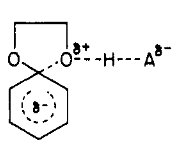
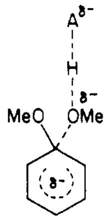


20



21

decomposition of the adducts does not occur via **20** (A = OMe). Should methanol act as a general acid in this process, the $k_{-2}/24.7$ values should fit the Brønsted plots of Figure 6 and be equal to about 2.4×10^{-5}, 4.5×10^{-7}, and 1.5×10^{-6} L mol^{-1} s^{-1} for **8a**, **8b**, and **10**, respectively. Instead, the experimentally found $k_{-2}/24.7$ values are equal to 0.085, 2.55×10^{-4}, and 1.01×10^{-3} L mol^{-1} s^{-1}. Thus, the noncatalyzed decomposition of the three spiro adducts studied is certainly a unimolecular reaction.

In contrast with that of **8a** and **8b**, the decomposition of the *gem*-dimethoxy adducts **6a** and **6b** was not found to be general acid catalyzed. This confirms recent observations by Bernasconi that catalysis of the decomposition of such adducts by carboxylic acids is generally weak and hardly detectable.[35] However, some catalysis of this process was observed in using cationic catalysts like pyridinium ions.[35] On this basis, the different behavior of spiro and *gem*-dimethoxy adducts was interpreted in terms of electrostatic effects arising from a different balance in the degree of proton transfer and C–O bond breaking in the transition states for acid decomposition of these complexes.[33] Thus, the experimental observations suggest substantial positive charge development on the departing oxygen atom in the transition state for the spiro adduct systems, as visualized in **20**, but either very little charge or some negative charge on the departing oxygen in the transition state for the dimethoxy adduct systems, as shown in **21**.[33] As a consequence, carboxylic acids may be effective catalysts in the case of the spiro adducts but not in that of the dimethoxy adducts. For these latter systems, the opposite situation prevails, and it is the cationic catalysts which will be more efficient.[33] The occurrence of these electrostatic interactions are of interest in that they provide indirect support to our proposal (vide supra) that the origin of the abnormal behavior of the benzofuroxan spiro adduct **8b** relative to its benzofurazan analogue **8a** must be understood in terms of electrostatic transition-state destabilization.

Experimental Section

Materials. 7-(2-Hydroxyethoxy)-4-nitrobenzofurazan (**7a**) and -benzofuroxan (**7b**) were prepared as previously described: **7a**, mp 115 °C; **7b**, mp 124 °C.[10] 4-Methoxy-7-nitrobenzofurazan (**4a**) and -benzofuroxan (**4b**) were also obtained according to literature procedures: **4a**, mp 116 ° (lit. mp 115–116 °C);[2b,36] **4b**, mp 162 °C (lit. mp 160–163 °C).[2a,37]

Methanolic benzenesulfonic acid and potassium methoxide solutions were prepared as previously described.[5] Buffer solutions were made up from the best available commercial grades of reagents, which were recrystallized or distilled before use.

Rate and pH Measurements. Stopped-flow determinations were performed on a Durrum stopped-flow spectrophotometer, the cell compartment of which was maintained at 20 ± 0.2 °C. All kinetic runs were carried out in triplicate with a substrate concentration in the range $3\text{–}5 \times 10^{-5}$ M. Observed pseudo-first-order rate constants are accurate to ±3%.

The pH values were measured with a Tacussel Isis 2000 pH meter and are relative to the standard rate in pure methanol.

Registry No. **4a**, 18333-73-8; **4b**, 18378-09-1; **6a**, 64882-54-8; **6b**, 63153-26-4; **7a**, 66770-00-1; **7b**, 66770-02-3; **8a**, 98540-90-0; **8b**, 98540-91-1; **9**, 6478-31-5; **10**, 54846-61-6.

Supplementary Material Available: Tables of first-order rate constants for the formation and decomposition of **6a**, **6b**, **8a**, **8b**, and **10**, representative oscilloscope traces illustrating the decomposition of **8b**, an illustration of the effect of [$CHCl_2COOH$] on k_{obsd} for **8b**, and the UV–vis spectra for **4a**, **4b**, **6a**, **6b**, **6aH$^+$**, and **6bH$^+$** (6 pages). Ordering information is given on any current masthead page.

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(36) Dal Monte, D.; Sandri, E.; Mazzaracchio P. *Boll. Sci. Fac. Chim. Ind. Bologna* **1968**, *26*, 165.

(37) Ghosh, P. B.; Whitehouse, M. W. *J. Med. Chem.* **1968**, *11*, 305 and references therein.

Decomposition Reactions of a Cis-Diacyl Diimide. 4-Phenyl-1,2,4-triazoline-3,5-dione[1]

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The cis-diacyl diimide 4-phenyl-1,2,4-triazoline-3,5-dione (**1**) was decomposed in a variety of solvent systems. In nonnucleophilic solvents under 80 °C **1** underwent nitrogen evolution and was converted to 2,6-diphenyltriazolo[1,2-*a*]-*s*-triazole-1,3,5,7-tetrone (**2**). At higher temperatures **1** gave phenyl isocyanate (**3**). In nucleophilic solvent systems (acetic acid, alcohols, or water) **1** underwent loss of nitrogen and formed mixtures containing varying amounts of **2**, 1-(*N*-phenylcarbamoyl)-4-phenylurazole (**5**), 4-phenylurazole (**11**), diphenylurea (**12**), *N*-phenylcarbamates (**13**), and 1-(alkoxycarbonyl)-4-phenylurazoles (**14**), depending on the decomposition conditions employed. The mechanistic pathways leading to the various products are discussed.

Cis-diacyl diimides are cyclic electron-deficient azo compounds that react readily with olefinic and acetylenic sites. As such they have been employed as intermediates in the synthesis of a wide variety of heterocyclic systems. They are in general unstable compounds and often must be generated and trapped in solution at low temperatures. The 4-substituted triazoline-3,5-diones, often referred to as RTAD, are the most extensively utilized derivatives of this class of compounds principally because of their high reactivity and the fact that they can be isolated and stored under inert conditions.[2,3] When subjected to thermolysis,

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(1) (a) Presented in part at the 181st National Meeting of the American Chemical Society, Atlanta, GA, April 1980; ORGN 178. (b) Presented in part at the 189th National Meeting of the American Chemical Society, Miami Beach, FL, May 1985; ORGN 116.

(2) Cookson, R. C.; Gupte, S. S.; Stevens, I. D. R.; Watts, C. T. "Organic Syntheses"; Wiley: New York, 1971; Vol. 51, p 121.

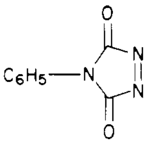
0022-3263/85/1950-4589$01.50/0

Table I. Decomposition Products of 4-Phenyl-1,2,4-triazoline-3,5-dione (1)

	dec conditions		product % yield							
solvent	temp,[j] °C	time	2	3	5	11	12	13	14	other products (%)
C_6H_6	78	4 mo[a]	64		28					
CH_2Cl_2	40	3 mo[a]	51		48					
C_6H_5Br	156	6 h[b]	12	41						**7** (9)
C_6H_5–C_6H_{11}	165	2–3 min[b]	0.5	4						**8** (15)[c]
HOAc, $Pb(OAc)_2$, Ac_2O, CH_2Cl_2[e]	RT	12 h[a]	21		33	*d*	11			**15** (2)
abs EtOH–CH_2Cl_2 (15:85)	RT	20 min[b]	*k*		2	11		33 (R = Et)	46[f] (R = Et)	
t-BuOH–CH_2Cl_2 (10:90)	RT	1–2 weeks[b]	2		60	18		18 (R = *t*-Bu)		
H_2O–EtOAc (5:95)	RT	12 h	*k*		39	28	15			
CH_3OH (1 equiv)–C_6H_6[g]	RT	48 h[b]	1					20–25[h]		**16** (R = Me) (7)[h] (2)[i]

[a] The decomposition was carried out in the presence of atmospheric moisture. [b] The decomposition was carried out under a nitrogen atmosphere. [c] See the Experimental Section for a description of the unidentified products. [d] 11 could not be quantitatively isolated from the lead salts which formed in the oxidation of 11 with $Pb(OAc)_4$. [e] 1 was formed in solution by oxidation of 11 with $Pb(OAc)_4$ and allowed to decompose in the reaction mixture. [f] Estimated yield. 14 (R = Et) was isolated solvated with CCl_4–$CHCl_3$ following recrystallization. [g] Equivalent amounts of 1 and CH_3OH were used as described in ref 7. [h] Estimated yield from HPLC data. [i] Isolated yield. [j] RT = room temperature. [k] Trace.

photolysis, or nucleophilic solvents, however, the triazoline-3,5-diones rapidly decompose with gas evolution. To date neither the identity of the decomposition products nor the mechanisms of their formation have been extensively studied. The results that have been reported are concerned mainly with the decomposition reactions of 4-phenyl-1,2,4-triazoline-3,5-dione (1).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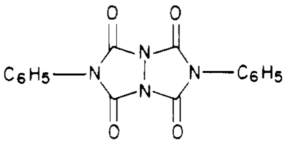
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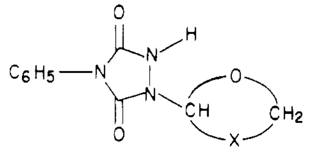
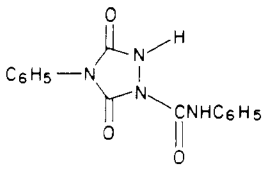

4, X = $(CH_2)_2$, CH_2OCH_2

The triazolo[1,2-*a*]-*s*-triazole 2 has been reported as a decomposition product of 1 under photolytic conditions and thermal conditions and in the presence of nucleophilic solvents.[4-8] Both photolytic decomposition of 1 in nonnucleophilic solvents[5] and thermal decomposition of 1 in the solid phase near its decomposition temperature[4,5] gave high yields of phenyl isocyanate (3). Wamhoff and Wald reported that 1 decomposed in cyclic ethers under both photolytic and thermal conditions to yield the addition products 4.[5] The carbamoylurazole 5 was formed as the major decomposition product of 1 in the presence of water and pyridine.[5] Dao and Mackay reported that 1 reacted with methanol and ethanol to produce 1-(alkoxycarbonyl)-2-(*N*-phenylcarbamoyl)-4-phenylurazoles (6) in near quantitative yield.[6,7] Reaction of 1 with other primary and secondary alcohols gave low to moderate yields of 6. In these instances oxidation of the alcohols by 1 to aldehydes and ketones was a competing process.[7] In the present study the decomposition behavior of 1 in a variety of nonnucleophilic and nucleophilic solvent systems is described.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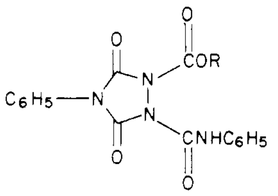
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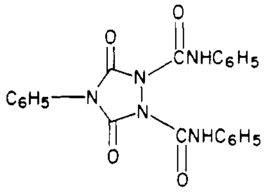
Results and Discussion

The decomposition products, percent yields, and reaction conditions resulting from the decomposition of 1 in various solvent systems are summarized in Table I. The percent yield of each product is the mole percentage of 1 that was consumed to form it.

The decompositions carried out in nonnucleophilic solvents resulted in the formation of 2 in all cases. Compound 2 was the major product in the two lower boiling solvents (benzene and methylene chloride) and a relatively minor product in the two higher boiling solvents (bromobenzene and phenylcyclohexane). The carbamoylurazole 5 was isolated only when the decompositions were carried out in the presence of atmospheric moisture. The decomposition proceeded at a faster rate in methylene chloride than in the higher boiling benzene. In the two higher boiling solvents phenyl isocyanate (3) was produced. Additionally compound 7 precipitated over a 4-week period from the decomposition in bromobenzene,[9] and compound 8 was isolated from the decomposition in phenylcyclohexane. The presence of 3 was demonstrated by gas

$C_6H_5N{=}C{=}O$

3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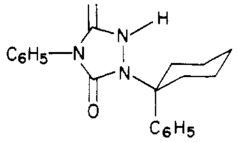
8

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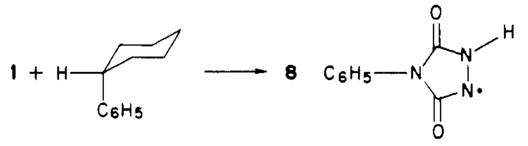
(3) Wamhoff, H.; Wald, K. *Org. Prep. Proced. Int.* **1975**, *7*, 251.
(4) Stolle, R. *Chem. Ber.* **1912**, *45*, 273.
(5) Wamhoff, H.; Wald, K. *Chem. Ber.* **1977**, *110*, 1699.
(6) Dao, L. H.; Mackay, D. *J. Chem. Soc., Chem. Commun.* **1976**, 326.
(7) Dao, L. H.; Mackay, D. *Can. J. Chem.* **1979**, *57*, 2727.
(8) Hall, J. H.; Kaler, L.; Herring, R. *J. Org. Chem.* **1984**, *49*, 2579.

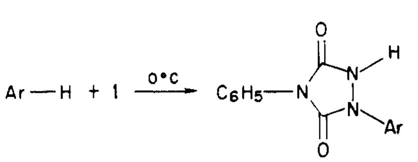
(9) Compound 2 rather than 7 was isolated when 4-phenylurazole (11) was allowed to react with 2 equiv of 3 in the presence of triethylamine. Presumably 7 underwent ring closure under the basic conditions: Capuano, L.; Müller, K. *Chem. Ber.* **1977**, *110*, 1691.

chromatography (reaction in phenylcyclohexane[10]) and by its conversion to diphenylurea upon the addition of water to the product solutions. Moreover, carbon monoxide evolution was evidenced. The evolved gases from the reaction in bromobenzene gave a precipitate of manganese dioxide when passed through an acidified solution of potassium permanganate containing silver nitrate.[11] The production of 3 in the higher temperature reactions is consistent with earlier reports.[4,5] The formation of compound 8 probably arises by free-radical addition of the benzylic C–H bond of phenylcyclohexane across the nitrogen-to-nitrogen double bond of 1 initiated by the traces of urazolyl radicals 9 that are present in solutions of 1.[5,12,13]



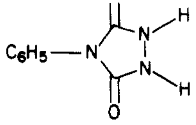
9

This reaction is analogous to the reported thermal addition of cyclic ethers to 1 to produce 4.[5] It has been recently demonstrated that electron-rich aromatic rings react readily with 1 at 0 °C to give aromatic substitution products 10.[8,14] It would appear that the aromatic rings of benzene, bromobenzene, and phenylcyclohexane are not reactive enough with 1, and, therefore, the decompositions must proceed by higher energy processes in these solvents.



10

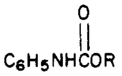
The decompositions carried out in the nucleophilic solvent systems generally produced relatively low yields of 2 and moderate yields of 5. 4-Phenylurazole (11) was formed in each instance. Additionally diphenylurea (12) was produced in the acetic acid and the aqueous solvent systems, and *N*-phenylcarbamates 13 and (alkoxycarbonyl)urazoles 14 were produced in the alcohol solvent systems. A small quantity of acetanilide (15) was isolated in the acetic acid solvent system. The fact that 5 was isolated from all of the nucleophilic solvent systems implies that it was formed from a similar type of intermediate in each case. The structure of this intermediate is ascribed to 16. Thus 16 (R = OAc) can conceivably react with acetic acid to give 5 plus acetic anhydride in the presence of the acetic acid solvent system, and 16 (R = H) would spontaneously decarboxylate to give 5 in the aqueous solvent system. In the alcohol systems 16 (R = alkyl) can react with the alcoholic solvents by two different pathways as shown in Scheme I. The results indicate that a steric effect is operative here, for while decomposition in the ethanol solvent system led mainly to path B products 13 (R = Et) and 14 (R = Et), decomposition in the *tert*-butyl alcohol system led to a moderately high yield of the path A product 5 and no path B product 14 (R = *t*-Bu).



11

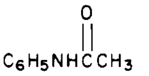
$C_6H_5NHC(=O)NHC_6H_5$

12



$C_6H_5NHC(=O)OR$

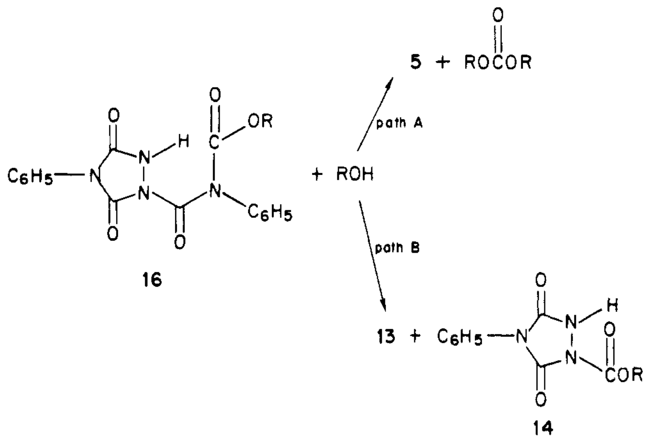
13



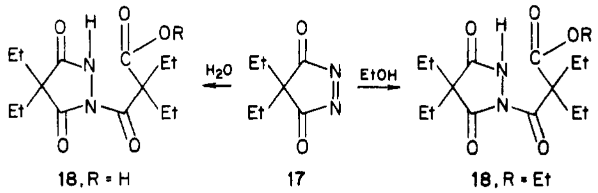
$C_6H_5NHC(=O)CH_3$

15

Scheme I



In order to rule out the possibility that products 5 and 14 were formed by a route different from that depicted in Scheme I, several test reactions were run. Thus it was found that in methylene chloride at room temperature, 11 does not react with diethyl carbonate to give 14 (R = Et), and it reacts slowly with 3 to give a very low yield of 5 (2–3% after 24 h).[15] In addition it was found that 5 does not react with refluxing ethanol. Therefore, products 11, 13 (R = Et), or 14 (R = Et) were not produced from 5. It is most likely then that products 5 and 13 (R = Et) were formed from 16. Although 16 cannot be isolated under the various decomposition conditions used, its existence can be inferred from the fact that the analogous compounds 18 (R = H and R = Et) were isolated in good yields (25–30% each) from the decomposition of the pyrazoline-3,5-dione 17 with water[16] and ethanol,[17] respectively.



The urazole 11 has not been previously reported as a decomposition product of 1. It is a reduction product resulting from the net transfer of two hydrogen atoms to 1. It is possible that in the case of decomposition in ethanol–methylene chloride that 11 was produced by the oxidation of ethanol by 1. However, this type of oxidation is not possible in the decompositions in the water and *tert*-butyl alcohol systems. To prove that 11 arose only as a primary decomposition product of 1 and not from the conversion of any of the other decomposition products, either under the reaction conditions or during workup, a

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(10) Both 3 and bromobenzene had nearly identical GC retention times on the columns available.

(11) Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley: New York, 1972; p 440.

(12) Hall, J. H.; Bigard, W. E.; Fargher, J. M.; Jones, M. L. *J. Org. Chem.* **1982**, *47*, 1459.

(13) Alberti, A.; Pedulli, G. F. *J. Org. Chem.* **1983**, *48*, 2544.

(14) Hall, J. H. *J. Org. Chem.* **1983**, *48*, 1708.

(15) Compound 5 is produced when 3 and 11 are heated in the presence of base for several hours: E. I. du Pont de Nemours & Co. U.S. Patent 3 141 023, 1964; *Chem. Abstr.* **1964**, *61*, 8317c. See also ref 5 and 9.

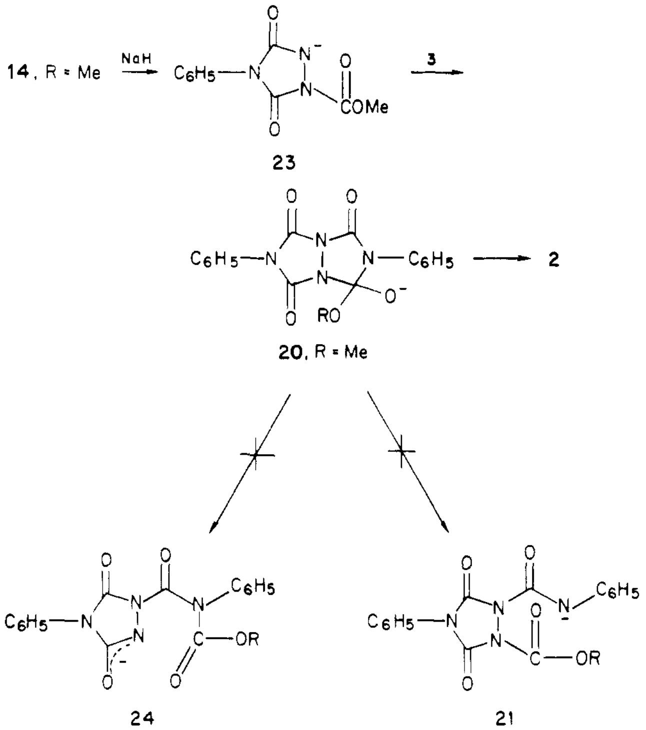
(16) Gillis, B. T.; Izydore, R. A. *J. Org. Chem.* **1969**, *34*, 3181.

(17) Izydore, R. A.; Johnson, H. E., unpublished results.

number of test reactions were carried out. It was found that **2** was recovered quantitatively when it was stirred in water for 24 h or heated under reflux in ethanol for 7 h or in bromobenzene for 21 h. Attempted reaction of methylene chloride solutions of **14** (R = Et) with absolute ethanol for 21 h, *tert*-butyl alcohol for 6.5 weeks, or methanol for 6 days led in all cases to a quantitative recovery of **14** (R = Et). It should be noted that **14** (R = Et) contains a less sterically hindered and a more reactive carbonyl group at N-1 of the urazole ring than either **5** or intermediate **16**. Therefore, **2**, **5**, and **14** (R = Et) were not converted to **11** by the nucleophilic solvents. In a separate set of experiments it was shown that **11** was present in the original reaction products before workup. Following decomposition of **1** in the *tert*-butyl alcohol solvent system under nitrogen, the solvent and alcohol were evaporated under vacuum. To the residue was added a quantity of dry methylene chloride. The insoluble solid residue was filtered, and its IR spectrum showed it to be a mixture of **2**, **5**, and **11**. Addition of water dissolved a portion of the residue to give an acidic solution, and subsequent filtration and evaporation of the aqueous filtrate produced pure **11**. In another decomposition of **1** in the *tert*-butyl alcohol system under nitrogen, an aliquot of the product solution was removed and to it were added a few drops of *tert*-butyl hypochlorite. The solution immediately turned deep red, consistent with the presence of **1**. Addition of a few drops of ethyl diazoacetate to the red solution immediately decolorized it accompanied by gas evolution.[18] To the remainder of the product solution was added a quantity of *tert*-butyl hypochlorite followed by *trans,trans*-1,4-diphenyl-1,3-butadiene (**19**). Following workup the neutral fraction was shown to contain the Diels–Alder adduct derived from **1** and **19** by comparison of its ^{1}H NMR spectrum and high-performance liquid chromatogram with those of an authentic sample.[19-21] Thus the above experiments show that **11** was present prior to the workup of the reaction mixture and was not formed from **2**, **5**, or **15**.

As noted earlier Dao and Mackay reported that **1** reacted with methanol and ethanol to produce **6** (R = Me, Et).[6,7] They also observed a trace of **2**.[7] Compounds **6** (R = Me, Et) were reportedly formed in near quantitative yielded when (1) equimolar quantities of **1** and alcohol (10 mmol each) were allowed to react in benzene for 2 days at room temperature, (2) **1** (10 mmol) was allowed to react with a large excess of alcohol (10 mL) for 30 min at room temperature, and (3) equimolar quantities of **1**, alcohol, and pyridine (1 mmol each) in benzene were allowed to react for 1 h at room temperature.[7] A curious mechanism involving the intermediacy of anions in neutral solution was proposed for the formation of **6** under conditions 1 and 2. Anion **20** was formulated as the final intermediate leading to **6** under both neutral and basic decomposition conditions. The conclusion was made that cleavage from **20** of resonance-stabilized anion **21** rather than loss of methoxide ion would occur.[7] Our results for the decomposition of **1** in the various nucleophilic solvents are obviously in disagreement with these findings. As described above we observed that **2**, **5**, and **11** were present in the crude product mixture from the experiments carried out in *tert*-butyl alcohol. In a separate experiment the solvent was removed under vacuum from the product solution of **1** and 15% absolute ethanol–methylene chloride. The sticky residue was placed in ethyl acetate, and the insoluble solids were removed by filtration. Analysis of the filtrate by high-performance liquid chromatography (HPLC) on a silica column showed the presence of **13** (R = Et) as a major component as well as some **14** (R = Et).

Scheme II



Several attempts were made to directly synthesize **6** (R = Me). A suspension of equimolar quantities of **11** and sodium hydride in dry tetrahydrofuran (THF) was allowed to react with phenyl isocyanate (**3**) and methyl chloroformate (**22**) by the reported procedure,[7] but no **6** (R = Me) was obtained. The only compounds isolated following workup were **5**, **14** (R = Me), and a little **12**. When a suspension of equimolar quantities of **5** and sodium hydride in dry THF was allowed to react with **22**, a white solid was produced whose melting point behavior, after recrystallization from chloroform–hexane, showed decomposition with gas evolution over a wide temperature range, 170–287 °C. When the solid was subjected to mass spectrometry, peaks at *m/z* 296, 235, and 212 resulted. These peaks correspond to **5**, **14** (R = Me), and **12**, respectively. The solid was not further characterized. Evaporation of

$$\mathbf{5} + \underset{\mathbf{22}}{\mathrm{ClCO_2Me}} \xrightarrow{\mathrm{NaH}} \mathbf{3} + \mathbf{12} + \mathbf{14}\ (\mathrm{R = Me})$$

the filtrate from the recrystallization of the solid gave a gummy residue containing **3** as indicated by its odor and its IR spectrum, which contained a moderate absorption peak at 2140 cm^{-1}. In a similar manner phenyl isocyanate (**3**) was added to a suspension of equimolar quantities of **14** (R = Me) and sodium hydride in dry THF. A precipitate formed, which was identified as **2** (28% yield). Also isolated were unreacted **14** (R = Me) and **3**. The formation of **2** is consistent with the intermediacy of **20** (R = Me) via **23**. Intermediate **20** apparently undergoes loss of methoxide ion to yield **2** rather than cleavage of a C–N bond to give **21** or the resonance-stabilized anion **24** (Scheme II).[9] These latter two anions would be expected to lead upon protonation to **6** (R = Me) and **16** (R = Me),

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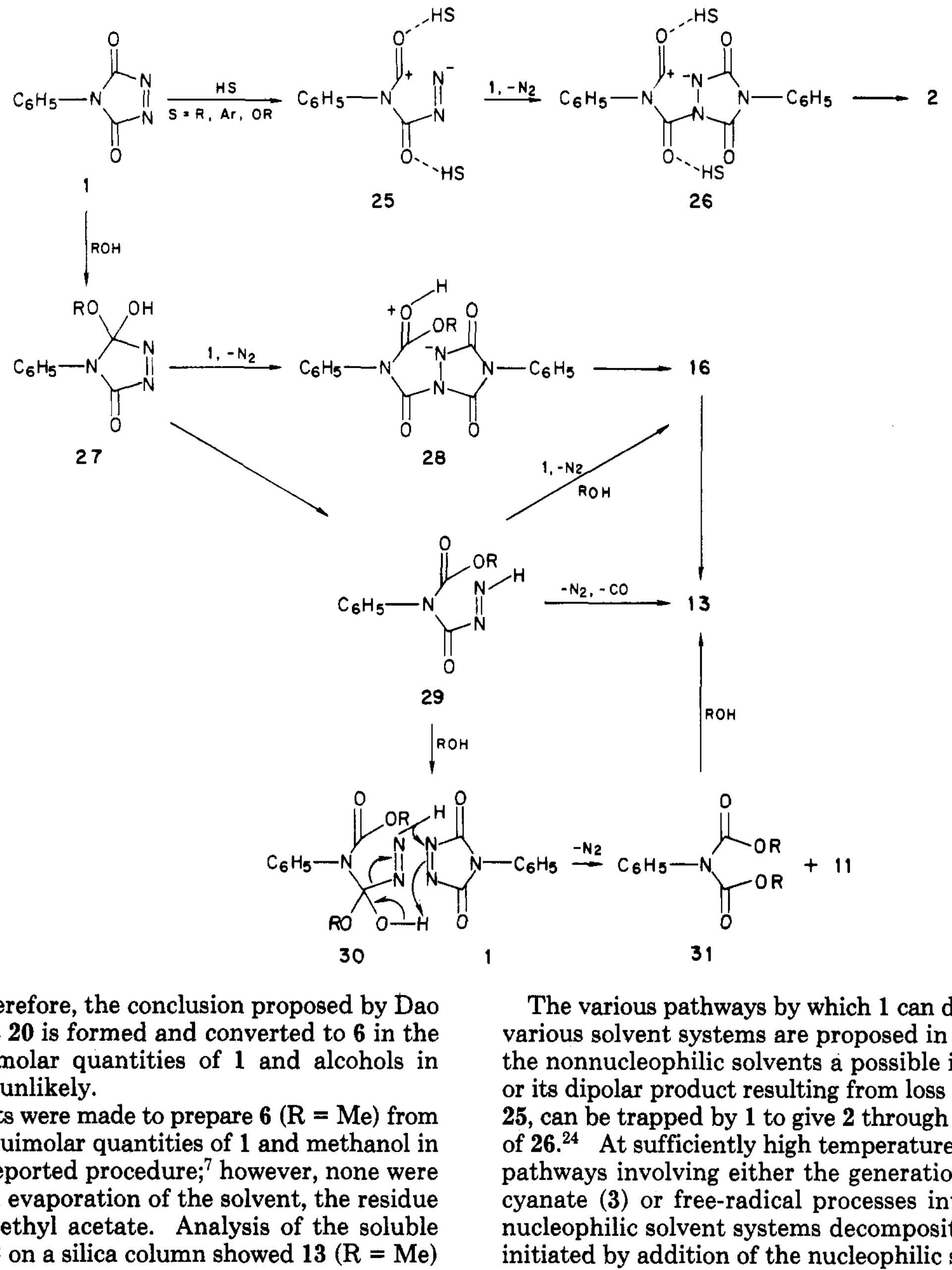
[18] Izydore, R. A.; McLean, S. *J. Am. Chem. Soc.* **1975**, *97*, 5611.

[19] Gillis, B. T.; Hagarty, J. D. *J. Org. Chem.* **1967**, *32*, 3130.

[20] Burrage, M. E.; Cookson, R. C.; Gupte, S. S.; Stevens, I. D. R. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1325.

[21] Addition of *tert*-butyl hypochlorite to a solution of **5** in CH_2Cl_2 turned the solution dark in an apparent reaction. However, addition of **19** to the dark solution did not give a Diels–Alder product.

Scheme III



respectively. Therefore, the conclusion proposed by Dao and Mackay that **20** is formed and converted to **6** in the reaction of equimolar quantities of **1** and alcohols in benzene is quite unlikely.

Several attempts were made to prepare **6** (R = Me) from the reaction of equimolar quantities of **1** and methanol in benzene by the reported procedure;[7] however, none were successful. Upon evaporation of the solvent, the residue was treaed with ethyl acetate. Analysis of the soluble portion by HPLC on a silica column showed **13** (R = Me) as the major component and several minor components. In one instance we were able to isolate one of the minor components by repeated recrystallizations from $CHCl_3$–CCl_4 to give 2% of a white solid, mp 226–230 °C (gas evolution). The solid showed m/z 354.0968 ($C_{17}H_{14}N_4O_5$). It had IR carbonyl absorptions at 1699, 1730, and 1750 cm^{-1} and a sharp absorption at 3398 cm^{-1}. The ^1H NMR spectrum contained a broad singlet (1 H) at δ 9.0, an aromatic multiplet (10 H) at δ 7.45, and a singlet (3 H) at δ 3.99. The spectral data are consistent with **16** (R = Me) or its hydroxyimide tautomer (C(OH)=N) at N-2 of the heterocyclic ring.[22] This conclusion is based on the frequency of the sharp IR absorption at 3398 cm^{-1}. The alternate structure **6** (R = Me) would be expected to show an N–H absorption similar to those of **5** and **7**. These appear at 3220 and 3317 cm^{-1}, respectively. Moreover, it is likely that **16** (R = Me) would be stable to the reaction conditions as no excess alcohol was present to further react with it.[23]

The various pathways by which **1** can decompose in the various solvent systems are proposed in Scheme III. In the nonnucleophilic solvents a possible intermediate **25**, or its dipolar product resulting from loss of nitrogen from **25**, can be trapped by **1** to give **2** through the intervention of **26**.[24] At sufficiently high temperatures, other reaction pathways involving either the generation of phenyl isocyanate (**3**) or free-radical processes intervene. In the nucleophilic solvent systems decomposition of **1** may be initiated by addition of the nucleophilic solvent to one of the carbonyl groups of **1**. The initially formed intermediate **27** can add to **1** accompanied by loss of nitrogen to yield **16** via either **28** or **29**.[25] The moderately high yields of **5** observed in the decompositions in methylene chloride and benzene probably resulted through decarboxylation of **16** (R = H) as these decompositions were carried out in the presence of atmospheric moisture. A similar proposal was made by Wamhoff and Wald to account for the production of **5** from the decomposition of **1** in aqueous pyridine.[5] Intermediate **28** does not close to **2**, since only low yields of **2** were obtained in the nucleophilic solvent systems. Addition of a nucleophilic solvent molecule to the carbonyl group of **29** leads to **30**.[26] Reaction of in-

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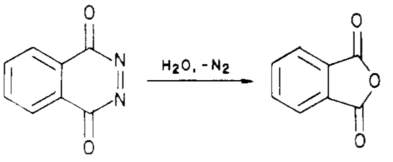
[22] Dao and Mackay (ref 7) reported that their **6** (R = Me) had mp 180–187 °C dec and gave no molecular ion in the mass spectrum.

[23] Compound **16** (R = Me) was not isolated in sufficient quantity to test its reactivity.

[24] It is possible that a free-radical process involving urazolyl radicals **9** can contribute to the decomposition (See ref 5).

[25] An alternate route to **16** is through **26** (S = OR). The production of **16** by this route is possible if formation of **25** (S = OR) is the rate-determining step and if the rate of formation of **25** (S = OR) is sufficiently enhanced by the effect of the hydrogen bonding between **1** and solvent (S = OR).

termediate **30** with **1** gives **31** and **11**. It is possible that diimide is involved as an intermediate in this conversion. Several examples of the isolation of oxidation products analogous to **31** from the decompositions of cis-diacyl diimides in the presence of nucleophiles have been reported. These include the formation of diethylmalonic acid derivatives from the decomposition of **17** in the presence of acetic acid[16] or hydrogen chloride[27] and the formation of phthalic anhydride from the decomposition of phthalazine-1,4-dione in the presence of atmospheric moisture.[28]



The carbamate products **13** can conceivably arise through three routes. Decomposition of product **16** (Scheme I, path B), product **31**, and intermediate **29** could all lead to **13**. Although **29** is a possible intermediate in

$$31 + \mathrm{ROH} \longrightarrow 13 + \mathrm{RO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OR}$$

the decomposition scheme, its presence is not required. Thus, the percent yield of **13** (R = Et) is near the sum of the yield of **11** and one-half the yield of **14** (R = Et), and it can be concluded that **13** (R = Et) arose primarily through products **16** (R = Et) and **31** (R = Et).[29] Similarly, the yields of **13** (R = *t*-Bu) and **11** are nearly equal in the decomposition in *tert*-butyl alcohol, and it seems likely that these two products were formed via **30** (R = *t*-Bu). Finally the presence of **12** in the aqueous and acetic acid solvent system implies the formation of aniline. The aniline can react with **1** to give **12**. In the case of decomposition in the acetic acid solvent system, it can also react with the acetic anhydride present to yield **15**.

In summary, we have shown that **1** can decompose in solution by several different reaction pathways. Both the nature of the solvent system and other decomposition conditions determine which reaction pathways are followed.

Experimental Section

Melting points were taken on a Mel-Temp melting point apparatus and are uncorrected. Infrared spectra were recorded on a Beckman IR-10 or Acculab 10 spectrophotometer. NMR spectra were obtained on a Varian EM-360A nuclear magnetic resonance spectrometer. Mass spectra were determined on an AEI-902 mass spectrometer at the Research Triangle Institute of Mass Spectrometry, Research Triangle Park, NC. High-performance liquid chromatograms were obtained either on a Waters Associates HPLC system or on a Varian Model 5000 liquid chromatograph, and gas chromatography was performed on a Varian 3700 gas chromatograph. Elemental analyses were determined by MHW Laboratories, Phoenix, AZ.

General Procedure for the Decomposition Reactions. A. Nonnucleophilic Solvents. A solution containing 1.50 g (8.47 mmol) of 4-phenyl-1,2,4-triazoline-3,5-dione (**1**)[2] in 50–100 mL of solvent was heated at reflux. The decomposition was complete when the characteristic carmine red color of **1** had faded. Upon cooling, the precipitate of 1,3,5,7-tetrone (**2**) was removed by filtration: mp, sublimed above 300 °C; IR (Nujol) 1785, 1756, 1164, 1010, 740, 734, 717, 680 cm^{-1}; MS, *m/z* (relative intensity) 322 (58, M$^+$), 119 (100), 91 (21).

Anal. Calcd for $C_{16}H_{10}N_4O_4$: C, 59.65; H, 3.11; N, 17.39. Found: C, 59.34; H, 3.29; N, 17.36.

The filtrate was evaporated to dryness on a rotary evaporator to give 1-(*N*-phenylcarbamoyl)-4-phenylurazole (**5**), which was purified either by washing with chloroform or by recrystallization from ethanol–water: mp 195–198 °C; IR (Nujol) 3225, 1795, 1730, 1606, 1565, 1500, 1234, 762, 747, 711, 685 cm^{-1}; MS, *m/z* (relative intensity) 296 (5, M$^+$), 177 (100), 119 (73), 91 (34).

Anal. Calcd for $C_{15}H_{12}N_4O_3$: C, 60.81; H, 4.05; N, 18.92. Found: C, 60.59; H, 4.01; N, 18.66.

B. Nucleophilic Solvents. A solution was prepared which contained 1.50 g (8.47 mmol) of **1** dissolved in 50 mL of either methylene chloride or ethyl acetate. To the solution at room temperature was added 5–10 mL of the nucleophilic solvent with stirring. Stirring was continued until the decomposition was complete. The solvent was removed by rotary evaporation, and the residue was dissolved in 50 mL of methylene chloride. The insoluble precipitate of **2** was removed by filtration. The methylene chloride solution was washed with three 25-mL portions of water. The aqueous washings were evaporated to dryness by rotary evaporation to give 4-phenylurazole (**11**): mp 208–210 °C [lit.[2] mp 209–210 °C]. The methylene chloride solution was washed three times with 25-mL portions of 5% Na_2CO_3. The carbonate washings were acidified (HCl) to precipitate **5**, which was removed by filtration. In the case of the decomposition in ethanol–methylene chloride, the acidified carbonate washings were next washed with three 30-mL portions of methylene chloride. The methylene chloride washings were dried ($MgSO_4$) and evaporated to dryness by rotary evaporation to give 1-(ethoxycarbonyl)-4-phenylurazole (**15**, R = Et) as a white solid. Recrystallization from CCl_4–$CHCl_3$ gave a white solid, mp 120–121 °C. The liquid resolidified immediately and melted again at 131–132 °C. Mass spectral and elemental analyses of this solid showed that it contained approximately 80% **14** (R = Et) and 20% CCl_4–$CHCl_3$. Heating the solid at 140 °C for 15 min under a stream of nitrogen gave an analytical sample of **14** (R = Et): mp 131.5–132.5 °C; IR (Nujol) 3165, 3060, 1795, 1742, 1703, 1600, 1498, 1316, 1145 cm^{-1}; MS, *m/z* (relative intensity) 249 (7, M$^+$), 205 (6), 177 (100), 119 (34), 91 (21); ^{1}H NMR ($CDCl_3$) δ 8.05 (m, 6, Ar CH and NH), 4.60 (q, 2, OCH_3), 1.35 (t, 3, CH_3).

Anal. Calcd for $C_{11}H_{11}N_3O_4$: C, 53.01; H, 4.45; N, 16.86. Found: C, 52.79; H, 4.31; N, 17.02.

The original methylene chloride solution was dried ($MgSO_4$) and evaporated to dryness under reduced pressure to give either ethyl *N*-phenylcarbamate (**13**, R = Et) [EtOH-CH_2Cl_2 solvent system], *tert*-butyl *N*-phenylcarbamate (**13**, R = *t*-Bu)[30] [*t*-BuOH–CH_2Cl_2 solvent system], or diphenylurea (**12**) [H_2O–EtOAc solvent system]. These last three compounds were recrystallized by standard procedures[31] and identified by comparing their melting points and IR spectra with those of authentic samples.

Decomposition of 1 in Bromobenzene. A solution containing 1.40 g (8.00 mmol) of **1** in 50 mL of bromobenzene under nitrogen was heated at reflux for 6 h, after which decomposition of **1** was complete. The reaction mixture was allowed to stand at room temperature for 4 weeks during which a precipitate slowly formed. The precipitate was filtered, dried, and heated for 5 min in 10 mL of chloroform. The hot solution was filtered and the insoluble solids washed with 3 mL of hot chloroform to give 0.15 g (11.6%) of **2**. The filtrate was evaporated to dryness by rotary evaporation to give a solid residue. Recrystallization of the residue from chloroform–petroleum ether gave 0.10 g (9.0%) of 1,2-bis(*N*-phenylcarbamoyl)-4-phenylurazole (**7**) as a white solid: mp 202–206 °C; IR (Nujol) 3317, 1997, 1747, 1603, 1540, 1498, 1277, 1238, 759, 741, 687 cm^{-1}; MS, *m/z* (relative intensity) 296 (11, M – C_6H_5NCO), 177 (99), 119 (100), 91 (96).

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(26) An alternate route to **30** involves the addition of ROH to the carbonyl group of **27** followed by ring opening. This route is possible if addition of ROH to **27** is sufficiently competitive with the cleavage of the C–N bond in the conversion of **27** to **29**.

(27) Evnin, A. B.; Lam, A. Y.; Maher, I. I.; Blyskal, J. J. *Tetrahedron Lett.* **1969**, 4497.

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

(29) The percent yield of **14** (R = Et) was calculated on the basis that 2 equiv of **1** gave 1 equiv of **14** (R = Et), whereas the percent yield of **13** (R = Et) was calculated on the basis that 1 equiv of **1** gave 1 equiv of **13** (R = Et).

(30) The IR spectrum of the crude product showed bands corresponding to those of di-*tert*-butyl carbonate.

(31) Shriner, R. L.; Fuson, R. C.; Curtin, D. Y.; Morrill, T. C. "The Systematic Identification of Organic Compounds", 6th ed.; Wiley: New York, 1980.

Anal. Calcd for $C_{22}H_{17}N_5O_4$: C, 63.61; H, 4.10; N, 16.87. Found: C, 63.57; H, 4.05; N, 17.05.

To the original bromobenzene filtrate was added 10 mL of water and the resulting mixture stirred overnight. The mixture was filtered to give after drying 0.35 g (41%) of **12**: mp 238–240 °C [lit.[31] 238 °C]. The bromobenzene solution was dried ($MgSO_4$) and distilled to give a small amount of gummy residue, which was not characterized.

Decomposition of 1 in Phenylcyclohexane. A solution containing 1.85 g (10.5 mmol) of **1** in 50 mL of phenylcyclohexane in a 100-mL three-necked flask was kept under a nitrogen atmosphere with stirring. The flask was heated in an oil bath. When the temperature reached 160–165 °C, rapid decomposition occurred, which was complete after 2–3 min. Upon cooling to room temperature, a small quantity of suspended solid was filtered to yield 0.0085 g (0.50%) of **2**. The filtrate was distilled under reduced pressure at 94–98 °C (10 mm). Gas chromatographic analysis of the distillate on a 5% OV-1 column at 145 °C showed the presence of a small quantity of phenyl isocyanate (**3**). Addition of 5 mL of water to the distillate produced 0.045 g (4.0%) of diphenylurea (**12**). The residue from the distillation was heated at 180 °C (0.05 mm) to remove most of the remaining phenylcyclohexane. To the moist solid residue was added 15 mL of chloroform. The insoluble solid was filtered to give 1.04 g of a solid mixture, which was only partially melted at 330 °C. The filtrate was evaporated by rotary evaporation to give 1.34 g of a solid–liquid residue. To the residue was added 25 mL of carbon tetrachloride. After heating to reflux, 5 mL of chloroform was added to dissolve most of the solid. The hot mixture was filtered, and 40 mL of hot petroleum ether was added to the filtrate. Upon cooling, a precipitate of 1-(1-phenylcyclohexyl)-4-phenylurazole (**8**) weighing 0.54 g (15%) slowly formed as a white solid. The solid **8** was filtered and the filtrate concentrated by rotary evaporation to give 0.50 g of a liquid residue. Gas chromatographic analysis of this residue on 5% OV-101 column programmed from 145–220 °C showed the presence of ten components. Compound **8** was purified by recrystallization from the carbon tetrachloride, chloroform, petroleum ether system described above: mp 168.5–170.5 °C; IR (Nujol) 3150, 1760, 1715, 1654, 1263, 1201, 1162, 1151, 770, 696 cm^{-1}; MS, m/z (relative intensity) 178.0616 (6.7, $C_8H_8N_3O_2$), 159 (100, $C_{12}H_{15}$), 91 (78, C_7H_7); ^1H NMR ($CDCl_3$) δ 9.4 (br s, 1), 7.33 (m, 10), 2.8 (m, 2), 2.2 (m, 2), 1.7 (m, 6). Anal. Calcd for $C_{20}H_{21}N_3O_2$: C, 71.62; H, 6.31; N, 12.52. Found: C, 70.30; H, 6.50; N, 12.27.[32]

Decomposition of 1 in the Presence of Acetic Acid, Acetic Anhydride, and Lead Acetate. To a slurry consisting of 5.1 g (29 mmol) of **11** in 300 mL of methylene chloride at 0 °C was added over a 20-min period 14.8 g (30 mmol) of 90% lead tetraacetate with stirring. Three hours was required to complete the oxidation. The reaction mixture was filtered, and the filtered solids were washed with 50 mL of methylene chloride. The washings were combined with the filtrate, and the resulting solution was allowed to warm to room temperature and stand overnight for decomposition. The reaction mixture was filtered to remove 1.00 g (21.4%) of **2**. The methylene chloride solution was washed with two 100-mL portions of water and two 100-mL portions of 10% Na_2CO_3. The carbonate washings were acidified (HCl), and the precipitate was suction filtered to give 1.40 g (32.6%) of **5**. The aqueous washings were evaporated to dryness to give a solid residue containing **11** and lead diacetate. The original methylene chloride solution was dried ($MgSO_4$) and evaporated under reduced pressure to give a solid residue. The residue was heated in 20 mL of boiling water for 15 min and filtered. The aqueous filtrate was evaporated to dryness to give 0.090 g (2.3%) of acetanilide (**15**), which was identified by comparison of its mp and IR spectrum to those of an authentic sample. The filtered solid was heated in 10 mL of boiling chloroform for 10 min. The hot mixture was filtered and the filtrate evaporated to dryness to yield 0.35 g (11.4%) of **12**, which was identified by comparison of its mp and IR spectrum to those of an authentic sample.

Reaction of 1-(Methoxycarbonyl)-4-phenylurazole (14, R = Me) with 3. To a slurry of 0.25 g (5.0 mmol) of 50% NaH–mineral oil in 30 mL of dry THF was added 1.18 g (5.00 mmol) of **14** (R = Me) with stirring. After 15 min 0.60 g (5.0 mmol) of **3** was added. The mixture was stirred for 70 min at room temperature. The THF was evaporated, and the residue was washed twice with 25 mL of hexane. To the solid residue was added 100 mL of water. The insoluble solid was filtered to give 0.45 g (28%) of **2**. Acidification of the filtrate with concentrated HCl yielded 0.55 g of **14** (R = Me) (47% recovery). The hexane washings were evaporated to give a solid–liquid residue, which was shown to contain **3** and mineral oil by IR spectroscopy.

Reaction of Equimolar Quantities of 1 and Methanol. The reaction of 10 mmol each of **1** and methanol in benzene was carried out as described in ref 7. Following decomposition of **1**, 0.4 g of a precipitate containing **2** was filtered off. The solvent was evaporated to give a gummy solid. A small portion of the solid was placed in 5 mL of HPLC grade ethyl acetate. The soluble portion was analyzed by HPLC on a Partisil PXS 10/25 silica column by using a solvent flow rate of 3.0 mL/min, a detector wavelength of 266 nm, and a solvent mixture of hexane–ethyl acetate (75:25) for 0–4 min, which was programmed to 100% ethyl acetate from 4–5 min. Peaks appeared at t_R 2.06, 3.42, 4.33, 6.50, and 7.44 min. The peak at t_R 2.06 min (20%) corresponded to **13** (R = Me). To the gummy solid was added 15 mL of chloroform. The insoluble portion was removed by filtration, and the filtrate was slowly evaporated at room temperatuve to a volume of 3–4 mL. The solid that separated was filtered and washed with 8 mL of $CHCl_3$–CCl_4 (40:60). This solid was recrystallized twice from $CHCl_3$–CCl_4 (40:60) to give 40 mg (2%) of 1-(*N*-phenyl-*N*-methoxycarbonyl)-4-phenylurazole (**16**, R = Me) as a white solid: mp 226–230 °C (gas evolution); IR (Nujol) 1699, 1730, and 1750 (C=O), 3398 (N–H) cm^{-1}; MS, calcd for $C_{17}H_{14}N_4O_5$ 354.0962, found 354.0968; ^1H NMR ($CDCl_3$) δ 9.0 (br s, 1), 7.45 (m, 10), 3.99 (s, 3). Analysis by HPLC as described above showed that **16** (R = Me) corresponded to the peak at t_R 4.33 min (95% purity).

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Registry No. **1**, 4233-33-4; **2**, 32494-23-8; **3**, 103-71-9; **5**, 63376-35-2; **7**, 98304-07-5; **8**, 98304-08-6; **11**, 15988-11-1; **12**, 26763-63-3; **13** (R = Et), 101-99-5; **13** (R = Bu-*t*), 3422-01-3; **14**, 98304-09-7; **15**, 103-84-4; **16**, 98304-10-0; C_6H_6, 71-43-2; CH_2Cl_2, 75-09-2; C_6H_5Br, 108-86-1; $C_6H_5C_6H_{11}$, 827-52-1; HOAc, 64-19-7; $Pb(OAc)_2$, 301-04-2; Ac_2O, 108-24-7; EtOH, 64-17-5; *t*-BuOH, 75-65-0; H_2O, 7732-18-5; EtOAc, 141-78-6; CH_3OH, 67-56-1.

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(32) Analysis of recrystallized **8** by HPLC on a reversed-phase column showed the presence of 3–4% of an impurity. Further recrystallizations did not remove the impurity.