Hz, 1 H), 5.81 (d, J = 1.5 Hz, 1 H), 7.26 (br s, 5 H). The enol acetate (114 mg, 0.49 mmol) was treated with DDQ (161 mg, 0.71 mmol) in benzene (1 mL) at room temperature for 1.8 h. Workup and preparative TLC (20:1 dichloromethane–ethyl acetate) gave bullatenone (**7**) (92 mg, 99% yield). The overall yield from benzaldehyde to bullatenone was 81%.

Treatment of the enol acetate **2a** (33 mg, 0.14 mmol) with sodium methoxide (0.01 mmol) in methanol (1 mL) at room temperature for 0.7 h gave the dihydrofuranone **3a** (24 mg, 90% yield).

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(13) The synthetic material showed more than 97% purity of the *E* isomer as evidenced by ^{1}H NMR ($CDCl_3$): δ 6.73 (t, J = 6.0 Hz, 1 H, C(7)-H), 4.82 (d, J = 6.0 Hz, 2 H, C(8)=H_2) consistent with the literature values, 6.64 and 4.82 (ref 3a), 6.77 and 4.87 (ref 11b), 6.90 and 4.95 (ref 11c).

Photoexcitation of Nonconjugated, Strained, Saturated Hydrocarbons. Relationship between Ease of Oxidation and Quenching of Naphthalene Fluorescence by Saturated Hydrocarbons

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Recently, we have examined in detail the oxidation of strained, saturated hydrocarbons.[2] The relative ease with which these hydrocarbons released electrons (0.4–2.1 V vs. SCE[2]) suggested that (a) they might all be effective fluorescence quenchers[3] through

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