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REACTION OF THE SILVER SALT OF PHENYLNITROACETONITRILE WITH CARBON DISULPHIDE

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The silver salt of phenylnitroacetonitrile (I) reacts in unusual and complicated ways. Thus with triphenylmethyl chloride it gives one of the stereoisomeric α,α′-bis(triphenylmethanoazo)-stilbenes[1]. During study this reaction[2] it was found that (I) reacts with carbon disulphide at 40° to give a white crystalline product $C_{16}H_{10}N_4O_3$ (II) (≈5%) of m.p. 122-123° dec., together with carbonyl sulphide and silver sulphide:

$$2\ \left(C_6H_5-C(CN)(NO_2)\right)^-Ag^+ + CS_2 \xrightarrow{\Delta} C_{16}H_{10}N_4O_3 + COS + Ag_2S$$

I II

Compound (II) is also formed in some alkylation reactions[3] of (I).

Compound (II) showed weak i.r. absorption at 2240 cm^{-1} (C≡N) and two strong at 1585 and 1327cm^{-1}, an nmr multiplet centered at τ 2.3, and a uv maximum at 272 nm (ε 14.000). The mass spectrum gave no peak for the molecular ion, even at 15 eV, but instead prominent peaks at 260 m/e (M-46) and at 131, 105 and 77 m/e, which are attributed to the ions $(C_6H_5COCN)^+$, $C_6H_5CO^+$ and $C_6H_5^+$ respectively. The osmometric M.W. of II was 303 (theor. 306.3). Thermal decomposition of (II) gave benzoic acid and reduction with Adams catalyst in methanol afforded benzoylcyanide and ethyl benzoate.

The above and other data do not lead to an unequivocal structure.

Therefore the problem was solved by X-ray structure analysis*, which clearly showed that the product (II) is an oxime ether of benzoylcyanide oxime (III).

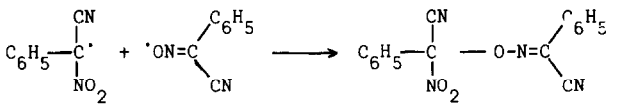
Crystal data are as follows: $C_{16}H_{10}N_4O_3$, monoclinic crystals from ether-petroleum ether (40-60°), with unit cell dimensions a=13.0346, b=9.8186, c=12.0830 Å, β=101.60°, z=4, space

* A detailed crystal structure analysis carried out by S. Kokkou and P. Rentzeperis, will be published in the Acta Crystallographica.

group $P2_{1/n}$. Intensities were measured in a PHILIPS automatic single crystal diffractometer (3094 reflections). The structure was solved by direct methods and refined to a final R=0.077. The bond lengths and angles found are given in figures 1 and 2 respectively.

Bond lengths and angles agree with literature values for similar systems, except that C_1-N_1 at 1.617 Å which is greater than the normally 1.50 Å for the C-N bond in nitro compounds, although some values up to 1.54 Å have been reported[4]. This larger C_1-N_1 distance is considered real. Mass spectral data show easy abstraction of the nitro group from the molecular ion $M^{+\cdot}$ which also suggests a weak and long C_1-N_1 bond.

Concerning the reaction mechanism we propose that the product (III) is formed by coupling species (IV) and (V) which are formed by homolytic decomposition of the silver salt (I):



IV V III

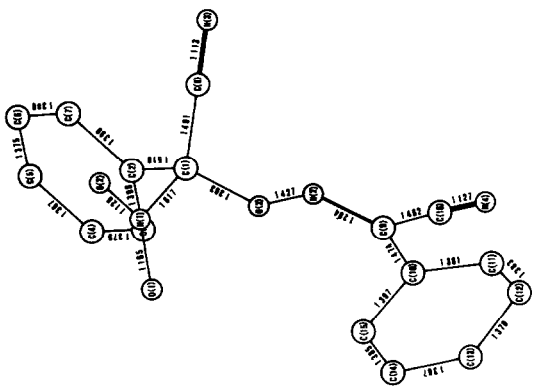


Fig. 1. Bond lengths of compound (III).

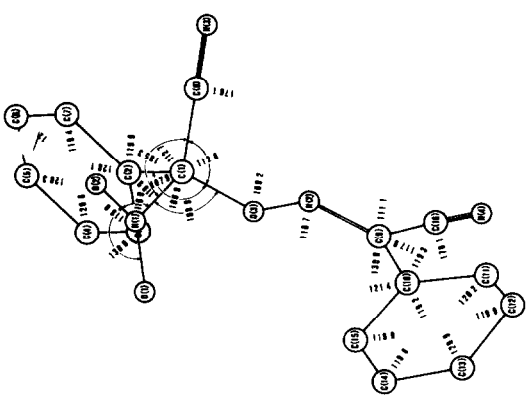


Fig. 2. Bond angles of compound (III).

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R E F E R E N C E S

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