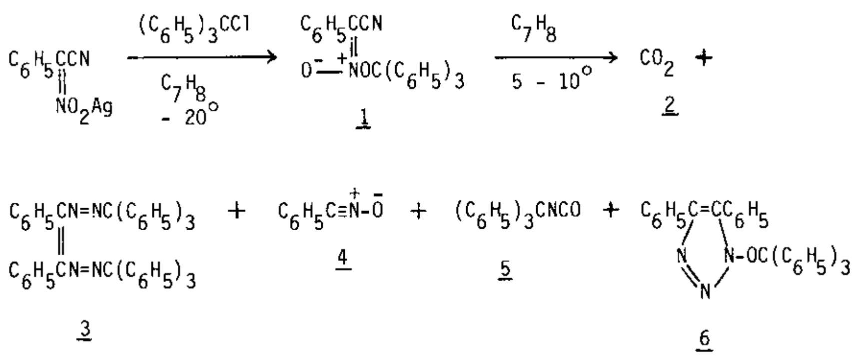
THE FORMATION AND FACILE CONVERSION OF TRITYL PHENYLCYANOMETHANE NITRONATE

Joseph H. Boyer* and Thanikavelu Manimaran

Chemistry Department, University of New Orleans, New Orleans, La. 70148, U.S.A.

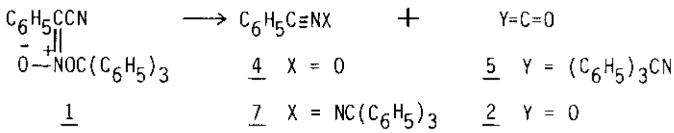
Abstract - Trityl chloride and silver phenylcyanomethane nitronate in toluene at -20°C gave trityl phenylcyanomethane nitronate 1, an unstable ester that rearranged and fragmented at 5-10°C to 1-triphenylmethoxy-4,5-diphenyl-1,2,3-triazole 6 with coproducts carbon dioxide, α,α'-bis(triphenylmethaneazo)stilbene 3, benzonitrile-N-oxide 4, and trityl isocyanate 5.

A product $C_{33}H_{25}N_3O$ obtained from an unexplained reaction[1] between silver phenylcyanomethane nitronate and trityl chloride in toluene at 0°C has been identified by X-ray crystallographic analysis as 1-triphenylmethoxy-4,5-diphenyl-1,2,3-triazole 6[2]. Coproducts included carbon dioxide 2, α,α'-bis(triphenylmethaneazo)stilbene 3, benzonitrile-N-oxide 4, and trityl isocyanate 5, eq(1)[1]. Trityl phenylcyanomethane nitronate 1 has now been identified as the initial product of the reaction at -20°C by comparative infra-red spectroscopic analysis (-20°C) of the ester 1 and the related benzyl[3] and benzhydryl[4] phenylcyanomethane nitronates (decomposition at 25°C)[5]. The conversion, eq(1), is important as a rare example of a transfer at low temperature of the oxygen atoms in a nitronate group to a carbon atom and is pertinent to explosive reactions of nitro compounds in which carbon dioxide may be similarly produced.

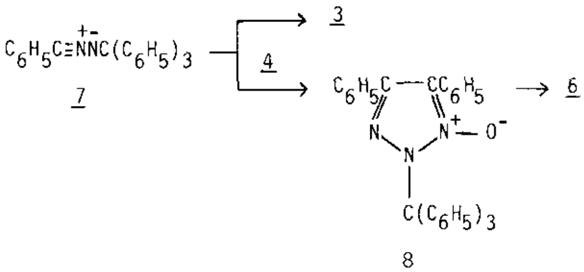


eq(1)

Product analysis revealed two fragmentation modes for the ester 1: one afforded benzonitrile-N-oxide 4 and trityl isocyanate 5, while the other differed by an interchange of oxo and tritylimino substituents (X, Y) to afford carbon dioxide 2 and benzonitrile-N-tritylimine 7, eq(2)[6,7]. The intermediacy of the nitrilimine 7 accounted for the formation of the bisazostilbene 3 (18%) by dimerization[1,6,7] and the triazole 6 (24%) by a dipolar addition with benzonitrile oxide 4 to give 2-trityl-4,5-diphenyl-1,2,3-triazole-1-oxide 8 (unisolated) followed by migration of a trityl group from a nitrogen to an oxygen atom, eq(3)[8,9].

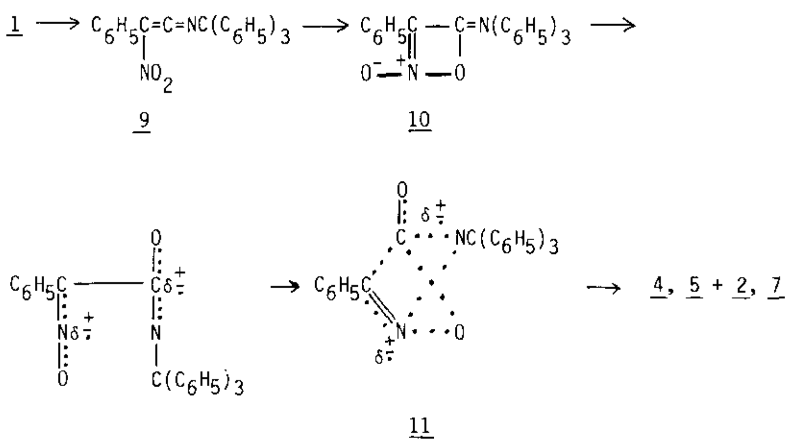


eq(2)



eq(3)

In a rationale for the dual fragmentation an initial isomerization of the ester 1 to the N-tritylimine 9 of phenylnitroketene,[10,11] ring-closure to the N-tritylimine 10 of 4H-3-phenyl-1,2-oxazet-4-one-2-oxide,[12,13] and ring opening by cleavage of a weak NO bond provided a model 11 as a precursor to compounds 4 and 5 by one fragmentation and to compounds 2 and 7 by another, eq(4). Further treatment of this complicated reaction will be dealt with in a longer report.



eq(4)

ACKNOWLEDGMENT

Financial support was received from ONR.

REFERENCES

1. D. Y. Curtin, R. J. Crawford, and D. K. Wedegaertner, J. Org. Chem., 1962, 27, 4300.

2. We are indebted to Dr. E. D. Stevens and Dr. C. L. Stevens for the X-ray analysis. The data will be published elsewhere.

3. J. T. Thurston and R. L. Shriner, J. Org. Chem., 1937, **2**, 183.

4. R. L. Shriner and G. B. Brown, J. Org. Chem., 1938, **2**, 561.

5. Since dual absorption bands near 1550 and 1350 cm^{-1}($-NO_2$) were absent at -20°C the formation of the nitronate esters predominated over the formation of the isomeric nitro compounds to be derived from C- and N-alkylation.

6. The nitrilimine 7 was previously abandoned as a precursor to the bisazostilbene 3 when benzonitrile-N-oxide 4 and trityl isocyanate 5 failed to give an adduct that might have fragmented to the nitrilimine 7 and carbon dioxide[7].

7. N. E. Alexandrou, J. Org. Chem., 1965, **30**, 1335.

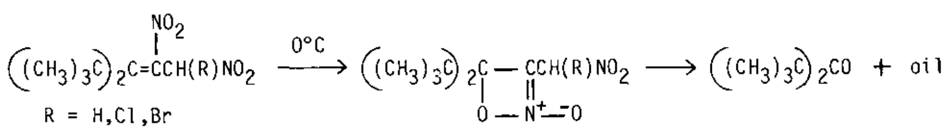
8. Attempts to realize independently a dipolar addition between benzonitrile-N-tritylimine 7 and benzonitrile-N-oxide 4 were abandoned when (a) tritylhydrazine and benzaldehyde failed to convert to the expected hydrazone (to be oxidized to the imine 7) and (b) N-tritylbenzohydrazidoyl chloride ($C_6H_5C(Cl)=NNHC(C_6H_5)_3$), to be dehydrochlorinated to the imine 7, was not obtained from β-N-tritylbenzohydrazide ($C_6H_5CONHNHC(C_6H_5)_3$) upon treatment with either thionyl chloride or phosphorus pentachloride.

9. The combined yield (42%) of compounds 3 and 6 is in good qualitative agreement with the yield (50%) reported for carbon dioxide[1].

10. The 1-5 sigmatropic isomerization 1 → 8 represented a formal change from O- to N-tritylation of a cyanomethane nitronate anion.

11. Attempts to prepare compound 8 by a reaction between trityl isocyanide and the sodium salt of phenylchloronitromethane were unsuccessful[7].

12. The formation of 4,4-di-t-butyl-3-methyl-4H-1,2-oxazete-2-oxide from 3-t-butyl-4,4-dimethyl-2-nitro-2-pentene on standing at 25°C was the first recognized example of an isomerization of an α,β-unsaturated nitro compound to a four-membered heterocycle. It underwent facile dissociation to give di-t-butyl ketone and an oil[13].



13. A. Berndt, Angew. Chem. Int. Ed. Eng., 1968, **7**, 637; K. Wieser and A. Berndt, ibid., 1975, **14**, 69, 70.

Received, 15th May, 1986