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NEW FORMATION OF A 1,3-DIPOLE IN THE REACTION OF ADAMANTANONE AZINE WITH TRIAZOLINEDIONES: IN CONNECTION WITH REACTIVITY TOWARD SINGLET OXYGEN

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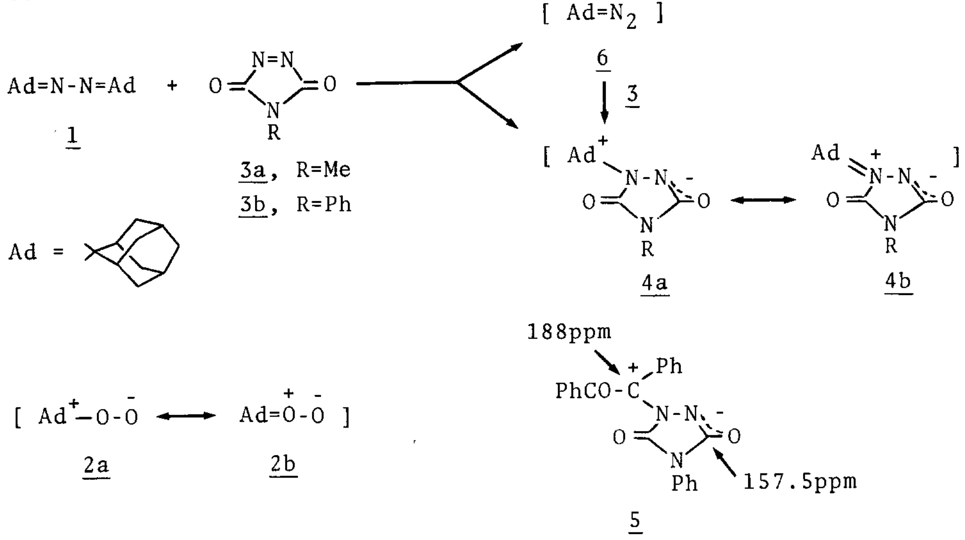
Summary: Tricyclo[3.3.1.1]decanone azine (adamantanone azine) reacts with 4-substituted 1,2,4-triazoline-3,5-diones under elimination of diazo adamantane to give a 1,3-dipole ("azomethinimine"), which on treatment with dipolarophiles affords the [2 + 3]-cycloadducts. The reaction is compared with singlet oxygen oxidation.

The reactions of azines with dienophiles represent a valuable enlargement to synthetic heterocyclic chemistry.[1)] Azines derived from aromatic aldehydes or hexafluoroacetone undergo the so-called criss-cross addition with two equivalents of dienophile to give diazabicyclooctane derivatives. Azines of cyclic ketones add dienophiles in Michael- or ene synthesis, affording the corresponding ring-substituted products. Meanwhile, 4-substituted 1,2,4-triazoline-3,5-diones (TAD) might be an interesting and useful substrate for exploring [2 + 2]-[2)] and [2 + 4]-cycloaddition[3)] and ene reaction of olefins.[4)] Its reaction modes also resemble those of singlet oxygen.[2-4)] Recently, we have found that the photooxygenation of tricyclo[3.3.1.1]decanone azine (adamantanone azine, 1) produces a carbonyl oxide intermediate (2) by elimination of diazo adamantane.[5)] These results have prompted us to investigate the reactivity of azines toward TAD in comparison with singlet oxygen oxidations.

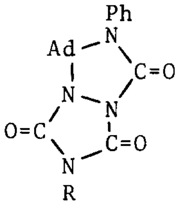
To 4-methyl-1,2,4-triazoline-3,5-dione (3a, 1 mmol) was added a methylene chloride solution of azine 1 (1 mmol) at room temperature under nitrogen atmosphere. An exothermic reaction[6)] immediately took place with evolution of nitrogen and the red color of reaction mixture turned to dark green. When the reaction mixture was chromatographed on silica gel, adamantanone and N-methylurazole were obtained in 75% and 73% yields, respectively, accompanied with recovered 1 (43%). When 2 mmol of 3a was used under the same condition, 1 was completely consumed (adamantanone; 180%, N-methylurazole; 95%) and the criss-cross addition products were not obtained at all. Very similar results were obtained with 4-phenyl derivatives (3b). A suspected intermediate would be a 1,3-dipole ("azomethinimine" form, 4),[6-8] which was stable in anhydrous solution, but could not be isolated (Scheme). A characteristic feature of azomethinimine intermediate 4 is seen in the ^{1}H-NMR spectra, where the resonances due to the α-hydrogen atoms adjacent to the cationic carbon appear at 4.10(bs s,1H) and 4.75(br s,1H) ppm; in the ^{13}C-NMR spectra, the cationic carbon and anionic carbon resonances are assigned at 181.6 and 156.5 ppm, respectively, by comparison with those found for the corresponding benzil derivatives (5).[6] These spectra data may demonstrate the large contribution of the structure 4b. One plausible rationale for these observations is that the reaction of azine 1 with triazolinediones 3 would initially form azomethinimine intermediate 4 by eliminating diazo adamantane (6).[5] A subsequent reaction [6,7] of 6 with another molecule of 3 might also produce 4 as shown in Scheme, followed by formation of the hydrolyzed products, i.e., adamantanone and N-methylurazole.

Scheme.



To test these possibilities, the following experiments have been done. In order to trap the dipole intermediate 4, the cycloaddition was attempted with some dipolarophiles. The reaction[9] in the presence of phenylisocyanate and acetylenedicarboxylic acid dimethyl ester[6] afforded the corresponding adducts, 7[10] and 8,[11] in substantial yields, respectively. When the reaction mixture[9] was quenched with methanol, the corresponding urazole 9[12] was obtained. These results clearly show the actual existence of azomethinimine intermediate 4. Meanwhile, carbonyl oxide 2 produced in the singlet oxygen oxidation of 1 can also be trapped with p-nitrobenzaldehyde and methanol to form the same type of adducts, 10 and 11, in moderate yields, respectively.[13]

Thus, a new type of reaction of azine 1 with triazolinediones 3 afforded a 1,3-dipole 4 ("azomethinimine") instead of the criss-cross adducts under elimination of diazo adamantane and may have some relations with relatively low oxidation potential of 1 or conformation similar to the reaction with singlet oxygen.[5] The studies with TAD might provide the more detailed insight for the singlet oxygen oxidation of azines.



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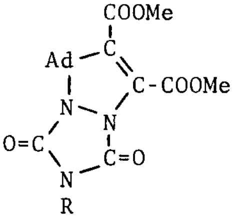

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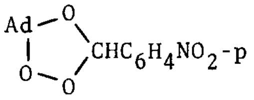

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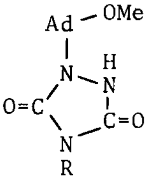

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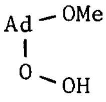

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References and Notes:

1) Warner-Jauregg, T., Synthesis, 1976, 349; references cited therein.

2) Körner von Gustorf, E.; White, D. V.; Kim, B.; Hee, D.; Leitich, J., J. Org. Chem., 1970, 35, 1155; Pasto, D. J.; Chen, F. T., Tetrahedron Lett., 1973, 713; Hoffman, R. W., Angew. Chem. Int. Ed. Eng., 1972, 11, 324;

Adam, W.; De Lucchi, O., Tetrahedron Lett., 1981, 22, 929.

3) Adam, W.; De Lucchi, O., Angew. Chem. Int. Ed. Eng., 1980, 19, 762; Burrage, M. E.; Cookson, R. C.; Gupte, E. S.; Stevens, I. D. R., J. Chem. Soc. Perkin Trans. 2, 1975, 1325.

4) Hoffmann, H. M. R., Angew. Chem. Int. Ed. Eng., 1969, 8, 556; Gopalan, A,; Moerck, R.; Magnus, P., J. Chem. Soc. Chem. Commun., 1979, 548; Seymour, C. A.; Greene, F. D., J. Am. Chem. Soc., 1980, 102, 4806.

5) Ando, W.; Sato, R.; Sonobe, H.; Akasaka, T., Tetrahedron Lett., 1984, 25, 853.

6) Bethäuser, W.; Regitz, M.; Theis, W., ibid., 1981, 22, 2535.

7) Bettinetti, G. F.; Capretti, L., Gazz. Chim. Ital., 1965, 95, 33; Ried, W.; Lim, S. H., Liebigs Ann. Chem., 1973, 1141.

8) Huisgen, R., Angew. Chem. Int. Ed. Eng., 1963, 2, 565; Fahr, E.; Lind, H., ibid., 1966, 5, 372; Moody, C. J., In "Advences In Heterocyclic Chemistry", Katritzky, A. R.; Boulton, A. J., Ed.; Academic Press: New York, 1982, 30: p 1.

9) Two equivalents of 3 was used to azine 1.

10) 6a: 76%; mp 186-188°C; m/e 366(M$^+$); IR(KBr) ν 1750, 1720 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ 7.28-7.60(m,5H), 3.13(s,3H), 2.39-2.86(m,4H), 1.50-2.10(m,10H) ppm; Anal. Calcd for $C_{20}H_{18}O_3N_4$: C,65.24; H,6.01; N,15.16. Found: C,65.55; H,6.05; N,15.29. 6b: 79%; mp 140-142°C; m/e 428(M$^+$); IR(KBr) ν 1780, 1720 cm^{-1}; ^{1}H-NMR(CDCl$_3$) δ 7.35-7.70(m,10H), 2.50-3.0(m,4H), 1.50-2.10(m,10H) ppm.

11) 7a: 36%; mp 179.5-181°C; m/e 389(M$^+$); IR(KBr) ν 1810, 1740 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ 3.95(s,3H), 3.87(s,3H), 3.08(s,3H), 2.30-3.0(m,4H), 1.55-2.10 (m,10H) ppm; Anal. Calcd for $C_{19}H_{23}O_6N_3$: C,58.60; H,5.95; N,10.79. Found: C,58.12; H,5.96; N,10.65. 7b: 57%; mp 176-178°C; m/e 451(M$^+$); IR(KBr) ν 1780, 1720 cm^{-1}; ^{1}H-NMR(CDCl$_3$) δ 7.45-7.65(m,5H), 3.95(s,3H), 3.87(s,3H), 2.30-3.0(m,4H), 1.50-2.10(m,10H) ppm.

12) 8a: quant.; ^{1}H-NMR(CDCl$_3$) δ 3.28(s,3H), 3.10(s,3H), 1.60-2.20(m,14H) ppm. 8b: quant.; ^{1}H-NMR(CDCl$_3$) δ 7.30-7.65(m,5H), 3.30(s,3H), 1.25-2.20(m,14H) ppm.

13) Ando, W.; Sato, R.; Akasaka, T., to be published.

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