

temperature or in a THF glass at $-105\text{ }^{\circ}\text{C}$. In contrast, both **2** and **3** are paramagnetic;^{11,12} the effective magnetic moment per titanium corresponding to a spin-only value at room temperature is completely consistent with the magnetic separation of two d^1 Ti(III) $\text{Ti}(\text{C}_5\text{H}_5)_2$ fragments by a tetradentate $\text{C}_2\text{X}_4^{2-}$ ligand ($\text{X} = \text{O}, \text{NR}$) such that the singlet-triplet energy gap must be small (i.e., weak antiferromagnetic coupling¹¹). A cyclic voltammogram of **1** in either CH_2Cl_2 or THF displays two reversible one-electron reductions and no oxidations,¹⁴ whereas both **2** and **3** can be oxidized to their dications. A reasonable interpretation of these electrochemical data is that oxidation to give the d^0 Ti(IV) dications occurs in **2** and **3** (but not in **1**) because the removed electrons are predominantly metal-localized in **2** and **3** (and hence in more energy-destabilized HOMO's).

The four dititanium tetrathiolene-bridged molecules in **1** per unit cell lying on crystallographic inversion centers possess analogous solid-state geometries with the bridging C_2S_4 ligand coordinated to the two centrosymmetrically equivalent $\text{Ti}(\text{C}_5\text{H}_5)_2$ moieties via side-on, 1,2-dithio-chelating C_2S_2 ring linkages (Figure 1). Although the C_2S_4 part of the central $\text{TiS}_2\text{C}_2\text{S}_2\text{Ti}$ fragment corresponds within experimental error to a planar $D_{2h}-2/m2/m2/m$ configuration, inclusion of the titanium atoms lowers the pseudo symmetry to $\text{C}_{2h}-2/m$ because each of the two TiS_2 planes is inclined by 46° with respect to the $\text{S}_2\text{C}_2\text{S}_2$ plane. This angle of trans folding in **1** is remarkably similar to the observed folding (of $43\text{--}46^\circ$ range) of the TiS_2 plane from the dithiolene S_2C_2 plane about the S...S line in four structurally characterized dicyclopentadienyltitanium dithiolene complexes.¹⁸ This common structural feature implies that the degree of electron delocalization of each TiS_2C_2 ring in the dititanium tetrathiolene complex **1** is similar to that in each of the monotitanium dithiolene complexes.

Major variations between the molecular geometry of **1** and those of **2**¹⁰ and **3**¹² directly point to much greater electron delocalization of the C_2X_4 -bridged ligand in **1**. The C-C distances of 1.54 (1) Å in **2** and 1.504 (6) Å in **3** approximately conform to single-bond values in harmony with the C_2X_4 -bridged ligand (with $\text{X} = \text{O}, \text{NR}$) being formulated as a dianion. As electron density is donated by the metal centers onto the C_2X_4 ligand one would expect the C-C bond length to decrease with the limit of charge-transfer corresponding to a $\text{C}_2\text{X}_4^{4-}$ tetraanion which formally contains a C-C double bond. The average C-C distance (mean, 1.41 Å; 1.40 (2)–1.42 (2) range for four independent half molecules) in **1** suggests (from a valence-bond formalism) that the C_2S_4 ligand in **1** is in an intermediate oxidation state between the dianion and tetraanion. In other words, the tetrathiooxalate ligand is a much better acceptor of electron density and thus can be regarded as a tetrathiolene-like ligand. Another salient structural difference which supports this view is that the tilt of each of the two TiX_2 planes out of the C_2X_4 plane is only 11° for both **2**¹⁰ and **3**¹² compared to 46° for **1**. The considerably larger folding angle in **1** is readily attributed to the much better overlap (and hence much greater molecular stability by electron delocalization) achieved in the HOMO between the titanium $3d_{z^2}$ and $d_{x^2-y^2}$ AO's¹⁹ and the π -acceptor $2b_u$ C_2X_4 orbital for $\text{X} = \text{S}$ (i.e., for a folding angle of 0° , the resulting titanium- C_2X_4 orbital overlap in the HOMO is zero).

Current studies include completion of theoretical MO calculations on **1**, **2**, and **4** with the nonparameterized Fenske-Hall model,²⁰ attempted isolation of the monoanion of **1** for a comparative structural-bonding analysis, and possible transfer reactions of the C_2S_4 ligand of **1** to other metals.

Acknowledgment. This research was supported by the National Science Foundation. We are particularly grateful to Dr. R. B. Cody (Nicolet Analytical Instruments) for obtaining a mass spectrum of **1** with a Nicolet FT-MS 1000 mass spectrometer. Special thanks are also due to Professor Brock Spencer (Beloit College) for his help in carrying out the EPR measurements.

(19) (a) Petersen, J. L.; Lichtenberger, D. L.; Fenske, R. F.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6433-6441. (b) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729-1742.

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Supplementary Material Available: Tables listing the atomic parameters and intramolecular distances and bond angles for $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}]_2(\text{C}_2\text{S}_4)$ (**1**) (6 pages); table listing the observed and calculated structure factor amplitudes for **1** (21 pages). Ordering information is given on any current masthead page.

Conventional and Laser-Jet Photochemistry of 2-Methylbenzophenone¹

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The current interest in high-intensity laser photochemistry in solution² has prompted us to construct a laser-jet photochemical apparatus with which it becomes possible to conduct multiple photon reactions in solution on a substantially enhanced scale. By use of this laser-jet apparatus, the solution to be irradiated is ejected at high velocity from a capillary nozzle (diameter = 100 μm) into the focal region of an argon ion laser. This irradiation configuration allows one to achieve useful CW fluences in the range of $10^{22}\text{--}10^{23}$ photons $\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ (3 W, 333-364 nm laser lines). At these intensity levels it should be possible to obtain isolable quantities of photoproducts from absorbing transients having lifetimes as short as about 100 ns.³

In this initial work, we have applied the laser-jet technique to the previously studied 2-methylbenzophenone (**1**) system.⁴ This system provides (1) a readily accessible target intermediate, the photoenol **E-2** (Scheme I), with a lifetime in the range of several seconds; (2) only one other suitably long-lived intermediate, **3**, which might efficiently absorb a second photon under jet conditions;⁵ and (3) a known, albeit very inefficient, photocyclization of **E-2** to the dihydroanthrone tautomer **3**, which ultimately is oxidized to anthrone (**4**).⁶ Furthermore, under low-intensity conditions, the *E*- and *Z*-photoenols were thought to revert almost exclusively to the starting ketone **1**.

Therefore, during low-intensity control studies, we were surprised to observe that **1** afforded a rather complex mixture of products (Scheme II and Table I).⁷ Products **7-11** have never before been reported from this parent photoenol system.⁸ The

(1) Presented at the XI IUPAC Symposium on Photochemistry, Lisbon, Portugal, July 21-Aug 1, 1986.

(2) (a) Turro, N. J.; Aikawa, M.; Butcher, J. A., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 5127. (b) Scaiano, J. C.; Wagner, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 4626. (c) Bromberg, A.; Schmidt, K. H.; Meisel, D. *J. Am. Chem. Soc.* **1985**, *107*, 83. (d) Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396. (e) Scaiano, J. C.; McGimpsey, W. G.; Casal, H. L. *J. Am. Chem. Soc.* **1985**, *107*, 7204. (f) Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 2349.

(3) To date this laser-jet apparatus has been used to successfully reproduce the extraordinary photochemistry of 1,1,5,5-tetraphenyl-1,5-pentadienyl ($\tau = 900$ ns) first reported by Johnston and Scaiano (ref 2f; we thank Dr. Scaiano for his assistance in repeating this work) as well as to initiate the photochemistry of other shorter lived biradicals. The details of this work as well as a full description of the laser-jet apparatus will be reported in a full paper at a later date.

(4) (a) Sammes, P. G. *Tetrahedron* **1976**, *32*, 405 and references therein. (b) Wilson, R. M. *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1985; Vol. 7, Chapter 5 and references therein. (c) Haag, R.; Wirz, J.; Wagner, P. *J. Helv. Chim. Acta* **1977**, *60*, 2595.

(5) It is conceivable that the triplet photoenols might also be excited further under jet conditions, but with lifetimes in the range of 30-50 ns, these species would probably undergo very inefficient excitation.

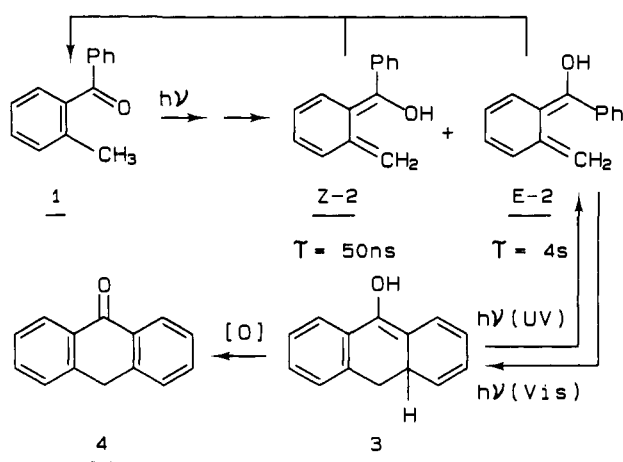
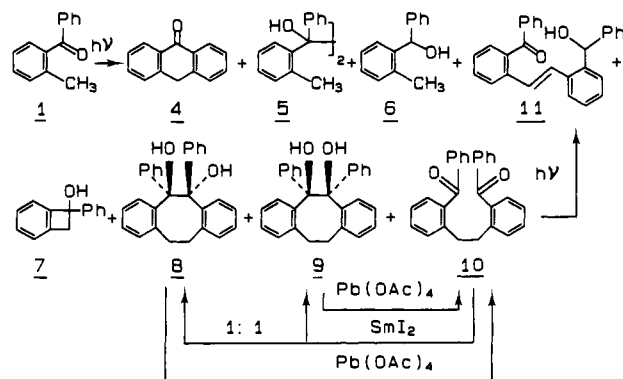
(6) (a) Ullman, E. F.; Huffman, K. R. *Tetrahedron Lett.* **1965**, 1863 (b) Heindel, N. D.; Molnar, J.; Pfau, M. *J. Chem. Soc., Chem. Commun.* **1970**, 1373.

(7) The structures of all products were consistent with their spectral properties: *d,l*-**5**, mp $154\text{--}155\text{ }^{\circ}\text{C}$; *meso*-**5**, mp $140\text{--}141\text{ }^{\circ}\text{C}$; **6**, mp $89\text{--}91\text{ }^{\circ}\text{C}$; **8**, mp $162\text{--}165\text{ }^{\circ}\text{C}$; **9**, mp $140\text{--}141\text{ }^{\circ}\text{C}$; **10**, mp $106\text{--}107\text{ }^{\circ}\text{C}$; **11**, mp $120\text{--}130\text{ }^{\circ}\text{C}$ dec.

Table I. Product Yields in the Photolysis of 2-Methylbenzophenone as a Function of Solvent, Light Intensity, and Wavelength

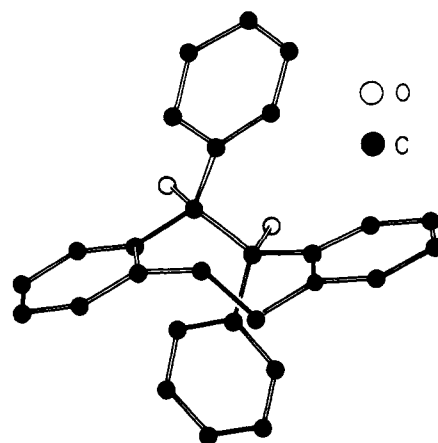
irradiation conditions	conversion (%)	yields (%) ^a						11
		4	5 ^b	6	7 ^c	8-9 ^{c,d}	10 ^e	
Low Intensity								
Rayonet, 350 nm, $C = 5.4 \times 10^{-2}$ M								
(1) <i>i</i> -PrOH, 11 h	74		60	7	30			
(2) benzene, 20 h	89	0.5	6		39	16	3	3
High-Intensity Single Beam								
argon laser-jet ^f UV lines, benzene $C = 2 \times 10^{-2}$ M								
(3) 2.6 W, 6 h	35	23			15	15	13	
(4) 0.55 W, 45 min	31	11					6	
(5) 1.30 W, 45 min	24	22					6	
(6) 2.85 W, 45 min	31	24					8	
Double Beam								
(7) same as run 6 except second beam visible lines, 9 W; focused ca. 0.1 mm below UV beam	34	34					6	

^aYields determined by HPLC for all products $\geq 3\%$ and based upon consumed starting material. For runs 4-7, only the yields for 4 and 10 were determined. ^bMeso and *d,l* forms present in a ratio of ca. 1:2. ^cThe ratio of monomer to dimers 7:(8 + 9) is concentration dependent: 2:1 ($C = 1.4 \times 10^{-2}$ M), 0.9:1 ($C = 2.9 \times 10^{-1}$ M). ^dThe ratio 8:9 varied from 1:5 to 1:9 (see ref 15). ^eThe diketone 10 yield is very sensitive to traces of oxygen which are especially difficult to excluded under jet conditions. ^fStandard jet conditions: conducted in a sealed jet chamber under an argon atmosphere with argon purged solutions, UV lines 334-364 nm, visible lines 458-514 nm, solutions recycled ca. 7 times, pump rate ca. 2 mL/min, nozzle diameter = 100 μ m, beams focused to 100 μ m.

Scheme I**Scheme II**

failure to observe cyclobutanol 7 in this parent system has contributed to the development of complex mechanistic arguments that rationalize the formation of cyclobutanols in more sterically hindered 2-alkylbenzophenones.⁹ In fact, this photoreaction would

(8) (a) The only cyclobutanol reported from a simple photoenol is that from 2-methylbenzaldehyde which is formed in low yield. Arnold, B. J.; Mellows, S. M.; Sammes, P. G. *J. Chem. Soc., Perkin Trans. 1* 1974, 401. (b) Diketone coupling products related to 10 have been found in the photo-reactions of 2,4-dimethylacetophenone (Becker, H.-D. *J. Org. Chem.* 1967, 32, 2140), and 2-methylacetophenone (Morrocchi, S., personal communication). (c) In other studies of this and related photoenol systems, GLC analysis and purification schemes involving distillation probably have caused the thermal decomposition of 7-9 and related heat-sensitive products.

**Figure 1.** Structure of compound 8 as determined by a single-crystal X-ray diffraction study.

seem to constitute the method of choice for the synthesis of 7 in moderate quantities.¹⁰

The structures of these new photoproducts were established as follows. The known benzocyclobutanol 7^{7,10b,c} was shown to undergo thermal reversion to the starting ketone 1^{10a,b} via the intermediate *E*-enol (*E*-2) which could be efficiently trapped by dienophiles.^{9b,11} Special attention was devoted to the novel dibenzocyclooctadiol isomers 8 and 9. The regiochemistries of these isomers were established by chemical correlations with the diketone 10 as shown in Scheme II. The stereochemistry of 9 was correlated with that of 8 by means of an NMR study with a chiral shift reagent,¹² and the structure of 8 was firmly established through a single-crystal X-ray structure determination (Figure 1).¹³ It

(9) (a) Matsuura, T.; Kitaura, Y. *Tetrahedron* 1969, 25, 4487. (b) Kitaura, Y.; Matsuura, T. *Tetrahedron* 1971, 27, 1597. (c) Heine, H.-G. *Liebigs Ann. Chem.* 1970, 732, 165. (d) Carre', M.-C.; Viriot-Villaume, M.-L.; Caubère, P. *J. Chem. Soc., Perkin Trans. 1* 1979, 2542. (e) Ito, Y.; Umehara, Y.; Hijiya, T.; Yamada, Y.; Matsuura, T. *J. Am. Chem. Soc.* 1980, 102, 5917. (f) Ito, Y.; Nishimura, H.; Umehara, Y.; Yamada, Y.; Tone, M.; Matsuura, T. *J. Am. Chem. Soc.* 1983, 105, 1590.

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(11) For details of this work see: Wilson, R. M.; Hannemann, K.; Heineman, W. R.; Kirchhoff, J. R. *J. Am. Chem. Soc.*, following paper in this issue.

(12) Tris[3-((trifluoromethyl)hydroxymethylene)-(+)-camphero]europium(III) complex was used as the chiral NMR-shift reagent: 8, δ 8.22 (d, $J = 8$ Hz, 2 H) expanded to two doublets in the presence of the shift reagent; 9, addition of shift reagent had no effect upon the 300-MHz ¹H NMR spectrum.

is interesting to note that the samarium diiodide reduction¹⁴ of **10** affords low yields of **8** and **9** in about a 1:1 ratio but that **9** is the predominant isomer by far in the photoreaction (Table I).¹⁵ No head-to-tail or spiro dimers¹⁵ were detected in this photoreaction. A similar propensity for head-to-head dimerization of thermally generated, unsymmetrical *o*-quinodimethanes has been observed.^{16b,17} At present very little can be said about the mechanism of this highly stereospecific photoenol dimerization except to note that the formation of these dimers does not appear to depend upon light intensity (Table I, runs 2 and 3). Thus, this is probably not a photodimerization. Furthermore, these dimers cannot be detected when the photoenols are generated thermally at 80–120 °C from neat cyclobutanol **7**. However, this may be due to the thermal lability of these dimers.¹⁵ Finally, the stilbene **11** is the major of several secondary photoproducts from the known diketone **10**¹⁸ whose photochemistry will be described in a separate publication. The diketone **10** itself seems to arise from the oxidation of the photoenol perhaps through hydrogen abstraction by ³**1**.^{8b,11}

High-intensity irradiation of **1** in the laser-jet apparatus using a single UV argon ion laser beam afforded a significant light intensity dependent increase in the yield of only a single product, anthrone (**4**), at the expense of the other products shown in Scheme II (Table I). The two-photon formation of anthrone (**4**) from **1** has been reported previously in ca. 1% yield.⁶ The extremely low yield of this transformation is not only due to the intrinsic inefficiency of its two-photon mechanism but also to the photoreversibility of the formation of the dihydroanthrone tautomer **3** (Scheme I).⁶ It might be expected that this photoreversion of **3** to **E-2** might be favored by the high-energy UV photons required to generate **E-2** from **1** but that it might be less favorable with lower energy visible photons which should readily convert the photoenol **E-2** ($\lambda_{\text{max}} = 417 \text{ nm}$) to the dihydroanthrone **3**. In order to test this hypothesis, the laser-jet irradiation of **1** was repeated by using two crossed laser beams (Table I), a UV beam to generate the photoenol **E-2** from **1**, and a visible beam to convert **E-2** to **3**. That this double-beam technique is quite effective is shown by a further substantial enhancement in the yield of anthrone. Since this intensity study was conducted under an inert atmosphere, the enhanced efficiency for the formation of **4** under jet conditions must be due in large part to the high concentrations of hydrogen abstracting species such as radicals and ³**1**, which will facilitate the oxidation of **3** to **4**.

In conclusion, these studies have served not only to redefine the chemistry of this parent photoenol system but also to provide some indication of the potential of the laser-jet technique as a method for extending high-intensity photochemical phenomena into the realm of synthetic utility.

Acknowledgment. We thank the National Science Foundation (NSF CHE-8409628) and the Deutsche Forschungsgemeinschaft for financial support. K. H. also thanks the Deutschen Akademischen Austauschdienst for a NATO travel grant. The NMR and mass spectrometry facilities used in this work were partially funded through National Science Foundation grants (CHE-8102974 and PCM-8219912) for which we are most grateful.

Supplementary Material Available: X-ray data for **8** and Tables 1–5 listing atomic numbering scheme, X-ray operations, results

(13) See supplementary material paragraph.

(14) Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693.

(15) The ratio of **8:9** is somewhat variable (see Table I). Control experiments showed that diols **8** and **9** decompose slowly at ca. 50 °C and under the irradiation conditions, as well as partially isomerize into one another upon standing in solution. It could not be determined whether **8** is a primary dimerization product or is formed through the isomerization of **9** during irradiation.

(16) (a) Moss, R. J.; White, R. O.; Rickborn, B. *J. Org. Chem.* **1985**, *50*, 5132. (b) Errede, L. A. *J. Am. Chem. Soc.* **1961**, *83*, 949.

(17) Quinkert, G.; Opitz, K.; Wiersdorff, W. W.; Weinlich, J. *Tetrahedron Lett.* **1963**, 1863.

(18) Huang, R. L.; Lee, H. H. *J. Chem. Soc. C* **1966**, 929. The structure of diketone **10** was also confirmed by an independent synthesis: Wilson, R. M.; Hannemann, K., unpublished results.

and procedure, atomic coordinates and isotropic thermal parameters, bond lengths, bond angles, anisotropic thermal parameters, and H-atom coordinates and isotropic thermal parameters (7 pages); Table 6 listing calculated and observed structure factors (23 pages). Ordering information is given on any current masthead page.

Laser-Jet Delayed Trapping: Electron-Transfer Trapping of the Photoenol from 2-Methylbenzophenone¹

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During the course of the development of the argon ion laser-jet technique for the study of high-intensity photochemistry,² it became apparent that the laser jet provided a unique opportunity for the trapping of relatively long-lived photochemical intermediates. Thus, the jet solution containing the photochemical substrate could be passed through the focal region of the laser just before it was injected into a "fountain" of a solution containing the trapping agent. Through the partitioning of the photochemical and trapping steps in this way, it should be possible to employ unusual trapping agents that would quench the formation of the photointermediate or would themselves initiate undesired photochemistry, if they were present during the irradiation phase. One can estimate on the basis of the parameters of the current jet apparatus³ that photochemical intermediates with lifetimes of about 10⁻² s or greater should be amenable to trapping by this delayed trapping technique. The *E*-photoenol **1** derived from 2-methylbenzophenone (**2**) (Scheme I) would seem to be an ideal candidate for this type of trapping experiment since it is known to have a lifetime of several seconds.⁴ In this report, we describe the first application of this laser-jet delayed trapping technique⁵ and the unusual photoenol chemistry observed during the course of this study.

The *E*-photoenol **1** and related species are readily trapped in Diels–Alder reactions such as the first reaction shown in Table I.⁶ The reactions listed in Table I have been studied under both photochemical (conventional and jet) and thermal conditions.⁷ A distinct limitation of the delayed trapping technique is that only a single pass through the laser beam is possible. Once quenched in the "fountain", the solution cannot be recycled. Thus, even though the reactions are quite clean, the conversion usually is only

(1) Presented at the XI IUPAC Symposium on Photochemistry, Lisbon, Portugal, July 21–Aug 1, 1986.

(2) Wilson, R. M.; Hannemann, K.; Peters, K.; Peters, E.-M. *J. Am. Chem. Soc.*, preceding paper in this issue.

(3) A jet nozzle diameter of 100 μm provides a laminar stream velocity of about 4.25 m s⁻¹ and a residence time in the laser focal region of about 25 μs . In the experiments described here, the laser beam is focused about 5 mm above the trapping solution which affords a delay time of about 1 ms between irradiation and quenching in the trapping solution.

(4) (a) Sammes, P. G. *Tetrahedron* **1976**, *32*, 405 and references therein. (b) Wilson, R. M. *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1985; Vol. 7, Chapter 5 and references therein. (c) Haag, R.; Wirz, J.; Wagner, P. J. *Helv. Chim. Acta* **1977**, *60*, 2595.

(5) We thank a referee for calling our attention to the fact that this delayed trapping laser-jet technique is the liquid-phase analogue of the classical gas-phase lead mirror delayed trapping of methyl radicals: Paneth, F.; Hofeditz, W. *Ber. Dt. Chem. Ges.* **1929**, *62*, 1335.

(6) (a) Arnold, B. J.; Sammes, P. G.; Wallace, T. W. *J. Chem. Soc., Perkin Trans. 1* **1974**, 415. (b) Nerdel, F.; Brodowski, W. *Chem. Ber.* **1968**, *101*, 1398.

(7) All products of these trapping experiments were either identical with authentic material or had spectral properties which were consistent with the proposed structures: maleic anhydride adduct, ref 6b; naphthoquinone adduct, mp 175 °C dec, IR (KBr) 3420, 1675, 1660 cm⁻¹; **4**, yellow oil, IR (CCl₄) 1665, 1600, 1580 cm⁻¹; **5**, mp 106–107 °C, IR (KBr) 1655, 1600, 1580 cm⁻¹; **7**, mp 60–64 °C, IR (KBr) 3300–3100, 1770, 1710, 1695, 1655 cm⁻¹; **8**, mp 184–185 °C, IR (KBr) 1725 cm⁻¹; **9**, mp 117–120 °C, IR (KBr) 3440, 1670, 1660 cm⁻¹; **10**, yellow oil, IR (KBr) 1670, 1660, 1600 cm⁻¹.