

Nitrodibromoacetonitrile: An Agent for Bromination and for the Formation of Adducts Formally Derived from Cyanonitrocarbene

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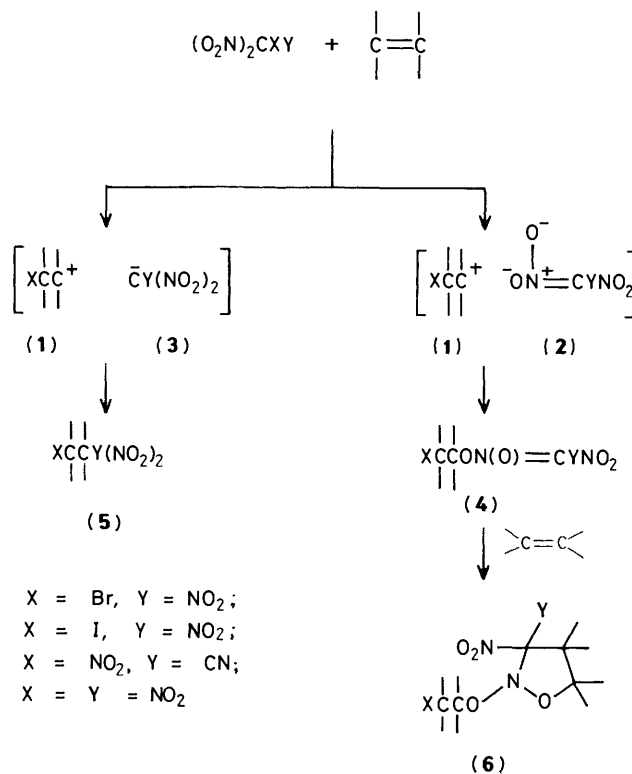
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The reactions of nitrodibromoacetonitrile (NDBA) with alkenes, aromatic compounds, amines, and sulphides have been studied. Products were formally derived from bromine or nitrocyano-carbene except for bis(2-bromocyclohexyl)nitroacetonitrile (**13**), an adduct (2:1) obtained from cyclohexene and NDBA. 2,3-Dimethylbut-2-ene was converted into 3-cyano-4,4,5,5-tetramethyl-4,5-dihydroisoxazole 2-oxide (**15**) and 2,3-dibromo-2,3-dimethylbutane (**16**). *meso*-1,2-Dibromo-1,2-diphenylethane was obtained from *trans*-stilbene. In a reaction catalysed by copper, benzene and NDBA gave benzoyl cyanide. From anthracene, phenol, and cupric acetylacetonate, 9,10-dibromoanthracene, 4-bromo-phenol, and cupric bromoacetylacetonate were obtained respectively. Dimethyl sulphide, tetrahydrothiophene, and triethylamine afforded the corresponding sulphonium-(**30**) and (**31**) and ammonium cyanomethylide-(**33**)[†] derivatives and, with the latter, co-formation of triethylammonium bromide. Rationales for the reactions are discussed.

Abstraction of a 'positive' substituent from bromotrinitromethane,¹ iodotrinitromethane,² trinitroacetonitrile,³ and tetranitromethane⁴ by an alkene lead to the formation of nitronate esters (**4**) [isolated as isoxazolidine derivatives (**6**) and polynitro compounds (**5**)].⁵ Carbenium nitronates (**1, 2**) \longleftrightarrow polynitromethanides (**1, 3**) have been proposed as intermediates⁴ (Scheme 1).

Certain metal trinitromethanide salts reacted with cyclohexene in aprotic solvents at 20–50 °C to give 3a,4,5,6,7,7a-hexahydro-3-nitro-1,2-benzisoxazole 2-oxide (**7**),⁵ Scheme 2. Polynitromethanide salts and alkenes generally gave similar reactions.^{5,6} The intermediacy of dinitrocarbene (**8**) was considered;⁷ however, it was not established that ejection of the elements of the metal nitrite occurred prior to the formation of the heterocycle. Isoxazolidine 2-oxide anions (**9**) were proposed as intermediates from the addition of aryl nitromethanenitronate anions to alkenes,⁶ and a similar anion (**10**) was a proposed intermediate from alkaline hydrolysis of a silyl ether (**11**).⁸ Each anion [(**9**) and (**10**)] with sodium, potassium, or other 'hard' counterions thermolysed to give a dihydroisoxazole along with a metal nitrate. None or only trace amounts of the dihydroisoxazole 2-oxide and a metal nitrite were produced; however, this was the preferred product pair when the counterion was silver, a soft cation.⁶ It is, therefore, unlikely that anion (**9**) is precursor to dihydroisoxazole 2-oxide in reactions between alkenes and 'hard' metal trinitromethanide salts thus strengthening the case for the intermediacy of dinitrocarbene (**8**). The generality of the formation of dihydroisoxazole 2-oxides from 'hard' metal trinitromethanide salts and alkenes under ambient conditions tends to preclude the intervention of the anion (**2**) \longleftrightarrow (**3**) as a discrete intermediate in reactions between an alkene and covalent derivatives of polynitromethane (Scheme 1), none of which have so far produced dihydroisoxazole 2-oxides.

The present investigation was undertaken to (a) investigate abstraction of a 'positive' group from nitrodibromoacetonitrile (NDBA), (b) find an example of the formation of dihydroisoxazole 2-oxide from the alkene and NDBA, and (c) investigate the intermediacy of nitrocyano-carbene in certain reactions.

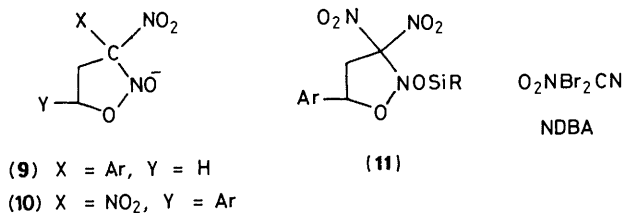
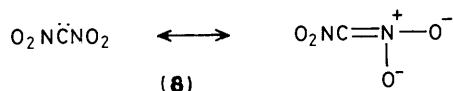
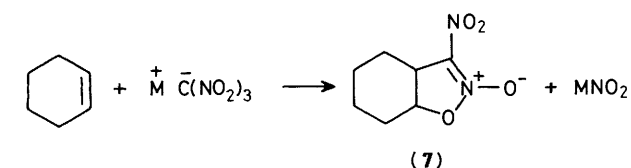


Scheme 1.

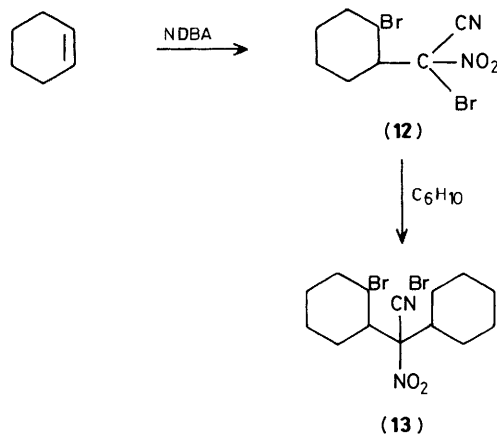
Results and Discussion⁹

With one exception the formation of products involved the abstraction of one or both bromo groups from NDBA by

[†] Named by IUPAC rules of nomenclature these would be sulphonium and ammonium cyanomethanides.



Scheme 2.



Scheme 3.

various alkenes, aromatic compounds, amines, and sulphides. Competitive abstraction of the nitro and cyano groups was not detected.

Alkenes.—A simple 1:1 adduct between an alkene and NDBA (from the ammonium salt of nitroacetonitrile and bromine)¹⁰ was not found; however, such an adduct (12) was assumed to explain the ultimate formation of the 2:1 adduct, bis(2-bromocyclohexyl)nitroacetonitrile (13) (9%) (stereochemistry unknown), from cyclohexene and NDBA by a C-alkylation pathway (see Scheme 3). The proposed structure (13) was compatible with its elemental analysis, molecular weight determination and characteristic nitro-group stretching frequencies ν_{max} . 1 550 and 1 390 cm⁻¹. Thermolysis of a putative nitronate ester, *cf.* (4), produced by O-alkylation was assumed to account in part for the intractable portion of the product mixture. That the ester was not converted into an isoxazolidine adduct, *cf.* (6), was in agreement with the known limited ability of cyclohexene to function as a dipolarophile. [Cyclohexene added to the nitronate ester obtained from the olefin and tetranitromethane to give a low yield (18%) of the expected isoxazolidine].^{4a}

The assumption that a dihydroisoxazole 2-oxide could be produced in a reaction between an olefin and a halogenonitro-

methane, presumably *via* a carbenium nitromethanide salt, was dependent on a nitromethanide anion with severely limited ability to undergo C- and/or O-alkylation by the counterion and consequently an opportunity to combine with the electron rich olefin to give the heterocycle along with the ejection of an inorganic anion. NDBA was chosen for investigation since the corresponding bromocyanonitromethanide anion was assumed to be planar and weakly nucleophilic as a consequence of the replacement of a nitro group in the cyanodinitromethanide anion (3; Y = CN) (planar and weakly nucleophilic)¹¹ with the sterically comparable bromo group. A consideration of electron rich symmetrically substituted alkenes capable of abstracting not only the 'positive' bromine from NDBA but also subsequently accepting an ejected bromide anion led to the successful choice of 2,3-dimethylbut-2-ene.

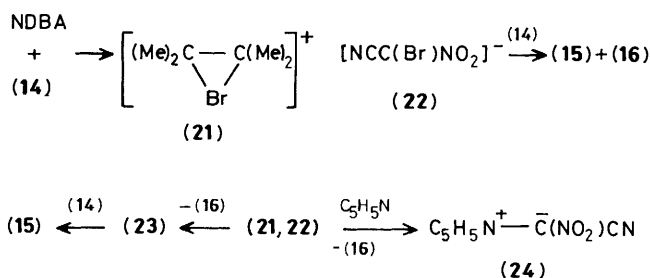
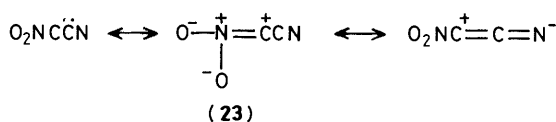
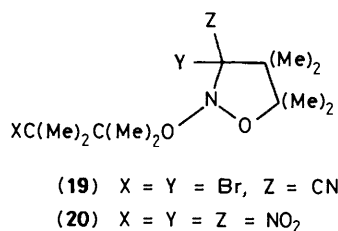
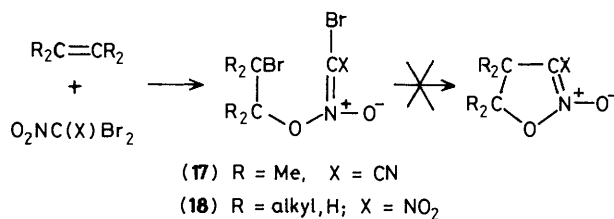
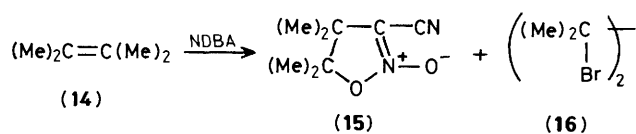
2,3-Dimethylbut-2-ene (14) (2 mol) and NDBA in dichloromethane at 25 °C gave 3-cyano-4,4,5,5-tetramethyl-4,5-dihydroisoxazole 2-oxide (15) (45%) and 2,3-dibromo-2,3-dimethylbutane (16) (42%) (Scheme 4). The structure of the new heterocyclic compound (15) was confirmed by an X-ray crystallographic analysis.* An explanation for the formation of the heterocycle (15) by cyclization from a nitronate ester (17), an adduct from NDBA and the olefin (14), was considered unlikely since similar cyclizations from β -bromoalkylnitronates (18), known adducts from trinitroacetomethane and olefins,¹ were not observed. Support for the intermediacy of the nitronate ester (17) was further diminished by the failure to detect the formation of an isoxazolidine derivative (19), the dipolar adduct from the alkene (14) and the ester (17). [A comparable isoxazolidine (20), was obtained^{4b} from the olefin (14) and the ester O₂NC(Me)₂C(Me)₂ON(O)=C(NO₂)₂].

That the formation of neither the heterocycle (15) nor the dibromide (17) proceeded from a radical precursor was shown by a lack of inhibition in product formation by the added presence of either di-*t*-butyl nitroxide or tetracyanoethylene (radical scavengers), an observation supported by an absence of a CIDNP signal for the reaction. It is proposed that the reaction proceeded through the formation of a bromonium methanide (21), (22). The formation of the heterocycle (15) and the dibromide (16) was attributed to a straightforward interaction between the intermediate and the olefin (14) (Scheme 4) without differentiation between concerted and stepwise pathways that required additional intermediates. The results are most compatible with an explanation based on the dissociation of the intermediate (21), (22) to the dibromide (16) and nitrocyano-carbene (23) and addition of the latter, either on formation or subsequently, to the olefin (14) to produce the heterocycle (15). It is anticipated that the dihydroisoxazole 2-oxide (15) will also be produced by a reaction between 2,3-dimethylbut-2-ene and bromodinitroacetonitrile;¹² an investigation is planned.

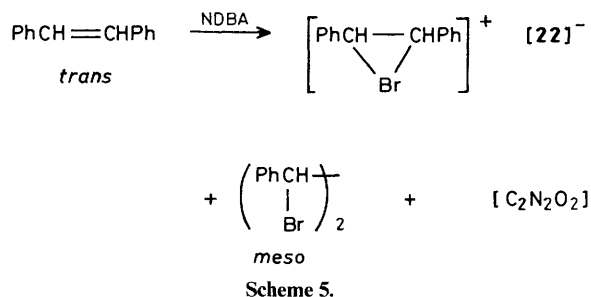
Support for the proposed intermediate (21), (22) was found in the complete suppression of the formation of the heterocycle (15), and the absence of any effect on the formation of the dibromide (16), by the added presence of pyridine in the reaction mixture. Pyridinium cyanonitromethylide (24), an expected product, was not detected in the complex product mixture (Scheme 4).

Although alkylation was not detected in the conversion of *trans*-stilbene to *meso*-1,2-dibromo-1,2-diphenylethane¹³ (10%) by treatment with NDBA, a rationale for the reaction was based on the intermediacy of a bromonium bromocyanonitromethanide salt. A dissociation of the intermediate anion (22) was proposed to provide a bromide anion required to combine with the bromonium cation for product formation (Scheme 5);

* We are indebted to Dr. R. Gilardi and Dr. C. George, Naval Research Laboratory, Washington, D.C. for the X-ray analysis. The data will be published elsewhere.



Scheme 4.



however, the remainder of the intermediate methanide anion was not accounted for. NDBA was unreactive to both diphenyl- and dimethyl-acetylene but reacted with bistriethylsilylacetylene to give an intractable mixture.

Aromatic Compounds.—Although a trace of benzoyl cyanide (26) was detected in the reaction mixture, NDBA tended to be unreactive to benzene at 80 °C for 20 h and was recovered (80%). A more efficient formation of the cyanide (26) occurred

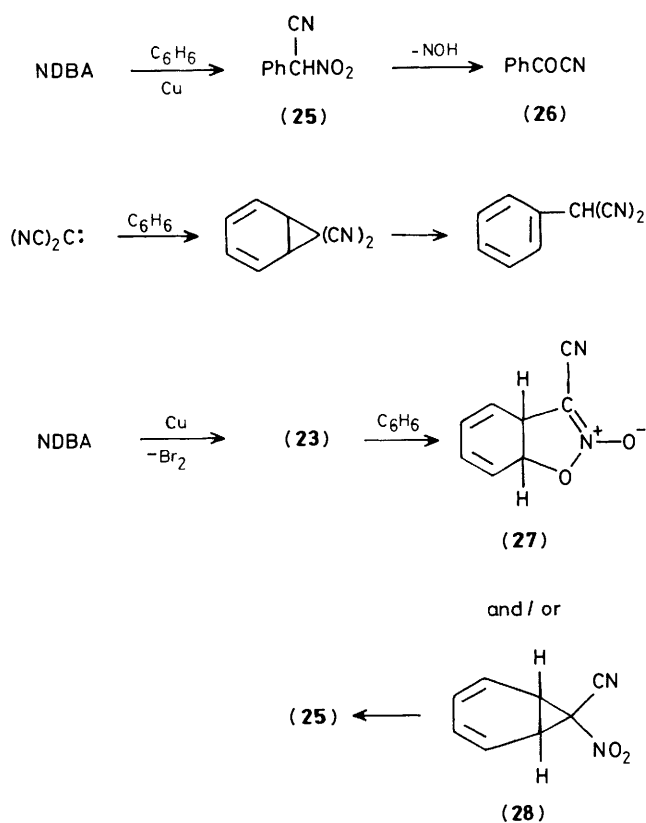
when the reaction was carried out in the presence of copper (Scheme 6). The proposed intermediacy of nitro(phenyl)acetonitrile (25) was supported by an independent quantitative conversion of compound (25) under similar conditions into the acyl cyanide (26). The conversion (25) → (26) is reminiscent of the facile thermolysis of an aryl bromonitroacetonitrile to the acyl cyanide, ArCOCN.¹⁴ It was suggested that these α-nitro nitriles underwent initial isomerization to a nitrite ester, ArC(ONO)XCN (X = H, Br) and that the cyanide (26) was produced by an elimination of nitroxyl (Scheme 6) whereas an elimination of nitrosyl bromide from ArC(ONO)BrCN occurred. The isomerizations of α-nitro nitriles to nitrite esters were described as radical processes.¹⁵ Debromination was presumably promoted by copper and afforded an interaction with benzene to produce a formal adduct from cyanonitrocarbene. Since dicyanocarbene (from dibromodicyanomethane and copper) reacted with benzene by addition to an unsaturated bond rather than by direct insertion into a CH bond (Scheme 6),¹⁶ it is proposed that cyanonitrocarbene was an intermediate that added to benzene to give a dihydrocyanobenzisoxazole oxide (27) and/or the isomeric norcaradiene (28); however, the formation of intermediate (25) by isomerization of adducts (27) and/or (28) has not been differentiated from formation by direct insertion of the carbene into a benzene CH bond (Scheme 6).

Anthracene and phenol underwent typical aromatic brominations at ambient temperatures to give 9,10-dibromoanthracene¹ and 4-bromophenol¹⁷ on treatment with NDBA. In a similar reaction NDBA converted cupric acetylacetonate to its bromo derivative. The mild conditions required for aromatic bromination (assumed to be ionic) by NDBA are reminiscent of those required for tetranitromethane to form charge transfer complexes with electron rich olefins and certain aromatic compounds.¹ Only upon irradiation did the latter give nitroaromatic derivatives.¹⁸

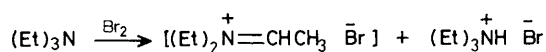
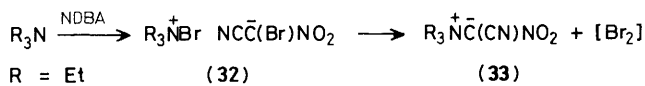
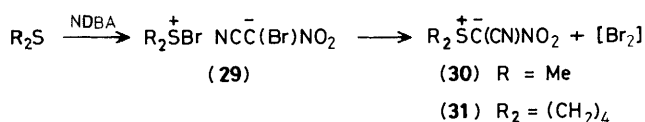
Nucleophiles.—A variety of nucleophiles reacted with NDBA, Scheme 7. Dimethyl sulphide (2 equiv.) when treated with NDBA in dichloromethane at 0 °C for 30 min gave a high yield of dimethylsulphonium cyanonitromethylide (30), previously obtained from nitroacetonitrile and dimethyl sulphoxide.¹⁹ Tetrahydrothiophene gave tetrahydrothiophenium cyanonitromethylide (31) by similar treatment. An excess of triethylamine in benzene or carbon tetrachloride reacted with NDBA to give triethylammonium cyanonitromethylide (33) in low yield and triethylammonium bromide. It is proposed that these reactions proceeded from intermediate onium methanides (29) and (32). The formation of triethylammonium bromide from triethylamine and bromine was previously reported.²⁰ Attempts to liberate and capture cyanonitrocarbene (23) from its adducts (30) by treatment with either thiocyanogen or dimethoxy disulphide²¹ were unsuccessful; however, the formation of dimethyl sulphide was detected.

Experimental

Spectral data was obtained on the following instruments: Pye-Unicam SP 200 IR, Varian A-60 and JEOL FX 90 Q NMR, and Hatachi R MU-6 mass spectrometers. Elemental analyses were obtained from Micro-Tech Laboratories, Skokie, IL. NDBA¹⁹ and nitro(phenyl)acetonitrile²² were obtained by the reported methods. Freshly precipitated copper powder²³ was used. Anthracene, cupric acetylacetonate, cyclohexene, dimethyl sulphide, phenol, tetrahydrothiophene, 2,3-dimethylbut-2-ene, and triethylamine were commercially available. All ¹H n.m.r. (60 MHz) spectra were run in CDCl₃ with tetramethylsilane as internal standard. The mass spectra were electron impact (70 eV).



Scheme 6.



Scheme 7.

Bis(2-bromocyclohexyl)nitroacetone (13).—A solution of NDBA (12.2 g, 50 mmol) in an excess of cyclohexene (50 ml) was stirred overnight at 25 °C. The mixture was concentrated to give the adduct (13) (1.9 g, 9%) as a colourless solid, m.p. 198–199 °C (decomp.) (Found: C, 41.0; H, 5.1; Br, 39.25; N, 6.9%; *M*⁺, 408. C₁₄H₂₀Br₂N₂O₂ requires C, 41.2; H, 4.9; Br, 39.2; N, 6.9%; *M*, 408); *v*_{max}. 1 550, and 1 390 cm⁻¹ (NO₂); δ_H 1.3–2.5 (18 H, m, CH₂), 4.3 (1 H, m, CH), and 4.8 (1 H, m, CH).

3-Cyano-4,4,5,5-tetramethyl-4,5-dihydroisoxazole 2-Oxide (15) and 2,3-Dibromo-2,3-dimethylbutane (16).—To a stirred solution of NDBA (4.9 g, 20 mmol) in dichloromethane (20 ml) at 25 °C a solution of 2,3-dimethylbut-2-ene (14) (3.4 g, 40 mmol) in dichloromethane (30 ml) was added dropwise. Stirring was continued for 30 min after which solvent was removed, and the residue chromatographed over neutral alumina. Hexane (3 × 100 ml) eluted 2,3-dibromo-2,3-dimethylbutane (16) (2.1 g, 42%), m.p. 168–169 °C (decomp.) (from hexane) (lit.²⁴ m.p. 166–168 °C). The same solvent (4 × 100 ml) then eluted 3-

cyano-4,4,5,5-tetramethyl-4,5-dihydroisoxazole 2-oxide (15) (1.5 g, 45%), m.p. 68–69 °C (from hexane) (Found: C, 56.6; H, 7.3; N, 16.5%; *M*⁺, 168. C₈H₁₂N₂O₂ requires C, 57.1; H, 7.1; N, 16.7%; *M*, 168); *v*_{max}. 2 220 (C≡N), 1 605, and 1 350 cm⁻¹; δ_H 1.31 (3 H, s, Me) and 1.44 (3 H, s, Me); δ_C (90 MHz; CDCl₃) 109.69 (C-3), 103.53 (CN), 90.84 (C-5), 48.79 (C-4), 21.08 (Me at C-5), and 20.72 (Me at C-4). There was no change in the reaction when the solvent dichloromethane was replaced by benzene or cyclohexane.

Benzoyl Cyanide (26).—NDBA (12.2 g, 50 mmol) and copper powder (6.4 g, 100 mmol) were heated in dry benzene (100 ml) at 80 °C for 15 h. After removal of insoluble inorganic material and the solvent the residue was distilled in a Kugelrohr apparatus (130 °C, 0.1 Torr) to give benzoyl cyanide (26) (1.85 g, 28%), m.p. 30–32 °C (lit.¹⁴ m.p. 30–32 °C). Nitro(phenyl)acetone (25) (4.05 g, 25 mmol) and copper powder (3.2 g, 50 mmol) were heated in dry benzene (50 ml) at 80 °C for 10 h to give benzoyl cyanide (26) (3.2 g, 97%).

Brominations.—Anthracene (1.8 g, 10 mmol) in dichloromethane (30 ml) was treated with NDBA (4.9 g, 20 mmol) in dichloromethane (20 ml). The mixture was stirred for 3 h and concentrated to give 9,10-dibromoanthracene (2.2 g, 65%) as yellow needles, m.p. 218–220 °C (lit.¹ m.p. 220 °C).

A solution of NDBA (2.4 g, 10 mmol) in dichloromethane (25 ml) was added to a solution of phenol (0.5 g, 5 mmol) in dichloromethane (25 ml) and stirred for 4 h. The solvent was removed and the residue was placed on a neutral alumina chromatography column. Elution with ethyl acetate afforded 4-bromophenol (0.4 g, 46%), m.p. 63–64 °C (lit.¹⁷ m.p. 63 °C).

To a solution of cupric acetylacetonate (2.6 g, 10 mmol) in acetone (50 ml) NDBA (4.9 g, 20 mmol) was added dropwise and the mixture was stirred for 1 h to give cupric bromoacetylacetonate that separated as dark green needles (1.9 g, 56%), m.p. 226–227 °C (decomp.) [lit.²⁶ m.p. 220 °C (decomp.)] (Found: C, 28.6; H, 2.8. C₁₀H₁₂Br₂O₄Cu requires C, 28.60; H, 2.86%).

Sulphonium Cyanonitromethylides (30) and (31).—To a stirred solution of dimethyl sulphide (2.5 g, 40 mmol) in dichloromethane (20 ml) at 0–5 °C a solution of NDBA (4.9 g, 20 mmol) in dichloromethane (50 ml) was added dropwise. Stirring at 0–5 °C was continued for 30 min. Dimethylsulphonium cyanonitromethylide (30) (2.7 g, 80%) was isolated as a colourless solid, m.p. 213–214 °C (decomp.) (from water) [lit.¹⁹ m.p. 213–215 °C (decomp.)]; *v*_{max}. 2 200 (C≡N), 1 400, and 1 295 cm⁻¹ (NO₂).

A similar reaction with tetrahydrothiophene gave tetrahydrothiophenium cyanonitromethylide (31) (54%), m.p. 166–167 °C (decomp.) (from water) (Found: C, 41.3; H, 4.8; N, 16.3; S, 18.6. C₆H₈N₂O₂S requires C, 41.9; H, 4.65; N, 16.3; S, 18.6); *v*_{max}. 2 200 (C≡N), 1 395, and 1 300 cm⁻¹ (NO₂); δ_H 2.1–2.7 (2 H, m, CH₂) and 3.4–3.8 (2 H, m, CH₂).

Triethylammonium Cyanonitromethylide (33).—A solution of triethylamine (4.0 g, 40 mmol) in carbon tetrachloride (25 ml) was added dropwise to a stirred solution of NDBA (2.4 g, 10 mmol) in carbon tetrachloride at 25 °C. The mixture was stirred for 10 min. The solvent was removed and the residue was triturated with acetone (20 ml), separated by filtration, and triturated with dichloromethane (25 ml) to give the methylide (33) as a colourless solid (90 mg, 5%), m.p. 154–155 °C (decomp.) (Found: C, 51.2; H, 8.1; N, 23.0. C₈H₁₅N₃O₂ requires C, 51.9; H, 8.2; N, 22.7%; *v*_{max}. 2 200 (C≡N), 1 420 (NO₂), and 1 330 cm⁻¹ (NO₂); δ_H 1.50 (3 H, t, Me) and 3.17 (2 H, q, CH₂). The combined filtrates were concentrated to give triethylammonium bromide as a colourless solid (1.7 g, 45%), m.p.

248—249 °C (decomp.) [lit.,²⁷ m.p. 238—240 °C (decomp.)]. Similar results were obtained when benzene replaced carbon tetrachloride as solvent.

Acknowledgements

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