Triazolinediones. Conversion to Deaza Dimers by Electron-Transfer Catalysis. A Possible Radical Anion Diels–Alder Reaction[1]

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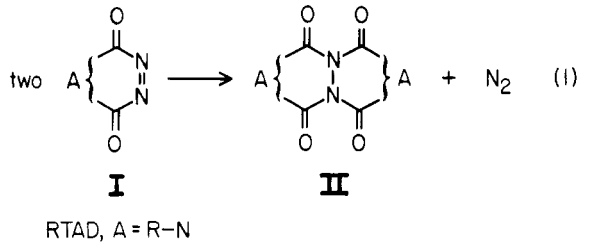
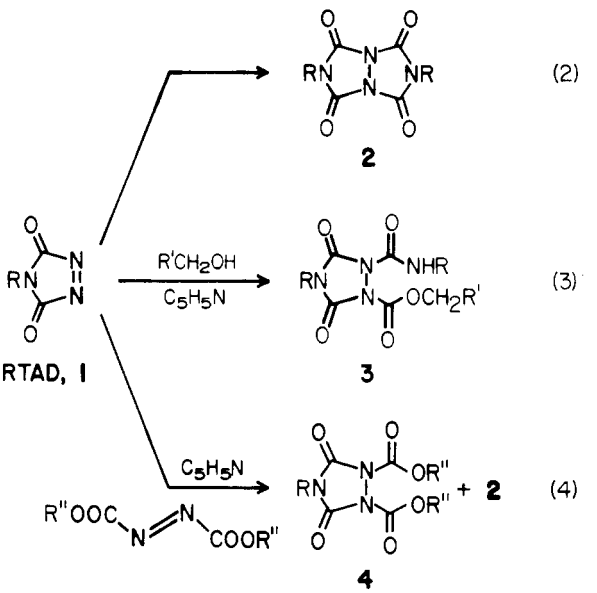
1,2,4-Triazolinediones, 4-RTAD (1), are converted to dimeric products (deaza dimers 2) with loss of dinitrogen by a variety of agents of which the most effective are good single-electron donors (sodium naphthalenide, sodium iodide, sodium metal). The reaction is retarded by tetracyanoethylene or lead tetraacetate (electron acceptors). A radical anion chain reaction is proposed (Scheme IV and eq 9–12) in which the overall result is the reaction of two RTAD → deaza dimer 2 + N_2, catalyzed by electron donors. The sequence suggested includes the [4 + 2] cycloaddition of RTAD$^{-\cdot}$ with the dienophile RTAD, the first example (of which we are aware) of a radical anion Diels–Alder reaction. In the presence of an alcohol (e.g., methanol) PhTAD is converted, again in a catalyzed reaction (e.g., sodium iodide), to a methanol addition product, formulated as **3a** (eq 5a, 15, and 17 and Scheme V).

Triazolinediones,[2] RTAD (1; also I with A = RN) exhibit a wide range of reactivity and reaction types[3,4] including some "self-reactions". This last group includes polymerization of RTAD by light[3g] and conversion of RTAD to "dimeric" products with loss of dinitrogen (eq 1).[3d] The



deaza dimer 2 (also II with A = RN) has been observed by several groups.[3d,5] The conversion of cyclic azodicarbonyl compounds to deaza dimers has also been observed in several other systems[6] (e.g., A = C_6H_4,[6a] A = C_2H_2,[6a] A = $(Et)_2C$[6b,c]).

The conversion of RTAD to deaza dimer 2 occurs on heating,[5] and it is more rapid in the presence of urazole[2] 5[5b] or pyridine (eq 2).[3d] In the presence of pyridine and an alcohol, PhTAD is converted to the substituted urazole 3 (eq 3) of composition equal to deaza dimer plus the alcohol.[3d,7] However, compound 3 does *not* arise by alcoholysis of deaza dimer 2, implying that the alcohol intercepts an intermediate. Also, in the pyridine-promoted conversion of PhTAD to deaza dimer, inclusion of a large excess of diethyl azodicarboxylate results in the formation of some substituted urazole 4 (eq 4),[3d] again pointing to the trapping of an intermediate.



We have obtained some results that provide new insight on the nature of the intermediates and on the course of these reactions.

(1) This work has been supported in part by the National Science Foundation and by the National Institutes of Health (under NCI Training Grant NIH-5-T32CA09112).

(2) We use here the common names *triazolinedione* for structure 1 and *urazole* for structures 3–5. The Chemical Abstracts name for structure 1 (R = Ph) is 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione; the name for structure 5 is 4-phenyl-1,2,4-triazolidine-3,5-dione.

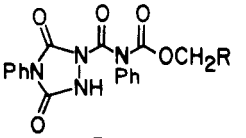
(3) (a) Cycloaddition, "ene" reaction, addition–rearrangement: see ref 4 (first paragraph and footnotes 2a–k). (b) Addition–rearrangement: Adam, W.; Carballeira, N. *J. Am. Chem. Soc.* **1984**, *106*, 2874. (c) Oxidation of alcohols: Cookson, R. C.; Stevens, I. D. R.; Watts, C. T. *J. Chem. Soc., Chem. Commun.* **1966**, 744. (d) Dao, L. H.; Mackay, D. *Can. J. Chem.* **1979**, *57*, 2727. (e) Aromatic substitution: Hall, J. H. *J. Org. Chem.* **1983**, *48*, 1708. (f) Aromatic substitution: Hall, J. H.; Kaler, L.; Herring, R. *J. Org. Chem.* **1984**, *49*, 2579. (g) Pirkle, W. H.; Stickler, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 7497.

(4) Cheng, C.-C.; Seymour, C. A.; Petti, M. A.; Greene, F. D.; Blount, J. F. *J. Org. Chem.* **1984**, *49*, 2910.

(5) (a) Stollé, R. *Chem. Ber.* **1912**, *45*, 273. (b) Wamhoff, H.; Wald, K. *Chem. Ber.* **1977**, *110*, 1699.

(6) (a) Kealy, T. J. *J. Am. Chem. Soc.* **1962**, *84*, 966. (b) Gillis, B. T.; Izydore, R. A. *J. Org. Chem.* **1969**, *34*, 3181. (c) Evnin, A. B.; Lam, A. Y.; Maher, J. J.; Blyskal, J. J. *Tetrahedron Lett.* **1969**, 4497. (d) Stetter, H.; Woernle, P. *Justus Liebigs Ann. Chem.* **1969**, *724*, 150.

(7) (a) Another possible structure for urazole 3 is the isomer **3-iso** suggested by Izydore, Johnson, and Horton (ref 7b). Spectral data do not appear to us to provide a distinction. The actual structure is, of course, of interest but it is not of mechanistic significance in the present context,



because a simple intramolecular acyl transfer could interconvert 3 and **3-iso**. The compound to which structure 3 is assigned is not extracted from an organic solvent by aqueous base; this is consistent with structure 3 rather than **3-iso** (the pK_A of urazoles with a hydrogen at N-1 or N-2 is approximately 5 [ref 28]); also see the Experimental Section of the present paper. For additional information on compounds of type 3 and **3-iso** see ref 3d and 7b. (b) Izydore, R. A.; Johnson, H. E.; Horton, R. T. *J. Org. Chem.* **1985**, *50*, 4589.

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Table I. Conversion of *N*-Phenyltriazolinedione (PhTAD) into Deaza Dimer 2[a]

PhTAD, M	catalyst, M[b]	solvent	time, h	deaza dimer 2, %
(0.10)	Pyr (0.040)	CH_2Cl_2	8.5	50
(0.10)	DMP (0.040)	CH_2Cl_2	3.5	70
(0.10)	TMP (0.040)	CH_2Cl_2	1	75
(0.20)	DTP (0.03)	CH_2Cl_2	100	35
(0.20)	NaNaph (0.0012)	THF	0.25	95
(0.20)	NaI (0.022)	Me_2CO	0.25	95
(0.40)	*t*-BuOK (0.037)	Me_2SO	1	100
(0.40)	Na (0.25)[c,d]	THF	25	95
(0.50)	CuCl (0.05)[c,d]	dioxane	25	75
(0.20)	CuCl (0.021)[c,d]	CH_2Cl_2	40	70
(0.10)	Cp_2Fe (0.05)[e]	CH_2Cl_2	3	45
(0.14)	$(t\text{-Bu})_2NO$ (0.14)[e]	CH_2Cl_2	5.5	60
(0.17)	*f*	THF	2[f]	60[g]

[a] Room temperature, 23 °C. [b] Pyr = pyridine, DMP = 2,6-dimethylpyridine, TMP = 2,4,6-trimethylpyridine, DTP = 2,6-di-*tert*-butylpyridine, Cp_2Fe = ferrocene, NaNaph = sodium naphthalenide. [c] Ratio of catalyst to PhTAD. [d] Heterogeneous. [e] See ref 10b. [f] Heat at 68 °C. [g] Plus 40% of 4-phenyl-1-(tetrahydro-2-furanyl)-1,2,4-triazolidine-3,5-dione; also, see ref 5b.

Table II. Effect of Tetracyanoethylene (TCNE) on the Conversion of PhTAD to Deaza Dimer 2 Catalyzed by 2,4,6-Trimethylpyridine[a]

TCNE, M	time, h[b]	deaza dimer 2, %
0	3	90
0.002	3	90
0.014	24	65
0.025	48	50

[a] Reactions were conducted with 0.50 mmol of PhTAD and 0.05 mmol of 2,4,6-trimethylpyridine in 4 mL of CH_2Cl_2 at room temperature. [b] Time for decolorization.

Results

Triazolinediones (e.g. 1, R = phenyl, methyl, benzyl) are converted to deaza dimer **2** (eq 2) upon heating in a variety of solvents. We have confirmed the observation of Dao and Mackay that the reaction is accelerated by pyridine and find that more hindered pyridines (e.g., 2,6-dimethylpyridine) are also effective. The observation that hindered pyridines accelerated the reaction suggested that they were not acting as nucleophiles (the role ascribed to them in the previous study[3d]) but possibly as bases or as electron donors. Several other types of electron donors were examined and found to accelerate the reaction of eq 2. The results are summarized in Table I. The most active systems are sodium naphthalenide in THF (fifth entry) and sodium iodide in acetone (sixth entry). Sodium metal in THF and potassium *tert*-butoxide in Me_2SO are also effective. Ferrocene (eleventh entry) accelerates the disappearance of PhTAD, but the reaction is now more complex, involving some consumption of ferrocene as well as ferrocene-promoted conversion of RTAD to deaza dimer **2**.

The amount of "initiator" needed is often small (e.g., sodium napthalenide is very effective even at a Na^+-$Naph^-\cdot$/PhTAD ratio of 0.005). Also, in the reaction of the third entry analysis by GC showed little or no consumption of the 2,6-dimethylpyridine.

Retardation of the Reaction. The conditions effective in promoting the reaction (Table I) pointed to the possibility of a chain reaction, and the types of agents further were suggestive of a radical anion chain. The effect of some additives on the 2,4,6-trimethylpyridine-promoted reaction was examined. Tetracyanoethylene (TCNE, Table II) and lead tetraacetate (Table III) retarded the rate.

Effect of R in RTAD. Three RTAD's have been examined: PhTAD, $PhCH_2TAD$, and MeTAD. In the reaction initiated by sodium naphthalenide in THF, the order of reactivity is PhTAD > $PhCH_2TAD$ ≫ MeTAD. Subjection of PhTAD and MeTAD in a 1:1 ratio to the reaction conditions afforded a mixture of the three possible deaza dimers, (Ph,Ph), (Ph,Me), and (Me,Me), shown by NMR to be present in the ratio of 1:2:1. In the reaction initiated by sodium iodide in acetone, PhTAD is again more reactive than MeTAD, but the difference is much less than that seen with sodium naphthalenide.

Table III. Effect of Lead Tetraacetate on the Conversion of PhTAD to Deaza Dimer 2 Catalyzed by 2,4,6-Trimethylpyridine[a]

$Pb(OAc)_4$, M	induction time[b]	time for decolorization, h	deaza dimer 2, %
0	30 s	6	90
0.004	90 min	12	90
0.01	6 h	22	85
0.022	26 h	33	80[c]
0.04	>50 h	72	75[c]

[a] Reactions were conducted with 1.0 mmol of PhTAD and 0.097 mmol of 2,4,6-trimethylpyridine in 5 mL of CH_2Cl_2 at room temperature. [b] Time before precipitation of deaza dimer. [c] Lead diacetate also present.

Table IV. Effect of Sodium Iodide and Methanol on the Consumption of PhTAD

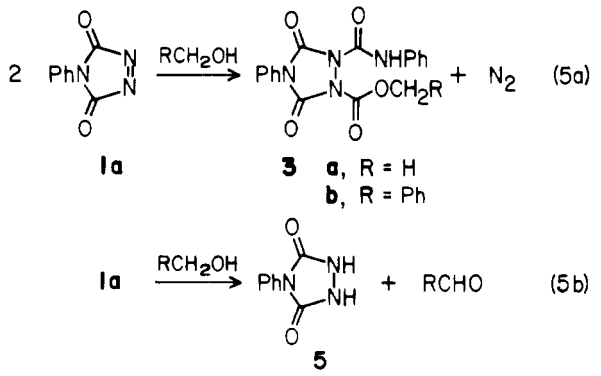
NaI, 10^3M	MeOH, M	time	products: 2	products: 3a
2.3[a]	0	45 min	√	×
4.5[a]	0	2.5 min	√	×
9.0[a]	0	1 min	√	×
22.0[a]	0	30 s	95%	×
0[b]	0.2	25 h	2%	68%
0.4[b]	0.2	6 h	4%	77%
2.0[b]	0.2	2.5 h	8%	71%
5.0[b]	0.2	1 h	11%	62%

[a] Reactions were conducted with 0.2 mmol of PhTAD in 1 mL of acetone at room temperature. [b] Reactions were conducted with 1.0 mmol of PhTAD in 5 mL of acetone at room temperature.

Effect of Solvent. (a) Acetic Acid. Addition of a solution of sodium iodide in acetone to PhTAD in acetic acid results in immediate reduction to the *N*-phenylurazole **5**.[5a,8]

(b) Alcohols. In the presence of methanol, PhTAD is converted to urazole **3a** (eq 5a) in a reaction that is markedly accelerated by sodium iodide (Table IV). As noted above, in the absence of the alcohol, PhTAD is converted by sodium iodide to the deaza dimer **2**. Table V summarizes some results for benzyl alcohol. In the absence of sodium iodide, the major reaction of PhTAD and benzyl alcohol is oxidation–reduction affording *N*-

(8) Clement, R. A. *J. Org. Chem.* **1960**, *25*, 1724.



phenylurazole **5** and benzaldehyde (eq 5b, R = phenyl). Sodium iodide increases the rate of consumption of PhTAD, favoring the formation of urazole **3b** (the major product) and deaza dimer **2** relative to benzaldehyde.

ESR Studies. The ESR spectra of the radical anions of PhTAD and MeTAD have been reported (well-resolved 15-line pattern for PhTAD).[9] Addition of a small amount of potassium *tert*-butoxide to a Me_2SO solution of PhTAD afforded this ESR signal. Solutions of PhTAD in THF with sodium naphthalenide or 2,4,6-trimethylpyridine and solutions of PhTAD in acetone containing sodium iodide afforded weak ESR signals, unlike the spectrum in Me_2SO containing potassium *tert*-butoxide.

Discussion

Several mechanisms have been suggested for the deaza dimerization reaction (Scheme I, eq 6,[5a] 7,[5b] and 8[3d]).

The principal findings of the present study are as follows: (a) a variety of agents effect the transformation of RTAD to deaza dimer; (b) the most effective agents are good single-electron donors; (c) in many instances, the agent need be present in only a small amount; (d) the transformation of RTAD to deaza dimer **2** and N_2 is retarded by certain electron acceptors (e.g., lead tetraacetate and tetracyanoethylene). These findings point to a mechanism as shown in Scheme II. Reactant is converted to product by a radical anion chain reaction in which initiation is effected by electron donation from, e.g., sodium metal, iodide ion, the naphthalene radical anion, etc. to RTAD.

In the presence of alternate electron acceptors [TCNE (tetracyanoethylene), lead tetraacetate, etc.] the concentration of $RTAD^{-}\cdot$ may be too low to carry on the chain at an adequate rate. Reduction potentials for some of the substances of this study are as follows ($E_{1/2}$ in acetonitrile vs. SCE): TCNE,[10] +0.24 V; chloranil (tetrachloro-1,4-benzoquinone),[10] +0.01 V; PhTAD,[3b] +0.05 V. The retarding effect of TCNE in the RTAD–deaza dimer reaction is in accord with these data. The observation that chloranil has very little effect may be ascribed to the substance acting in this reaction as a chain transfer agent for electrons rather than as an "electron sink".

Some alternatives to Scheme II are shown in Scheme III. Either $7^{-}\cdot$ or **7** could account for the ultimate formation of deaza dimer. However, the addition of an

(9) (a) Russell, G. A.; Blankespoor, R. L.; Mattox, J.; Whittle, P. R.; Symalla, D.; Dodd, J. R. *J. Am. Chem. Soc.* **1974**, *96*, 7249. (b) Alberti, A.; Pedulli, G. F. *J. Org. Chem.* **1983**, *48*, 2544. (c) Hall, J. H.; Bigard, W. E.; Fargher, J. M.; Jones, M. L. *J. Org. Chem.* **1982**, *47*, 1459.

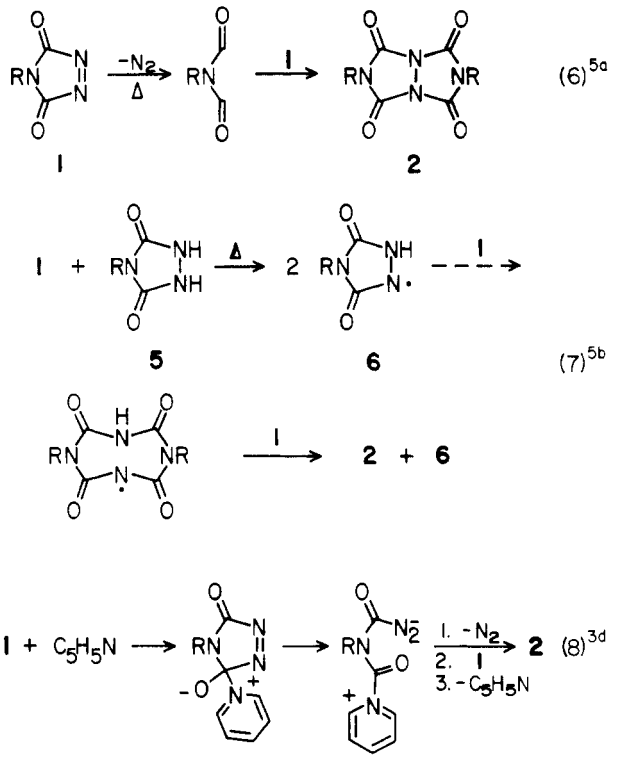
(10) (a) Meites, L.; Zuman, P. "Handbook Series in Organic Electrochemistry"; CRC Press: Cleveland, OH, 1977; Vol. I. (b) Oxidation potentials in acetonitrile vs. SCE: ferrocene, +0.35 V (ref 10a); di-*tert*-butylnitroxyl, +0.51 V [Sümmermann, W.; Deffner, U. *Tetrahedron* **1975**, *31*, 593. See also Semmelhack and Schmid (Semmelhack, M. F.; Schmid, C. R. *J. Am. Chem. Soc.* **1983**, *105*, 6732) for electrochemical generation and use of 1-oxo-2,2,6,6-tetramethylpiperidinium ion].

Table V. Effect of Sodium Iodide on the Reaction of Benzyl Alcohol and PhTAD[a]

NaI, 10^3M	2, %	3b, %	C_6H_5CHO, %
0[b]	0	20[b]	80[b]
0.025	0	0	65
0.1	0	≃10	40
0.5	5	major	10
5.0	20	major	1

[a] Reactions were conducted with 0.50 mmol of PhTAD, 0.500 mmol of benzyl alcohol and 0.163 mmol of *n*-tridecane in 2 mL of acetone at room temperature. [b] In benzene (ref 3d).

Scheme I



Scheme II

Initiation:

$$RTAD + B^{-}\cdot \text{ (or B)} \rightarrow RTAD^{-}\cdot + B \text{ (or } B^{+}\cdot) \quad (9)$$

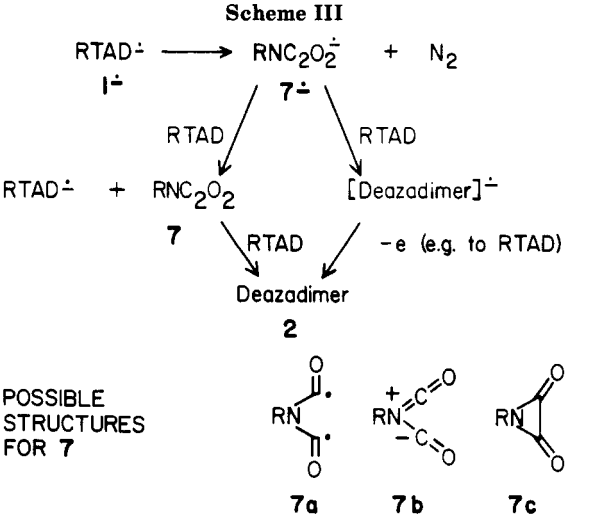
Propagation:

$$RTAD^{-}\cdot + RTAD \rightarrow [RTAD]_2^{-}\cdot \quad (10)$$

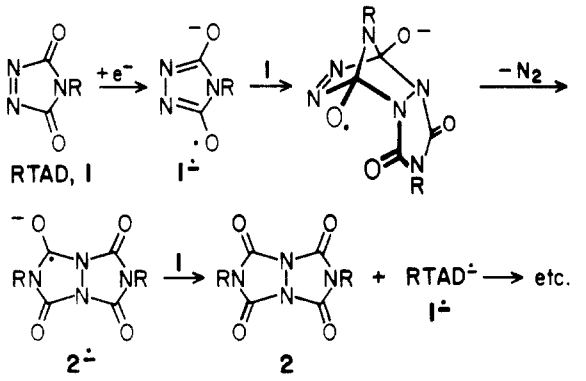
$$[RTAD]_2^{-}\cdot \rightarrow N_2 + [\text{deaza dimer}]^{-}\cdot \quad (11)$$

$$[\text{deaza dimer}]^{-}\cdot + RTAD \rightarrow \text{deaza dimer} + RTAD^{-}\cdot \quad (12)$$

Scheme III

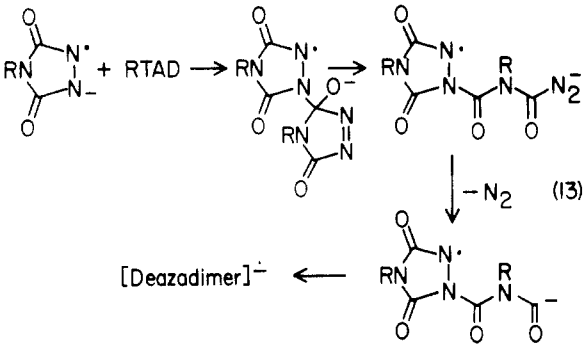


Scheme IV



electron to RTAD would be expected to *strengthen*,[11] not weaken, the carbonyl carbon to "azo" nitrogen bonds in RTAD⁻·. Secondly, the conversion of other types of azodicarbonyl compounds to deaza dimers (e.g., eq 1, A = R_2C[6b,c]) is in better accord with Scheme II than Scheme III; the structures corresponding to **7** in which "RN" is replaced by "R_2C" would be very unstable. Thirdly, the results of the RTAD–alcohol reaction (discussed below) also are in better accord with Scheme II than Scheme III.

Nature of the Dimerization Step (Scheme II, Eq 10). The problem is how best to put two RTAD's together with the overall loss of dinitrogen. One way is closely related to that proposed earlier by Dao and Mackay for the pyridine-catalyzed conversion of RTAD to deaza dimer (eq 8).[3d] The analogous step here would be nucleophilic addition of RTAD⁻· (instead of pyridine) to a carbonyl group of another RTAD (eq 13).



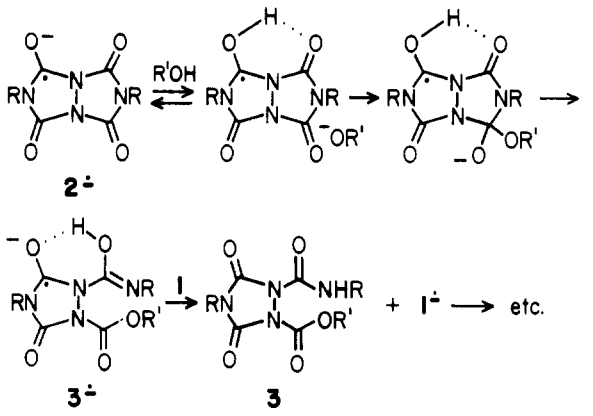
(13)

Another, and in our view superior, way is via cycloaddition as shown in Scheme IV. Simple variants on this scheme can also account for the formation of deaza dimers from other cyclic azodicarbonyl compounds.[6]

An important feature is the recognition that triazolinediones (RTAD's) are heterocyclic analogues of quinones; the one-electron reduction species, RTAD⁻·, may best be represented as shown in Scheme IV. In this form, one notes the "dienic" character and also the location of an alkoxide substituent that might be expected to provide acceleration in cycloaddition reactions.[12a] Furthermore, the reaction solution contains one of the most reactive dienophiles, RTAD. [4 + 2] cycloaddition[12b] and loss of dinitrogen affords the radical anion of the product, which then can transfer an electron to another RTAD.

Our preference for Scheme IV over eq 13 is based on several grounds, primarily the "trapping" experiments. RTAD is converted to the substituted urazoles **3** in the presence of alcohols and to the substituted urazoles **4** in the presence of dialkyl azodicarboxylates. Both of these reactions (discussed in more detail below) are promoted by electron-transfer agents, with the implication that the formation of deaza dimer **2**, urazole **3**, and urazole **4** proceed through common intermediates. The acyl anion of eq 13 would be expected to be protonated in the presence of an alcohol; problems also arise in the conversion of RTAD⁻· and dialkyl azodicarboxylates to urazole **4**. All three reactions (formation of deaza dimer **2**, urazole **3**, and urazole **4**) are accomodated by Scheme IV and simple extensions thereof (described below).

Scheme V



Effect of Other Additives. (a) Trapping by Azodicarboxylates. Dao and Mackay found that in the pyridine-promoted conversion of PhTAD to deaza dimer[3d] inclusion of a large excess of diethyl azodicarboxylate resulted in the formation of some of the substituted urazole **4** (eq 4), which they attributed to the addition of $^+$Py-CON(Ph)CO$^-$ (derived by loss of N_2 from the corresponding zwitterion in eq 8) to the azodicarboxylate, followed by cyclization and ejection of pyridine.[3d,13] Under sodium iodide catalysis, we also find that some **4** is formed from PhTAD in the presence of a large excess of an azodicarboxylate. We suggest that **4** is formed by the same type of reaction sequence shown in Scheme IV: cycloaddition of PhTAD⁻· with dimethyl azodicarboxylate,[14] followed by loss of dinitrogen to give **4**⁻·, and electron transfer from **4**⁻· to PhTAD.

(b) RTAD–Alcohol Reactions. RTAD in the presence of alcohols is converted to the substituted urazoles **3** (eq 5a), the deaza dimer **2** (now a minor product), and oxidation–reduction products (*N*-phenylurazole and the aldehyde or ketone corresponding to the alcohol, eq 5b). Sodium iodide and the pyridines accelerate the conversion of RTAD to deaza dimer *and to the substituted urazole*

$$\text{RTAD} \xrightarrow{\text{acetone, 25 °C}} \text{no reaction} \quad (14)$$

$$\text{RTAD} \xrightarrow[\text{slow}]{\text{acetone + MeOH (dilute)}} \text{substituted urazole } \mathbf{3a} \quad (15)$$

$$\text{RTAD} \xrightarrow[\text{fast}]{\text{acetone, NaI}} \text{deaza dimer } \mathbf{2} + N_2 \quad (16)$$

$$\text{RTAD} \xrightarrow[\text{fast}]{\text{acetone, MeOH, NaI}} \mathbf{3}\ (\text{major}) + \mathbf{2}\ (\text{minor}) \quad (17)$$

$$\mathbf{2} + \text{MeOH} \not\rightarrow \mathbf{3a} \quad (18)$$

(11) Based on simple MO considerations for the LUMO of RTAD.

(12) (a) Lutz, R. P. *Chem. Rev.* **1984**, *84*, 205. (b) An example of a [4 + 2] cycloaddition of PhTAD with a neutral cyclic 2,3-diaza 1,3-diene (4*H*-3,4,4,5-tetramethyl-1,2-pyrazole) has been reported: Evnin, A. B.; Arnold, D. R. *J. Am. Chem. Soc.* **1968**, *90*, 5330.

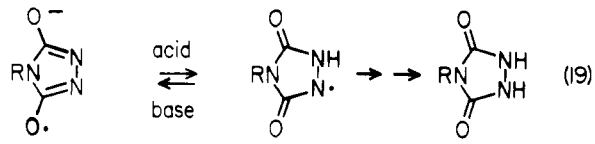
(13) Reference 3d also includes the possibility of formation of **4** by capture of **7** by azodicarboxylate.

(14) For comparison of PhTAD, dimethyl azodicarboxylate, and related species in cycloaddition reactions, see: Huisgen, R.; Xingya, L. *Tetrahedron Lett.* **1983**, *24*, 4185 and references cited therein.

3 but do not appear to enhance the oxidation–reduction reaction.

These observations suggest a relationship between the formation of deaza dimer **2** and substituted urazole **3**. A simple expansion of Scheme IV will suffice (Scheme V).[15] The observations of eq 14–18 have a bearing on some of the alternative routes shown in Scheme III; **7**$^{-}\cdot$ (**a**, **b**, or **c**), **7b**, and **7c** might be expected to react more rapidly with methanol than with PhTAD and to lead to RN(CHO)-$COOCH_3$ and/or $RNHCOCOOCH_3$ rather than to **3a**.

(c) Reaction in Acetic Acid. In acetic acid, the reaction of RTAD with sodium iodide takes a different course—reduction of PhTAD to *N*-phenylurazole rather than formation of the deaza dimer. This is also understandable in terms of Scheme IV: protonation of RTAD$^{-}\cdot$ to afford the urazolyl radical, followed by further reduction (eq 19).

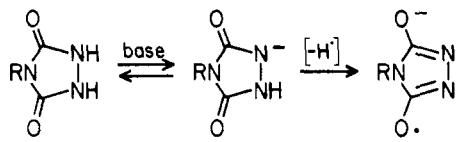


(19)

1$^{\cdot}$ **6** **5**

Initiation Step. Initiation of the radical anion chain reaction of Scheme II by electron donors such as sodium naphthalenide, sodium metal, or sodium iodide poses no problem. Less obvious is the promotion by *N*-phenylurazole (**5**, R = phenyl). Conversion of PhTAD to deaza dimer promoted by urazole **5** (a much slower reaction than those of Table I) has been suggested to proceed via a urazolyl radical. Although the route suggested[5b] (eq 7) has some drawbacks, the urazolyl radical, **6**, may indeed be present under those conditions.[16] We note that RTAD$^{-}\cdot$ is the conjugate base of the urazolyl radical (see eq 19); consequently a radical anion path (as in Scheme II) also may be operative in the urazole-promoted conversion of RTAD to deaza dimer **2**.

Still less obvious is the acceleration by pyridine and the alkyl-substituted pyridines. The marked retardation of the 2,4,6-trimethylpyridine-accelerated reaction by lead tetraacetate (e.g., ratio of PhTAD/2,4,6-trimethylpyridine/$Pb(OAc)_4$ = 1:0.1:0.02; see Table III) strongly implies that the pyridine-promoted conversion of RTAD to the deaza dimer is also a chain reaction. The pyridines are not notably good electron donors.[10,17] Could the pyridines be functioning as bases to convert some adventitious urazole or urazolyl radical to PhTAD$^{-}\cdot$ (eq 20, 19)?



(20)

5 **1**$^{\cdot}$

Addition of 10 mol % of urazole **5** to PhTAD and pyridine produces only a minor increase in the rate of consumption of PhTAD, thus providing no support for eq 20 as an explanation of the pyridine-promoted conversion of PhTAD to deaza dimer **2**. The possibility of **6** → **1**$^{-}\cdot$ is not excluded, although examination of the PhTAD in the ESR did not indicate the presence of the urazolyl radical **6**.[9b,c] Perhaps some complex of a pyridine and PhTAD is a better initiator than the pyridine alone.

The results of this study provide an interesting comparison with the $S_{RN}1$ reaction[18]—in particular, conversion of radical anions into radicals and anions and the reverse ($S_{RN}1$, eq 21 and 22) and conversion of radical anions into neutral species and new radical anions and the reverse (this study, eq 25 and 24).

$S_{RN}1$:

$$A^{-}\cdot \rightarrow C\cdot + D^{-} \quad (21)$$

$$C\cdot + B^{-} \rightarrow E^{-}\cdot \quad (22)$$

$$E^{-}\cdot + A \rightarrow E + A^{-}\cdot \quad (23)$$

net: $A + B^{-} \rightarrow E + D^{-}$

e.g., $ArI + RS^{-} \rightarrow ArSR + I^{-}$

This study:

$$A^{-}\cdot + B \rightarrow C^{-}\cdot \quad (24)$$

$$C^{-}\cdot \rightarrow D + E^{-}\cdot \quad (25)$$

$$E^{-}\cdot + A \rightarrow E + A^{-}\cdot \quad (26)$$

net: $A + B \rightarrow D + E$

e.g., TAD + TAD → N_2 + deaza dimer **2**

A key step in the proposed mechanism is the addition of RTAD$^{-}\cdot$ to another RTAD. The overall result suggested in Scheme IV is [4 + 2] cycloaddition. Questions of interest are the reversibility of the initial interaction and the stability of $A_2^{-}\cdot$. In its simplest form, $A_2^{-}\cdot$ is an "electron sandwich" of two A's (eq 27). How good are such species?

$$A^{-}\cdot + A \rightleftarrows A_2^{-}\cdot \quad (27)$$

One place to explore eq 27 is with A = benzoquinone (we have called attention to the relationship of triazolinediones as heterocyclic analogues of quinones). Meisel and Fessenden have studied the rate of exchange of an electron between benzoquinone radical anion (the "semiquinone") and benzoquinone.[19] Examination of their spectra reveals no evidence for the species $A_2^{-}\cdot$, and consequently the equilibrium constant for eq 27 must be unfavorable in that case. Another place to look for $A_2^{-}\cdot$ is with A = naphthalene. Here, also, studies[20] show no evidence for $[naphthalene]_2^{-}\cdot$. Thus, electron sandwiches composed of two π systems and an electron do not seem to be favorable arrays.[21] Consequently, such species probably are not providing much help in the dimerization reaction of RTAD. The simplest interpretation of this dimerization reaction is that suggested in Scheme IV—[4 + 2] Diels–Alder cycloaddition; the addition of an electron to RTAD

(15) The mode of reaction of methanol with PhTAD (eq 5a) in the absence of promoters (see ref 3d) may differ from the promoted route discussed here.

(16) Some crossover experiments reported in ref 5b strongly imply the presence of urazolyl radicals.

(17) Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S. "Handbook of HeI Photoelectron Spectra"; Halsted Press: New York, 1981.

(18) For reviews, see: Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413. Norris, R. K. In "The Chemistry of Functional Groups"; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1983; Chapter 16; Supplement D. Rossi, R. A.; de Rossi, R. H. *ACS Monogr.* **1983**, *No. 178*.

(19) Meisel, D.; Fessenden, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 7505.

(20) Howarth, O. W.; Fraenkel, G. K. *J. Chem. Phys.* **1970**, *52*, 6258. For studies of intramolecular "two π plus one electron" systems, see: Gerson, F.; Martin, W. B., Jr.; Wydler, C. *J. Am. Chem. Soc.* **1976**, *98*, 1318. These systems are of interest and call attention to the effect of solvent and of cation. However, for the intramolecular cases of "fast exchange", the ESR data do not distinguish between instantaneous delocalization over the two π systems and electron transfer between them at a rate greater than approximately 10^5 s^{-1}. See also: Staab, H. A.; Rebafka, W. *Chem. Ber.* **1977**, *110*, 3333.

(21) Electron-deficient sandwiches (two π systems minus an electron), $A_2^{+}\cdot$, do seem to be stable arrays (ref 20, $[naphthalene]_2^{+}\cdot$; see also: Chiang, T. C.; Reddock, A. H. *J. Chem. Phys.* **1970**, 52, 1371 $[perylene]_2^{+}\cdot$).

has converted it into a species with dienic character. This appears to be the first example of a radical anion Diels–Alder reaction.[22,23]

Experimental Section

General. All reactions were performed under argon at room temperature, with the exclusion of light, unless noted otherwise. Melting points, obtained on a Hoover Mel-Temp apparatus, are corrected.

Solvents were distilled as follows: CH_2Cl_2 and CH_3CN from CaH_2; THF and dioxane from sodium/benzophenone ketyl; acetone from B_2O_3; AcOH from Ac_2O/CrO_3; pyridine from BaO; 2,6-dimethylpyridine from $AlCl_3$; 2,4,6-trimethylpyridine from CaC_2; dimethyl sulfoxide (Me_2SO) from 3-Å molecular sieves.

Tetracyanoethylene (TCNE) was sublimed in vacuo to afford white crystals, mp 198–199 °C. 2,3,5,6-Tetrachloro-2,5-cyclohexadiene-1,4-dione (1,4-chloranil) was sublimed in vacuo to afford yellow crystals, mp 292–293 °C. CuCl was prepared according to the literature procedure.[24] $CuCl_2$ was Aldrich Gold Label, 99.999%. $Pb(OAc)_4$ was recrystallized from $AcOH/Ac_2O$ and stored protected from moisture. NaI was dried at 70 °C in vacuo for 2 days. Ferrocene was sublimed, mp 173–174 °C. Sodium naphthalenide was prepared and titrated according to the literature procedure.[25] 4-Phenyl-, 4-methyl-, and 4-(phenylmethyl)-3*H*-1,2,4-triazole-3,5(4*H*)-dione (PhTAD, MeTAD, and $PhCH_2TAD$ respectively) were prepared according to the literature procedures.[26] Dimethyl diazenedicarboxylate was also prepared according to the literature.[27]

Reaction of Pyridine and PhTAD. Pyridine (3.07 g, 38.8 mmol) was added to a stirred suspension of PhTAD (1.75 g, 10.0 mmol) in 10 mL of CH_2Cl_2. Gas evolved vigorously, and a solid precipitated. After 22 h, the initial red color had faded; the mixture was filtered, and the precipitate was washed with 5 mL of EtOH, leaving a pink powder. Recrystallization from Me_2SO yielded 1.21 g (75%) of white needles, 2,6-diphenyl-1*H*,5*H*-[1,2,4]triazolo[1,2-*a*][1,2,4]triazole-1,3,5,7(2*H*,6*H*)-tetrone (**2a**): mp >350 °C [lit.[5b] mp 345–350 °C]; IR (KBr) 1790 cm^{-1} (vs), 1760 (vs), 1500 (m), 1430 (s), 1165 (s), 1010 (m), 740 (s), 725 (s), 720 (m), 680 (s), 640 (m), 610 (m); ^1H NMR (CD_3SOCD_3) δ 7.50–7.65 (m, 10 H); ^{13}C NMR (CD_3SOCD_3) δ 126.7 (br), 129.3 (br), 129.8, 145.4. A control experiment established that PhTAD is stable in CH_2Cl_2 for at least 4 days.

Reaction of 2,6-dimethylpyridine and PhTAD was carried out by the above procedure, affording **2a**, mp >350 °C, 70% yield. In a separate experiment, analysis of the reaction mixture by gas chromatography (4% SE-30 on Chromosorb G, $^1/_8$ in. × 8 ft, 30 mL of He/min, 60–120 °C) after 24 h demonstrated that none of the 2,6-dimethylpyridine had been consumed in the reaction, relative to *n*-decane as an internal standard. Results of reaction of PhTAD with other substituted pyridines are summarized in Table I.

Reaction of PhTAD in the Presence of $CuCl_2$. Anhydrous $CuCl_2$ (13.4 mg, 0.100 mmol) was suspended in a stirred solution of PhTAD (175 mg, 1.00 mmol) in 2 mL of dioxane. After 54 h, the red suspension was diluted with 5 mL of CH_2Cl_2 and filtered, affording 27.7 mg of an orange-brown solid, a mixture of $CuCl_2$ and **2a**, mp >350 °C, identical with authentic **2a** by IR. The red filtrate was treated with an excess of 2,3-dimethyl-2-butene; evaporation of the solvents in vacuo gave 244.2 mg (94%) of a white residue, mp 128–130 °C, identical with 4-phenyl-1-(1,1,2-trimethyl-2-propenyl)-1,2,4-triazolidine-3,5-dione [lit.[28] mp 130–131 °C] by ^1H NMR.

Reaction of CuCl and PhTAD. Anhydrous CuCl (9.9 mg, 0.10 mmol) was suspended in a stirred solution of PhTAD (175 mg, 1.00 mmol) in 2 mL of dioxane. After 30 h, the red color had faded to brown, and a large amount of precipitate was evident. The mixture was diluted with 5 mL of CH_2Cl_2 after 54 h; filtration yielded 131 mg (75%) of a brown solid, mp >350 °C, identical with **2a** by IR. Reaction in CH_2Cl_2 instead of dioxane afforded a 70% yield of **2a**.

Reaction of Di-*tert*-butylnitroxyl and PhTAD. Di-*tert*-butylnitroxyl (100.2 mg, 0.6958 mmol) was added to a stirred solution of PhTAD (122.1 mg, 0.6973 mmol) in 5 mL of CH_2Cl_2. A precipitate slowly formed; after 5 h, the color of the solution had changed from dark red to pale green. Filtration of the mixture afforded 64.6 mg (58%) of a pink powder, mp > 350 °C, identical with **2a** by IR.

Effect of TCNE on the Reaction of 2,4,6-Trimethylpyridine and PhTAD. TCNE (13.1 mg, 0.102 mmol) and PhTAD (174.7 mg, 0.9977 mmol) were dissolved in 4 mL of CH_2Cl_2. 2,4,6-Trimethylpyridine (12.1 mg, 0.100 mmol) was added to the stirred solution, and gas evolution proceeded at a moderate pace. After 42 h, the red-orange mixture was filtered, affording 115.2 mg (72%) of an off-white powder, mp >350 °C, identical with **2a** by IR. The orange filtrate was treated with an excess of 2,3-dimethyl-2-butene, and the solvents were removed in vacuo. ^1H NMR analysis of the orange residue revealed a trace of the ene product and a disproportionately large number of aryl protons. Product yields of **2a** under other conditions are summarized in Table II.

Effect of $Pb(OAc)_4$ on the Reaction of 2,4,6-Trimethylpyridine and PhTAD. 2,4,6-Trimethylpyridine was added to stirred solutions of PhTAD and $Pb(OAc)_4$ in 5 mL of CH_2Cl_2. The reactions had varying induction periods before the beginning of decolorization and precipitation of **2a**. All precipitates were nearly identical with **2a** by IR. Amounts of reagents, yields of **2a**, induction times, and times to completion are listed in Table III. Yields of **2a** in entries 4 and 5 of Table III are corrected for coprecipitated $Pb(OAc)_2$ (determined by ^1H NMR). A control experiment showed that $Pb(OAc)_4$ and 2,4,6-trimethylpyridine did not react in CH_2Cl_2 for at least 24 h.

Reaction of Ferrocene and PhTAD. Ferrocene (93.0 mg, 0.500 mmol) was added to a stirred solution of PhTAD (175.2 mg, 1.000 mmol) in 10 mL of CH_2Cl_2. Over 30 min, the solution became black and a precipitate formed. After 3 h the mixture was filtered, affording 71.0 mg (44%) of an off-white powder, **2a**, mp >350 °C. Column chromatography of the filtrate (alumina I/hexane) afforded 50.7 mg (55%) of ferrocene. In another experiment, PhTAD (175 mg, 1.00 mmol) and ferrocene (9.0 mg, 0.05 mmol) gave 46.8 mg (29%) of **2a**. Also, when PhTAD (175 mg, 1.00 mmol) in 10 mL of CH_2Cl_2 was added, over 2 h, to a stirred solution of ferrocene (180 mg, 0.968 mmol) in 4 mL of CH_2Cl_2, filtration after 3 h gave 35.4 mg (22%) of **2a**.

Reaction of Na and PhTAD. Na (10.8 mg, 0.470 mmol) was added to a stirred solution of PhTAD (350.0 mg, 1.999 mmol) in 5 mL of THF. Gas began to evolve, and a precipitate began to form in 1 min. After 27 h, the colorless mixture was filtered to afford 310.7 mg (96%) of a white solid, identical with **2a** by IR. In a separate experiment, PhTAD was allowed to react with a Na mirror (PhTAD (83.0 mg, 0.474 mmol) in 4 mL of THF), yielding 76.2 mg (100%) of **2a** in 30 min.

Reaction of Sodium Naphthalenide and PhTAD. A solution of PhTAD (349.2 mg, 1.994 mmol) in 10 mL of THF was connected to a thermostated gas buret. A solution of sodium naphthalenide in THF (100 μL, 0.119 M, 11.9 μmol) was added to the stirred PhTAD solution. Vigorous gas evolution began, and a precipitate formed. After 4 h, the total volume of gas

(22) Acceleration of cycloaddition reactions by electron acceptors and interpretation in terms of radical cation Diels–Alder reactions have been reported. See: Pabon, R. A.; Bellville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1984**, *106*, 2730. Bauld, N. L.; Bellville, D. J.; Pabon, R.; Chelsky, R.; Green, G. *Ibid.* **1983**, *105*, 2378 and references cited therein. For a distinction between aminium radical cation- and acid-catalyzed Diels–Alder reactions, see: Gassman, P. G.; Singleton, D. A. *Ibid.* **1984**, *106*, 7993. See also: Jones, C. R.; Allman, B. J.; Mooring, A.; Spahic, B. *Ibid.* **1983**, *105*, 652. Calhoun, G. C.; Schuster, G. B. *Ibid.* **1984**, *106*, 6870.

(23) For examples of pericyclic radical anion reactions, see: Fox, M. A.; Hurst, J. R. *J. Am. Chem. Soc.* **1984**, *106*, 7626 and references cited therein (in particular, footnote 11).

(24) Keller, R. N.; Wycoff, H. D. In "Inorganic Syntheses"; Fernelius, W. C., Ed.; McGraw-Hill: New York, 1946; Vol. II, p 1.

(25) Scott, N. D.; Walker, J. F.; Hansley, V. L. *J. Am. Chem. Soc.* **1936**, *58*, 2442.

(26) (a) Cookson, R. C.; Gupte, S. S.; Stevens, I. D. R.; Watts, C. T. In "Organic Syntheses"; Benson, R. E., Ed.; Wiley: New York, 1971; Vol. 51, p 121. (b) Stickler, J. C.; Pirkle, W. H. *J. Org. Chem.* **1966**, *31*, 3444. (c) Burrage, M. E.; Cookson, R. C.; Gupte, S. S.; Stevens, I. D. R. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1325.

(27) Kauer, J. C. In "Organic Syntheses"; Rabjohn, N., Ed.; Wiley: New York, 1963; Collect. Vol. IV, p 411.

(28) Ohashi, S.; Leong, K.; Matyjaszewski, K.; Butler, G. B. *J. Org. Chem.* **1980**, *45*, 3467.

produced was 33.4 mL (approximately 100% yield of N_2 after correcting for the vapor pressure of THF). One half of the N_2 had been evolved after 1 min. Filtration of the reaction mixture yielded 305.0 mg (95%) of **2a**.

Reaction of NaI and PhTAD. A solution of NaI in acetone (1.00 M, 110 μL, 0.110 mmol) was added to a stirred solution of PhTAD (175.5 mg, 1.002 mmol) in 5 mL of acetone. Gas evolved immediately and vigorously; a precipitate formed instantaneously. After 15 min, the tan suspension was filtered to afford 150.2 mg (93%) of a light pink powder, identical with **2a** by IR. Results under other conditions are summarized in Table IV.

Dimethyl 4-Phenyl-3,5-dioxo-1,2,4-triazolidine-1,2-dicarboxylate (4, R = Ph, R″ = Me). Sodium hydride (0.96 g, 50% oil dispersion, 20 mmol) was added to a suspension of 4-phenyl-1,2,4-triazolidine-3,5-dione (1.77 g, 10.1 mmol) in 50 mL of dioxane. After stirring 30 min, methyl chloroformate (1.90 g, 20.1 mmol) was added; a precipitate slowly formed. After 18 h, the mixture was filtered, the precipitate was washed with 2 × 20 mL of THF, and the filtrate was evaporated in vacuo to yield a tan solid. Recrystallization from benzene/heptane afforded 3.11 g of white needles, mp 116–118 °C, which had occluded benzene. Sublimation [140 °C (0.005 mmHg)] afforded a white solid, 4 (R = Ph, R″ = Me): mp 127–128.5 °C (phase transition around 70 °C); IR ($CHCl_3$) 1840 cm^{-1} (m), 1770 (vs), 1405 (s), 1290 (vs), 1190 (vs), 1070 (m), 1040 (m), 970 (m); ^1H NMR ($CDCl_3$) δ 4.05 (s, 6 H); 7.4–7.6 (m, 5 H). Anal. Calcd for $C_{12}H_{11}N_3O_6$: C, 49.15; H, 3.78; N, 14.33. Found: C, 48.89; H, 3.70; N, 14.06.

Trapping by Dimethyl Diazenedicarboxylate (DMAD) of an Intermediate in the "Dimerization" Reaction of PhTAD. PhTAD (195.0 mg, 1.114 mmol) and DMAD (5.00 g, 34.3 mmol) were dissolved in 4 mL of acetone and stirred for 5 min. A solution of NaI in acetone (0.30 mL, 0.45 M, 0.14 mmol) was added, and vigorous gas evolution ensued. After 40 min, the initial red color had faded to the orange color of DMAD. Filtration of the mixture and washing of the precipitate with 2 × 2 mL of acetone afforded 111.3 mg (62%) of an orange powder, **2a**, mp >350 °C. The filtrate was concentrated in vacuo and then distilled in a Kugelrohr apparatus [20 °C (0.005 mmHg)], thus removing 4.4 g of excess DMAD. The residue was dissolved in EtOAc/acetone (2 mL of each) (more insoluble material appeared at this point) and chromatographed on SiO_2 (4:6 EtOAc/hexane). Fractions containing the compound of R_f 0.25 were pooled and evaporated in vacuo to yield 71.2 mg (0.243 mmol, 22%) of a tan semisolid, shown to be mainly dimethyl 4-phenyl-3,5-dioxo-1,2,4-triazolidine-1,2-dicarboxylate (**4**, R = Ph, R″ = Me) by ^1H NMR analysis. Recrystallization from CCl_4 afforded 32.5 mg of white crystals. Sublimation afforded a white solid, mp 127–128 °C (phase transition around 70 °C), identical by IR and ^1H NMR with **4** (R = Ph, R″ = Me).

Reaction of MeOH and PhTAD. CH_2Cl_2. MeOH (42 μL, 33 mg, 1.0 mmol) was added to a stirred solution of PhTAD (175 mg, 1.00 mmol) in 5 mL of CH_2Cl_2. No gas evolution was apparent. The reaction became cloudy after 15 min and decolorized after 17 h. Filtration afforded 13.2 mg of a white solid, mp 235 °C dec, then 340 °C dec. The filtrate was concentrated, and the residue was triturated with 5 mL of hexane. The off-white residue was partitioned between $CHCl_3$ (15 mL) and saturated aqueous $NaHCO_3$ (10 mL). The $CHCl_3$ layer was dried ($MgSO_4$) and concentrated in vacuo to give 138.9 mg (78%) of an off-white solid, mp 160 °C, resolidify, 234 °C dec; ^1H NMR ($CDCl_3$) δ 4.08 (s, 3 H), 7.14–7.56 (m, 10 H), 9.05 (br s, 1 H). Recrystallization from $CHCl_3$ afforded methyl 4-phenyl-2-[(phenylamino)carbonyl]-3,5-dioxo-1,2,4-triazolidine-1-carboxylate (**3a**) as white needles: mp 180 °C, resolidify, 242 °C dec [lit.[3d] mp 180–187 °C]; IR (KBr) 3384 cm^{-1} (s), 1821 (s), 1754 (vs), 1604 (s), 1553 (s), 1501 (s), 1449 (s), 1422 (vs), 1303 (vs), 1234 (vs), 1186 (m), 749 (s); ^1H NMR ($CDCl_3$) δ 4.08 (s, 3 H), 7.14–7.56 (m, 10 H), 9.05 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 55.81, 120.06, 125.16, 126.07, 129.24, 129.47, 129.59, 129.64, 136.12, 145.33, 146.33, 148.92, 150.16. A similar experiment performed in CD_2Cl_2 indicated that the crude product (before trituration or extraction) contained a 6.5:1 mixture of **3a** and **8**.

Acetone. MeOH (42 μL, 33 mg, 1.0 mmol) was added to a stirred solution of PhTAD (175 mg, 1.00 mmol) in 5 mL of acetone. Very slight gas evolution was apparent. The red color faded to light peach in 25 h. Filtration removed 3.5 mg (2%) of a white solid, **2a**, mp >350 °C. The filtrate was treated as above to afford 121.0 mg (68%) of an off-white solid, **3a**: mp 160 °C, resolidify, 230 °C dec. This material was identical by ^1H NMR with that produced from PhTAD and MeOH in CH_2Cl_2.

Reaction of MeOH, NaI, and PhTAD. A solution of NaI in acetone (1.0 M, 2.0 μL, 2.0 μmol) was added to a stirred solution of PhTAD (175 mg, 1.00 mmol) and MeOH (42 μL, 33 mg, 1.0 mmol) in 5.0 mL of acetone. Vigorous gas evolution ensued, and a precipitate began to form after 20 min. After 6 h, the pale yellow mixture was filtered and washed with 5 mL of CH_2Cl_2, affording 7.2 mg (4%) of **2a**, mp >350 °C. The filtrate was concentrated in vacuo, redissolved in 15 mL of CH_2Cl_2, and extracted with 10 mL of saturated aqueous $NaHCO_3$ containing 0.5 g of $Na_2S_2O_3 \cdot 5H_2O$. The CH_2Cl_2 layer was dried ($MgSO_4$) and evaporated to yield 135.6 mg (77%) of a yellowish solid, mp 230–240 °C dec. ^1H NMR analysis of the crude product indicated only **3a**. In a separate experiment, the crude product was recrystallized from $CHCl_3$/hexane 7 times to afford analytically pure white needles. The melting point, which depended on the rate of heating, varied between 233–234.5 °C dec and 236–238 °C dec. Anal. Calcd for $C_{17}H_{14}N_4O_5$: C, 57.62; H, 3.98; N, 15.81. Found: C, 57.38; H, 3.87; N, 15.84. Results under other conditions are summarized in Table IV.

4-Phenyl-1-[(phenylamino)carbonyl]-1,2,4-triazolidine-3,5-dione (9). A suspension of 4-phenyl-1,2,4-triazolidine-3,5-dione (885 mg, 5.00 mmol) in 8 mL of dioxane was treated with NaH (240 mg, 50% oil dispersion, 5.00 mmol). After the mixture was stirred for 15 min, phenyl isocyanate (595 mg, 5.00 mmol) was added; a precipitate quickly formed, and the mixture became very thick. After 30 min, the mixture was quenched with water, brought to pH 2 with 1 M HCl, and extracted with EtOAc (2 × 50 mL). The EtOAc solution was dried ($MgSO_4$) and concentrated in vacuo to yield 1.45 g of a white solid, mp 195 °C. Recrystallization from EtOH afforded 1.0 g (68%) of white needles, **9**: mp 200–202 °C; ^1H NMR (CD_3SOCD_3) δ 7.11–7.58 (m, 10 H), 9.79 (s, 1 H), 12.2 (br, 1 H). This material was identical with that prepared from PhTAD, H_2O, and pyridine as described by Wamhoff and Wald.[5b]

Synthesis of 2a from Methyl 4-Phenyl-3,5-dioxo-1,2,4-triazolidine-1-carboxylate (8). Compound **8**[3d] (235 mg, 1.00 mmol) was suspended in a mixture of 3 mL of phenyl isocyanate and 5 mL of THF. The suspension was heated to approximately 70 °C; most of **8** dissolved. Et_3N (18 mg, 0.18 mmol) was added. Within 15 s, all of compound **8** dissolved, and a new precipitate appeared. The mixture was cooled to room temperature and filtered to give 250.0 mg (78%) of fine white crystals, **2a**, mp >350 °C.[29]

Reaction of Benzyl Alcohol, NaI, and PhTAD. Benzyl alcohol (54.0 mg, 0.500 mmol) was added to a solution of PhTAD (87.5 mg, 0.500 mmol) and *n*-tridecane (30.0 mg, 0.163 mmol) (internal standard) in 2 mL of acetone. After the mixture was stirred for 10 s, a varying amount of NaI (in acetone) was added. After the red color had faded, the mixture was filtered to afford **2a**; yields of benzyl alcohol and benzaldehyde were determined by gas chromatography and the approximate amount of the triazolidinedione **3b** by NMR (from an experiment in CD_3COCD_3). Amounts of NaI used and yields of the various products are listed in Table V.

Reaction of NaI and PhTAD in AcOH. A solution of PhTAD (0.525 g, 3.00 mmol) in 15 mL of AcOH was treated with a solution of NaI (0.900 g, 6.00 mmol) in 4 mL of acetone. The dark red solution instantly became brown-black. After being stirred for 5 min at room temperature, the mixture was poured into 200 mL of ice–water and immediately extracted with 5 × 125 mL of CCl_4. The pale yellow aqueous layer was acidified with concentrated HCl to pH 0. After removal of the water in vacuo (60 °C), the residue was extracted with 4 × 10 mL of acetone; removal of the acetone in vacuo afforded 0.50 g of a light brown solid, mp 198–205 °C (95%). Extraction of this solid with 3.5 mL of a solution of 1.0 g of $NaHSO_3$ in 10 mL of 1 M HCl and 10 mL of saturated aqueous NaCl, followed by extraction with 1 mL of 1 M HCl afforded, after drying, 0.4053 g (76%) of a pale yellow solid, 4-phenyl-1,2,4-triazolidine-3,5-dione, mp 205–207 °C [lit.[26a] mp 209–210 °C]. Recrystallization from EtOH raised the melting point to 206–207 °C, and the IR spectrum of this material was identical with that of authentic 4-phenyl-1,2,4-triazolidine-3,5-dione. PhTAD was unchanged after 24 h in AcOH in the

absence of NaI, as determined in a control experiment.

Thermal Decomposition of PhTAD in THF.[5b] A solution of PhTAD (0.15 g) in 5 mL of THF was heated at reflux. A precipitate appeared after 5 min; after 2 h, the color had faded from dark red to yellow. Filtration of the mixture yielded 79.6 mg (58%) of a white powder, mp >350 °C, identical with **2a** by IR. Evaporation of the filtrate afforded 81.5 mg (39%) of 4-phenyl-1-(tetrahydro-2-furanyl)-1,2,4-triazolidine-3,5-dione as a yellow solid. Recrystallization twice from benzene gave off-white crystals: mp 161–162 °C [lit.[5b] mp 163 °C]; ^{1}H NMR ($CDCl_3$) δ 1.95–2.35 (m, 4 H), 3.90 (dd, J = 7.5, 14.5 Hz, 1 H), 4.10 (dd, J = 6.5, 14.5 Hz, 1 H), 5.89 (t, J = 5.5 Hz, 1 H), 7.30–7.45 (m, 5 H), 9.10 (br, 1 H).

Reaction of Na and $PhCH_2TAD$. $PhCH_2TAD$ (378 mg, 2.00 mmol) was added to Na (11 mg, 0.48 mmol) in 5 mL of THF, and the mixture was stirred. Gas evolved, and a precipitate slowly formed. After 21 h, the pale yellow mixture was filtered, and the precipitate was washed with pentane to afford 327 mg (93%) of a white powder, mp 207–211 °C. Recrystallization from Me_2SO/H_2O yielded a white solid, 2,6-bis(phenylmethyl)-1*H*,5*H*-[1,2,4]triazolo[1,2-*a*][1,2,4]triazole-1,3,5,7(2*H*,6*H*)-tetrone (**2c**): mp 208–209 °C; IR (KBr) 1790 cm^{-1} (vs), 1760 (vs), 1440 (vs), 1410 (s), 1350 (s), 1140 (s), 1025 (s), 730 (vs), 690 (s), 640 (s); ^{1}H NMR (CD_3COCD_3) δ 4.68 (s, 4 H), 7.30–7.40 (m, 10 H); ^{13}C NMR (CD_3COCD_3) δ 44.5, 129.0, 129.3, 129.7, 135.3, 146.6. Recrystallization from CH_2Cl_2/hexane afforded analytically pure needles: mp 213.5–214 °C. Anal. Calcd for $C_{18}H_{14}N_4O_4$: C, 61.71; H, 4.03; N, 15.99. Found: C, 61.43; H, 3.99; N, 15.69.

Attempted Methanolysis of 2c (2, R = $PhCH_2$). Compound **2c** (112.3 mg, mp 210–211 °C) was dissolved in 5 mL of CH_2Cl_2; 5 mL of MeOH was added, and the homogeneous solution was stirred at room temperature for 12 h. Removal of the solvents in vacuo afforded 117.2 mg of a white solid, mp 208–210 °C, mixed melting point with **2c** 209–211 °C.

Reaction of Pyridine and MeTAD. Pyridine (3.07 g, 38.8 mmol) was added to a suspension of MeTAD (1.13 g, 10.0 mmol) in 10 mL of CH_2Cl_2. Vigorous gas evolution ensued, and a solid precipitated. After 22 h, the mixture was filtered, and the solid was washed with 5 mL of EtOH to afford a pink powder. Recrystallization from Me_2SO yielded 0.28 g (28%) of white crystals, 2,6-dimethyl-1*H*,5*H*-[1,2,4]triazolo[1,2-*a*][1,2,4]triazole-1,3,5,7-(2*H*,6*H*)-tetrone (**2b**): mp 297–299 °C [lit.[30] mp 305 °C]; IR (KBr) 1780 cm^{-1} (vs), 1430 (s), 1380 (s), 1255 (s), 1080 (m), 750 (s), 620 (m); ^{1}H NMR (CD_3SOCD_3) δ 2.97 (s, 6 H); ^{1}H NMR ($CDCl_3$) δ 3.22 (s, 6 H); ^{13}C NMR (CD_3SOCD_3) δ 25.7, 146.8.

Reaction of Sodium Naphthalenide and MeTAD. A solution of sodium naphthalenide in THF (100 μL, 0.119 M, 11.9 μmol) was added to a solution of MeTAD (239.6 mg, 2.120 mmol) in 5 mL of THF. Gas evolved vigorously, and a precipitate slowly appeared. After 28 h, the decolorized mixture was filtered to afford 162.4 mg (77%) of a white powder, mp 294–296 °C, identical with **2b** by IR.

Comparison of the Reactivity toward "Dimerization" of PhTAD, MeTAD, and $PhCH_2TAD$. Sodium naphthalenide (NaNaph) in THF (100 μL, 0.070 M, 7 μmol) was added to 1.00 mmol of a TAD dissolved in 5 mL of THF. PhTAD decolorized in 5 min, $PhCH_2TAD$ in 40 min, and MeTAD in 20 h. Also, a mixture of 0.50 mmol each of PhTAD and MeTAD in 5 mL of THF, when treated with 7 μmol of NaNaph, decolorized in 2 h, after losing all of the deep red color due to PhTAD in 1 min. ^{1}H NMR of the crude reaction mixture indicated that the three possible deaza dimers Ph–Ph, Ph–Me,[30] and Me–Me were present in a 1:2:1 ratio. Also, NaI in acetone (100 μL, 1.00 M, 0.10 mmol) was added to 1.00 mmol of a TAD dissolved in 5 mL of THF. PhTAD decolorized in 1 min; MeTAD, 3 min.

ESR Studies. All solvents were degassed by three freeze–pump–thaw cycles. ESR spectra were obtained on a Varian E-Line spectrometer at 0.3360 T. The spectra were obtained at room temperature, and g values were calibrated with solid DPPH. **Me_2SO**: PhTAD (21.9 mg) was dissolved in 2.5 mL of Me_2SO (0.0500 M). Potassium *tert*-butoxide (265 μL of a 0.0473 M solution in Me_2SO) was added to the PhTAD solution (PhTAD/KO-*t*-Bu = 10). Moderate gas evolution occurred, and the red solution became purple/blue. An intense ESR signal was observed at g = 2.0036, consisting of 15 lines: a_N = 475 μT, 175 μT. This signal slowly lost intensity over 2 h; the purple/blue color faded simultaneously. No other signals were observed. **THF**: PhTAD (2.0 mg) was dissolved in 1 mL of THF (0.011 M); 2,4,6-trimethylpyridine (5 μL) was added (PhTAD/2,4,6-trimethylpyridine = 0.3). A strong ESR signal immediately appeared at g = 2.0056, consisting of at least 19 overlapping lines. Gas evolved slowly; the solution did not change color nor did the ESR signal decrease much in intensity. In another experiment, PhTAD (1.7 mg) was dissolved in 1 mL of THF (0.0097 M); a solution of sodium naphthalenide in THF (0.1 M, 1.5 μL) was added (PhTAD/sodium naphthalenide = 58). An ESR signal identical to that observed with 2,4,6-trimethylpyridine was seen. **CH_2Cl_2**: PhTAD (9.5 mg) was dissolved in 1 mL of CH_2Cl_2 (0.054 M); 2,4,6-trimethylpyridine (7.2 μL) was added (PhTAD/2,4,6-trimethylpyridine = 1.0). A strong ESR signal immediately appeared at g = 2.0060, consisting of at least 16 overlapping lines, with unresolved fine structure. This signal was not the same as the signal seen in THF. **Acetone**: PhTAD (22.4 mg) was dissolved in 2.5 mL of acetone (0.0512 M); a solution of NaI in acetone (0.020 M, 150 μL) was added (PhTAD/NaI = 43). A very weak ESR signal was detected at g = 2.0051, which bore a superficial resemblance to the signals in THF.

Note Apped in Proof: We thank Dr. Izydore for correspondence and spectral data pertaining to the **3,3-iso** problem. At this point the structural problem is unresolved (see footnote 7); however, IR and H NMR data show strong similarity between compound **16** of the Izydore paper (Izydore, R. A.; Johnson, H. E.; Horton, R. T. *J. Org. Chem.* **1985**, *50*, 4589) and compound **3a** of this paper.

Registry No. **1a**, 4233-33-4; **1b**, 13274-43-6; **1c**, 57964-81-5; **2a**, 32494-23-8; **2b**, 55029-98-6; **2c**, 100084-84-2; **3a**, 60290-33-7; **3b**, 60290-39-3; **4** (R = Ph, R′ = Me), 100084-85-3; **8**, 60290-34-8; **9**, 63376-35-2; $CuCl_2$, 7447-39-4; CuCl, 7758-89-6; $Pb(OAc)_4$, 546-67-8; Na, 7440-23-5; NaI, 7681-82-5; MeOH, 67-56-1; TCNE, 670-54-2; DMAD, 2446-84-6; pyridine, 110-86-1; 2,6-dimethylpyridine, 108-48-5; di-*tert*-butylnitroxyl, 2406-25-9; 2,4,6-trimethylpyridine, 108-75-8; ferrocene, 102-54-5; sodium naphthalenide, 3481-12-7; methyl chloroformate, 79-22-1; phenyl isocyanate, 103-71-9; benzyl alcohol, 100-51-6; 4-phenyl-1,2,4-triazolidine-3,5-dione, 15988-11-1; 4-phenyl-1-(tetrahydro-2-furanyl)-1,2,4-triazolidine-3,5-dione, 63376-27-2.

(29) Formation of **2a** from **8** has also been reported in ref 7b.
(30) Capuano, L.; Müller, K. *Chem. Ber.* **1977**, *110*, 1691.