Duality of Pathways in the Reaction of *N*-Phenyltriazolinedione with Alcohols

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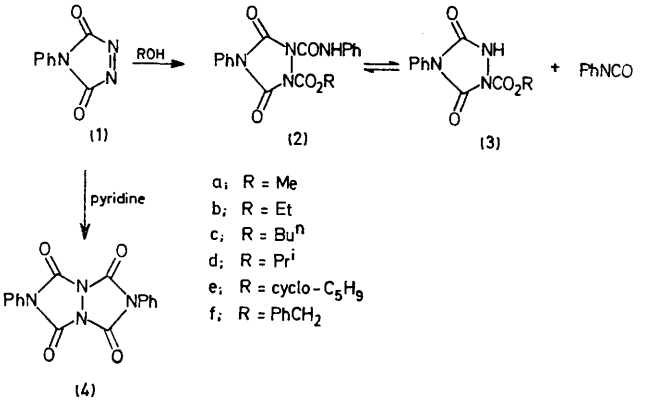
Summary *N*-Phenyltriazolinedione (**1**) in benzene gives 1-alkoxycarbonyl-2-*N*-phenylcarbamoyl-4-phenyl-1,2,4-triazolidine-3,5-diones (**2**) as the major product with simple primary aliphatic alcohols, and a minor one with secondary alcohols which are mainly oxidized to the carbonyl compound; the oxidation can, however, be suppressed in favour of the formation of (**2**) by addition of pyridine.

4-PHENYL-1,2,4-TRIAZOLINE-3,5-DIONE (**1**) is best known in its role as a dienophile in Diels–Alder reactions, but it has been used in other reactions as well, including insertion at C–H bonds in conjugated dienes[1] and in tropolone,[2] cycloaddition to alkenes,[3] formation of reactive dipoles with vinyl ethers,[4] vinyl esters,[5] and diazoacetic ester,[6] and oxidation of alcohols to carbonyl compounds.[7]

We now report that the last reaction is efficient only with easily oxidizable alcohols, especially arylalkyl methanols. The main or exclusive reaction with simple primary aliphatic alcohols, and a competing one with secondary aliphatic alcohols, involves formation of a compound (**2**) from two molecules of (**1**) and one of the alcohol with loss of one molecule of nitrogen.



Thus reaction of (**1**) at room temperature with 1 equiv. of methanol in benzene (*ca.* 2 days for a 0·1 M solution) or more rapidly in methanol as solvent, gave the sparingly soluble (**2a**) whose spectra included:† *m/e* 235 (M − PhNCO$^+$); ν(Nujol) 3398 (NH), 1828, 1760, and 1700 cm^{-1} (C=O); δ($CDCl_3$) 4·05 (OMe). It was thermally unstable, decomposing without melting to give a volatile liquid identified as phenyl isocyanate by conversion into ethyl phenylcarbamate. The phenylcarbamate was also obtained when (**2a**) was heated in ethanol, along with the other product of thermal decomposition (**3a**), m.p. 229—230 °C, which crystallized from the hot solution: *m/e* 235 (M^+); ν(Nujol) 3150 (NH), 1800, and 1754 cm^{-1} (C=O); δ($CDCl_3$) 3·94 (OMe). The identities of (**2a**) and (**3a**) were confirmed by synthesis, (**3a**) from 4-phenyl-1,2,4-triazolidine-3,5-dione with methyl chloroformate and (**2a**) from (**3a**) with phenyl isocyanate, both reactions being carried out in pyridine.

The decomposition of (**2a**) at 35 °C to (**3a**) and phenyl isocyanate was negligible in benzene or chloroform, but was rapid and reversible in pyridine (K_{eq} 0·75 for a 0·17 M solution at 35 °C, determined by ^{1}H n.m.r. analysis). The equilibrium position could be varied in either direction by the use of suitable mixtures of pyridine and chloroform as solvents. Urea-isocyanate equilibria of this kind have been occasionally noted recently.[8]

^{1}H N.m.r. analysis of the reaction of (**1**) and methanol in C_6D_6 showed that the formation of (**2a**) was quantitative; an isolated yield of 95% was obtained by allowing the reaction mixture to evaporate to a small volume at room temperature.

The possible formation of compounds of type (**2**) in benzene was examined for a number of representative alcohols. Ethanol and n-butanol gave (**2b**) (>95%) and (**2c**) (60%), no aldehyde being detected (^{1}H n.m.r. analysis in C_6D_6). Oxidation to the carbonyl compound with formation of 4-phenyl-1,2,4-triazolidine-3,5-dione was however, the dominant pathway in the reaction with propan-2-ol (68%), cyclopentanol (60%), and benzyl alcohol (80%), the balance being compound (**2**).

Pyridine had a marked catalytic effect on the formation of (**2**) but little or none on the oxidation. Inclusion of 1 equiv. in the reaction with propan-2-ol resulted in only 5% of oxidation (an amount not significantly changed by varying the pyridine content over the range 0·5—10 equiv.); the extent of oxidation of cyclopentanol similarly was only 20%, and benzyl alcohol 30%. Thus (**2d—f**) could be obtained in good yield.

In the absence of alcohol, pyridine caused the quantitative formation of (**4**) [a known product of thermal decomposition of (**1**)[9]], a compound not detected in the presence of alcohol. The intermediacy of (**4**) in the pathway to (**2**) can be discounted (though they may have a common precursor, which is very reactive to alcohol), since (**4**) is stable to methanol or ethanol under the reaction conditions.‡

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† Satisfactory elemental analyses were obtained for this and all other new compounds.

‡ Compound (**4**) is stable even in the neat alcohol at reflux. It is, however, slowly converted into (**2a**) by sodium methoxide in dimethylformamide.

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