1,2,4-TRIAZOLINE-3,5-DIONE - AN ELUSIVE CYCLIC AZO COMPOUND

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The compound 1,2,4-triazoline-3,5-dione (2a) is of interest theoretically[1] but it has never been isolated and characterized. Its preparation was first claimed by Stolle.[2] Recently it was generated at low temperature and trapped in situ with several dienes and the melting points of the adducts reported.[3] Recently, an ultraviolet spectrum of 2a was obtained but an extinction coefficient was not reported.[1] We wish to report the results of our work on the preparation of 2a in solution, its spectral properties, and some preliminary data on its decomposition.

| 1 | 2 | 3 | 4 | a) R = H |
| | | | | b) R = Et |
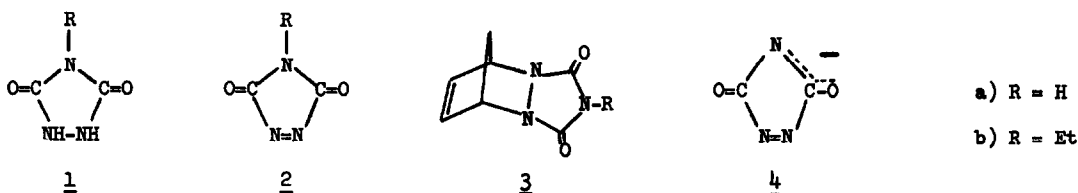
The dropwise addition of a solution of N_2O_4 (4 mmol) in CH_2Cl_2 (25 ml) to a suspension of urazole (1a) (5 mmol) in CH_2Cl_2 (250 ml) at 0° resulted in the gradual formation of a deep pink solution.[4] Addition of cyclopentadiene to this solution at 0° immediately discharged the pink color and the Diels-Alder adduct, 3a, was formed in 84% yield based on urazole consumed; mp, 210-212° dec (EtOAc) [lit.[3] mp 214-216° (EtOH)]. The structure of 3a is consistent with analytical and spectral data.[5] Similar results were obtained by using lead tetraacetate as the oxidant. By analogy with the reported oxidation of substituted urazoles,[4] the known dienophilic character of triazolinediones[3,6] and the structure of adduct 3a, we conclude that 2a is generated by both methods.

Qualitatively, the pink color of 2a persists in solution at 0° for several hours, suggesting a greater stability than had been supposed from prior reports. We generated 2a in several

solvents by adding N_2O_4 to a urazole solution (or suspension) and recorded the ultraviolet spectrum (Table 1).

Table 1. Spectral Data for 2a and 2b

Conditions	2a (0°)		2b (25°)	
	$\bar{\nu}$ (C=O), cm^{-1}	λmax (ϵmax), nm[a]	$\bar{\nu}$ (C=O), cm^{-1}	λmax (ϵmax), nm
DMF		523(209)		519(174)
DMF + NaOAc[b,c]		524sh, 542, 562		520
DMF + NH$_3$[b]		525sh, 543, 563		525sh, 541, 562
CH$_2$Cl$_2$	1790	500sh, 518(203), 539(237), 562(199)	1782	520, 534, 562
Diglyme	1778	515sh(182), 531(213), 552sh(159)		527
Diglyme + NH$_3$[b]		520sh, 537, 559		519, 538, 558
CH$_3$CN[d]	1790	510sh, 529, 549		
CCl$_4$[e]		548		544(230)

(a) The concentration of 2a was determined by titrating (0°) with a solution of cyclopentadiene while concurrently recording the uv spectrum.[7] ϵ was thus calculated and the average of several determinations is reported. (b) 2a does not react with cyclopentadiene under these conditions, uv data attributed to 4. (c) DMSO gave similar spectra. (d) 25°. (e) Ref. 1.

In some cases, anhydrous Na_2SO_4 or $MgSO_4$ was added to remove any water generated by the oxidation reaction.[9] These drying agents had no effect on the uv spectrum of 2a. However, in other cases, noted in Table 1, anhydrous NaOAc was used both as a desiccant and as a buffering agent for removing acidic oxidation products.[9] These spectra exhibit bathochromic shifts with the appearance of additional bands. The effect also occurs with dissolved ammonia. In the presence of NaOAc or ammonia, the pink oxidation product does not undergo immediate reaction with cyclopentadiene. With the addition of concentrated HCl, however, the spectrum reverts to its original form and reaction with cyclopentadiene then occurs rapidly. The spectrum of 2a also exhibits a longer wavelength maximum with the appearance of additional bands in CH_2Cl_2 (Table 1). However, reaction with cyclopentadiene is rapid under these conditions. These various spectral forms exhibited by 2a are shown in Figure 1.

The spectral changes resulting from a change in solvent polarity are in the direction expected for $n-\pi^*$ transitions.[10] The extent to which these changes also reflect possible changes in the position of keto-enol equilibrium for 2a has not been established unambiguously. The spectral changes caused by the addition of base (NaOAc or NH_3) must be due to something other than a simple solvent effect, since this alone does not explain the poor reactivity

Figure 1. Ultraviolet Spectra of
1,2,4-Triazoline-3,5-Dione; (a) in Methylene
Chloride, (b) in DMF, (c) in DMF Containing
Excess Anhydrous Sodium Acetate.
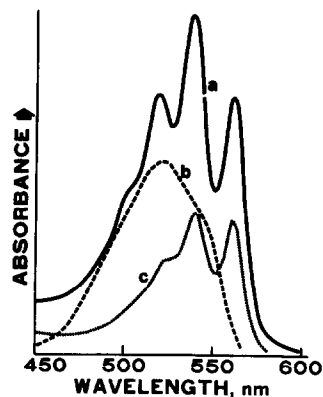
towards cyclopentadiene. We interpret these results to mean that 2a is converted to its anion

($\underline{4}$), whose formation is reversed on addition of acid. The failure of anion $\underline{4}$ to react with

cyclopentadiene is not unexpected; dienophiles with electron-donating groups are generally

less reactive.[11] In support of this, the ethyl-substituted triazolinedione, 2b, for which

neutralization is not possible, reacts with cyclopentadiene under all conditions listed in

Table 1.[12]

Infrared spectra were obtained for both 2a and 2b. Solutions of 2a were unstable in the

spectrophotometer beam at ambient conditions, permitting only a few rapid scans of the carbonyl

region (Table 1) before the material had completely decomposed.

The stability of 2a in solution (typically 0.01-0.03 $\underline{M}$) is quite variable. At 0 to 3°, a

DMF solution of 2a, prepared by the addition of 2.6 mmol of N_2O_4 to 2.5 mmol of urazole in

50 ml of dry DMF, decomposes with a half-life of 200 min. Prepared the same way in diglyme at

0°, 2a is essentially unchanged after 2 hr; at 25° its half-life is approximately 30 min, and

in the presence of a two-fold excess of NaOAc (anhyd.), its half-life is approximately one hr.

In water at room temperature, its decomposition is complete in a few minutes. In all solvents

investigated, the decomposition of 2a is accelerated by both acids and water, substances which

are difficult to exclude in the in situ preparations reported here.

The decomposition products from 2a were examined briefly by oxidizing urazole with N_2O_4

at room temperature and collecting the evolved gases. Urazole (50 mmol) in DMF or DMSO was

treated with N_2O_4 (55 mmol) to yield, typically, N_2 (37.5 mmol), CO_2 (20-35 mmol), and CO

(0.5-1.0 mmol). Cyanuric acid was also present among the nonvolatile products. In a

comparable experiment containing NaOAc (100 mmol), product analysis gave N_2 (48 mmol), CO_2

(17.5 mmol), CO (2.4 mmol), and a nitrate salt which was not further characterized.

We expected $\underline{2a}$ to follow the simple decomposition scheme of some cyclic α-carbonyl azo compounds,[8,13] to yield N_2, CO, and HNCO, in equimolar amounts. The high yields of CO_2 strongly suggest that a hydrolysis reaction is occurring. Since water and acids are undoubtedly reactive by-products from the N_2O_4 oxidation, this result is not surprising. In the presence of NaOAc, both neutralization of acids and ionization of $\underline{2a}$ to $\underline{4}$ can occur. Most of the resulting processes are not fully understood. It has not been possible to generate $\underline{2a}$ by the oxidation of urazole without introducing additional reactants. However, in work now in progress, evidence has been found supporting a simple decomposition of $\underline{2a}$ to N_2, CO, and HNCO under conditions not involving the use of oxidizing agents. This will be the subject of a future report.

<div align="center">REFERENCES</div>

(1) A. V. Pocius and J. T. Yardley, J. Amer. Chem. Soc., 95, 721 (1973).

(2) R. Stolle, Ber., 45, 273 (1912).

(3) M. G. de Amezua, M. Lora-Tamayo and J. L. Soto, Tetrahedron Lett., 2407 (1970).

(4) J. C. Stickler and W. H. Pirkle, J. Org. Chem., 31, 3444 (1966).

(5) Anal. Calc. for $C_7H_7N_3O_2$: C, 50.9; H, 4.3; N, 25.4; mol. wt., 165; Found: C, 51.1; H, 4.3; N, 25.4; mol. wt., 168 (determined by DMF by vapor phase osmometry). Nmr (DMSO-d_6): δ 1.90 (2H, q), 4.93 (2H, s), 6.35 (2H, s), 11.21 (1H, s); fine structure is evident in all but the lowest-field signal. Ir (KBr): 1750 cm^{-1} (s), 1725 (s) and 1380 (s).

(6) B. T. Gillis and J. D. Hagarty, J. Org. Chem., 32, 330 (1967).

(7) The end point was taken at the complete disappearance of the pink color. The reaction with cyclopentadiene was assumed to be quantitative. The reactivity of cis-α,α'-dicarbonyl azo compounds as dienophiles is well-documented making this assumption a reasonable one.[8]

(8) B. T. Gillis and R. Weinkam, J. Org. Chem., 32, 3321 (1967).

(9) N_2O_4 oxidation products include nitrous and nitric acids; see F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience Publishers, N. Y. 1972, 3rd Ed., pp 357-60, for a discussion of N_2O_4.

(10) The more polar solvents shift the maximum to shorter wavelengths. See J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", John Wiley and Sons, Inc., New York, 1966, pp 255-57.

(11) "1,4-Cycloaddition Reactions", J. Hamer, Ed., Academic Press, New York, 1967, Chapter 6.

(12) 4-Ethyl urazole ($\underline{1b}$) was obtained from N,N'-diethylazobisformamide by photolysis in DMSO. Its structure was consistent with nmr, ir, mol wt and combustion analysis data. The details of this work will be described in a forthcoming publication.

(13) B. T. Gillis and J. G. Dain, J. Org. Chem., 36, 518 (1971).