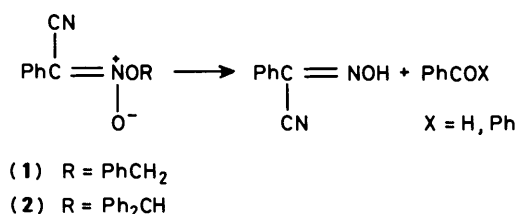# Triphenylmethyl Phenylcyanomethylenenitronate: Formation and Thermolysis

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The previously reported formation of carbon dioxide, α,α'-bis(trityl)stilbene (4), benzonitrile N-oxide (5), trityl isocyanate (6), and $C_{33}H_{25}N_3O$ (11) from a mixture of trityl chloride and silver phenylcyanomethylenenitronate in toluene is now attributed to the initial formation at $-20\,^{\circ}C$ of trityl phenylcyanomethylenenitronate (3) and its dissociations at $5\,^{\circ}C$. The ester (3) was characterized by conversion into bromonitrophenylacetonitrile (7) by treatment with bromine, to p-nitrobenzoyl cyanide (8) by treatment with dinitrogen tetraoxide, to trityl alcohol by hydrolysis, and to a mixture of trityl alcohol and trityl peroxide by exposure to the atmosphere. The bisazostilbene (4) (18%) and $C_{33}H_{25}N_3O$, identified by X-ray crystallographic analysis to be 4,5-diphenyl-1-triphenylmethoxy-1,2,3-triazole (11) (24%), were obtained from the nitronate ester (3) in toluene at $5\,^{\circ}C$; the nitrile oxide (5) and the isocyanate (6) were obtained in low yields from the ester (3) in dimethyl sulphoxide at $25\,^{\circ}C$. Hydrolysis converted the triazole (11) into 1-hydroxy-4,5-diphenyl-1,2,3-triazole (12) and trityl alcohol. Silver p-bromophenylcyanomethylenenitronate and trityl chloride afforded α,α'-bis-(tritylazo)-p,p'-dibromostilbene and its thermolysis product, p,p'-dibromodiphenylacetylene. Fragmentation of the ester (3) in the presence of added phenyl isocyanate gave the bisazo compound (4) and 3,4-diphenyl-1,2,4-oxadiazol-5-one (18). A similar mixture stored at $-20\,^{\circ}C$ gave the triazole (11) and the oxadiazolone (18). Aroyl nitrile oxides as well as phenyl isocyanate suppressed the formation of the red bisazostilbene (4). The intermediacy of the N-trityl imine (14) of $4H$-3-phenyl-1,2-oxazet-4-one 2-oxide in the thermolysis of the nitronate (3) was discussed.
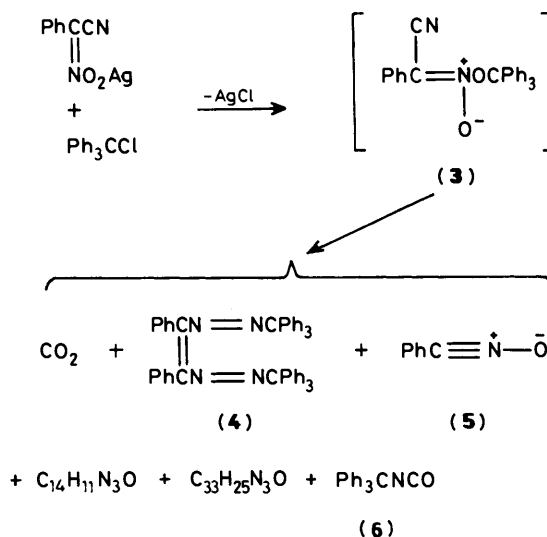
Phenylcyanomethylene nitronates and esters of other nitronic acids tend to be thermally unstable. Methyl phenylcyanomethylenenitronate had a half-life of several hours (25 °C).[1] Neither the benzyl (1) nor the benzhydryl ester (2) was isolated and each fragmented to the oxime of benzoyl cyanide and an appropriate carbonyl derivative (Scheme 1).[2] The formation of

(1) R = PhCH₂
(2) R = Ph₂CH

Scheme 1.

trityl phenylcyanomethylenenitronate (3) from a mixture of trityl chloride and silver phenylcyanomethylenenitronate in toluene was not previously detected.[3–5] (An α-oxo triphenyl-methylenenitronate was obtained from trityl chloride and the sodium salt of α-nitrocamphor.[6]) Instead, products whose formations were not explained included carbon dioxide, α,α'-bis(tritylazo)stilbene (4), benzonitrile N-oxide (5), trityl isocyanate (6), and two unidentified compounds $C_{33}H_{25}N_3O$ and $C_{14}H_{11}N_3O$ (Scheme 2).
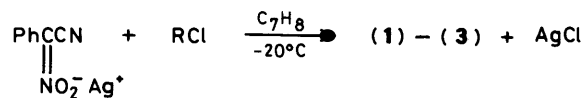
A re-investigation of this reaction was undertaken to determine structures for the unidentified products and to explain the formation of all products.[7] The formation of carbon dioxide was unique and of particular interest since the reaction, carried out in the absence of air, required the facile transfer of both oxygen atoms in the nitronate group to a carbon atom. This phenomenon is pertinent to detonations that produce carbon dioxide from organic nitro compounds.
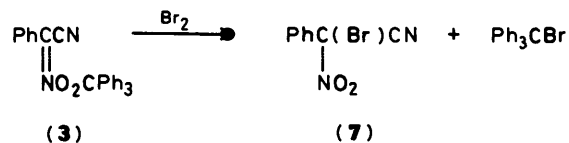
Scheme 2.

Results and Discussion

The formation of benzyl (1), benzhydryl (2), and trityl phenylcyanomethylenenitronate (3) by O-alkylation of the corresponding silver nitronate in toluene at $-20\,^{\circ}C$ (Scheme 3), was established by similarities throughout the i.r. spectra ($-20\,^{\circ}C$) for the three esters. In particular, the intense azomethine absorption at 1 590 (1), 1 580 (2), and 1 585 cm⁻¹ (3)[1b] and the absence of dual absorption near 1550 and 1350 cm⁻¹, characteristic of the nitro group,[1c] eliminated the presence of significant amounts of the isomeric products from C- and N-tritylation.

$$\underset{\underset{NO_2^- Ag^+}{\overset{\parallel}{\text{PhCCN}}}}{} + \text{RCl} \xrightarrow[-20°C]{C_7H_8} (1) - (3) + AgCl$$
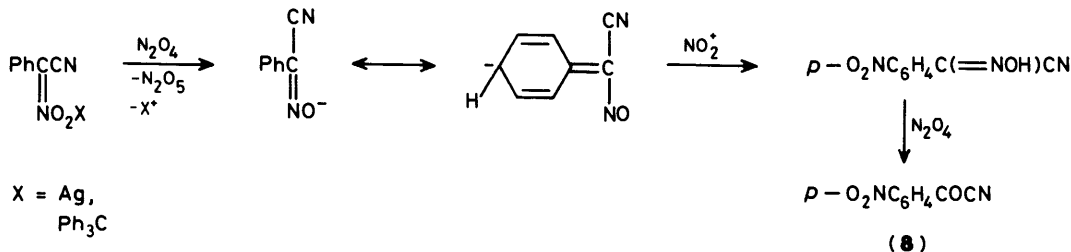
R = PhCH$_2$, Ph$_2$CH , Ph$_3$C

Scheme 3.

Just as bromination of sodium phenylcyanomethylene-nitronate gave bromonitrophenylacetonitrile (7),[8a,b] the trityl nitronate (3) gave bromonitrophenylacetonitrile (7) (53%) and trityl bromide (69%) on treatment with bromine (Scheme 4).

$$\underset{\underset{NO_2CPh_3}{\overset{\parallel}{\text{PhCCN}}}}{} \xrightarrow{Br_2} \underset{\underset{NO_2}{\overset{|}{\text{PhC(Br)CN}}}}{} + Ph_3CBr$$
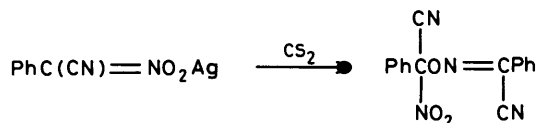
(3)   (7)

Scheme 4.

Conversion into p-nitrobenzoyl cyanide (8) (23%) was brought about by treatment with dinitrogen tetraoxide (Scheme 5). These reactions were compatible with the ester structure (3) but not with the isomeric C- and/or N-trityl structures. Silver phenylcyanomethylenenitronate and dinitrogen tetraoxide also gave the cyanide (8) (43%) (Scheme 5). It was proposed that both the nitronate salt and the nitronate ester (3) were converted initially into the oxime anion of benzoyl cyanide as dinitrogen tetraoxide was oxidized to dinitrogen pentaoxide. A facile nitration of the intermediate oxime anion followed by an independently established reaction between the oxime of p-nitrobenzoyl cyanide and dinitrogen tetraoxide completed the conversion into the cyanide (8) (Scheme 5).[9]

phenylcyanomethylenenitronic acid (9) nor nitro(phenyl)aceto-nitrile (10) were detected. (Hydrolysis of nitronate esters are competitive with the Nef reaction, the formation of hydroxamic acids, and auto-oxidation-reduction.[11]) Exposure to moist air at −20 °C converted the ester (3) into trityl alcohol (38%) and trityl peroxide (3%) (Scheme 7). Formation of the peroxide

$$Ph_3COH \xleftarrow{H_2O} (3) \xrightarrow{O_2} Ph_3COOCPh_3$$

PhC($=NO_2H$)CN   PhCH(NO_2)CN

(9)   (10)
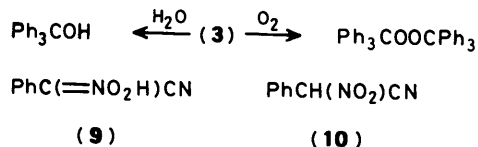
Scheme 7.

required attack by oxygen on the ester or an equivalent inter-mediate, insofar as neither trityl alcohol nor the corresponding chloride under similar conditions gave the peroxide.

The ester (3) fragmented (Scheme 8), when its toluene

$$\underset{\underset{NO_2CPh_3}{\overset{\parallel}{\text{PhCCN}}}}{} \xrightarrow[5°C]{C_7H_8}$$

(3)

$$CO_2 + (4) + (5) + (6) + Ph\underset{\underset{N}{\overset{}{\diagdown}}\,N}{\overset{}{\diagup}}NOX$$

(11) X = CPh$_3$
(12) X = H

Scheme 8.

solution was warmed to 5 °C and stored for 15 h. X-Ray crystallographic analysis* showed the product, $C_{33}H_{25}N_3O$, to be 4,5-diphenyl-1-triphenylmethoxy-1,2,3-triazole (11). It was hydrolysed by hydrochloric acid to trityl alcohol and 1-hydroxy-4,5-diphenyl-1,2,3-triazole (12) ($C_{14}H_{11}N_3O$). Contact with atmospheric moisture slowly brought about the same conversion (11) → (12) (Scheme 8).[4] The fragmentation was not noticeably affected by the added presence of either di-t-butyl nitroxide (a radical scavenger) or benzoyl peroxide (a radical source).

A partial extension of the overall conversion was realized in the production of α,α′-bis(tritylazo)-p,p′-dibromostilbene (2%) and p,p′-dibromodiphenylacetylene (28%) from silver p-bromo-

$$\underset{\underset{NO_2X}{\overset{\parallel}{\text{PhCCN}}}}{} \xrightarrow[{-X^+}]{\overset{N_2O_4}{\underset{-N_2O_5}{}}} \underset{\underset{NO^-}{\overset{|}{\text{PhC}}}}{\overset{CN}{|}} \longleftrightarrow \underset{H}{\diagup}\hspace{-2pt}\bigcirc\hspace{-2pt}\diagdown = \underset{\underset{NO}{\overset{|}{C}}}{\overset{CN}{|}} \xrightarrow{NO_2^{\cdot}} p-O_2NC_6H_4C(=NOH)CN$$

$$\downarrow N_2O_4$$

X = Ag,
Ph$_3$C

$$p-O_2NC_6H_4COCN$$

(8)

Scheme 5.

The reaction (Scheme 5) is reminiscent of the conversion of silver phenylcyanomethylenenitronate in carbon disulphide at 40 °C into the O-nitrocyanobenzyl derivative of the oxime of benzoyl cyanide (Scheme 6), for which radical intermediates were proposed.[10]

$$PhC(CN)=NO_2Ag \xrightarrow{CS_2} \underset{\underset{NO_2}{\overset{|}{\text{PhCON}}}}{}=\underset{\underset{CN}{\overset{|}{\text{CPh}}}}{}$$

Scheme 6.

Hydrolysis of the ester (3) at −20 °C was partially successful (Scheme 7). Water containing a few drops of hydrochloric acid converted the ester (3) into trityl alcohol (48%) but neither
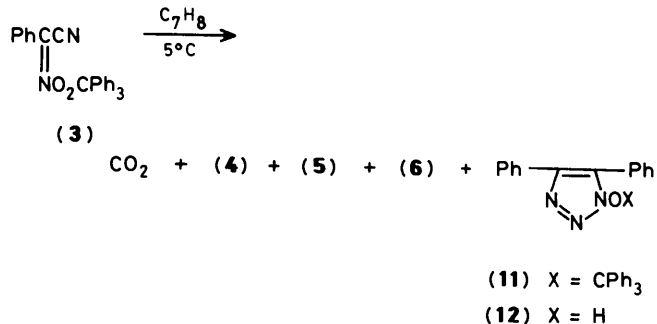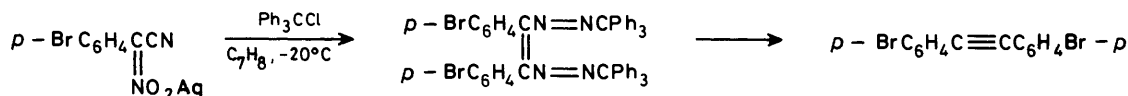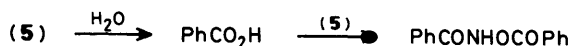

Scheme 9.

phenylcyanomethylenenitronate and trityl chloride (Scheme 9). Just as thermolysis of the bisazostilbene (4) in benzene at 80 °C in the presence of air gave diphenylacetylene (86%) and trityl peroxide (75%),[4] the bisazo-p,p'-dibromostilbene afforded p,p'-dibromodiphenylacetylene. In the absence of air trityl peroxide was not a co-product.

Attempts to bring about a reaction between triphenylsilyl chloride and silver phenylcyanomethylenenitronate under comparable conditions were unsuccessful and afforded recovery (95%) of the silyl chloride. Attempts to alkylate sodium phenylcyanomethylenenitronate with trityl chloride were also unsuccessful.

In dimethyl sulphoxide at 25 °C under nitrogen, silver phenylcyanomethylenenitronate and trityl chloride gave trityl isocyanate (6) (10%) and O-benzoylbenzhydroxamic acid (29%) after the mixture was treated with water. It was assumed that benzonitrile N-oxide (5) (an initial product) and benzoic acid (by hydrolysis) combined to form the hydroxamic acid (Scheme 10).[12]
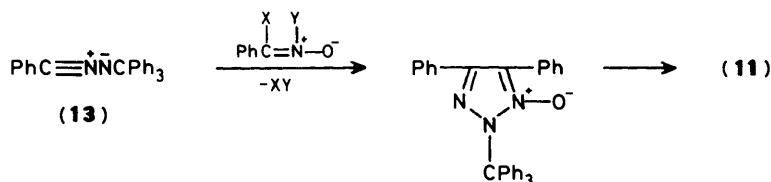

Scheme 10.

The deep-seated changes in the spontaneous reaction (Scheme 8) required the cleavage of at least five and the formation of at least seven bonds. Product analysis revealed two pathways for fragmentation of the ester (3) ($C_{27}H_{20}N_2O_2$): one afforded carbon dioxide and $C_{26}H_{20}N_2$, the other gave benzonitrile N-oxide (5) (C_7H_5NO) and trityl isocyanate (6) ($C_{20}H_{15}NO$) (Scheme 11). The intermediate $C_{26}H_{20}N_2$ was
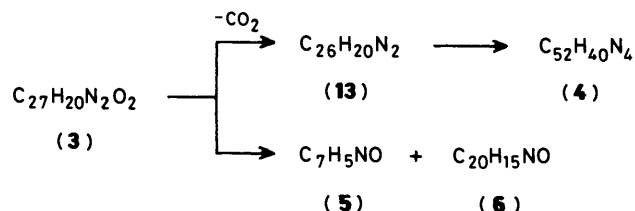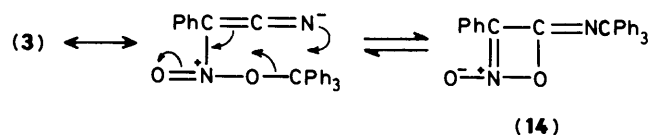

Scheme 11.

assigned the structure of benzonitrile–trityl imine (13) to provide for the formation of the bisazostilbene (4) ($C_{52}H_{40}N_4$) by dimerization and the triazole (11) by a migration of the trityl group from a nitrogen to an oxygen atom after a dipolar addition with benzonitrile N-oxide (5) (or an equivalent dipolarophile) gave 4,5-diphenyl-2-trityl-1,2,3-triazole 1-oxide (Schemes 11 and 12). [The nitrile imine (13) was previously abandoned as a precursor to the bisazostilbene (4) when benzonitrile N-oxide (5) and trityl isocyanate (6) failed to give an adduct that would

ostensibly afford the nitrilimine (13) and carbon dioxide by fragmentation.[5]]

The intermediacy of the N-trityl imine (14) of 4H-3-phenyl-1,2-oxazet-4-one 2-oxide was proposed to accommodate the fragmentation. Availability of the imine (14) depended on isomerization of the ester (3) for which both a direct pathway (Scheme 13) and an indirect pathway via N-trityl phenyl-nitroketene imine (15) (Scheme 14) were envisaged but not
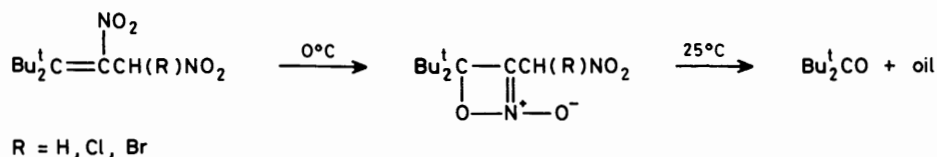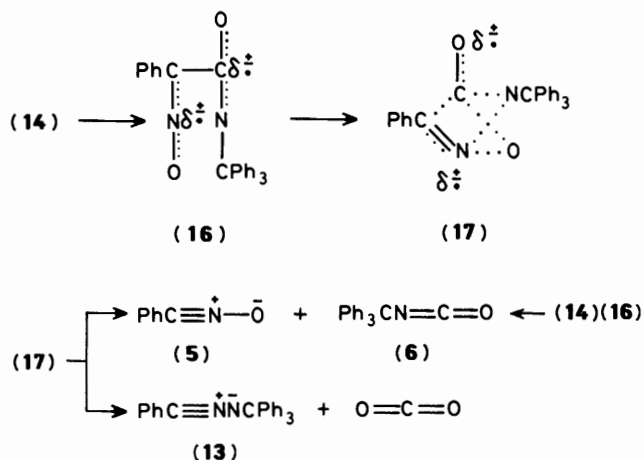

Scheme 13.
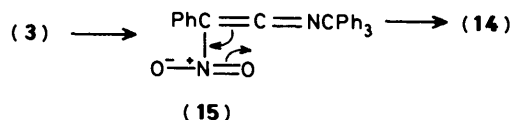
Scheme 14.

differentiated. Generation of the keteneimine (15) constituted a formal change from O- to N-tritylation of the phenylcyanomethylenenitronate anion. [Attempts to prepare the ketenimine (15) by a reaction between trityl isocyanide and the sodium salt of chloro(nitro)phenylmethane were unsuccessful.[5]] Although C-nitroketene imines are virtually unknown, the N-t-butylimine of dinitroketene, $(O_2N)_2C=C=NBu^t$, was produced from the anion of dinitrocyanomethane and t-butyl bromide. It was not isolated and was instead immediately converted into N-t-butyldinitroacetamide, $(O_2N)_2$-$CHCONHCBu^t$.[13] Ring closure of the nitroketenimine (15) to the intermediate oxazete (14) was reminiscent of the facile ring closure to 3-methyl-4,4-di-t-butyl-4H-1,2-oxazete 2-oxide from 3-t-butyl-4,4-dimethyl-2-nitropent-2-ene with time at 25 °C. This 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 (Scheme 15).[14]

The known facile dissociation of trialkyloxazetes[14] was extended to a cleavage of the oxazete (14) to account for a formation of benzonitrile N-oxide (5) and trityl isocyanate (6) (Scheme 16). A bond reorganization was required to account for fragmentation to benzonitrile–N-trityl imine and carbon dioxide. Ring-opening by cleavage of the oxazete N–O bond to afford an intermediate model in which new CO and NN bonding developed as CC, CN, and NO bonding deteriorated was proposed (Scheme 17). [A rearrangement of an O–N–O–C=N' system, to an N'–N–O–C=O system, prior to, or with dissociation, (14) → (13) + CO_2, is involved. A related
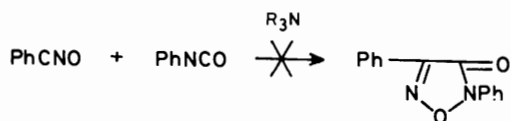

Scheme 12.

Scheme 15.
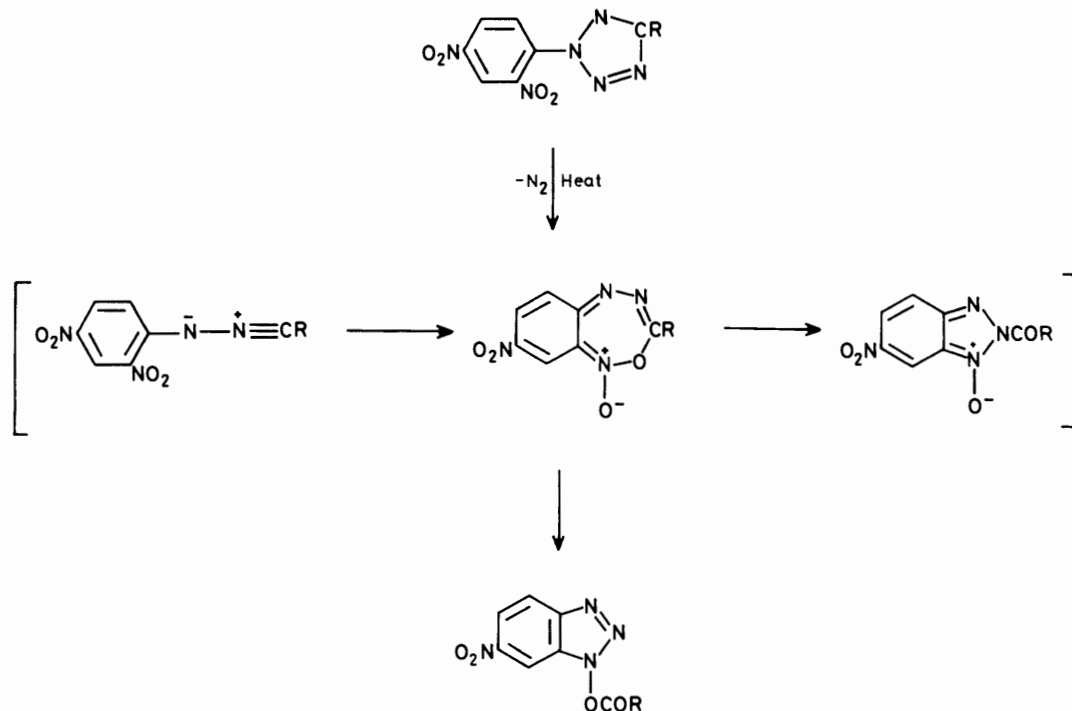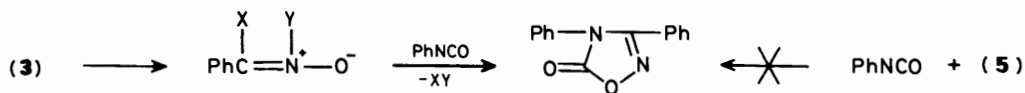

Scheme 16.

fragmentation reaction mixture at 5 °C afforded 3,4-diphenyl-1,2,4-oxadiazol-5-one (18) (8%) (Scheme 18) and the bisazostilbene (4). Since independent investigations revealed that phenyl isocyanate did not combine with benzonitrile N-oxide (5) under comparable conditions to give a dipolar adduct, it was assumed that the isocyanate captured the oxazete (14), or an equivalent intermediate dipolarophile, in an addition–elimination reaction to give the oxadiazolone (18) (Scheme 18). [The formation of 2,4-diphenyl-1,2,5-oxadiazol-3-one from a reaction between benzonitrile N-oxide (5) and phenyl isocyanate in the presence of triethylamine or sodium hydroxide has been reported (Scheme 19).[16,17] Our attempts to reproduce this

Scheme 19.

Scheme 17.

Scheme 18.

rearrangement was previously encountered in an explanation of the thermolysis of a 5-aryl-2-(2,4-dinitrophenyl)tetrazole to 1-aroyloxy-6-nitrobenzotriazole (Scheme 17).[15]]

Addition of an equimolar amount of phenyl isocyanate to the

result were unsuccessful. Phenyl isocyanate has a low order of dipolarophilic activity. It gave 4-mesityl-3-phenyl-1,2,4-oxa-diazol-5-one (76%) in a reaction with mesitonitrile N-oxide at 25 °C that required 15 months.[17]] When the fragmentation

reaction mixture was treated with phenyl isocyanate and stored at −20 °C the products isolated were the triazole (11) and the oxadiazolone (18). Formation of the red bisazostilbene (4) was suppressed.

Formation of the red azostilbene (4) was also suppressed by addition of an extra amount of benzonitrile N-oxide (5) or of phenylacetylene to the reaction mixture (Scheme 8). [The addition of radioactive benzonitrile N-oxide (5) showed not only that it was not a precursor but also that in sufficient amount it could be an inhibitor for the formation of the stilbene (4).[5] This inhibition is compatible with the competitive formation of compounds (4) and (11) (Schemes 11 and 12). Added phenylacetylene diminished the formation of the stilbene (4).[4] The probability that phenylacetylene and benzonitrile–N-triphenylmethyl imine (13) can form an adduct has not been established.] A similar suppression has been brought about by the addition of either p-chloro- or p-methyl-benzonitrile N-oxide. The possibility that interaction between a nitrile oxide and the stilbene (4) accounted for the diminished yield of the latter was shown to be invalid when independent experiments established that no reaction occurred between compound (4) (recovered 88%, 80%) and (5) or its p-chloro derivative. Dimerization of the nitrile oxides gave the expected diarylfuroxanes (66%, 60%).

Attempts to produce the N-trityl imine (13) independently were abandoned when (a) tritylhydrazine and benzaldehyde failed to undergo conversion to the expected hydrazone desired for dehydrogenation to compound (13) and (b) β-N-tritylbenzohydrazide gave benzohydrazide (43%, 60%) in an unexpected replacement of the trityl group with hydrogen upon treatment with either thionyl chloride or phosphorus pentachloride; N-tritylbenzhydrazidoyl chloride desired for dehydrochlorination to compound (13) was not detected (Scheme 20). Attempts to
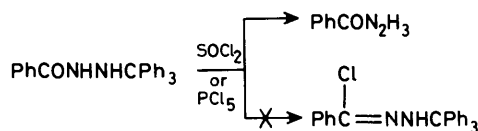
Scheme 20.

prepare the oxime (20) of the monotritylhydrazone (19) of benzil were unsuccessful. The oxime (20) was desired for an oxidative cyclization to 4,5-diphenyl-2-trityltriazole 1-oxide, an intermediate in Scheme 12. (A similar oxidation of the monoxime monophenylhydrazone of benzil to 2,4,5-triphenyl-1,2,3-triazole 1-oxide has been reported.[18])

The thermal stability of 3-phenyl-4-trityl-1,2,4-oxadiazol-5-one (21) ($C_{27}H_{20}N_2O_2$), decomp. >250 °C, precluded the heterocycle as an intermediate in the fragmentation reaction (Scheme 8) and as a precursor to carbon dioxide and the nitrile imine (13) (Scheme 11).[5] [Benzonitrile N-oxide (5) failed to give

(19) X = O

(20) X = NOH

(21)

Scheme 21.

an adduct with either trityl isocyanate (6)[5] or phenyl isocyanate. A more reactive dipolarophilic intermediate, e.g. the oxazete (14), combined with phenyl isocyanate to give the adduct (18) but failed to combine with trityl isocyanate (14) + (6) —×→ (21) + (6).]

Experimental

Reaction of Silver Phenylcyanomethylene nitronate and Trityl Chloride.—Trityl chloride (13.9 g, 0.05 mol) in toluene (100 ml) was added slowly to a stirred suspension of silver phenylcyanomethylenenitronate (13.3 g, 0.05 mol) in toluene (50 ml) at −20 °C under a nitrogen atmosphere. The mixture was stirred for 3 h at −20 °C. Silver chloride (6.58 g, 92%) was removed by cold filtration to leave trityl phenylcyanomethylnitronate (3) in toluene. On storage at 5 °C the bisazoethylene (4) was precipitated and was isolated after washing with benzene as a red crystalline solid (3.3. g, 18%), m.p. 144—145 °C (decomp.) [lit.,[4] m.p. 145 °C (decomp.)]; $v_{max.}$(KBr) 3 090, 3 060, 3 030, 1 600, 1 495, 1 450, 1 040, 910, 760, 700, and 650 cm^{-1}.

The filtrate was concentrated and treated with benzene to precipitate 1-triphenylmethoxy-4,5-diphenyl-1,2,3-triazole (11) as a colourless solid (2.85 g, 24%), m.p. 217—219 °C (lit.,[4] m.p. 216—219 °C) after recrystallization from benzene; $v_{max.}$(KBr) 3 070, 1 605, 1 490, 1 450, 880, 760, and 700 cm^{-1}; δ (CDCl$_3$) 7.0—7.7 (Found: C, 82.55; H, 5.55; N, 8.5. Calc. for $C_{33}H_{25}N_3O$: C, 82.65; H, 5.25; N, 8.76). In a further run the cold filtrate, after separation from silver chloride, was stirred for 1 h at 0 °C with water (50 ml) containing a few drops of concentrated hydrochloric acid. The reaction mixture was kept at 5 °C for 16 h, treated with benzene to give trityl alcohol, m.p. 161—162 °C[19] (3.1 g, 48%). No other product was isolated from the intractable mixture.

In a further experiment air was bubbled through the cold filtrate after removal of silver chloride for 2 h at −20 °C and the solution was stored at 5 °C for 16 h. The clear yellow solution was concentrated under reduced pressure. The residue was treated with benzene (25 ml) and the solid was filtered off and washed with a little benzene to give trityl alcohol, m.p. 161—162 °C (2.50 g, 38%). The mother liquor was left at room temperature for a few days; a small amount of trityl peroxide (0.10 g, 3%) was isolated, m.p. 183—185 °C (lit.,[20] m.p. 187 °C). [Modification in work-up determined the isolation of carbon dioxide,[3,4] and trityl isocyanate (5).[3]] Benzonitrile N-oxide (5) was trapped in a dipolar addition reaction as 3,5-diphenylisoxazole (DPI) by the added presence of phenylacetylene.[4] The formation of DPI by the dipolar addition of phenylacetylene to the nitrile oxide (5) has not been differentated from a dipolar addition–elimination reaction with the oxazete (14) [(14) + PhC≡CH ⟶ DPI + (6)].[3,4]

Bromine and the Nitronate (3).—Trityl chloride (6.95 g, mmol) in benzene (50 ml) was slowly added to a suspension of the silver salt of nitro(phenyl)acetonitrile (6.65 g, 25 mmol) in benzene (50 ml) at 0—5 °C under nitrogen. After the mixture had been stirred for 2 h at 0—5 °C, silver chloride was filtered off and a slight excess of bromine (2.4 g 30 mmol) was slowly added with stirring to the filtrate at 0—5 °C. The reaction mixture was kept at 5 °C for 16 h. T.l.c. of this mixture showed only two spots identical with those for bromonitro(phenyl)-acetonitrile and trityl bromide. Solvent was removed from the reaction mixture to give trityl bromide (5.56 g, 69%), m.p. and mixed m.p. with an authentic sample was 153—154 °C,[21] isolated by filtration. The filtrate was found to be bromonitro-(phenyl)acetonitrile (3.2 g, 53%) by comparison (t.l.c. and i.r.) with an authentic sample prepared by a reported procedure.[22]

Dinitrogen Tetraoxide and the Nitronate (**3**).—After removal of silver chloride the filtrate in toluene ($-20\,^\circ$C) (above) was treated with an excess of dinitrogen tetraoxide, stirred at $-20\,^\circ$C for 3 h, stored at $5\,^\circ$C for 40 h, concentrated, and combined with anhydrous ether (50 ml) to give *p*-nitrobenzoyl cyanide (1.0 g, 23%) as colourless crystals, m.p. 114—115 $^\circ$C (lit.,[23] m.p. 116 $^\circ$C). Trityl alcohol (2.8 g, 43%), m.p. 161—162 $^\circ$C was obtained from the mother liquor on concentration.

Phenyl Isocyanate and the Nitronate (**3**).—(*a*) After removal of silver chloride the filtrate (above) in toluene was treated at $-20\,^\circ$C with phenyl isocyanate (3.0 g, 25 mmol), stored at $5\,^\circ$C for 16 h, and filtered to remove the bisazo compound (**4**) as a red solid (1.80 g, 20%). From the filtrate stored at 25 $^\circ$C for a few days 3,4-diphenyl-1,2,4-oxadiazol-5-one (**18**) (0.48 g, 8%) separated as a colourless crystalline solid, m.p. 166—167 $^\circ$C (lit.,[24] m.p. 167 $^\circ$C).

(*b*) After removal of silver chloride the filtrate (above) was treated at $-20\,^\circ$C with phenyl isocyanate (3.0 g, 25 mmol) and stored at $-20\,^\circ$C for 2 days. The clear yellow solution was warmed to 25 $^\circ$C as it turned red-orange. After storage at 25 $^\circ$C for a day the yellow colour of the solution was restored. The solvent was removed and the residue was treated with ether (50 ml) to give the triazole (**11**) as a colourless solid (0.85 g, 14%), m.p. 215—217 $^\circ$C. The filtrate was stored at room temperature to bring about the precipitation of the oxadiazolone (**18**) isolated as a colourless solid (0.65 g, 11%), m.p. 165—167 $^\circ$C.

Benzonitrile Oxide and Phenyl Isocyanate.—Benzhydroxamic acid chloride [PhC(=NOH)Cl] (3.88 g, 25 mmol) and phenyl isocyanate (3.00 g, 25 mmol) in toluene (50 ml) were stirred at $-20\,^\circ$C under nitrogen. Triethylamine (2.6 g, 25 mmol) in toluene (30 ml) was added dropwise and stirring was continued for 2 h. The reaction mixture was filtered to remove triethylamine hydrochloride (2.82 g, 82%) and the filtrate was left at room temperature overnight. Filtration gave diphenylurea (1.20 g, 45%), m.p. 238—239 $^\circ$C (lit.,[25] m.p. 235 $^\circ$C). The filtrate was concentrated and the residue was recrystallized from methylene dichloride—hexane to give 3,4-diphenylfuroxane (1.7 g, 58%), m.p. 113—114 $^\circ$C (lit.,[26] m.p. 114 $^\circ$C).

Dimethyl Sulphoxide as Solvent.—Silver phenylcyanomethylenenitronate (13.3 g, 50 mmol) dissolved in dimethyl sulphoxide (45 ml) was treated with a solution of trityl chloride (13.9 g, 50 mmol) in dimethyl sulphoxide (45 ml) added slowly at room temperature under nitrogen. The mixture was stirred for 1 h and added to cold water (400 ml) layered with benzene (200 ml). After three extractions (3 × 100 ml) with benzene, the combined benzene extracts were washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. The residue, a waxy solid, was treated with benzene (20 ml) to give *O*-benzoylbenzhydroxamic acid as a colourless solid (1.72 g, 29%), m.p. 164—165 $^\circ$C (lit.,[27] m.p. 166 $^\circ$C) after washing with benzene and filtration. The mother liquor was concentrated to give trityl isocyanate (**6**) (1.45 g, 10%), m.p. 92—93 $^\circ$C (lit.,[28] m.p. 93 $^\circ$C).

p-Nitrobenzoyl Cyanide Oxime with Dinitrogen Tetraoxide.—An excess of dinitrogen tetraoxide was added to a solution of *p*-nitrobenzoyl cyanide oxime (0.191 g, 1 mmol) in benzene (20 ml) and stirred at room temperature for 6 h. The solvent was removed under reduced pressure and the residue was recrystallized from methylene dichloride–hexane to give *p*-nitrobenzoyl cyanide (0.140 g, 80%), m.p. and mixture m.p. with an authentic sample m.p. 114—115 $^\circ$C.

Silver p-*Bromophenylcyanomethylenenitronate and Trityl Chloride.*—To a suspension of silver *p*-bromophenylcyanomethylenenitronate (7.0 g, 20 mmol) in benzene (25 ml), a solution of trityl chloride (5.6 g, 20 mmol) in benzene (50 ml) was

added dropwise with stirring at 0—5 $^\circ$C under a nitrogen atmosphere. The mixture was stirred at 0—5 $^\circ$C for 4 h and filtered to remove silver chloride. The clear filtrate was left at room temperature for a day. α,α'-Bis(tritylazo)*p*-bromostilbene was precipitated as a red solid, (0.15 g, 2%), m.p. 143—144 $^\circ$C (decomp.); $\nu_{max.}$(KBr) 1 600, 1 495, 1 455, 1 020, 810, and 705 cm^{-1}; (Found: C, 70.65; H, 4.55; N, 6.4. Calc. for $C_{52}H_{38}Br_2N_4$: C, 71.07; H, 4.33; N, 6.38).

From the filtrate, di-*p*-bromophenylacetylene was isolated by concentration (0.95 g, 28%), m.p. 181—182 $^\circ$C (lit.,[29] m.p. 183 $^\circ$C).

3-Phenyl-4-trityl-1,2,4-oxadiazol-5-one (**21**).—To a solution of 3-phenyl-1,2,4-oxadiazol-5-one[30] (1.62 g, 10 mol) in a mixture of benzene and dimethylformamide, sodium hydride (slight molar excess) was added with stirring. Within a few minutes the sodium salt of the heterocycle was precipitated. Trityl chloride (2.78 g, 10 mmol) was added and the reaction mixture refluxed for 110 h. The unchanged sodium salt was filtered off and gave, on acidification, recovery of the oxadiazolone (65%). The organic layer was concentrated, dissolved in ethyl acetate, and the solution washed with water, and dried ($MgSO_4$). Removal of the solvent left a residue (2.7 g) chromatographically separated from a silica gel column to give trityl alcohol (800 mg), recovered starting oxadiazolone (300 mg, 20%), and 3-phenyl-4-trityl-1,2,4-oxadiazol-5-one (**21**) (400 mg, 65% yield based on recovered starting oxadiazolone), m.p. 188—189 $^\circ$C (chloroform–hexane); $\nu_{max.}$(CHCl$_3$) 1 770 cm^{-1}; δ (CDCl$_3$) 7.0—7.4 (m); *m/z* (70 eV) 404 (100%, *M*), 360 (40), 359 (19), 301 (36), 284 (26), 283 (56), 257 (17), 256 (12), 243 (28), 180 (16), 167 (25), 166 (45), 165 (90), 152 (19), 141 (13), 103 (14), 77 (14), and 44 (50) (Found: C, 80.0; H, 4.9; N, 6.9. Calc. for $C_{27}H_{20}N_2O_2$: C, 80.18; H, 4.98; N, 6.93%). [The assignment (**21**) was made in accordance with a similar methylation of 3-phenyl-1,2,4-oxadiazol-5-one to give the 4-methyl derivative, differentiated from the alternative *N*- and *O*-methyl derivatives by direct examination of the three compounds.[31]]

4,5-Diphenyl-1,2,3-triazol-1-ol (**12**).—The triazole (**11**) (1 g, 2.1 mmol) was dissolved in chloroform (10 ml) and stirred with 5M hydrochloric acid (10 ml) for 20 h. More chloroform (50 ml) was added after which the chloroform layer was washed with water and dried. The solvent was removed and the residue was treated with ether (20 ml), and the mixture was filtered to give the hydroxytriazole (**12**) as a colourless solid (0.13 g, 26%), m.p. 178—180 $^\circ$C (lit.,[3] m.p. 182 $^\circ$C). From the filtrate, trityl alcohol (0.29 g, 53%), m.p. 160—162 $^\circ$C was isolated.

Benzil Monotritylhydrazone (**19**).—Benzil monohydrazone[32] (11.2 g, 50 mmol), trityl chloride (16.8 g, 60 mmol) and magnesium sulphate (3 g, 25 mmol) in absolute ether (200 ml) were stirred under a nitrogen atmosphere. Dry pyridine (5 ml, 60 mmol) was added dropwise and the mixture was gently refluxed for 10 h. The mixture was cooled to 5 $^\circ$C. The insoluble material was filtered off and washed several times with water to give recovery of unchanged benzil monohydrazone (2.8 g). The ethereal filtrate was washed with dilute hydrochloric acid, aqueous sodium hydrogen carbonate, and water and then dried ($MgSO_4$). The solution was concentrated to precipitate benzil monotrityl hydrazone (**19**) (11.8 g, 67%), m.p. 151—152 $^\circ$C; $\nu_{max.}$(KBr) 3 320 (NH), 1 635 (C=O), 1 600, 1 540, 1 495, 1 450, 1 340, 1 240, 1 185, 1 030, 880, and 700 cm^{-1}; δ (CDCl$_3$) 6.9—7.8 (m, ArH) (Found: C, 85.0; H, 5.55; N, 6.1. Calc. for $C_{33}H_{26}N_2O$: C, 84.55; H, 5.77; N, 6.16). Attempts to prepare the oxime (**20**) of benzil monotritylhydrazone were unsuccessful.

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