abstraction reactions from alkanes (k_{sec}/k_{pri} = ~10 and k_{tert}/k_{pri} = ~36 at 25 °C).[11] However, a polar factor involving the electron-donor characteristics of the alcohol and electron-acceptor qualities of the hydroxyl radical may markedly lower the activation energy requirement for the abstraction of an α-hydrogen from the alcohol by the hydroxyl radical. The very long kinetic chain lengths observed in reactions involving the *tert*-butoxyl radical with secondary alcohols strongly suggest that this radical displays a high degree of selectivity toward the α-hydrogens of alcohols.[12] It is also possible that the reactivity of the hydroxyl radical in protic solvents is moderated by extensive hydrogen bonding with the solvent and would therefore be expected to display kinetic properties different from those observed in the gas-phase reactions of this species.

Experimental Section

Reagents. Hydrogen peroxide (Fisher, 30% aqueous solution) and acetic acid (Fisher, Anal. Reagent Grade) were used without further purification. Isopropyl alcohol (Mallinckrodt, Anal. Reagent Grade) was refluxed over stannous chloride, distilled from calcium oxide, and stored under nitrogen. Before using, it was subjected to gas chromatographic analysis to assure the absence of any acetone. An authentic sample of 2,5-hexanediol was prepared by sodium borohydride reduction of 2,5-hexanedione (Eastman Kodak). Ferrous ammonium sulfate and ferrous sulfate (Fisher, ACS Certified) were used without further purification.

Peroxyacetic Acid. The peroxyacetic acid used in this work was prepared by careful addition of glacial acetic acid (51 g, 0.85 mol) to a solution of 0.5 mol of hydrogen peroxide (30% solution) in 57 mL of concentrated sulfuric acid. The resulting solution was refluxed at 20 °C at 11 torr for 20 min and then distilled through a 20-cm column packed with glass helices. The first 5 mL of distillate were discarded. The remaining distillate was collected at 22 °C at 11 torr and amounted to 40 mL. Analysis (see below) showed this material to be 71% by weight peroxyacetic acid, 20.2% acetic acid, and 0.22% hydrogen peroxide.[13] The analytical procedure indicated no diacetyl peroxide was present. The remainder (8.38% by weight) was assumed to be water.

Differential Peroxide Determination. The hydrogen peroxide, peroxyacetic acid, and acetyl peroxide content of the starting reagent and of the reaction mixtures was determined by the method of Greenspan and MacKellar.[14] This method consisted of determining the hydrogen peroxide content by titration with standardized ceric sulfate solution to a ferroin indicator endpoint. The peroxyacetic acid content of the resulting solution was obtained by determining at room temperature the iodine liberated from a 10% potassium iodide solution added to the mixture. Acetyl peroxide concentration, although not present in our samples, can be determined from the amount of iodine resulting from heating the reaction mixture. All initial peroxide determinations were performed in triplicate. Corresponding blank solutions were also run.

Acetic acid was determined by potentiometric titration with standardized sodium hydroxide.

Oxidations of 2-Propanol with Peroxyacetic Acid and Hydrogen Peroxide. The following general procedure was employed for these oxidation reactions. All reactions involving the higher concentrations of ferrous ion were performed in an aqueous medium required to dissolve the ferrous salts at pH of about 1. The lower concentrations of ferrous ion were attainable in solutions consisting mainly of the alcohol. In all cases, the peroxidic reagent (peroxyacetic acid or 30% hydrogen peroxide) was weighed out into a volumetric flask with the 2-propanol. The ferrous ion was added, either as aqueous solution or weighed out salt, and dissolved in the mixture, which was then diluted to adjust the concentration. At the time intervals indicated (see Tables I–III) aliquots were removed, the peroxide content was measured as described, and the acetone content was determined by gas chromatrographic analysis on a polyglycol column (Dow E600 on Chromasorb W) using benzene or 2-butanone as the internal standard. A sample was also analyzed by gas chromatography on a Carbowax 20M on Chromasorb W for the 2,5-hexanediol. At the end of the reaction, an aliquot of the mixture was subjected to a potentiometric titration with standard sodium hydroxide solution to determine the total amount of acetic acid so that the acetic acid produced in the reaction could be determined.

Registry No. 2-Propanol, 67-63-0; peroxyacetic acid, 79-21-0; hydrogen peroxide, 7722-84-1; ferrous ion, 15438-31-0; 2,5-hexanediol, 2935-44-6; 2-propanone, 67-64-1; hydrogen, 1333-74-0; hydroxyl radical, 3352-57-6; ferrous ammonium sulfate, 10045-89-3; ferrous sulfate, 7720-78-7.

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[11] R. F. Hampson, Jr., and D. Garvin, *NBS Spec. Publ. (U.S)*, 513 (1978); A. C. Lloyd, K. R. Darnall, A. M. Winer, J. N. Pitts, Jr., *J. Phys. Chem.*, **80**, 789 (1976); N. R. Greiner, *J. Chem. Phys.*, **53**, 1070 (1970).

[12] C. Walling and J. C. Azar, *J. Org. Chem.*, **33**, 3888 (1968).

[13] The concentration of peroxyacetic acid prepared in this manner may be in a detonable range even at low temperatures, particularly if metal ion impurities are present. See D. Swern, "Organic Peroxides", Vol. I, D. Swern, Ed., Wiley-Interscience, New York, 1970, Chapter VII, p 477.

[14] E. P. Greenspan and D. G. MacKellar, *Anal. Chem.*, **20**, 1061 (1948).

Interaction of Electron-Deficient 1,2,4-Triazoline-3,5-diones with Electron-Rich Polyalkoxybenzenes

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4-Substituted-1,2,4-triazoline-3,5-diones have been found to form charge-transfer complexes with 1,3,5-trimethoxybenzene, 1,3-dimethoxybenzene, and 1,4-dimethoxybenzene but not with anisole. In the cases of 1,3,5-trimethoxybenzene and 1,3-dimethoxybenzene a reaction occurs to give aromatic substitution; the relative rates are 1,3,5-trimethoxybenzene > 1,3-dimethoxybenzene > 1,4-dimethoxybenzene. The rate of reaction of 4-butyl-1,2,4-triazoline-3,5-dione (*n*-BuTAD) with 1,3,5-trimethoxybenzene (TMB) *increases* with *decreasing* temperature to give apparent activation parameters: $\Delta H^* = -5.9$ kcal/mol, $\Delta S^* = -78$ cal deg^{-1} mol^{-1}. The rate is also dependent on the length of time that solutions of the *n*-BuTAD are exposed to ambient light, suggesting involvement of the urazolyl radical. It is suggested that the overall rate expression is $-[d(n\text{-BuTAD})/dt] = k_1K_{eq}(n\text{-BuTAD})(\text{TMB})(\text{Ur}\cdot)$, where (Ur·) is the urazolyl radical concentration, K_{eq} is the equilibrium constant for charge-transfer complex formation, and k_1 is the rate constant for attack of Ur· on the charge-transfer complex.

In a previous paper, the reactions of 4-phenyl- and 4-alkyl-1,2,4-triazoline-3,5-diones (RTAD's) with vinyl ethers were examined, and evidence was presented that 1,4-dipoles are involved in the reactions.[1] However, changing

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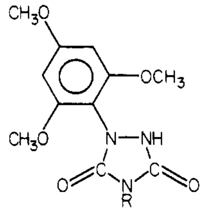
the polarity of the solvent had no clear-cut effect on the rate of reaction. In order to explain this result, it was postulated that formation of the 1,4-dipole is not the initial step in the reaction, but that there is an initial formation of a charge-transfer complex, which collapses to give the 1,4-dipole, i.e.

$$\text{RTAD} + \text{ROCH}{=}\text{CH}_2 \rightleftharpoons \text{CT complex} \rightarrow \text{1,4-dipole} \rightarrow \text{products}$$

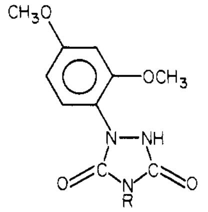
However, no direct evidence for the existance of the CT complex could be found. Therefore we initiated a search to find examples where RTAD's could interact with unsaturated electron-rich compounds to give more stable CT complexes.

It was reasoned that since RTAD's are highly electron deficient, there might be a good possibility that they would form stable complexes with electron-rich aromatic compounds. In order to test this idea we chose initially to look at the interaction of RTAD's with polyalkoxybenzenes.

When a methylene chloride solution of PhTAD was mixed with a methylene chloride solution of 1,3,5-trimethoxybenzene, the solution became dark red. After 2 min the solution was considerably lighter in color, after 10 min it was light, red and after 1 h it was light orange. It was quite clear that a dark-red complex had formed but that a reaction had occurred. Workup of the mixture gave a 74% yield of **1a**. The ^{1}H NMR of **1a** showed a singlet at δ 3.77 for the methoxy groups, a singlet at δ 6.11 for hydrogens ortho to the methoxy groups, a multiplet at δ 7.4 for the phenyl on nitrogen, and a very broad peak at δ 8.4 for the NH. The IR showed a strong peak at 1695 and a weaker peak at 1762 cm^{-1} for the carbonyls, a pattern characteristic of urazoles, as well as a broad peak at 3150 cm^{-1} for NH.



1a, R = C_6H_5
b, R = n-C_4H_9



2a

A similar reaction was observed when n-BuTAD was reacted with 1,3,5-trimethoxybenzene except the reaction took 5 h; **1b** was isolated in 68% yield.

In order to see if the same reaction could be observed with less activated aromatic rings, PhTAD was allowed to react with 1,3-dimethoxybenzene. On mixing, a deep blood-red color appeared. The red color disappeared after about 12 h to give a yellow-brown solution. Removal of the solvent gave a resinous material that solidified on treatment with ether. The crude reaction mixture contained some polymer and about 10–15% of unreacted 1,3-dimethoxybenzene, suggesting formation of some 2:1 adducts. Extraction of the urazoles with base, followed by recrystallization, gave a 34% isolated yield of the major product **2a**.

When solutions of PhTAD were mixed with 1,4-dimethoxybenzene, the blood-red complex formed, but no aromatic substitution occurred. The color was eventually discharged after 1 month at room temperature, but only thermal decomposition products of PhTAD were isolated.

When PhTAD was placed in a methylene chloride solution containing anisole, it not only did not react with it but neither was the red complex formed. Thus it appears that at least two methoxy groups are required to produce the complex in detectable concentration.

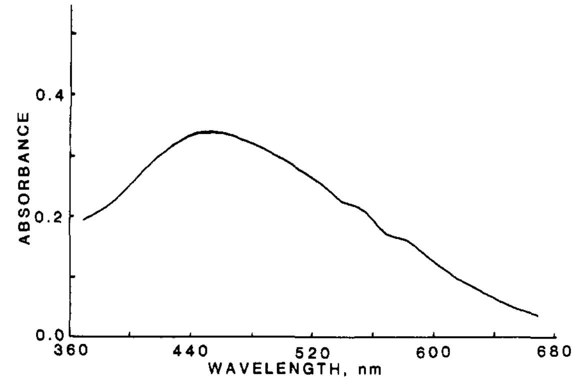
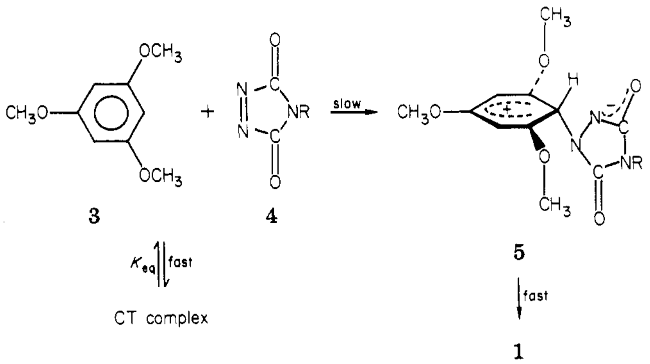


Figure 1. Visible spectrum of charge-transfer complex of 1,4-dimethoxybenzene with 4-phenyl-1,2,4-triazoline-3,5-dione.

Scheme I



The relative rate of reaction with PhTAD is 1,3,5-trimethoxybenzene > 1,3-dimethoxybenzene > 1,4-dimethoxybenzene. This is what would be expected for normal electrophilic aromatic substitution, since the position of substitution in these compounds is activated by three, two, and one methoxy groups, respectively. The decreased rate of reaction of n-BuTAD with 1,3,5-trimethoxybenzene compared to PhTAD is consistent with other reported kinetic studies on RTAD's.[1,2]

By running spectra of dilute solutions (5–50 mM) of RTAD's in concentrated (1.0–0.5 M) solutions of the alkoxybenzenes, it was possible to obtain some visible spectral information on complex formation. In the case of PhTAD there is considerable overlap of its spectrum with that of the complex. However by using a difference technique, the spectrum of the complex of PhTAD with 1,3-dimethoxybenzene ($\lambda_{\max}$ 456 nm) and with 1,4-dimethoxybenzene could be determined (Figure 1). The latter exhibited a maximum at 457 nm with longer wavelength shoulders at 545 and 580 nm. The absorbance at $\lambda_{\max}$ was directly proportional to both the PhTAD and 1,4-dimethoxybenzene concentrations over the range studied. It was not possible to obtain the molar extinction coefficient for the complex. However, if it is assumed that the complex has about the same molar extinction coefficient as the long-wavelength absorption of RTAD's (ϵ = 100–500),[3] then an estimate of the association equilibrium constant would be in the range of 2–0.1.

A solution of n-BuTAD in a saturated solution of 1,4-dimethoxybenzene in methylene chloride showed only a

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(1) J. H. Hall and M. L. Jones, *J. Org. Chem.*, **48**, 822 (1983).

(2) M. E. Burrage, R. C. Cookson, S. S. Gupte, and I. D. R. Stevens, *J. Chem. Soc., Perkin Trans. 2*, 1325 (1975).

Scheme II

$$3 + 4 \underset{\text{rapid}}{\overset{K_{eq}}{\rightleftharpoons}} \text{CT complex} \xrightarrow[\text{slow}]{k_1} 5 \xrightarrow[\text{fast}]{} 1$$

Table I. Effect of TMB Concentration on Rate of Reaction with *n*-BuTAD at 31.1 °C in CH_2Cl_2

10^2k_{obsd}, s^{-1}	10^2[TMB], mol L^{-1}	k_2,[b] L mol^{-1} s^{-1}
3.85	3.92	0.982
7.75	7.69	1.008
12.6	11.7	1.076
16.2	14.8	1.095
14.3	14.8	0.966
10.7	11.3	0.947
8.14	7.69	1.058
4.10	3.92	1.046

[a] k_{obsd} = pseudo-first-order rate constant. [b] k_{obsd}/(TMB).

weak RTAD absorption, suggesting that the bulk of the material was complexed.

There seems to be more than one interpretation of these observations. One would be to view these reactions as normal, direct electrophilic substitution reactions as shown in Scheme I. In support of this mechanism is the well-known highly electrophilic character of 4-substituted-1,2,4-triazoline-3,5-diones in Diels–Alder and other reactions[4] as well as the increasing rate of reaction as the position of substitution is activated by increasing numbers of methoxy groups. In this scheme the complex is viewed as a side reaction unrelated to the substitution. One difficulty with this view point is that, as shown above, a large portion of RTAD and polymethoxybenzene are tied up as complex. One would expect that K_{eq} for 1,3,5-trimethoxybenzene would be much larger even than that for 1,4-dimethoxybenzene and that there would be little free RTAD in such a solution. If the mechanism above is correct, formation of a more stable charge-transfer complex ought to slow the reaction down due to the decreased concentration of the reactants.

What would be more reasonable is that the charge-transfer complex is the precursor of the dipolar species as shown in Scheme II. The overall rate constant for this scheme would be given by $k_2 = K_{eq}k_1$. Since K_{eq} would be expected to increase with increasing numbers of methoxy groups and since k_1 would increase with the number of activating methoxy groups, one would expect the k_2 to increase as observed.

In order to obtain additional information about the reaction, a kinetic study of the rate of reaction of *n*-BuTAD with 1,3,5-trimethoxybenzene (TMB) was undertaken. The rate was studied under pseudo-first-order conditions, using a 10–40-mol excess of TMB. The rate was followed spectrophotometrically by monitoring the *n*-BuTAD absorption at 537 nm. As seen in Table I, the reaction was first order in both *n*-BuTAD and TMB.

The effect of temperature on the reaction is given in Table II. As can been seen from this data, the observed rate constant *decreases* with *increasing* temperature. These data give an apparent $\Delta H^* = -5.9 \pm 1.5$ kcal mol^{-1} and an apparent $\Delta S^* = -78 \pm 5$ cal deg^{-1} mol^{-1}. This inverse temperature effect on the reaction is readily accommodated by Scheme II. As the temperature is raised, the charge-transfer complex becomes less stable, i.e., K_{eq} decreases. On the other hand, k_1 should increase with increasing temperature. However, if K_{eq} decreases faster than k_1 increases, $k_2 = k_1K_{eq}$ will decrease with increasing temperature. This inverse temperature effect cannot be explained by Scheme I.

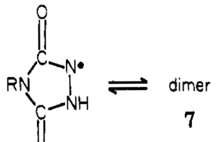
Table II. Effect of Temperature on Rate of Reaction of *n*-BuTAD with TMB[a]

temp, °C	10^2k_{obsd}, s^{-1}	k_2, L mol^{-1} s^{-1}
9.6	17.3	2.25
12.8	10.1	1.31
16.4	10.5	1.36
22.7	9.66	1.26
24.8	8.34	1.08
31.1	7.95	1.03
38.3	5.85	0.761

[a] $[TMB]_0 = 7.69 \times 10^{-2}$ M (20-fold excess). $k_2 = k_{obsd}/[TMB]_0$.

However, during the course of these studies, it was also discovered that the pseudo-first-order rate constant depended on the history of the *n*-BuTAD solution. A 0.01 M stock solution was prepared in methylene chloride. This solution was stored in the dark. This stock solution was diluted to 0.004 M for use in the kinetic measurement. The 0.004 M solution was allowed to stand at room temperature in normal laboratory fluorescent light. The pseudo-first-order rate constants (k_{obsd}) were determined with use of a 20-fold excess of TMB at 31.1 °C. The rate constant depended on the length of time the 0.004 M solution stood in the light before use. For example, one series of experiments gave the following results: (time in hours, k_{obsd} in reciprocal seconds) 1.3, 4.34×10^{-4}; 2.0, 9.12×10^{-3}; 4.3, 1.73×10^{-2}; 5.9, 3.40×10^{-2}; 13, 7.75×10^{-2}; 72, 7.75 × 10,–,2. As can be seen, the rate increased rapidly as the solution stood at room temperature in ambient light and leveled off after the solution had stood about 12 h. All of the data in Tables I and II were obtained with these "light equilibrated" solutions.

It has been shown that solutions of RTAD's contain urazolyl radicals 6.[5] On photolysis of alkyl TAD's in methylene chloride this radical concentration increases rapidly, reaching a steady-state concentration in normal laboratory light. This radical is also in equilibrium with a dimer as shown by a dramatic increase in intensity of the ESR spectrum as the alkyl-TAD sample is warmed from 25 to 50 °C.[5,6]



7

6

These results suggest that the urazolyl radical (Ur•) is involved in the reaction prior to or during the rate-determining step. Also, since this radical is used up during the rate-determining step, it must be regenerated in a later step, otherwise the reaction would not be cleanly first order in *n*-BuTAD. Thus the overall rate equation is:

$$-\frac{d(n\text{-BuTAD})}{dt} = k_1K_{eq}(n\text{-BuTAD})(\text{TMB})(\text{Ur}\cdot)$$

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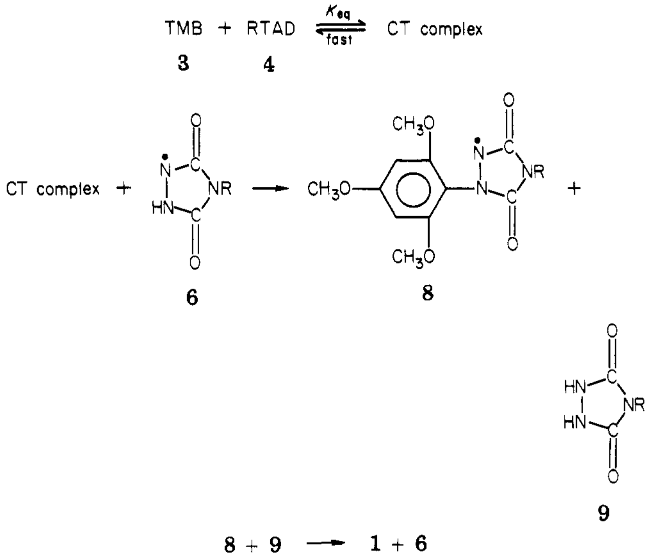
[3] (a) J. Herweh and R. M. Fantazier, *Tetrahedron Lett.*, **23**, 2101 (1973); (b) A. V. Pocius and J. T. Yardley, *J. Am. Chem. Soc.*, **95**, 721 (1973); (c) *J. Chem. Phys.*, **61**, 2779 (1974).

[4] J. Sauer and B. Schröder, *Chem. Ber.*, **100**, 678 (1967).

[5] J. H. Hall, W. E. Bigard, J. M. Fargher, and M. L. Jones, *J. Org. Chem.*, **47**, 1459 (1982).

[6] (a) W. H. Pirkle and P. L. Gravel, *J. Am. Chem. Soc.*, **96**, 3335 (1974); (b) W. H. Pirkle and J. C. Stickler, *ibid.*, **92**, 7497 (1970); (c) H. Wamhoff and K. Wald, *Chem. Ber.*, **110**, 1699 (1977).

Scheme III

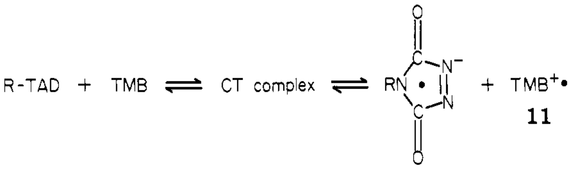


where $k_{obsd} = k_1K_{eq}$(Ur·).

A mechanism consistent with these results is given in Scheme III. In this scheme, the slow step is postulated to be the reaction of the 4-butylurazolyl radical **6** with the charge-transfer complex to give the radical **8** and 4-butylurazole. The 4-butylurazolyl radical is then regenerated by hydrogen abstraction. Radicals such as **8** are quite stable in the absence of hydrogen atom donors.[5,6]

An attempt was made to inhibit the reaction of *n*-BuTAD with TMB by addition of triphenylmethane. It was anticipated that the urazolyl radical would abstract hydrogen from the triphenylmethane rather than from the charge-transfer complex and slow down the reaction. However, no inhibition was observed. Apparently the urazolyl radical is more stable than the triphenylmethyl radical.

During the course of this investigation we were concerned that the charge-transfer complex might be dissociated into radical cations and anions, i.e. The RTAD



10

radical anion **10** is easily generated at −50 °C by reaction with potassium *tert*-butoxide in DMF.[5,7] Solutions (0.1 M in CH_2Cl_2) of *n*-BuTAD and 1,3,5-trimethoxybenzene (1.0 M in CH_2Cl_2) were carefully degassed and mixed at −78 °C. An attempt was made to observe the ESR spectra of radicals **10** and **11** over a temperature range of −78 to 50 °C. Neither radical could be detected. Only radical **6** could be detected. At 50 °C radical **6** disappeared rapidly as reaction occurred to give **1b**.

Experimental Section

Melting points are uncorrected. The IR spectra were recorded on a Perkin-Elmer 297 spectrophotometer. The visible spectra were obtained on a Perkin-Elmer 340 spectrophotometer. The NMR spectra were obtained with a 90-MHz Perkin-Elmer R32 spectrometer. The elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

The 4-substituted-1,2,4-triazoline-3,5-diones were prepared by oxidation of the urazole with *N*-bromosuccinimide.[8] PhTAD was purified by recrystallization from methylene chloride at −10 °C prior to use. *n*-BuTAD was purified by sublimation. The polyalkoxybenzenes were purchased commercially except for 1,3,5-trimethoxybenzene, which was prepared by the procedure of Mannich.[9]

Kinetic Studies. Standard solutions (0.004 M) of RTAD's were prepared in methylene chloride and allowed to stand in laboratory light for 1 or 2 days before use. A standard solution 1.0 M of TMB in methylene chloride was prepared. The solution of RTAD was placed in the spectrometer cell and temperature equilibrated. The TMB solution was temperature equilibrated in the constant temperature bath connected to the spectrometer. Aliquots of the TMB solution were then added to the RTAD solution in the cuvette to give solutions that contained a 10–40-fold excess of TMB. The absorbance of the RTAD at 537 nm was then recorded as a function of time.

Visible Spectrum of Charge-Transfer Complexes. These spectra were recorded with double-compartment cells. The reference cell contained the TMB solution in one compartment and the R-TAD solution in the other compartment. The sample cell contained the RTAD–polyalkoxybenzene mixture in both compartments.

Reaction of 4-Phenyl-1,2,4-triazoline-3,5-dione. A. 1,3,5-Trimethoxybenzene. 4-Phenyl-1,2,4-triazoline-3,5-dione (0.175 g, 0.001 mol) was dissolved in 5 mL of methylene chloride. To this solution was added 0.168 g (0.001 mol) of 1,3,5-trimethoxybenzene in 2 mL of methylene chloride. The solution turned from a bright red to blood red. After 10 min, the solution was light red. After 75 min, the solution (now light orange) was evaporated to give a resinous-looking material. Addition of a few milliliters of ether induced crystallization. The ether was evaporated and the solid recrystallized from 3 mL of absolute ethanol at −10 °C: yield, 0.287 g (74%) of 1-(2,4,6-trimethoxyphenyl)-4-phenylurazole with 1 mol of ethanol of crystallization; ^{1}H NMR ($CDCl_3$) δ 1.16 (3 H, t), 2.13 (1 H, s, 3.63 (2 H, q, 3.77 (9 H, s), 6.11 (2 H, s), 7.24–7.62 (5 H, m), 8.4 (1 H, vbr s); ^{13}C NMR Me_2SO-d_6) δ 55.6 (4-CH_3O), 56.1 (2,6-CH_3O), 91.0, 105.1, 158.4, and 162.3 (C-3, C-1, C-2, and C-4 of tetrasubstituted ring), 126.6, 128.4, 129.5, and 131.3 (C-2, C-4, C-3, C-1 of phenyl), 152.1 (C=O's); IR (Nujol) 3150 (NH, b), 1762 and 1692 (C=O), 1138 (CO) cm^{-1}.

Anal. Calcd for $C_{17}H_{17}N_3O_5$·C_2H_5OH: C, 58.60; H, 5.95; N, 10.79. Found: C, 59.05; H, 5.96; N, 10.76.

On heating the ethanol of crystallization was lost at about 130 °C and the solid changed crystalline form; the new solid melted at 193–194 °C. The NMR of this material was identical with the original material, except the peaks at 1.16, 2.13, and 3.63 ppm due to the ethanol were missing. Comparison of the NMR of the crude product with that of the purified material showed the absence of additional products, indicating that the reaction was essentially quantitative.

B. 1,3-Dimethoxybenzene. 4-Phenyl-1,2,4-triazoline-3,5-dione (0.350 g, 0.002 mol) and 1,3-dimethoxybenzene (0.276 g, 0.002 mol) were dissolved in 20 mL of methylene chloride. After standing at room temperature for 12 h, the solution had turned a yellow-brown. The solution was extracted with 20 mL of 0.24 M potassium hydroxide in two portions. The methylene chloride solution was dried over magnesium sulfate and then evaporated to give 0.083 g of recovered 1,3-dimethoxybenzene. The potassium hydroxide solution was decolorized with a liberal portion of charcoal, filtered, and then acidified to give 0.492 g of white solid, which was a mixture of product and polymer. It recrystallized very slowly from 3 mL of 1,3-dioxane at room temperature to give 0.147 g (34%) of 1-(2,4-dimethoxyphenyl)-4-phenylurazole: mp 183.5–185.0 °C; ^{1}H NMR ($CDCl_3$) δ 3.81 (3 H, s), 3.83 (3 H, s), 6.54 (2 H (ortho to CH_3O's), m, 7.3–7.6 (6 H, m), 8.7 (1 H, vbr s); IR (Nujol) 3195 (NH, br), 1758, 1691 (C=O), 848, 822, 758, 720 cm^{-1}.

Anal. Calcd for $C_{16}H_{15}N_3O_4$: C, 61.33; H, 4.83; N, 13.41. Found: C, 61.42; H, 4.89; N, 13.69.

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(7) G. A. Russell, R. L. Blankespoor, J. Mattox, P. R. Whittle, D. Symalla, and J. R. Dodd, *J. Am. Chem. Soc.*, **96**, 7249 (1974).

(8) H. Wamhoff and K. Wald, *Org. Prep. Proced. Int.*, 7(5), 251 (1975).

(9) C. Mannich, *Arch. Pharm.* (*Weiheim, Ger.*), **242**, 506 (1904).

Reaction of 4-Butyl-1,2,4-triazoline-3,5-dione with 1,3,5-Trimethoxybenzene. The reaction was carried out as above with the 4-phenyl compound. After a 5-h reaction time, the solvent was removed under vacuum to give a resinous residue. Addition of ether induced crystallization. The product was filtered, washed, and recrystallized from ethanol at −10 °C to give a 68% yield of product, mp 156–157 °C. Ethanol of crystallization was removed by heating to 130 °C for 30 min. ^{1}H NMR (CDCl$_3$) δ 0.95 (3 H, t), 1.2–1.9 (4 H, m), 3.59 (2 H, t), 3.79 (6 H, s), 3.81 (3 H, s), 6.13 (2 H, s), 7.99 (1 H, br s); ^{13}C NMR, (CDCl$_3$) δ 13.7, 19.7, 30.0, and 39.2 (*n*-butyl), 55.6 (4-CH$_3$O), 56.1 (2,6-CH$_3$O), 91.1, 106.3, 158.5, and 162.4 (C-3, C-1, C-2, and C-4 of aryl ring), 153.6 and 155.7 (C-3 and C-5 of urazole).

Anal. Calcd $C_{15}H_{21}N_3O_5$: C, 55.71; H, 6.55; N, 13.00. Found: C, 55.72; H, 6.75; N, 12.80.

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Registry No. 1a, 84751-99-5; **1b**, 84752-00-1; **2a**, 84752-01-2; 1,4-dimethoxybenzene–4-phenyl-1,2,4-triazoline-3,5-dione complex, 84752-02-3; 4-phenyl-1,2,4-triazoline-3,5-dione, 4233-33-4; 4-butyl-1,2,4-triazoline-3,5-dione, 13482-57-0; 1,3,5-trimethoxybenzene, 621-23-8; 1,3-dimethoxybenzene, 151-10-0; anisole, 100-66-3.

Photochemistry of Epoxyquinone. 5. Photoinduced Cycloadditions of Epoxynaphthoquinone to Aldehydes, Ketones, and Oxygen[1,2]

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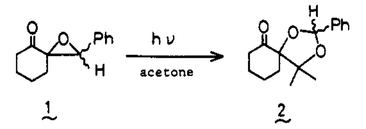
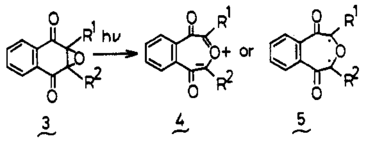
Irradiation of a benzene solution of 2,3-dihydro-2,3-dimethyl-2,3-epoxy-1,4-naphthoquinone (**3a**) in the presence of aldehydes gives the primary 1,3-dioxolane adducts in good yields. Upon further irradiation, the primary adducts undergo photorearrangement to give alkylidenephthalides. A similar photocycloaddition reaction of **3a** with aliphatic ketones was realized by their use as the reaction medium. When irradiated in the presence of oxygen in benzene, **3a** was converted into 3-acetyl-3-acetoxyphthalide and 3-acetoxy-3-methylisochroman-1,4-dione presumably via the reaction of singlet oxygen with a carbonyl ylide, **4a**. In contrast to 2,3-dialkylepoxynaphthoquinones **3a–d**, the photoinduced cycloaddition of 2,3-dihydro-2,3-diphenyl-1,4-naphthoquinone (**3e**) to carbonyl compounds did not occur. The photoinduced cycloadditions of epoxynaphthoquinones to carbonyl compounds are believed to be HOMO-controlled reactions on the basis of substituent effects at the 2- and 3-positions of epoxynaphthoquinones and at the para position of the dipolarophiles, namely, aromatic aldehydes.

Ring-opening reactions at C–C bonds of oxiranes have attracted considerable interest from both synthetic and mechanistic standpoints.[3,4] Especially, 1,3-dipolar cycloaddition of carbonyl ylides to carbonyl compounds constitues among the most convenient methods for the synthesis of 1,3-dioxolane compounds. While several examples of 1,3-dipolar cycloaddition reactions of thermally generated carbonyl ylides with less volatile carbonyl compounds can be found in literature,[5] relatively little is known about the cycloaddition of photogenerated carbonyl ylides to carbonyl compounds. In one system, Pête et al. have recently described the photocycloaddition reaction of the α,β-epoxy ketone **1** to acetone leading to the formation of the 1,3-dioxolane **2**[6] (eq 1). Recently, we have reported that irradiation of several epoxynaphthoquinones gives carbonyl ylides **4** or 1,3-diradical **5** (eq 2), which may be trapped by alkenes or dipolarophiles such as 2-norbornene and *N*-phenylmaleimide.[7] When irradiated in a benzene solution (0.1 M) in the absence of 1,3-dipolarophile, 2,3-dimethyl-2,3-dihydro-2,3-epoxy-1,4-naphthoquinone (**3a**) is converted into dimers **6a** and **6b** (eq 3) in good yields via the cycloaddition of **4a** or **5a** to the carbonyl group of another molecule of **3a**.[1] This result prompted to investigate the possibility of trapping of 4 or 5 with simple aldehydes and ketones. In this paper, the photolyses of epoxynaphthoquinones in the presence of various aldehydes and ketones were examined and the 1,3-dipolar cycloadditions of 4 or 5 to aldehydes and ketones as well as

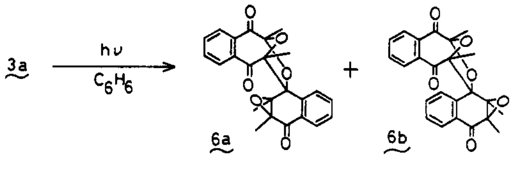


(1)



(2)

a; R^1=R^2=Me,
b; R^1=R^2=Et,
c; R^1=Me, R^2=$CH_2C(CH_3)_3$
d; R^1=Me, R^2=$CH_2C(CH_3)_2Ph$
e; R^1=R^2=Ph



(3)

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(1) Part 4: Maruyama, K; Osuka, A. *J. Org. Chem.* **1980**, *45*, 1898.

(2) For preliminary reports on some aspects of the present study, see: (a) Maruyama, K.; Osuka, A. *Chem. Lett.* **1979**, 77. (b) Maruyama, K.; Osuka, A.; Suzuki, H. *Chem. Lett. Ibid.* **1979**, 1477. (c) Maruyama, K.; Osuka, A.; Suzuki, H. *J. Chem. Soc. Chem. Commun.* **1980**, 723.

(3) (a) Linn, W. J.; Benson, R. E. *J. Am. Chem. Soc.* **1965**, *87*, 3657. (b) Ullman, E. F.; Milks, J. E. *Ibid.* **1962**, *84*, 315; **1964**, *86*, 3814. (c) Petrellis, P. C.; Dietrich, H.; Meyer, E.; Griffin, G. W. *Ibid.* **1967**, *89*, 1967. (d) Do-Minh, T.; Trozzolo, A. M.; Griffin, G. W. *Ibid.* **1970**, *92*, 1402. (e) Huisgen, R.; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 572 and references cited therein.

(4) (a) Houk, K. N.; Sims, J.; Duke, R. E., Jr.; Stroziew, R. W.; George, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 7287. (b) Houk, K. N.; Sims, J.; Watts, C. R.; Luskus, L. J. *Ibid.* **1973**, *95*, 7301. (c) Bigot, B.; Sevin, A.; Devaquet, A. *Ibid.* **1979**, *101*, 1095; **1979**, *101*, 1101.

(5) Robert, A.; Pommeret, J. J.; Foucaud, A. *Tetrahedron* **1972**, *28*, 2085.

(6) Muzart, J.; Pête, J. ep. *Tetrahedron Lett.* **1977**, 303.

(7) Arakawa, S. *J. Org. Chem.* **1977**, *42*, 3800.

0022-3263/83/1948-1712$01.50/0