presence of platinum oxide (20 mg) to give, after workup and distillation, **5**: 0.14 g (96% yield); bp 92–94 °C (0.2 torr); VPC (3 m, 10% Reoplex, 150 °C) single peak; IR 3490 (OH), 1740 (C=O) cm^{-1}; ^1H NMR (CCl_4) δ 3.75 (s, 6, 2 OCH_3), 3.60 (s, 1, OH), 1.96 (br t, 2, CH_2-1), 0.92 (t, 3, J = 7.2 Hz, CH_3). Anal. Calcd for $C_{10}H_{18}O_5$: C, 55.01; H, 8.31. Found: C, 55.38; H, 8.37.

Photochemical Isomerization of 4. A solution of **4** (0.4 g) in hexane (100 mL) under nitrogen was irradiated with ultraviolet light (Philips 250 W, max 240 nm). The reaction was monitored by VPC (3 m, 10% Reoplex, 160 °C). The initial ratio of isomers (9:1) reached the equilibrium value (10:7) after 4 h. Chromatography on a silica gel column (40 g, 200–300 mesh) and distillation gave **4**: 0.22 g (55% yield); bp 97–99 °C (0.2 torr); VPC two peaks 10:7;[29] IR 3490 (OH), 1740 (C=O), 970 (CH=CH) cm^{-1}. Anal. Calcd for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07. Found: C, 66.21; H, 10.31.

Catalytic Isomerization of 3a and 4. 3a (VPC 7:3)[30] or **4** (VPC 10:7) was treated in dichloromethane solution at room temperature for 18 h with 1 mol equiv of Lewis acid ($SnCl_4$, BF_3, $AlCl_3$). After workup the recovered adducts **3a** and **4** showed an unchanged ratio of isomers by VPC.

Kinetic Procedure. The reactions were followed kinetically in the temperature range 110–150 °C by the ampule technique. The pseudo-first-order experiments were run with a 12–14 molar excess of alkene to at least 70–80% completion. The second-order rate constants were calculated with constant molar ratios of the reactants (1:1) over the first 50–60% of reaction.

Product Analysis. To the reaction mixture was added an appropriate amount of 2,4-dimethylnitrobenzene or *m*-dinitrobenzene as internal standard, followed by carbon tetrachloride to make the solution homogenous. Samples were withdrawn at 1–2 h intervals, quenched by cooling to −20 °C, and analyzed by VPC on a 10% Reoplex 1 m column (Chromosorb W) by using a column temperature of 100–130 °C. Peak areas were measured by weight, and the amount of adduct was calculated from the calibration against the internal standard. For each sample three VPC analyses were performed. In the case of (*E*)- and (*Z*)-2-pentene, in order to measure separately the formation of the geometrical isomers, the adducts were analyzed after silylation.[31]

Solvent Effect. Solvent effect was studied for solutions in carbon tetrachloride, bromobenzene, and methyl cyanide under the pseudo-first-order conditions (1–2% solution for dimethyl mesoxalate and 7–10% solution for the alkene). Effects were temperature independent. Table I gives results for 140 °C.

Treatment of the Data. Reaction order was determined by a graphic method. A linear plot was obtained for the pseudo-first-order data [log ($X_\infty - X$) vs. t (where X_∞ is the concentration after termination of the reaction and X is the concentration at time t)] and for the second-order ($1/(X_\infty - X)$ vs. t). Rate constants of the pseudo-first-order (k') reactions were calculated from a least-squares treatment of log ($X_\infty - X$) against t. Second-order rate constants (k) were obtained from the relation $k = k'/A$ (where A = alkene concentration). Energies of activation were obtained by a least-squares method from the log k against T^{-1} data. Entropies of activation were obtained from the Eyring equation. The estimated precision is ca. ±7 kJ mol^{-1} in E_a and ±12.5 kJ mol^{-1}/K^{-1} in ΔS^*.

Registry No. 1a, 109-67-1; **1b**, 592-41-6; **1c**, 563-45-1; **1d**, 760-20-3; **1e**, 816-79-5; **1f**, 646-04-8; **1g**, 627-20-3; **2**, 3298-40-6; (*E*)-**3a**, 72844-70-3; (*Z*)-**3a**, 72844-71-4; (*E*)-**3b**, 72844-72-5; (*Z*)-**3b**, 72844-73-6; **3c**, 72844-74-7; (*E*)-**3d**, 72844-75-8; (*Z*)-**3d**, 72844-76-9; **3e**, 72844-77-0; **3f**, 72844-78-1; **3g**, 72844-79-2; (*E*)-**4**, 18016-36-9; (*Z*)-**4**, 72844-80-5; **5**, 72844-81-6; butyl glyoxylate, 6295-06-3.

Mechanistic Studies of the Reaction of 4-Substituted 1,2,4-Triazoline-3,5-diones with β-Dicarbonyl Compounds

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4-Substituted 1,2,4-triazoline-3,5-diones were found to add to the α position of β-diketones and β-diketo esters, yielding both 1:1 and 2:1 adducts. The 1:1 adducts showed a dramatic stabilization of the enolic tautomer when compared to the original β-dicarbonyl compounds as evidenced by a large increase in percent enol in all solvents. Kinetic studies support reaction through the 1,4-dipolar pathway involving triazolinedione and the enolic form of the β-dicarbonyl compound. This reaction was also found to demonstrate a strong solvent dependency, hydrogen bonding solvents being rate enhancing.

Kinetic investigations[1] have shown 4-phenyl-1,2,4-triazoline-3,5-dione (PhTD) to be one of the most powerful dienophiles known. It is 10^3 times more reactive than tetracyanoethylene (TCNE) and 2×10^3 times more reactive than maleic anhydride. A significant result is the ability of PhTD to undergo reactions at room temperature, a factor which makes it an excellent dienophile for poorly reactive and unstable electrocyclic substrates. PhTD was treated with butadiene and cyclopentadiene by Cookson, Gilani, and Stevens[2] to yield the (4 + 2) cycloaddition products. This led to extensive further research with (4 + 2) cycloadditions.[3-8]

The Diels–ene pathway is also taken with PhTD. Pasto and Chen[9] first observed this reaction. They treated (4-phenylbutylidene)cyclopropane with PhTD to form the "ene" reaction product. This reaction was found to be ~30 000 times faster than that employing conventional azodicarboxylates.[10]

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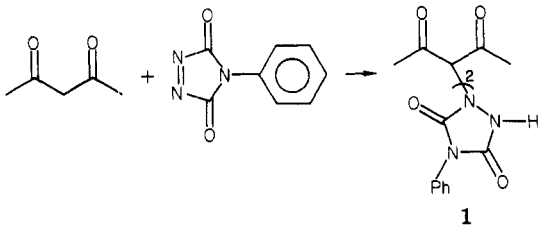
Combinations of these reaction pathways have been observed in the reaction of PhTD with double Diels–Alder and Diels–Alder–ene sequences in the reaction of PhTD with styrenes. Cookson, Gilani, and Stevens[11] isolated a double Diels–Alder adduct with styrene. Guilbault, Turner, and Butler[12] showed that both the double Diels–Alder and the Diels–Alder–ene products were formed with styrene in a 1:2 ratio. Turner, Guilbault, and Butler[13] and Wagener and Butler[14] have shown that PhTD cleaves enol esters via an intramolecular rearrangement of the initially formed 1,4-dipolar intermediate.

PhTD has been shown to undergo reaction with acetone to form 2-(acetomethyl)-4-phenyl-1*H*-1,2,4-triazoline-3,5-dione by both Cookson, Gilani, and Stevens[11] and Ruch.[15] Although no mechanistic study was conducted, Ruch[15] postulated that reaction occurred through the extremely low concentration of enol structure in a manner analogous to that suggested by Diels[16] and Diels and Wulft[17] for the reaction of β-dicarbonyl compounds with azodicarboxylates. No investigations dealing with the reaction of triazolinediones with β-dicarbonyl compounds have been reported, although two separate studies[18,19] have been conducted to show that azodicarboxylates undergo reaction with the sodio derivative of β-dicarbonyl compounds to yield the 1:1 adducts only.

This paper deals with a kinetic study of the reaction of triazolinediones with β-dicarbonyl compounds, identification of both the 1:1 and the 2:1 addition products, and postulation of a mechanism which is supported by the data.

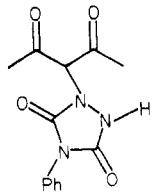
Results and Discussion

Adducts of 2,4-Pentanedione (PD) and PhTD. 2,4-Pentanedione was added to a solution of PhTD in acetonitrile in a molar ratio of 1:1. Reaction was complete in approximately 1 h as noted by disappearance of the characteristic red color of the triazolinedione. NMR and elemental analysis indicated the 2:1 adduct 1 to be the



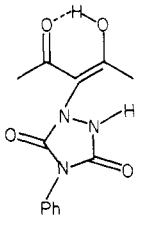
1

reaction product. Assuming kinetic preference for the 2:1 adduct, a second attempt was made to synthesize the 1:1 adduct. The reactants were mixed as before in acetonitrile, employing a 4:1 excess of PD. The reaction was complete in 15 min. Subsequent workup resulted in a stable white powder which was recrystallized from ethanol–water. Elemental and mass spectral analysis of the compound indicated the structure to be the 1:1 adduct **2a**. The NMR spectrum, however, showed no α-proton absorption and



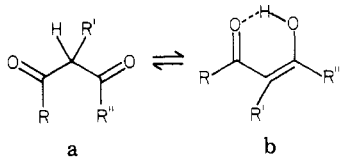
2a

a marked shift of the pendent methyl signals upfield (in Me_2SO-d_6) from 2.4 to 1.9 ppm. Further inspection showed a broad band at δ 16.0 which by integration was shown to be equivalent to one proton. The shift in the methyl absorption and appearance of the peak at δ 16.0 are both indicative of a highly stabilized β-dicarbonyl enol tautomer. (See the paragraph at the end of the paper about Supplementary Material). Infrared (IR) absorption characteristics of a chelated enol are found at 1640 cm^{-1}. Ultraviolet spectral analysis (UV) likewise supports this conclusion as a characteristic chelated absorption was observed at 272 nm. This information allows assignment of **2** as the structure of the 1:1 product.



2

The percentage of enolization of β-dicarbonyls is known to be solvent dependent, more polar hydrogen-bonding solvents being the most suppressive. The absence of an α-proton absorption in Me_2SO implies this adduct to be essentially 100% enolized in all solvent systems since Allen and Dwek[20a] have shown that at infinite dilution the enol content of 2,4-pentanedione is only 60% in Me_2SO in comparison to 75% in acetone, 94% in CCl_4, and 95% in cyclohexane. For β-diketones the nonbonded van der Waals interaction between R and R″ is an important consideration in keto–enol equilibria.[20b] As a result equilibrium favors the enol tautomer. Examination of models indicates no steric interaction with the 1:1 adduct **2** in either tautomer a or b. The stabilization resulting



a b

from the chelation and conjugation is therefore assumed to be increased through the electron-withdrawing nature of the α-substituted urazole, resulting in the observed tendency toward formation of the enol tautomer relative to the pure β-diketone.

Mechanistic Study of the β-Diketone–PhTD Reaction. Reaction of equimolar quantities of the 1:1 adduct **2** with PhTD resulted in quantitative formation of the 2:1 adduct **1**. The reaction pathway in Scheme I can thus be envisioned. This finding implies that reaction occurs through the enol tautomer in formation of the adducts as formation of the 2:1 adduct from the 1:1 adduct apparently takes place through this route. Adduct reaction rates with various other β-diketones and β-keto esters to be discussed

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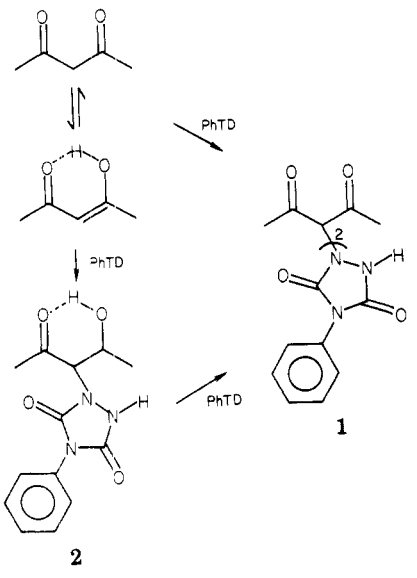
Scheme I



Scheme II

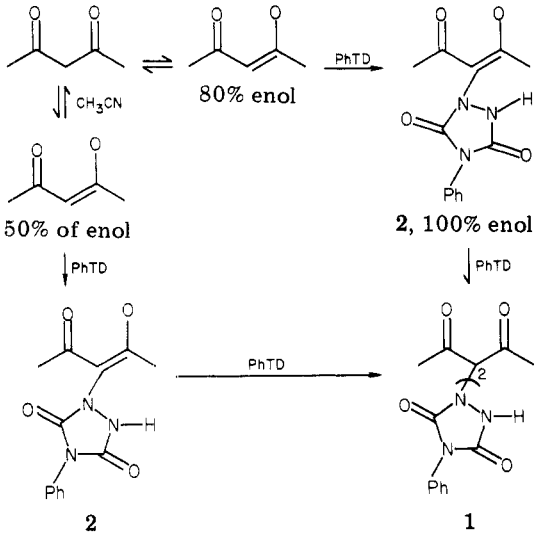


Table I. Adduct Ratios of PhTD-PD Reaction

solvent	reactant ratio[b]	% enol[a]	% 2:1 adduct
CH_2Cl_2	1:1	80	17
EtAc	1:1	70	40
CH_3CN	1:1	50	95

[a] Based on NMR integration of PD. [b] β-Diketone/PhTD.

later in this paper were found to be dependent on the amount of enol initially present in the diketone. As a test of this theory, PD was treated with PhTD in a 1:1 molar ratio in methylene chloride, ethyl acetate, and acetonitrile. The percent enolization in these solvents was found to be 80, 70, and 50%, respectively, as determined by NMR. Similar NMR studies of the 1:1 adduct in these solvents showed it to have the expected 100% enolization. Scheme II was then considered. Assuming the enolic form of the β-diketone to be the reacting species, the amount of 1:1 adduct vs. 2:1 adduct formed in this reaction could be a function of the ratio of enolic content for 2,4-pentanedione and the 1:1 adduct 2 in a particular solvent. Formation of the 2:1 adduct 1 would therefore be favored in solvents decreasing this ratio due to an increase in the probability of PhTD encountering a reactive form, the enol, with the 1:1 adduct due to its complete enolization in the solvents

Scheme III

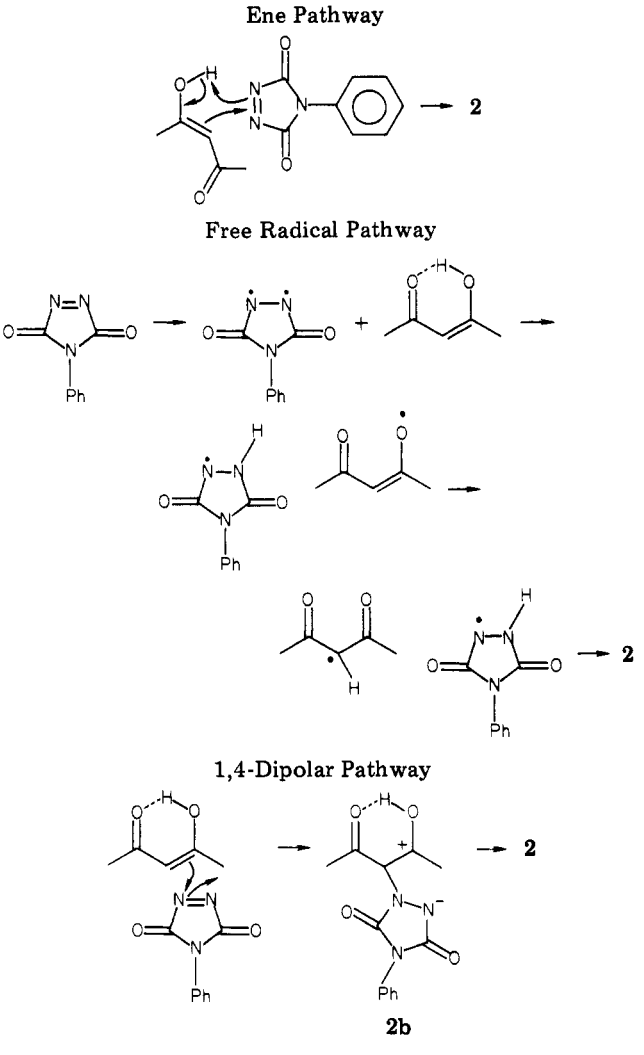


Table II. Results of the Kinetic Study of PhTD and 2 in Different Solvents

solvent	K, L mol^{-1} s^{-1} [b]	COC	solvent dipole
THF[c]	70.5	0.978[a]	1.63
1,4-dioxane	13.29	0.999	0.00
EtAc	2.60	0.999	1.78
$(CHCl_2)_2$	1.07×10^{-3}	0.999	1.32

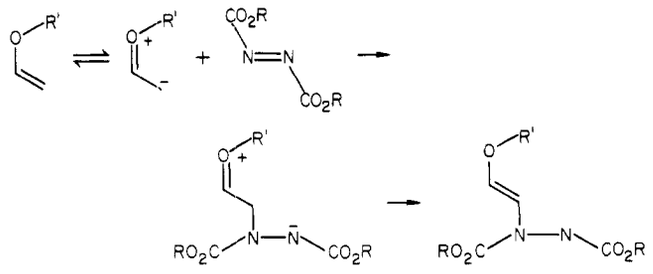
[a] Poor COC attributed to rapid reaction relative to mixing. [b] Calculated by the method of least squares. [c] Distilled fresh from Na.

studied. Reaction occurring through the keto form would be expected to reverse these product ratios. This argument also assumes the relative rates of 1:1 and 2:1 adduct formation to remain the same in each solvent. As Table I shows, the relationship between the 1:1 and 2:1 adducts under the various conditions employed is as expected, giving support to the theory of reaction through an enolic substrate.

Possible Mechanisms. In an attempt to postulate the most probable mechanism, the possible reaction pathways for an enolic substrate were considered and subsequently compared to kinetic and spectral information obtained. Three potential reaction pathways can be rationalized (see Scheme III).

The ene and dipolar pathways would be expected to proceed via second-order kinetics, with the free radical yielding a complex kinetic scheme. In an attempt to obtain kinetic data on the system, the reaction of PhTD and the

Scheme IV



1:1 adduct **2** was studied spectroscopically by monitoring the PhTD visible absorbance in $(CHCl_2)_2$ at 545 nm. Application of the data obtained to the second-order equation gives a rate of 1.072×10^{-3} L mol^{-1} s^{-1} by the least-squares method (COC = 0.9997). This reaction was chosen for the kinetic work due to the singular product it affords, namely, the 2:1 adduct **1**. Subsequent kinetic studies undertaken to determine possible solvent effects (Table II) indicate an unusually strong solvent dependency for the system. The rate change from slowest to fastest is approximately 70 000, a finding difficult to explain in terms of the ene reaction. As an electrocyclic concerted reaction, the ene reaction is characterized as a "no mechanism" path and as such is not expected to be dramatically affected by solvent changes. Wagener[21] noted a small solvent influence in the Diels–Alder–ene reaction of PhTD with styrene. This rate influence was of low magnitude and opposite to that observed with this reaction system. This conclusion is supported by the reaction of PhTD and 4-methyl-1-pentene to give the 1:1 ene adduct which was found to have a similar rate change with solvent influence. The ene reaction mechanism, therefore, appears to be an unlikely choice as the most probable mechanism for these adduct formations and was ruled out.

Esters of azodicarboxylic acid undergo reaction with vinyl ethers[22,23] through a dipolar intermediate as depicted in Scheme IV. Butler, Wagener, and Turner[14,24] give substantial evidence for a similar reaction pathway with PhTD and vinyl ethers and esters. It is generally thought that dipolar reactions should show pronounced solvent effects. The results of a solvent study of the vinyl ethers[24] with PhTD show no correlation with solvent polarity. Since both monomers are highly polar, it was reasoned that they could experience enough ground-state solvation to effectively cause the solvation of the transition state to be undetectable. Therefore, it is plausible to suspect a similar mechanism with the β-diketone system. As Table II shows, the rate does not parallel solvent polarity. The greatly enhanced rate would, at best, be difficult to explain simply by polarity stabilization in view of previous evidence.

Enol tautomers exist in the hydrogen-bonded species for both PD and the 1:1 adduct **2**. Wheland[25] estimates that the intramolecular hydrogen bond of pentanedione stabilizes the enol tautomer by 5–10 kcal, and the conjugated system further stabilizes this by 2–3 kcal. The effect of substitution of an electron-withdrawing substituent on this has been shown by Yoshida et al.[26] to increase the percentage of enol in the adduct. If the intermediate **2b** shown in the 1,4-dipolar pathway above shares this stability, its decay would have an influence on the overall reaction rate. Making this assumption the following kinetic scheme was proposed:

Table III. Chemical Shifts of Chelated Enolic Protons of 2 and 5

solvent	system	shift, ppm	solvent	system	shift, ppm
acetone	2	15.8	$CHCl_3$	2	16.0
Me_2SO	2	11.2	$(CHCl_2)_2$	5	13.0
$(CHCl_2)_2$	2	15.2	THF	5	12.0
dioxane	2	15.0			

Table IV. Solvent Dependency of Pseudo-First-Order Kinetics for PhTD Adducts of CHD and Pd

system	solvent	K, s^{-1}	ΔK	COC
PD + PhTD	$(CHCl_2)_2$	1.10×10^{-4}	1000	0.9996
PD + PhTD	THF	10^{-1}		
CHD + PhTD	$(CHCl_2)_2$	9.50×10^{-3}	5.6	0.9997
CHD + PhTD	THF	5.33×10^{-2}		0.9997

$$\text{PhTD} + \text{enol} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{dipolar intermediate} \xrightarrow{k_2} \text{adduct}$$

Steady-state treatment of the intermediate results in the rate = $k'k_2$[PhTD][enol], where $k' = k_1/(k_{-1} + k_2)$. A study of the chemical shift of the enolic OH (Table III) shows a small deviation upfield as the H-bonding tendency of the solvent increases. We assume, therefore, the function of oxygen-containing solvents in the observed rate increase is twofold: (1) weakening the intermediate, **2b**, allowing it to collapse to product, and (2) acting as a transfer agent for the proton from the weakened chelate to the amide position.

For this theory to be tested, a system was needed which would not be expected to display this type of solvent dependency. This required that it not be capable of forming the stabilizing chelation and exist completely in the free enolic form. 1,3-Cyclohexanedione (CHD) is such a ketone and is prevented from the intramolecular chelation due to the methylene bridge. NMR provides proof of this in the appearance of the OH chemical shift at δ 10 as a sharp singlet in chloroform. The methylene bridge and 1,3-dicarbonyl moiety force the carbonyl groups and the α-carbon into coplanarity, allowing the compound to exist in a resonance-stabilized enolic state which is 100% in most solvents. Stabilization of the intermediate formed from reaction of this compound with PhTD cannot be a factor in its kinetics. The solvent may exert an effect only if it is acting as a proton-transfer agent. A comparison of the rates of PD and PhTD in THF and $(CHCl_2)_2$ with those of CHD and PhTD in the same solvents should show a dramatic variance in the differential solvent rates. The overall rate would also be expected to be high for the unstabilized system.

In order to preclude any steric problems with the 1:1 → 2:1 reaction, we chose for this study the reaction of the pure diketones, PD and CHD, with PhTD. As both the 2:1 and 1:1 adducts may form under conditions employed for the secondary rate determination, pseudo-first-order rate conditions employing a tenfold excess of diketone were used. Trial reactions were run under these conditions. After complete reaction, solvent was stripped away and the crude solid analyzed with NMR. No indication of the 2:1 adduct was found.

For each of the four systems, one 2-mL volumetric flask was prepared. The one containing PhTD was added to the sample vial. The diketone was injected with sufficient

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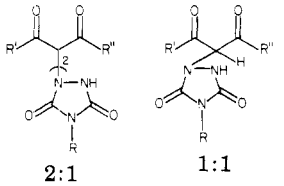
Table V.
Identification of the Adducts of the 4-Substituted 1,2,4-Triazoline-3,5-dione-β-Dicarbonyl Reaction



2:1

1:1

compd	R	R′	R″	adduct ratio[a]	mp, °C
1	Ph	CH_3	CH_3	2:1	215 d[b]
2	Ph	CH_3	CH_3	1:1	171-173
3	Ph	$-(CH_2)_3-$		1:1	211 d
4	Ph	$-(CH_2)_3-$		2:1	180 d
5	Ph	CH_3	OC_2H_5	1:1	153-154
6	Ph	CH_3	OC_2H_5	2:1	199-202
7	*p*-tol	CH_3	OC_2H_5	2:1	228-231
8	*p*-tol	CH_3	CH_3	1:1	190-192
9	Ph	Ph	Ph	1:1	189-191
10	Ph	Ph	Ph	2:1	160 d
11	CH_3	Ph	Ph	2:1	170-172 d
12	CH_3	Ph	Ph	2:1	164-166 d
13	CH_3	$-CH_2C(CH_3)_2CH_2-$		2:1	218 d

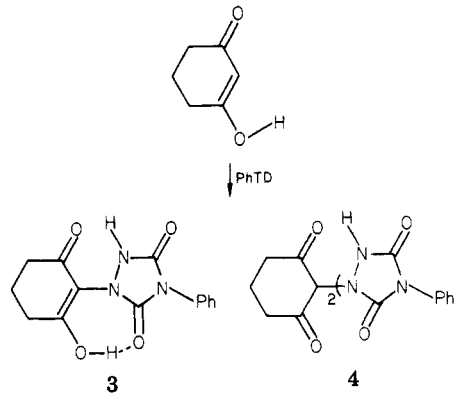
[a] Triazolinedione-β-dicarbonyl compound ratio. [b] With decomposition.

force to effect mixing of the two reactants. The THF run with PD was too rapid to follow accurately, making it necessary to make a conservative estimate of the rate based on data obtained. To assure this reaction was indeed following the kinetics of the other samples, we measured its rate at a depressed temperature (5 °C) and found that it gave the desired correlation to the first-order equation. Table IV shows the expected decrease in solvent dependency for 1,3-cyclohexanedione.

Adducts of PhTD with β-Diketones and β-Diketo Esters. Having established an enol monomer which increases its ability to add the triazolinedione moiety in formation of the 1:1 addition product by increasing the percentage of reactive species, namely, the enolized ketone, we studied other β-dicarbonyls to determine if this trend would be followed. Those employed in this study along with the adducts are listed in Table V.

Adducts of Ethyl Acetoacetate (EtAA) with PhTD. Treatment of equimolar quantities of PhTD and EtAA in methylene chloride gives complete decoloration in 24 h. Analysis and spectral data show the 2:1 adduct **6** to be obtained in 60% yield after recrystallization. As EtAA is only 7% enolized in this solvent, the 2:1 adduct is expected to be greatly favored if the 1:1 adduct shows significantly increased enolization relative to the pure β-diketo ester. As this was suspected to be the case after obtaining 2:1 adduct under the above conditions, the 1:1 adduct **5** was synthesized for spectral study. PhTD was mixed with a sixfold excess of EtAA in methylene chloride. Reaction was complete in 5 min. The NMR spectrum (Figure 2 of the Supplementary Material) of this compound in $CDCl_3$ shows it to exist to the extent of 90% in the enolized form. The composition of the equilibrium mixture is determined by integration of the NMR signal for the keto form as observed in the presence of mixed ethyl multiplets and methyl and α-hydrogen absorptions at δ 2.4 and 5.6, respectively.

Adducts of CHD and PhTD. Reaction of PhTD with CHD in a 2:1 molar ratio in 150 mL of dry methylene chloride gave complete reaction in 4 h. Analysis of this product indicated it to be the 1:1 hydrated 2:1 adduct **4**. Attempts to remove the water of hydration by vacuum



3 4

drying at 130 °C and 0.05 mmHg resulted in decomposition of the product. NMR gave a sharp singlet at δ 6.3 which slowly exchanges with D_2O and is unique to this 2:1 adduct. On the basis of a model study, this singlet was assigned as an absorption due to a strongly hydrogen bonded amide proton.

Reaction between equimolar quantities of PhTD and CHD resulted in immediate formation of the 1:1 adduct **3**. This compound gave the expected 100% enolization in Me_2SO-d_6 as evidenced by a broad signal at δ 12.5 and absence of vinylic signals.

Adducts of Dibenzoylmethane (DBzM) and PhTD. The 1:1 adduct **9** of DBzM with PhTD was obtained by reaction of a fivefold excess of the β-diketone with PhTD in THF. Reaction was instantaneous under these conditions. The 2:1 adduct **10** was obtained by reaction of a 2:1 molar quantity of PhTD and β-diketone. This system proved to be somewhat different from the others studied. Although dibenzoylmethane is essentially 100% enolized in less polar solvents, the 1:1 adduct **9**, which in previous cases demonstrated an increase in enol content at equilibrium, appeared in this case to result in decreased enolization. A sharp singlet in the upfield proton of the aromatic region (δ 7.2) which did not appear in **10** was suspected of being the α-proton of the keto form (Figure 3 of the Supplementary Material).

In an attempt to clarify the spectra in this region and determine the extent of keto form, we employed 4-methyl-1,2,4-triazoline-3,5-dione (MeTD) in formation of the adducts. The δ 7.2 signal with this 1:1 adduct, **11**, clearly separated from the aromatic signals, disappeared on addition of D_2O (Figure 4 of the Supplementary Material). This signal integrates to 60% of one proton in Me_2SO-d_6. The decreased enolization was supported by a model study which shows a great deal of steric problems with formation of the chelated conformation of this 1:1 adduct and that with PhTD, which explains the reluctance observed toward formation of **10** and **12**.

Spectral Data for the Adducts of β-Dicarbonyl Compounds with PhTD and MeTD. A summary of proton chemical shifts of the α-substituted adducts of the β-diketo carbonyl compounds studied is listed in Table I of the Supplementary Material. The methyl signals of the PD and EtAA adducts show a pronounced upfield shift to δ 2.1 in Me_2SO-d_6 for the 1:1 adducts while the methyl signals of the 2:1 adducts appear at δ 2.4. These shifts are compatible with the known methyl shift for the enol and keto forms of the pure β-dicarbonyls in this and other solvents. The chelated enolic proton for the 1:1 adducts with PD were found at δ 16.3 in $CHCl_3$ while those for EtAA and CHD were found further upfield at δ 12.3 and 12.5, respectively.

Data from UV and IR spectra are given in Table II of the Supplementary Material. All 1:1 adducts show strong

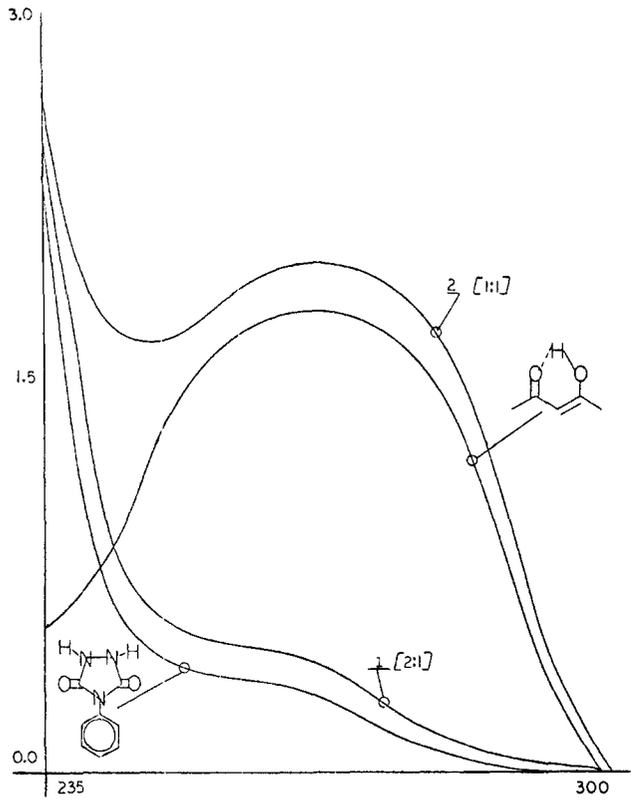
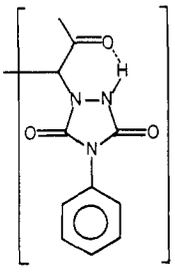


Figure 1. UV spectra: adducts 1 and 2, 2,4-pentanedione, and 4-phenylurazole.

absorption in the 1580–1560-cm^{-1} region (KBr) which is attributed to the C=O stretching vibration strongly perturbed by hydrogen bonding and superimposed with the C—C stretching vibration. The 2:1 adducts all show a strong amide band at 3300 cm^{-1}. A model study indicates that this adduct may form a six-membered hydrogen bonded conformer which would be expected to prevent the amide proton from undergoing tautomerization with the 3-one of the urazole ring as it is known to do.



The UV spectrum shows in each of the 1:1 adducts the appearance of an absorption in acetonitrile which is not found in the spectra of the 2:1 adducts. This band was most obvious in the case of the 1:1 adduct of PD (Figure 1).

Experimental Section

Equipment and Data. All temperatures are reported uncorrected. Nuclear magnetic resonance spectra were measured with a Varian A-60A analytical NMR spectrometer. All chemical shifts are relative to tetramethylsilane. Infrared spectra were obtained with a Beckman IR-8 or IR-10 or with a Perkin-Elmer infrared spectrophotometer. Melting points were determined with a Thomas-Hoover melting point apparatus. Mass spectra were obtained with either a Hitachi Perkin-Elmer RMU mass spectrometer or a high-resolution computerized MS-30. Elemental analyses were performed by one of the following: Galbraith Laboratories, Heterocyclic Chemical Corp., or Microlab. Yields not reported in the preparative experiments were less than 20%.

Procedure for Kinetic Measurements. Two-milliliter portions of equimolar solutions of PhTD and the 1:1 adduct of PhTD and 2,4-pentanedione (PD) were pipetted into an ultraviolet (UV) cell which was maintained at constant temperature. The 1:1 adduct was used due to its previously established 100% enolization. Visible spectra at 545 nm (unless otherwise noted) were recorded vs. time, taking no less than seven readings. The reaction was determined to be second order overall due to its fit with the second-order rate expression

$$\frac{1}{A_t} = \frac{k}{a}t + \frac{1}{A_0}$$

where A = the absorbance at time t, a = the PhTD absorptivity times cell path length (1 cm), k = the second-order rate constant, and A_0 = the absorbance at time zero.

Pseudo-first-order rates were determined in a similar manner. Two-milliliter portions of solutions of PhTD–β-diketone in a 1:10 molar ratio were pipetted into the UV cell. Due to the speed of the reaction between PhTD and PD in THF the kinetics were run at reduced temperature to demonstrate the fit of the data to the first-order kinetic equation

$$\ln \frac{A_t}{a} = k_t + A_0$$

The UV cell was cooled to 6 °C via a constant-temperature circulating ethylene glycol system. Individual solutions were allowed to reach this temperature before mixing. All other runs were conducted at room temperature.

The opposite 10:1 (β-diketone–PhTD) reaction could not be carried out due to the possibility of a side reaction to form the 2:1 adduct.

4-Phenyl-1,2,4-triazoline-3,5-dione (PhTD) was prepared according to the method of Pirkle and Stickler.[10]

THF was obtained in high purity for the kinetic studies by vacuum-line distillation from the potassium salt of the dianion of benzophenone to assure freedom from peroxides.

1,1,2,2-Tetrachloroethane was purified by distillation over 3A molecular seives through a 10-in. Vigreux column.

1,4-Dioxane and ethyl acetate were purified by distillation over CaH_2 through a 36-in. Vigreux column.

Kinetics of 4-Substituted 1,2,4-Triazoline-3,5-diones with 4-Methyl-1-pentene. Pseudo-first-order kinetics of the substituted triazolinediones with 4-methyl-1-pentene were carried out in a manner identical with that used with PhTD and the β-diketones. Two-milliliter quantities of solutions of PhTD and 4-methyl-1-pentene in 1:10 molar ratios were mixed at constant temperature. Pseudo-first-order conditions were used due to the potential for higher than 1:1 adduct formation.

Synthesis of Adducts of 4-Substituted 1,2,4-Triazoline-3,5-diones and β-Dicarbonyl Compounds. 3,3-Bis(4-phenyl-2*H*-1,2,4-triazoline-3,5-dionyl)-2,4-pentanedione (1). PhTD (0.86 g, 0.0049 mol) in 50 mL of methylene chloride was added directly to 0.245 g (0.002 45 mol) of PD in 50 mL of the same solvent. The reaction was complete in approximately 20 h. Recrystallization yielded the 1:1 adduct **2** as the major product. The reaction was repeated in acetonitrile. Recrystallization of the crude solid from chloroform gave 0.5 g of white solid **1**: mp 215 °C dec; IR (KBr) 3150 (br), 1800 (s), 1720 (br), 1600 (s, m), 1510 (s), 1430 (s), 1380 (s), 1250 (br), 1180 (w), 1150 (s), 1080 (w), 1030 (s), 810 (s), 780 (s), 725 (w), 700 (s), 635 (br) cm^{-1}; NMR (Me_2SO-d_6) δ 2.40 (s), 7.45 (m), 10.6 (br s); no molecular ion observed in mass spectrum.

Anal. Calcd for $C_{21}H_{18}N_6O_6$: C, 56.00; H, 4.00; N, 18.67. Found: C, 56.08; H, 4.11; N, 18.74.

3-(4-Phenyl-2*H*-1,2,4-triazoline-3,5-dionyl)-2,4-pentanedione (2). PhTD (0.868 g, 0.0049 mol) dissolved in 25 mL of methylene chloride was added to 1.5 g (0.0147 mol) of PD in 25 mL of methylene chloride. The red color disappeared in about 15 min. Solvent was then evaporated and the resulting oil crystallized. Purification by recrystallization from an ethanol–water mixture yielded 1.2 g (87%) of white powder: mp 171–173 °C; IR (KBr) 3050 (br), 2800 (m), 1770 (s), 1600 (br), 1460 (s), 1410 (s), 1360 (s), 1250 (s), 1210 (s), 1150 (s), 1090 (s), 1000 (br), 910 (s), 820 (s), 750 (s), 720 (s), 690 (s), 630 (s) cm^{-1}; NMR

(acetone-d_6) δ 2.15 (s), 7.5 (s), 8.3 (br s), 15.9 (br s); mass spectrum, m/e 275 (molecular ion).

Anal. Calcd for $C_{13}H_{13}O_4N_3$: C, 56.72; H, 4.73; N, 15.23. Found: C, 56.42; H, 4.97; N, 14.90.

2-(4-Phenyl-2*H*-1,2,4-triazoline-3,5-dionyl)-1,3-cyclohexanedione (3). PhTD (0.44 g, 0.0025 mol) in 20 mL of CH_2Cl_2 was added dropwise to a rapidly stirred solution of 3.0 g (0.025 mol) of CHD in CH_2Cl_2. Reaction was instantaneous as noted by immediate decoloration. The solvent was rotoevaporated and the resulting solid recrystallized from 50 mL of $CHCl_3$: mp 211 °C dec; IR (KBr) 3120 (br), 1770 (s), 1700 (br), 1640 (br), 1560 (br), 1490 (s), 1410 (br), 1360 (s), 1350 (w), 1320 (s), 1280 (s), 1240 (br), 1180 (s), 1130 (s), 1060 (w), 980 (s), 905 (w), 880 (m), 760 (s), 740 (w), 720 (w), 690 (s) cm^{-1}; NMR (Me_2SO-d_6) δ 1.9 (m), 2.45 (m), 7.4 (s), 12.77 (s); mass spectrum, m/e 287 (molecular ion).

Anal. Calcd for $C_{14}H_{13}N_3O_4$: C, 58.54; H, 4.53; N, 14.63. Found: C, 58.57; H, 4.54; N, 14.57.

2,2-Bis(4-phenyl-2*H*-1,2,4-triazoline-3,5-dionyl)-1,3-cyclohexanedione (4). PhTD (1.0 g, 0.005 mol) in 25 mL of CH_2Cl_2 was added to 0.35 g (0.0029 mol) of CHD in 25 mL of CH_2Cl_2. The reaction was complete in 4 h. After removal of 50 mL of the solvent, crystallization occurred. The product was recrystallized from a CH_2Cl_2–acetone mixture: mp 179–182 °C; IR (KBr) 3370 (s), 3250 (s), 3100 (br), 2940 (s), 1770 (s), 1600 (br), 1580 (w), 1485 (s), 1400 (br), 1200 (br), 1130 (s), 1010 (w), 885 (w), 740 (br), 670 (br) cm^{-1}; NMR (acetone-d_6) δ 2.3 (m), 3.0 (t), 6.4 (s, exchanges with D_2O), 7.5 (s); no molecular ion observed in mass spectrum.

Anal. Calcd for $C_{22}H_{18}N_6O_6 \cdot H_2O$: C, 55.0; H, 4.16; N, 17.50. Found: C, 54.89; H, 4.19; N, 17.40.

Ethyl 2-(4-Phenyl-2*H*-1,2,4-triazoline-3,5-dionyl)-3-oxobutanoate (5). PhTD (1.0 g, 0.005 mol) in 25 mL of reagent-grade CH_2Cl_2 was added to 4.45 g (0.0342 mol) of EtAA. The reaction was complete in approximately 15 min. During rotoevaporation, a crystalline product was obtained (0.42 g, 24%) which was dried at 35 °C in a vacuum oven: mp 152–154 °C; IR (KBr) 3100 (br), 2850 (sh), 1780 (s), 1700 (s), 1660 (s), 1610 (s), 1500 (s), 1400 (s), 1320 (s), 1260 (w), 1220 (s), 1185 (s), 1140 (w), 1085 (w), 1060 (s), 1000 (w), 800 (br), 770 (w), 700 (br), 630 (w) cm^{-1}; NMR (acetone-d_6) δ 1.25 (t), 1.3 (t), 2.1 (s), 2.45 (s), 4.25 (q), 4.30 (q), 5.6 (s), 7.45 (s), 12.3 (br s, existed as 75% enolized tautomer in this solvent); mass spectrum, m/e 302 (molecular ion).

Anal. Calcd for $C_{14}H_{12}N_3O_5$: C, 55.08; H, 4.92; N, 13.77. Found: C, 55.06; H, 4.94; N, 13.82.

Ethyl 2,2-Bis(4-phenyl-2*H*-1,2,4-triazoline-3,5-dionyl)-3-oxobutanoate (6). PhTD (0.6 g, 0.0034 mol) in 20 mL of methylene chloride was added to 0.4 g (0.0034 mol) of EtAA in 20 mL of methylene chloride. The reaction was complete in 24 h as noted by decoloration. The solvent was rotoevaporated and the resulting oil dissolved in ethanol. Water was added to the warm solution until cloudiness persisted. This mixture was heated until solution was obtained. On slow cooling crystallization occurred: mp 199–202 °C; IR (KBr) 3520 (s), 3130 (br), 2960 (w), 2900 (w), 2820 (w), 1800 (s), 1740 (br), 1520 (s), 1430 (br), 1370 (s), 1290 (s), 1260 (s), 1230 (s), 1190 (s), 1160 (s), 1080 (s), 1015 (s), 870 (w), 810 (m), 770 (m), 715 (s), 700 (w), 680 (s), 640 (w) cm^{-1}; NMR δ 1.35 (t), 2.47 (s), 4.47 (q), 7.4 (s); no molecular ion observed in mass spectrum.

Anal. Calcd for $C_{22}H_{20}N_6O_7$: C, 55.00; H, 4.17; N, 17.45. Found: C, 54.65; H, 4.34; N, 17.12.

Ethyl 2,2-Bis[4-(*p*-methylphenyl)-2*H*-1,2,4-triazoline-3,5-dionyl]-3-oxobutanoate (7). 4-(*p*-Tolyl)-1,2,4-triazoline-3,5-dione (ToPD; 0.2 g, 0.0015 mol) in 20 mL of methylene chloride was added to 0.14 g (0.0015 mol) of EtAA in 20 mL of dry solvent. The reaction was complete in 24 h. On rotoevaporation of solvent, an oil was obtained which was recrystallized from an ethanol–water mixture: mp 228–231 °C; IR (KBr) 3540 (s), 3320 (br), 3120 (br), 2950 (w), 2820 (w), 1800 (s), 1730 (s), 1520 (s), 1430 (br), 1370 (s), 1290 (s), 1265 (s), 1230 (s), 1190 (s), 1160 (s), 1080 (s), 1020 (s), 870 (m), 810 (m), 770 (br), 717 (s), 680 (s), 650 (s) cm^{-1}; NMR δ 1.3 (t), 2.35 (2 s), 4.35 (q), 7.2 (s), 10.3 (br s); no molecular ion observed in mass spectrum.

Anal. Calcd for $C_{24}H_{24}N_6O_7$: C, 56.69; H, 4.72; N, 16.54. Found: C, 56.75; H, 4.78; N, 16.57.

3-[4-(*p*-Tolyl)-2*H*-1,2,4-triazoline-3,5-dionyl]-2,4-pentanedione (8). 4-(*p*-Tolyl)-1,2,4-triazoline-3,5-dione (ToPD, 0.92 g, 0.0049 mol) in 25 mL of methylene chloride was added to 1.5 g (0.014 mol) of PD in 25 mL of methylene chloride. The reaction was complete as noted by decoloration in approximately 15 min. The solvent was rotoevaporated to yield a crystalline product which was recrystallized from an EtOH–H_2O mixture to give 1.0 g (70%) of a white powder: mp 190–192 °C; IR (KBr) 3100 (br), 2900 (sh), 1770 (s), 1700 (br), 1600 (br), 1460 (s), 1410 (s), 1360 (s), 1250 (s), 1210 (s), 1150 (s), 1090 (s), 1000 (b), 910 (s), 820 (s), 750 (s), 720 (s), 690 (s), 630 (s) cm^{-1}; NMR ($CDCl_3$) δ 2.15 (s), 2.4 (s), 7.3 (s), 15.3 (br s); mass spectrum, m/e 289 (molecular ion).

Anal. Calcd for $C_{14}H_{15}N_3O_4$: C, 58.13; H, 5.19; N, 14.53. Found: C, 57.76; H, 5.24; N, 14.30.

2-(4-Phenyl-2*H*-1,2,4-triazoline-3,5-dionyl)-1,3-diphenyl-1,3-propanedione (9). PhTD (0.5 g, 0.002 85 mol) in 40 mL of THF was added dropwise to 40 mL of a rapidly stirred THF solution containing 3.1 g (0.0143 mol) of dibenzoylmethane (DBzM). The reaction was instantaneous as shown by decoloration to a pale yellow solution. Rotoevaporation followed by recrystallization from a THF–hexane mixture gave 1.1 g (97%) of product: mp 189–191 °C; IR 3500 (w), 3260 (br), 3080 (s), 2960 (s), 1790 (s), 1800 (b), 1600 (s), 1580 (s), 1500 (s), 1430 (m), 1280 (m), 1240 (m), 1200 (w), 1180 (w), 1140 (w), 1000 (s), 985 (w), 930 (w), 820 (m), 760 (m), 690 (m) cm^{-1}; NMR (acetone-d_6) δ 7.31 (s), 7.42 (s), 7.55 (m), 8.1 (m); mass spectrum, m/e 399 (molecular ion).

Anal. Calcd for $C_{23}H_{17}N_3O_4$: C, 69.18; H, 4.26; N, 10.53. Found: C, 69.40; H, 4.36; N, 10.64.

2,2-Bis(4-phenyl-2*H*-1,2,4-triazoline-3,5-dionyl)-1,3-diphenyl-1,3-pentanedione (10). PhTD (0.5 g, 0.002 85 mol) in 25 mL of THF was added to 0.32 g (0.001 42 mol) of DBzM. The reaction was complete in 24 h. Rotoevaporation followed by recrystallization from $CHCl_3$–hexane gave a fine white powder: mp 160–162 °C; IR (Nujol) 3200 (w), 2950 (s), 2860 (s), 1800 (s), 1740 (s), 1680 (s), 1600 (s), 1580 (w), 1500 (m), 1460 (s), 1420 (w), 1380 (w), 1260 (w), 1220 (w), 1150 (w), 1020 (w), 890 (w), 820 (w), 760 (w), 720 (w), 700 (w), 690 (w), 640 (w) cm^{-1}; NMR (acetone-d_6) δ 7.4 (m), 7.45 (s), 8.1 (m); no molecular ion observed in mass spectrum.

Anal. Calcd for $C_{31}H_{22}N_6O_6$: C, 64.81; H, 8.83; N, 14.63. Found: C, 64.72; H, 4.13; N, 14.42.

2-(4-Methyl-2*H*-1,2,4-triazoline-3,5-dionyl)-1,3-diphenyl-1,3-propanedione (11). 4-Methyl-1,2,4-triazoline-3,5-dione (MeTD; 0.25 g, 0.0023 mol) in 30 mL of acetone was added dropwise to 1.25 g (0.005 mol) of DBzM in 45 mL of the solvent. Reaction was complete in 15 min. Rotoevaporation followed by recrystallization from a THF–hexane mixture gave needle crystals: mp 170–172 °C; IR (Nujol) 3200 (m), 2900 (s), 1770 (w), 1720 (w), 1680 (s), 1610 (w), 1600 (w), 1580 (w), 1460 (s), 1380 (w), 1345 (w), 1295 (w), 1265 (w), 1180 (w), 1080 (w), 1040 (w), 1005 (w), 985 (w), 940 (w), 910 (w), 840 (w), 830 (w), 795 (w), 765 (w), 740 (w), 690 (w), 660 (w), 625 (w) cm^{-1}; NMR (Me_2SO-d_6) δ 3.1 (s), 7.18 (s, exchanged with D_2O), 7.6 (m), 8.1 (m).

Anal. Calcd for $C_{18}H_{15}N_3O_4$: C, 64.0; H, 4.45; N, 12.46. Found: C, 63.65; H, 4.90; N, 13.01.

2,2-Bis(4-methyl-2*H*-1,2,4-triazoline-3,5-dionyl)-1,3-diphenyl-1,3-propanedione (12). MeTD (0.25 g, 0.0023 mol) in 35 mL of acetone was mixed with 0.25 g (0.001 15 mol) of DBzM in 36 mL of acetone. After 48 h, the red color had disappeared. Rotoevaporation followed by recrystallization from a THF (minimum amount)–hexane mixture yielded a white solid: mp 164–166 °C; IR 3200 (w), 2900 (s), 1800 (m), 1720 (s), 1600 (w), 1580 (w), 1460 (m), 1400 (m), 1380 (w), 1290 (w), 1260 (w), 1220 (w), 1180 (w), 1000 (w), 940 (m), 920 (w), 900 (w), 820 (w), 800 (m), 760 (w), 730 (w), 690 (w), 640 (w), 610 (w) cm^{-1}; NMR (Me_2SO-d_6) δ 2.15 (s), 6.8 (m), 7.2 (m).

Anal. Calcd for $C_{21}H_{18}N_6O_6$: C, 51.85; H, 4.52; N, 17.20. Found: C, 51.99; H, 4.51; N, 16.88.

2,2-Bis(4-phenyl-2*H*-1,2,4-triazoline-3,5-dionyl)-5,5-dimethyl-1,3-cyclohexanedione (13). 5,5-Dimethyl-1,3-cyclohexanedione (DMCHD; 0.20 g, 1.43×10^{-3} mol) in 50 mL of ethyl acetate was added to 0.5 g (2.86×10^{-3} mol) of PhTD in 50 mL of this solvent. The reaction was complete in 1 h. Crystallization was accomplished by addition of hexane to cloudiness, heating to again obtain solution, and subsequent slow cooling: mp 218 °C dec; IR (Nujol) 3200 (m), 3100 (m), 2900 (s), 1792 (w), 1770 (m), 1740 (s), 1700 (s), 1600 (w), 1505 (m), 1495 (w), 1460 (s), 1415

(m), 1380 (m), 1320 (w), 1270 (m), 1240 (w), 1220 (w), 1185 (m), 1160 (m), 1080 (w), 1065 (w), 1030 (w), 1010 (w), 970 (w), 940 (w), 920 (w), 845 (w), 805 (w), 770 (m), 760 (w), 740 (w), 715 (w), 705 (w), 690 (w), 645 (m) cm^{-1}; NMR (Me_2SO-d_6) δ 7.5 (s, 5), 3.0 (s, 4), 1.1 (s, 6).

Anal. Calcd for $C_{24}H_{22}N_6O_6$: C, 58.78; H, 4.49; N, 17.14. Found: C, 59.02; H, 4.55; N, 17.49.

Registry No. 1, 72708-70-4; 2, 72708-71-5; 3, 72708-72-6; 4, 72708-73-7; 5, 72708-74-8; 6, 72708-75-9; 7, 72708-76-0; 8, 72708-77-1; 9, 72708-78-2; 10, 72708-79-3; 11, 72708-80-6; 12, 72708-81-7; 13, 72708-82-8; PhTD, 4233-33-4; PD, 123-54-6; CHD, 504-02-9; EtAA, 141-97-9; ToPD, 72708-83-9; DBzM, 120-46-7; MeTD, 13274-43-6; DMCHD, 126-81-8.

Supplementary Material Available: NMR spectra of compounds 2 (in Me_2SO-d_6, Figure 1), 5 (in $CDCl_3$, Figure 2), 9 (aromatic region, Figure 3), and 11 (aromatic region, in Me_2SO-d_6, Figure 4) before and after addition of D_2O and tabulation of NMR (Table I), IR, and UV (Table II) data for compounds 1–13 (6 pages). Ordering information is given on any current masthead page.

Photostimulated Reactions of *N,N*-Disubstituted Amide Enolate Anions with Haloarenes by the $S_{RN}1$ Mechanism in Liquid Ammonia [1]

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The photostimulated reactions of chloro-, bromo-, and iodobenzenes, 1-chloronaphthalene, and 9-bromophenanthrene with the enolate anion of *N*-methyl-*N*-phenylacetamide in liquid ammonia gave good yields of substituted products. In the dark, iodobenzene gave 34% of substitution product, but chlorobenzene did not react. The enolate anion of *N,N*-dimethylacetamide was only partially soluble in liquid ammonia, but good yields of substitution products were obtained. The enolate anion of *N*-acetylpiperidine was insoluble in liquid ammonia, but the enolate anion of *N*-acetylmorpholine was soluble and good yields of substitution products were obtained under photostimulation. It is suggested that these reactions occur by the $S_{RN}1$ mechanism of aromatic substitution.

Subsequent to the discovery that ketone enolate anions can be arylated by the photostimulated $S_{RN}1$ mechanism in liquid ammonia,[2] this type of reaction has been demonstrated to have wide applicability as to both the aromatic substrates and the ketone enolate anions that can be successfully employed.[3,4]

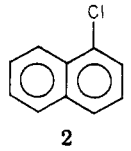
The photostimulated arylation of ester enolate anions, such as *tert*-butyl acetate enolate anion, has been carried out by several research groups.[5-7] The photostimulated arylation of enolate anions derived from aldehydes was attempted, but their very low reactivity and the high yields of dehalogenation products obtained make this reaction useless for synthetic purposes.[7]

We now report the reactions of haloarenes with several *N,N*-disubstituted amide enolate anions in liquid ammonia under photostimulation by the $S_{RN}1$ mechanism.

Results and Discussion

The anion of acetamide formed in liquid ammonia by acid–base reaction with amide ions failed to undergo photostimulated reaction with 1-chloronaphthalene (2). The reason is probably that the hydrogens attached to nitrogen are much more acidic than the hydrogens attached to the carbon atom; thus the enolate anion is not formed at all, and the nitranion nucleophile (eq 1) is apparently not a good nucleophile for the photostimulated $S_{RN}1$ reaction (eq 2). The p*K* for dissociation of the N–H

$$CH_3CONH_2 + NH_2^- \rightarrow \underset{1}{CH_3CONH^-} + NH_3 \quad (1)$$



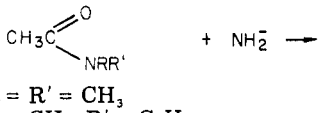
$$+ \ 1 \xrightarrow{h\nu} \text{no reaction} \quad (2)$$

2

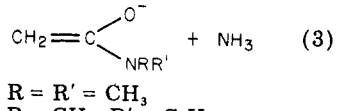
bond in acetamide is 25.5 in Me_2SO whereas the p*K* for dissociation of the C–H bond in *N,N*-dimethylacetamide is above 32.[8] Although these values are not known in liquid ammonia, it is reasonable to expect the same order, namely, $pK_{C-H} > pK_{N-H}$.

The nucleophile 1 and the anion derived from *N*-methylacetamide have been shown to be unreactive toward aryl radicals in reactions stimulated by electrons from an electrode.[9]

On the other hand, *N,N*-disubstituted amide enolate anions are known to be formed in liquid ammonia by acid–base reaction with amide ion (eq 3).[10]



3a, R = R′ = CH_3
b, R = CH_3, R′ = C_6H_5



(3)

4a, R = R′ = CH_3
b, R = CH_3, R′ = C_6H_5

(1) This research was supported in part by the Consejo Nacional de Investigaciones Científicas y Técnicas and the Secretaría de Ciencia y Tecnología, Argentina.
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