Bromonitromethane—A Versatile Electrophile

Brian R. Fishwick[a], David K. Rowles, and Charles J. M. Stirling[b]*
[a] *Research Department, I.C.I. Organics Division, Blackley, Manchester M9 3DA*
[b] *Department of Chemistry, University College of North Wales, Bangor LL57 2UW*

Pathways in reactions of bromonitromethane with a variety of nucleophiles have been investigated.

With thiolates, the electrophilic centre is bromine and the initial products are disulphides. When the thiolate ion itself carries an electrophilic centre such as carbonyl or cyano β-to sulphur, the product is a nitrothiophene derived from subsequent reaction of the first-formed disulphide with nitronate ion displaced in the initial process. This provides a generalisation of earlier nitrothiophene synthesis by this route.

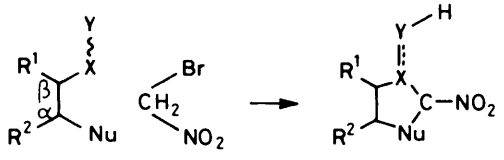
In reactions with arenesulphinate ion, the electrophilic centre is also bromine and equilibration between the initial reactants and the initial products, sulphonyl bromide and nitronate ion, is established. The components of the equilibrium subsequently react either with each other or with the solvent. Reactions with sulphides are slow and distal substituents such as hydroxy- or cyano- so much reduce reactivity that no reaction is observed. Dimethyl sulphide attacks bromonitromethane at the carbon atom, and subsequent attack on the nitromethyl sulphonium salt initially formed gives methylthionitromethane and trimethylsulphonium bromide.

Iodide ion attacks at bromine to give iodine, presumably *via* iodine bromide, but with tervalent phosphorus nucleophiles, attack is at oxygen giving the corresponding oxides and HCN in a double deoxygenation sequence. For hydroxide, methoxide, and hydride ions (from sodium borohydride), nucleophilic attack is at hydrogen and the nitronate ion produced is inert to further attack. There is no evidence of carbene formation by α-elimination.

When the anion of bromonitromethane is allowed to react with tributylboron, the anionic migration–displacement which follows boron–carbon bond formation, yields 1-nitropentane.

The anion of bromonitromethane is unreactive towards aldehydes and electrophilic alkenes.

The work described in this paper originated from an interest in the synthesis of aminothiophenes and their derivatives in connection with disperse dyestuffs. Our interest had been particularly attracted to the reactivity of bromonitromethane which had been shown to be a useful equivalent of a one-carbon nitro-functionalised synthon in the synthesis of heterocyclic nitro compounds. Thus, in the general system (**1**) the overall



(**1**)

reaction apparently involves displacement by the nucleophile at α-C and addition to the electrophile at β-C. Several variations on this general theme have been reported:

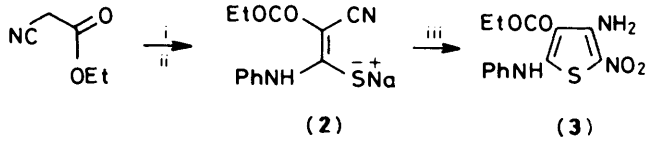
Nu = S; X ≈ Y = CN; R^1R^2 = benzo giving nitroaminobenzothiophene[1]

Nu = O; X ≈ Y = CN; R^1R^2 = benzo giving nitroaminobenzofuran[2]

Nu = O; X ≈ Y = C=O; R^1R^2 = benzo giving nitrobenzofuran[3-5]

Nu = OMe; X ≈ Y = C=O; R^1R^2 = benzo giving nitrobenzofurans[6]

Nu = S; X ≈ Y = C≡C; R^1 – NHAr; R^2 = H giving 2-nitro-5-arylaminothiophenes.[7]



(**2**) (**3**)

Reagents: i, NaOEt–EtOH; ii, PhNCS; iii, $BrCH_2NO_2$

With thiocarbonylamidines, the products are aminothiazoles.[8]

The common features of these reactions is the presence in the sulphur or oxygen nucleophile of an electrophilic centre β- to the nucleophilic atom. It is this combination of structures that produces the capability for cyclisation.

The use of bromonitromethane in this way has placed emphasis on the design and synthesis of appropriate co-reactants. In the first part of this paper we report work on this general theme.

The synthetic work excited our mechanistic curiosity and in the second part of the paper we present an investigation of the reactions of a variety of nucleophiles with this interesting and versatile electrophile.

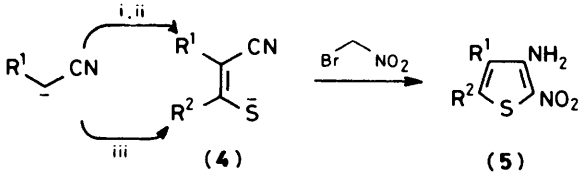
Synthesis of Nitrothiophenes and Related Compounds.—The use of bromonitromethane is exemplified as follows: using Lalibierte's[9] general method, treatment of the sodium salt of ethyl cyanoacetate with phenyl isothiocyanate gave the salt of the thioamide (**2**), which with bromonitromethane gave the nitrothiophene (**3**).

Nitroaminothiophenes obtained by variation of this pro-

Table 1. Synthesis of 3-amino-2-nitrothiophenes (5)

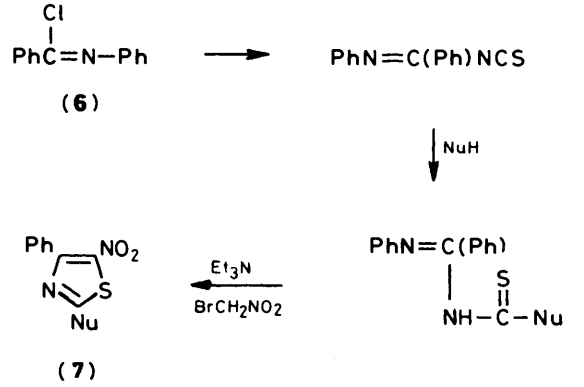
Series (5)	% Yield Thiol	% Yield Thiophene	M.p. °C	Formula	Found (%) (Required) C	H	N
a	95	40	172[a,b]	$C_{13}H_{13}N_3O_4S$	50.2 (50.8)	4.2 (4.2)	
b	33	60	218[c,f]	$C_{11}H_8N_4O_2S$	50.2 (50.8)	3.4 (3.1)	21.5 (21.5)
c	86	30	156[c]	$C_8H_{10}N_2O_4S_2$	38.4 (36.6)	3.8 (3.8)	10.7 (10.6)
d		55	248[d]	$C_6H_5N_3O_2S_2$	33.6 (33.4)	2.6 (2.3)	19.6 (19.5)
e	63	56	293[e]	$C_6H_7N_3O_3S_2$	30.7 (30.9)	3.3 (3.0)	18.1 (18.0)
f	96	70	192—194	$C_8H_{11}N_3O_4S$	38.9 (39.1)	4.5 (4.5)	16.9 (17.1)

[a] *m/z* 307 (*M*). [b] From toluene. [c] From butan-1-ol. [d] From butan-1-ol–DMF. [e] From DMF. [f] Found: S, 24.7; Calc: S, 24.4%.



a, $R^1 = CO_2Et$, $R^2 = NHPh$;
b, $R^1 = CN$, $R^2 = PhNH$;
c, $R^1 = CO_2Et$, $R^2 = SMe$;
d, $R^1 = CN$, $R^2 = SMe$;
e, $R^1 = CONH_2$, $R^2 = SMe$;
f, $R^1 = CO_2Et$, $R^2 = NHMe$;
g, $R^1 = PhSO_2$, $R^2 = NHPh$

Scheme 1. *Reagents*: i CS_2; ii MeI; iii RNCS



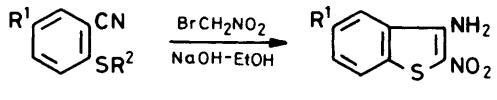
a; Nu = morpholino
b; Nu = piperidino
c; Nu = ethoxy

cedure (Scheme 1) are listed in Table 1. Again, bromonitromethane provides the 1-carbon doubly functionalised reagent.

We confirmed the conversion[8] of *N*-phenylbenzimidoyl chloride (**6**) into the thiazoles (**7a**) and (**7c**) and obtained the new thiazole (**7b**) in 60% yield. Again, the presence of the β-electrophile makes cyclisation possible.

o-Cyanobenzenethiols (**8**) are particularly significant intermediates for dyestuff synthesis and we have obtained high yields in conversions into the benzothiophenes (**9**) from the simple thiol (**8a**)[1] and the nitro derivative (**8b**).[10]

We have improved the synthesis of the starting thiol (**8a**) by treatment of *o*-chlorobenzonitrile with 2-cyanoethanethiolate in HMPA[11] with subsequent elimination[12] of the thiolate from the cyanoethyl sulphide (**8c**) (85%). We return to the reactions of these thiols with bromonitromethane below.



a; $R^1 = H$, $R^2 = H$
b; $R^1 = NO_2$, $R^2 = H$
c; $R^1 = H$; $R^2 = CH_2CH_2CN$

The common feature of all of these thiophene-forming reactions is ring formation, consequent upon nucleophilic attack of a β-electrophile-bearing thiolate ion upon bromonitromethane. In all cases, a new C–S bond is created but in no case was direct mechanistic information available about the reactions studied. The remainder of this paper is concerned with the reactivity of bromonitromethane towards these and other nucleophiles and with proposals as to the pathways of the reactions.

Reactions of Bromonitromethane with Thiolates.—The heterocyclic syntheses described above all depend upon the formation of a C–S bond in the process of the reaction between a β-functionalised thiolate ion and bromonitromethane. An obvious question, therefore, was whether this bond was formed directly by displacement of bromide from bromonitromethane. Reactions between tertiary and secondary α-nitro halides and thiolate ions are well known from the work of Kornblum[13] and Bowman.[14] These lead to the *products* of direct substitution but it is clear that in the case of tertiary α-nitro halides at least, reaction can occur by an $S_{RN}1$ mechanism, and reactions are inhibited by oxygen and *p*-dinitrobenzene.[15]

In our work, treatment of bromonitromethane with simple thiolates in ethanol rapidly gives disulphides in 75—95% yields (Table 2). Clearly, direct displacement of halide to give α-nitro sulphide is a negligible reaction under these conditions. A careful search revealed no trace of α-nitro sulphide and it was shown separately that phenylthionitromethane is stable to the reaction conditions, only deprotonation occuring. Formation of disulphide does *not* come about by displacement of the anion of nitromethane from an initially formed α-nitro sulphide. This is in line with earlier work[14] for uncatalysed reactions but Bowman[16] has shown, however, that under photocatalysis in DMF, α-nitro sulphides with strongly electron-acceptive conjugative groups attached to sulphur can undergo (slow) reactions with thiolates to give disulphides in yields up to 55%.

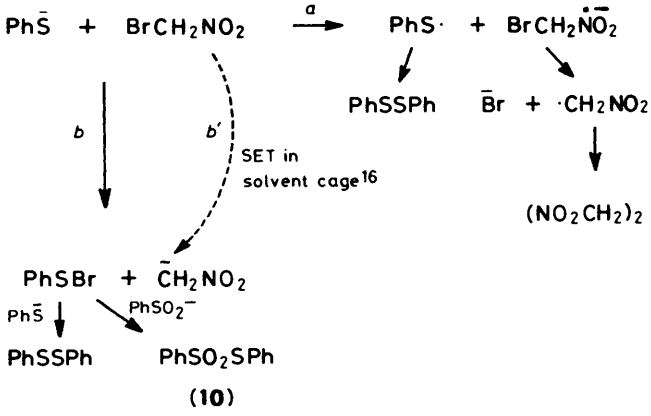
Table 2. Reactions of bromonitromethane with simple thiolates[a,b,c]

Thiolate	Product	Yield %
PhS^-	PhSSPh	95
EtS^-	EtSSEt	85[f]
$PhCH_2S^-$	$PhCH_2SSCH_2Ph$ $\bar{C}H_2NO_2$[j]	96[c,e] 82[d,e] 92[g] 99[k]
$o\text{-}NO_2C_6H_4S^-$	$(o\text{-}NO_2C_6H_4S)_2$	89
$EtOC(:S)S^-$[h]	EtOC(:S)SSC(:S)OEt	95[i]
Benzothiazole-2-thiolate	Dibenzothiazol-2-yl disulphiole	98[l]
$H_2\overset{+}{N}(NH_2)=C\bar{S}$[p]	$[H_2\overset{+}{N}(NH_2)=CS]_2$ (**16**)	48[o]
o-Cyanobenzenethiolate	3-Amino-2-nitrobenzo[*b*]thiophene (**9a**)	87[m] 82[n]

[a] Reactions in MeOH under N_2 with sodium thiolate:nitro-compound. [b] Na salt. [c] In methanol by addition of $BrCH_2NO_2$ to thiolate. [d] Inverse addition. [e] M.p. and mixed m.p., 69 °C (from MeOH). [f] B.p. 66 °C/32 mmHg; $\delta_H(CDCl_3)$ 1.32 (t) and 2.70 (q). [g] With ethyl bromonitroacetate. [h] K salt. [i] B.p. 106 °C/0.15 mmHg, $n^{21}{}_D$ 1.5971; δ_H ($CDCl_3$) 1.44 (t) and 4.73 (q) [lit., b.p. 107—109 °C/0.05 mmHg, m.p. 31.5—32.5 °C (G. Bulmer and F. G. Mann, *J. Chem. Soc.*, 1945, 674)]. [j] As Na salt (see Experimental section). [k] With 2-bromo-2-nitropropane-1,3-diol. [l] M.p. and mixed m.p. 179—181 °C. [m] Addition of thiolate to bromonitromethane. [o] As dinitrate, m.p. and mixed m.p. 115 °C. [p] Reaction in aqueous nitric acid.

The conditions employed were much more severe than for our reactions. Nitromethane anion is, however, the complementary product of the reaction in the case of, for example, the reaction with toluene-α-thiolate with which, for convenience, most reactions have been performed.

We have also shown that thiolates are not oxidised to disulphides by simple nitro compounds such as nitromethane or ethyl nitroacetate.



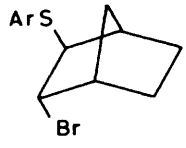
(**10**)

Scheme 2.

We believe that these results exclude an oxidative pathway to disulphide or one which depends upon direct nucleophilic displacement of bromide ion from bromonitromethane. Two reasonable alternatives remain, shown as path *a* and path *b* in Scheme 2.

The stoicheiometry of the reaction is 2:1 thiolate:nitro halide. This is evidence against the SET mechanism (path *a*) whose stoicheiometry is 1:1. Additionally, such reactions have been clearly shown in earlier work on secondary and tertiary α-nitro halides to be inhibited by oxygen and, for example, by *p*-dinitrobenzene. While our reactions were performed with careful exclusion of air to exclude direct oxidation of thiolate to disulphide, Bowman[17] has found that this is not a very rapid reaction. Formation of disulphides in our reactions was very rapid. Admission of air had no effect on yields or (qualitatively) on rates. Likewise, *p*-dinitrobenzene did not affect the yields of products or visibly affect their rates of formation.

On the basis of this evidence, the remaining pathway, path *b*, appeared possible. This involves nucleophilic attack by the thiolate on bromine, a type of reaction which is encountered particularly when the nucleophile is polarisable (soft) and the carbon leaving group is particularly stabilised as the anion.[18] Both of the products, disulphide and nitronate ion, and also the stoicheiometry, are consistent with this pathway. An initial product of the reaction is the sulphenyl bromide which is postulated to react with another thiolate ion. Alternatively, the same products may be generated by SET within a solvent cage.[16] This is a rapid process which makes diversion of the sulphenyl halide to other products difficult. When the thiolate–bromonitromethane reaction was carried out in the presence of norbornene, no adduct (**11**) could be isolated, despite the fact that in a study of the reactivity of 35 alkenes towards sulphenyl halides,[19] this alkene was one of the most reactive, more so than cyclohexene by a factor greater than 100. Cyclohexene also failed to trap sulphenyl halide.



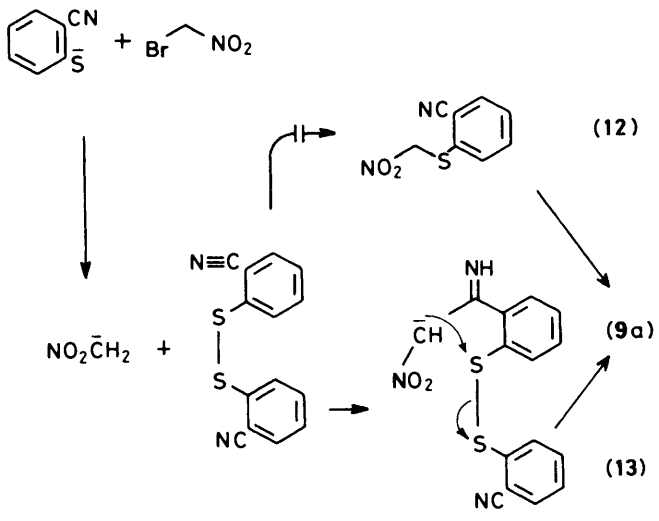
(**11**)

It was shown some time ago[20] that sulphenyl chlorides and bromides react rapidly with arene sulphinate ions to give thiolsulphonates. It will be seen (below) that sulphinate ions react with bromonitromethane but when benzenethiolate ion was allowed to react with bromonitromethane in the presence of sodium benzene sulphinate, *S*-phenyl benzenethiosulphonate (**10**) was obtained in low (15%) yield. Separate experiments showed that an alternative source of the ester (**10**) [equation (1)] was not viable under the reaction conditions. This trapping

$$PhS\bar{O}_2 + PhSSPh \longrightarrow PhSO_2SPh + PhS^- \quad (1)$$

procedure has also been used by Bowman and his collaborators[21] to implicate the formation of sulphenyl halides in X-philic[18] reactions of thiolates with 2-halogenomethyl-5-nitrofurans.

These experiments do not *establish* pathway *b*, but show that there is least contrary evidence for this possibility. This pathway is also suggested by the observation of transient brown colours on the addition of thiolate to the methanolic solution of



Scheme 3.

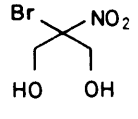
bromonitromethane. (Benzenesulphenyl bromide is dark brown.)

The anomalous result is the ready formation not of disulphide but of a thiophene in the reaction of *o*-cyanobenzenethiol. Our interpretation of this result against the background of the reactions with simple thiolates is that rapid disulphide formation is indeed the initial reaction. This is followed by attack of the liberated nitronate ion not at the disulphide linkage with subsequent intramolecular attack by the anion of the thio-nitro compound (**12**) (Scheme 3) but instead by attack of the nitronate ion on the nitrile function (**13**) with subsequent ring closure to give (**9a**).

A related sequence probably accounts for the formation of the thiophenes (**3**) and (**5**).

In separate experiments, we have not been able to detect any reaction between nitronate ions and simple aromatic nitriles, but the equilibrium is undoubtedly very much on the side of the initial reagents. In support of our ruling out of an attack on the disulphide linkage, the electronically similar di-*o*-nitrophenyl disulphide is inert to nitronate ion under the conditions in which di-*o*-cyanophenyl disulphide gives (**9a**). This is an important comparison. Bowman and his collaborators[16] have shown that nitronates *are* capable of displacement at sulphur in disulphides, $(RS)_2$, with formation of α-nitro sulphides provided that R is powerfully electronegative (*e.g.* 2-pyridyl) and if a large (typically tenfold) excess of nitronate over disulphide is employed.

In contrast with our results using bromonitromethane, reactions with the commercial fungicide 2-bromo-2-nitro-



(**14**)

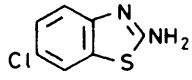
$[(HOCH_2)_2C(NO_2)]_2$

(**15**)

propane-1,3-diol (**14**) proceeded somewhat differently. Toluene-α-thiolate ion was converted (99%) into the disulphide but the complementary product was the dimer (**15**). Such a product is indicative of radical coupling and hence of an SET mechanism. This result suggests a delicate balance between the X-philic and SET pathways, a balance that may be decided by the stability of the radical ion produced. In the case of (**14**) of course, this is tertiary. The stoicheiometry is the same in either case. In reaction of toluene-α-thiolate with (**14**) on a 1:1 mole basis, the yield of (**15**) was 48%, and 49% of (**14**) was recovered.

Reactions of Bromonitromethane with other Sulphur Nucleophiles.—Thiourea. Reactions with thiourea in alcoholic solvents gave thick buff gums which were mainly sulphur and these conditions were not proceeded with. When, however, the reactions were performed in nitric acid, the disulphide dinitrate (**16**) (Table 2) was obtained in moderate yield.

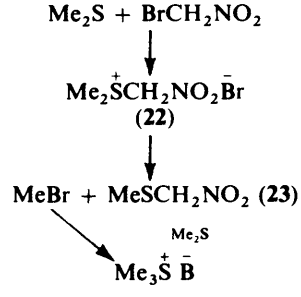
Thiocyanate ion. No clearly defined product could be obtained. On the basis of our other results, a reasonable expectation was the formation of thiocyanogen $(NCS)_2$, which reacts rapidly with *p*-chloraniline to give the crystalline benzisothiazole (**17**). None was obtained under conditions in which use of bromine as oxidising agent gave the compound in 90% yield.

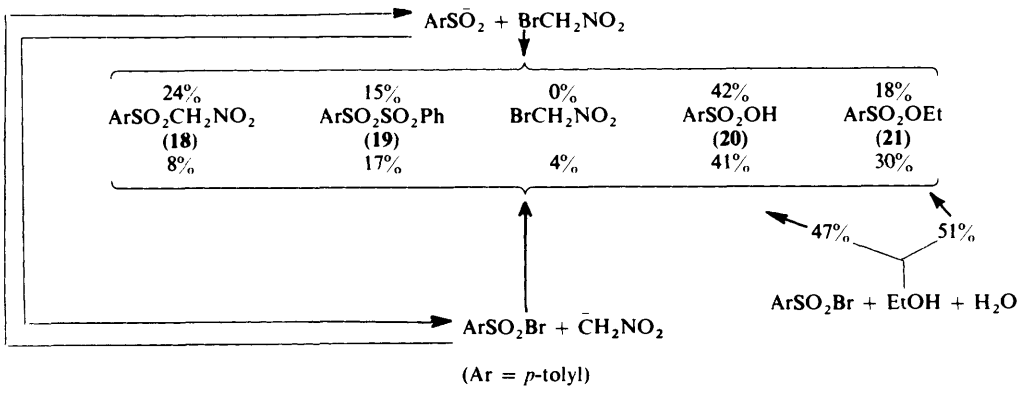


(**17**)

Toluene-p-sulphinate ion. In 50:50 v:v ethanol–water, reaction with bromonitromethane gave a series of products (Scheme 4). Formulation of the reaction as for the simple thiolates would suggest toluene-*p*-sulphonyl bromide and nitronate ion as the initial products. Toluene-*p*-sulphonyl bromide reacts readily with toluene-*p*-sulphinate ion to give the disulphone (**19**), accounting for its formation once equilibration between the four initial components of the reaction is established. That equilibration is occurring is strikingly confirmed by the formation of a small amount of bromonitromethane from the sulphonyl bromide and nitronate ion. Different behaviour from that of the thiolate reaction is clearly evident in the isolation of the nitro sulphone (**18**). This product *could* arise from direct displacement, as suggested for a sulphide nucleophile (below), or could be the cross combination product of an SET mechanism ($PhSO_2\cdot + \cdot CH_2NO_2$) together with bis-sulphone. We have no clear evidence on this point one way or the other at present; but the formation of disulphone (**19**) is unaffected by *p*-dinitrobenzene. Products of type (**18**) have previously been obtained[22] in unstated yield by treatment of a mixture of mono- and di-bromonitromethane in methanol with sulphinates. The acid (**20**) and ester (**21**) are entirely expected products once toluene-*p*-sulphonyl bromide has been generated. Solvolysis of the sulphonyl bromide in the medium gives broadly the same hydrolysis:ethanolysis ratio (Scheme 4).

Reactions with sulphides. Dimethyl sulphide in acetonitrile reacted very slowly (5 days at 50 °C) with bromonitromethane to give, as final products, trimethylsulphonium bromide (62%) and methylthionitromethane (**23**) (68%). These products are best accounted for as arising from slow S_N2 displacement of bromide from the nitrohalide and subsequent dealkylation of





Scheme 4.

the nitrosulphonium salt (**22**) by bromide. The methyl bromide thus generated is trapped by the excess of dimethyl sulphide.

In connection with generation of nitrothiophenes we were particularly interested in the possibility of intramolecular displacement by a nitronate ion in an appropriately substituted nitro sulphide. To this end we attempted similar reactions

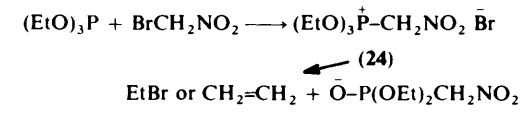
between bromonitromethane and 3-hydropropyl and 2-hydroxyethyl methyl sulphides. In neither case was any appreciable reaction observed under severe conditions over long periods.

Reactions with Other Nucleophiles.—Iodide ion. Potassium iodide in methanol reacted slowly with bromonitromethane liberating iodine (65%) after 36 h; the latter was determined by thiosulphate titration and by conversion of aniline into 4-iodoaniline. The potassium bromide recovered from the reaction was contaminated with traces of nitrite, perhaps derived from nitronate ion. Again, the results are consistent with nucleophilic attack on bromine with displacement of nitronate ion:

$$I^- + BrCH_2NO_2 \longrightarrow IBr + \bar{C}H_2NO_2$$

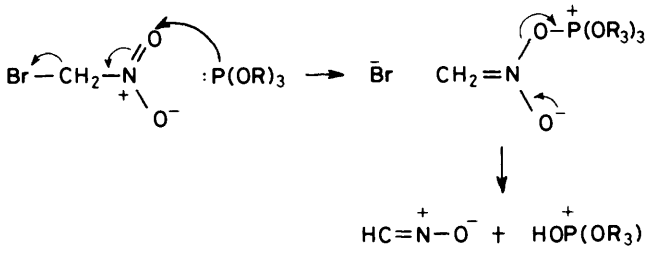
Nitromethane was identified (g.l.c.) in organic extracts of reaction mixtures buffered to pH 5.8.

Phosphorus nucleophiles. Triethyl phosphite, on reaction with bromonitromethane in diethyl ether, gave triethyl phosphate (94%) and HCN (66%) as cyanide, measured with a cyanide-sensitive electrode. This finding is in contrast to that of Arbuzov and his collaborators[23] who kept the initial products of the reaction (performed at 20 °C) at 160 °C. The products under these conditions were triethyl phosphate (55%), ethyl bromide (49%), and gaseous products which included ethylene. Such products could be accounted for as arising from an Arbuzov-like sequence (Scheme 5) involving subsequent displacement or elimination in the quasi-phosphonium salt (**24**).



Scheme 5.

This sequence does not, of course, account for the formation of triethyl phosphate for which ethyl bromide is a mutually exclusive product. We suggest that the most probable sequence involves attack by phosphorus at *oxygen* in a Perkow-type[24] sequence* (Scheme 6) and the nitrile oxide similarly is very susceptible to deoxygenation. The stoicheiometry of the reaction (2:1 phosphite:bromonitromethane) giving the observed yields is also consistent with this view of the reaction.



Scheme 6.

With an equimolar proportion of triphenylphoshpine in benzene, a quantitative yield of triphenylphosphine hydrobromide was obtained after 12 h together with triphenylphosphine oxide (82%), showing again a 2:1 phosphite:bromonitromethane stoicheiometry. Hydrogen cyanide (100%) was determined as before and 49% of the initial quantity of bromonitromethane was recovered. Again, this behaviour is consistent with that of ethyl phosphite, involving attack at oxygen with formation of phosphine oxide and nitrile oxide, which then undergoes deoxygenation. The overall result is at variance with an earlier report[25] of this reaction in which hydroxyiminomethyltriphenylphosphonium bromide (**25**) was obtained. We obtained *ca.* 10% of material with the properties of the material obtained earlier but we were unable to establish the presence of a P–CH= function by ^{1}H n.m.r.

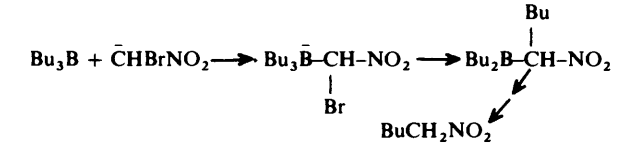
$$Ph_3\overset{+}{P}–CH=N=OH\ \bar{B}r\ (\mathbf{25})$$

Basic nucleophiles. In all of the previous instances, bromonitromethane has not been dissociated in the reaction medium. Its pK_a in 50% MeOH–H_2O is 8.7.[26] No reaction other than deprotonation occurred on treatment of bromonitromethane with phenoxide ion in methanol, with aqueous sodium hydroxide, or with methanolic sodium methoxide. Treatment

* We thank a referee for this suggestion which improves our original version.

with methanolic sodium borohydride allowed isolation of $NaCHBrNO_2$ (74% yield). All of these nucleophiles are poorly polarisable, a disadvantage for attack at bromine,[18] and are sufficiently basic to ionise the nitro compound almost completely. Under these conditions, therefore, it is not surprising that neither halogen nor carbon is the electrophilic site. The derived ion is a 'carbenoid', *i.e.* with the potential for α-elimination of bromide or nitrite, but we could find no evidence for carbene trapping in deprotonation reactions in the presence of cyclohexene.

Reaction of Bromonitromethane with Tributylborane.—The anion of bromonitromethane was generated using 2,6-di-t-butylphenolate[27] in THF as base, and treatment with tributylborane gave, in equimolar solutions at 0 °C, 1-nitropentane (57% isolated yield). The reaction can be formulated as shown in Scheme 7.



Scheme 7.

The reaction is a new example of migration–displacement processes, characteristic of boron chemistry.[28] It has obvious applications to the alkylation of nitro compounds and is to be further investigated. α-Halogenonitroalkanes are easily accessible and the reaction offers a real alternative to the unsatisfactory deprotonation–alkylation sequence.[29] The closest analogue of the bromonitromethane reaction is the electrolytic synthesis of nitroalkanes from trialkylborons and nitromethane.[30]

The Anion of Bromonitromethane as a Nucleophile.—We attempted a number of reactions of bromonitromethane with benzaldehyde and with acrylonitrile under basic conditions. In no case were we successful in obtaining the typical carbanion addition products. Our failures are reminiscent of those reported by Zeilstra and Engberts[31] with *p*-tolylsulphonyl nitromethane.

Conclusions.—Bromonitromethane is not only a valuable one-carbon nitro-functionalised fragment for the synthesis of heterocycles and nitro compounds, but has an intriguing range of reactivity much of which has received only preliminary attention. This small molecule has substantial potential.

Experimental

Extractions were with dichloromethane unless otherwise stated. M.p.s are uncorrected. Unless otherwise stated, all reactions were carried out under nitrogen. Known compounds were authenticated by mixed m.p., i.r. and n.m.r. spectra. 2-Nitrophenyl nitromethyl sulphide had m.p. 70 °C.[32]

Bromonitromethane was prepared by Slagh's method.[33] Nitromethane (0.1 mol) was added to a solution of sodium hydroxide (4 g, 0.1 mol) in water (135 cm^3). To the solution at 0 °C was added bromine (16 g, 0.1 mol) with stirring over 35 s, during which time the temperature rose to 17 °C. After 30 min, the pH was adjusted to 3 with HCl and extraction with dichloromethane and subsequent evaporation and distillation gave bromonitromethane (69%), b.p. 42 °C/12 mm Hg., $n^{20}D$ 1.4884 (lit.,[34] $n^{20}D$ 1.4880), ^1H n.m.r. (neat) δ 5.7 (s). Light petroleum refers to the fraction b.p. 40—60 °C; ether refers to diethyl ether.

3-*Amino*-2,5-*dinitrobenzo*[*b*]*thiophene* (**9b**).—Successive treatment of 2-chloro-5-nitrobenzonitrile (30 mmol) in dimethylformamide (100 cm^3) with sodium sulphide (36 mmol) in water (20 cm^3) at 5 °C under N_2 (20 min), and then with bromonitromethane (36 mmol) according to Beck's procedure,[10] gave the thiophene (**9b**) (87%), m.p. 296 °C raised to 304 °C (from DMP–butan-1-ol) (Found: C, 40.5; H, 2.3; N, 17.8. $C_8H_5N_3O_4S$ requires C, 40.2; H, 2.1; N, 17.6%). Inverse addition, *i.e.* of thiolate to bromonitromethane, gave the same product (m.p. and mixed m.p.) in 82% yield.

3-*Amino*-2-*nitrobenzo*[*b*]*thiophene* (**9a**).—2-Cyanoethanethiol[35] (11 mmol) and 2-nitrobenzonitrile (11 mmol) in HMPA (20 cm^3) at 20 °C were treated with lithium hydroxide (0.48 g, 20 mmol). After 2 h, addition to water (100 cm^3) and extraction with ether (3 × 50 cm^3) gave the sulphide (**9c**) (86%), m.p. 38 °C (from EtOH); (1.7 mmol) of this in DMF (15 cm^3) was treated with sodium hydroxide (0.32 g) in water (3 cm^3) at 0 °C. After 15 min, bromonitromethane (1.7 mmol) was added and, after the mixture had been stirred for 2 h at 17 °C, addition to ice–water and extraction with ether (3 × 50 cm^3) gave a residue (1.9 g) which on flash chromatography (ether–light petroleum) gave the thiophene (**9a**) (84%) m.p. 217 °C (from ethanol) (lit.,[36] m.p. 217—218 °C; lit.,[37] m.p. 218—218.5 °C).

Typical Thiophene Synthesis.—Ethyl cyanoacetate (2.3 g, 21 mmol) was added to a solution of sodium (0.48 g, 21 mmol) in dry ethanol (25 cm^3) at 0 °C. Phenyl isothiocyanate (21 mmol) was added and after 1 h at 18 °C, bromonitromethane (21 mmol) was added to give a yellow solution which deposited the crude thiophene (**5a**) (2.7 g, 40%), m.p. 157 °C raised to 171.5 °C (from acetone); δ ($CDCl_3$) 7.4 (s), 4.46 (q), and 1.46 (t).

5-*Nitro*-4-*phenyl*-2-*piperidinothiazole* (**7b**).—*N*-Phenylbenzimidoyl chloride (**6**) (46 mmol) in acetone (20 cm^3) at 0 °C was treated with piperidine (46 mmol) in acetone (60 cm^3) dropwise over 30 min with stirring. After 2 h, the solution was filtered and the filtrate evaporated; the residue in ether (300 cm^3) was treated with sodium ethoxide (1 g) in ethanol (30 cm^3). After 24 h at 20 °C, filtration and removal of ether from the filtrate gave the *amidine* (60%), m.p. 139 °C (from ethanol) (Found: C, 70.8; H, 6.7; N, 12.8. $C_{19}H_{21}N_3S$ requires C, 70.6; H, 6.5; N, 13.0%). The amidine (15 mmol) in acetone (60 cm^3) was treated with bromonitromethane (15 mmol) in acetone (10 cm^3) dropwise with stirring, followed immediately by triethylamine (15 mmol) in acetone (10 cm^3). The mixture was stirred under reflux for 45 min, when removal of solvent, addition of water to the residue, and extraction with chloroform gave the *thiazole* (**7b**) (4.36 g, 53%), m.p. 124 °C (from ethanol) (Found: C, 58.2; H, 5.0; N, 14.2; $C_{14}H_{15}N_2O_3S$ requires C, 58.1; H, 5.0; N, 14.2%).

Reactions of Thiolates with Bromonitromethane.—(*a*) *With toluene-α-thiolate.* Toluene-α-thiol (24 mmol) was added to a solution of sodium (0.96 g, 24 mmol) in ethanol (20 cm^3). Addition of bromonitromethane (24 mmol) caused immediate precipitation of dibenzyl disulphide (96%), m.p. 64 °C raised to 69 °C (from methanol) alone or mixed with an authentic specimen.

The reaction was repeated with sodium benzenethiolate (21 mmol) in ethanol (15 cm^3) added dropwise over 1 h to norbornene (21 mmol) and bromonitromethane (21 mmol). After 3 h, addition to water and extraction gave a residue (2.45 g), m.p. 52 °C raised to m.p. 60 °C (1.93 g, 95%), alone or mixed with an authentic specimen of diphenyl disulphide.

The reaction was repeated using sodium benzenethiolate (21

mmol) in ethanol (30 cm^3) at 0 °C added dropwise over 1 h to bromonitromethane (21 mmol) in cyclohexene (30 cm^3); work-up as before gave diphenyl disulphide (1.93 g, 95%), m.p. and mixed m.p. 60 °C.

Other reactions with thiolates were carried out similarly. Yields are given in Table 2.

(*b*) *With* o-*nitrobenzenethiolate.* Bromonitromethane (0.67 g, 4.8 mmol) in ethanol (10 cm^3) was added dropwise to sodium *o*-nitrobenzenethiolate (9.6 mmol) at 0 °C over 1 h. Addition of water and filtration gave di-*o*-nitrophenyl disulphide (89%), m.p. and mixed m.p. 197—201 °C. The filtrate was evaporated to half volume, adjusted to pH 4 (acetate buffer) and extracted to give the recovered thiol (0.24 g 13%), m.p. and mixed m.p. 52—53 °C.

No 2-nitrophenyl nitromethyl sulphide was formed and this compound was recovered by treatment with *o*-nitrobenzenethiolate under the same conditions.

The disulphide (1.0 g) was recovered after treatment with sodium nitromethane (1.1 g) in ethanol (25 cm^3) at 20 °C for 24 h, and subsequent addition to acetate buffer (pH 4.5) (50 cm^3).

Reaction of 2-*Bromo*-2-*nitropropane*-1,3-*diol with Toluene*-α-*thiolate Ion.*—Sodium (0.286 g, 13 mmol) was allowed to dissolve in methanol (25 cm^3) and toluene-α-thiol (12.4 mmol) followed by 2-bromo-2-nitropropane-1,3-diol (12.4 mmol) were added to the solution. After 1 h, filtration gave a residue (2.3 g) which, on trituration with ether provided 2,3-dinitro-2,3-bishydroxymethylbutane-1,4-diol (**15**) (0.729 g, 48%), m.p. 107 °C (from methanol); δ_C ($CDCl_3$) 58.4 and 118.3 p.p.m.; δ_H ($CDCl_3$) 4.1 (s) and 3.4—3.9 (br s). Evaporation of the ethereal solution gave dibenzyl disulphide (99%), m.p. and mixed m.p. 70 °C. Evaporation of the original methanol mother liquors gave recovered bromo nitro compound (49%).

Interception of Benzenesulphenyl Bromide in the Benzenethiolate–Bromonitromethane Reaction.—Sodium benzenesulphinate (22 mmol) was added to sodium benzenethiolate (20 mmol) in ethanol (30 cm^3) at 0 °C. Bromonitromethane (21 mmol) in ethanol (20 cm^3) was added dropwise with vigorous stirring over 15 min. Insoluble material (1.46 g) was filtered off and evaporation of the filtrate gave a residue (8.72 g). Leaching with ether (100 cm^3) gave further insoluble material (3.17 g) and flash chromatography of the filtrate in ether–light petroleum (1:1) gave first diphenyl disulphide (1.7 g, 74%) and then *S*-phenyl benzenethiosulphonate (0.75 g 15%), m.p. and mixed m.p. 45 °C (from ethanol).

Reaction of Di-o-*cyanophenyl Disulphide with Sodium Nitromethane.*—Nitromethane (1 mmol) was added to a solution prepared from sodium (0.02 g, 0.87 mmol) and ethanol (15 cm^3). After addition of the disulphide (0.86 mmol), the mixture was set aside for 15 h, when addition to water (50 cm^3) and extraction gave 3-amino-2-nitrobenzo[*b*]thiophene (**9a**) (100 mg, 63%), m.p. and mixed m.p. 216 °C. The aqueous layer was acidified and extracted to give *o*-cyanobenzenethiol (74%).

Reactions of Toluene-α-*thiolate with Nitroethyl Esters.*—Sodium methoxide (46 mmol) in methanol (25 cm^3) was treated with toluene-α-thiol (5.06 g, 46 mmol) and ethyl bromonitroacetate (46 mmol) in methanol (25 cm^3) was then added dropwise at 18 °C with stirring over 30 min. After 12 h, filtration gave dibenzyl disulphide (92%) (identified by m.p. and mixed m.p.).

Repetition with ethyl nitroacetate in place of ethyl bromonitroacetate gave, on filtration, the sodium salt of ethyl nitroacetate (74%), identified by dissolution in water and extraction to give the free ester.

Reaction of Toluene-p-*sulphinate Ion with Bromonitromethane.*—Bromonitromethane (17 mmol) was added at 24 °C to a solution of sodium toluene-*p*-sulphinate (17 mmol) in ethanol–water (1:1, v/v; 60 cm^3). After 2 h, filtration gave di-*p*-tolyl disulphone (0.79 g, 15%), m.p. 212 °C raised to 216 °C (from benzene) alone or mixed with an authentic specimen.* After 2 h, the mixture deposited *p*-tolylsulphonylnitromethane (0.58 g), m.p. 115 °C raised to 116 °C (lit.,[38] 116.6 °C) (from ethanol) (Found: C, 44.9; H, 4.05; N, 6.3. Calc. for $C_8H_9NO_4S$: C, 44.6; H, 4.2; N, 6.5%). Addition of the mother liquors to saturated brine (50 cm^3), adjustment of the pH to 2 and extraction gave a residue which on addition of ethanol at 0 °C gave further *p*-tolylsulphonylnitromethane (0.18 g), m.p. and mixed m.p. 114 °C. Distillation of the mother liquors gave ethyl toluene-*p*-sulphonate (0.6 g, 18%), b.p. 95 °C/0.6 mmHg; the i.r. spectrum was identical with that of an authentic specimen. The aqueous solutions were combined and evaporated to give a residue with an i.r. spectrum identical with that of sodium toluene-*p*-sulphonate. In a second experiment, addition of the reaction mixture was to water instead of brine and the residue (3.2 g) from evaporation of the aqueous solutions was titrated (Volhard) for bromide giving, by subtraction, a 42% yield of sodium toluene-*p*-sulphonate.

Addition of toluene-*p*-sulphonyl bromide (17 mmol) to ethanol–water (1:1, v/v) at 23 °C and extraction as before after 24 h, gave ethyl toluene-*p*-sulphonate (1.73 g, 51%), b.p. 95 °C/10.5 mmHg; and sodium toluene-*p*-sulphonate (1.12 g, 47%).

Reaction of Toluene-p-*sulphonyl Bromide with Sodium Nitromethanide.*—Toluene-*p*-sulphonyl bromide[39] (17 mmol) was added to sodium nitromethanide (1.5 g 18 mmol) in ethanol–water (1:1, v/v; 60 cm^3) at 23 °C. After 24 h, filtration gave di-*p*-tolyl disulphone (0.46 g, 17%), m.p. 215 °C raised to 216 °C alone or mixed with an authentic specimen. Addition of the mother liquors to water as before gave tolylsulphonylnitromethane (0.29 g, 8%) m.p. and mixed m.p. 116 °C. Distillation of the residue after removal of the solvent gave bromonitromethane (0.1 g, 4%), b.p. 48 °C/12 mmHg; and then ethyl toluene-*p*-sulphonate (1.7 g, 51%), b.p. 95 °C/0.5 mmHg. Neutralisation of the aqueous solutions (pH 7) and evaporation gave sodium toluene-*p*-sulphonate (0.97 g, 41%). When the reaction was repeated in the presence of *p*-dinitrobenzene (10 mol %) the yield of di-*p*-tolyl disulphone was unaffected.

Reaction of Toluene-p-*sulphonyl Bromide with Sodium Toluene*-p-*sulphinate.*—A rapidly stirred solution of sodium toluene-*p*-sulphinate (10 mmol) in ethanol–water (1:1, v/v; 12 cm^3) at 20 °C was treated with *p*-dinitrobenzene (1 mmol) and toluene-*p*-sulphonyl bromide (10 mmol). After 24 h, filtration gave a residue (0.72 g), m.p. 150 °C (decomp.) raised to 216 °C (from toluene) (0.46 g, 13%) alone or mixed with an authentic specimen.

Reactions of Other Nucleophiles with Bromonitromethane.—(*a*) *Triphenylphosphine.* Triphenylphosphine (19 mmol) in dry benzene (20 cm^3) was added dropwise over 15 min to bromonitromethane (21 mmol) in benzene (10 cm^3) at 18 °C. After 12 h, filtration gave triphenylphosphine oxide hydrobromide (3.4 g, 100%), m.p. 140—145 °C raised to 145—147 °C (from acetonitrile) (lit.,[40] m.p. 145—148 °C). Evaporation of the filtrate gave an oily residue which, on addition of ether (100 cm^3) gave triphenylphosphine oxide (2.29 g, 82%) (m.p. and mixed m.p. identical with authentic specimen). Removal of the solvent and distillation of the residue gave recovered

* Literature values range from 206 to 230, and our analytically pure specimens varied in m.p. between 205 and 216 °C.

bromonitromethane, b.p. 52 °C/13 mmHg (49%). In a separate experiment, the reaction mixture was washed with aqueous 1M-sodium hydroxide and determination of cyanide in the solution with a cyanide sensitive electrode type after suitable dilution showed the yield of HCN to be 100%.

(*b*) *With triethyl phosphite.* Bromonitromethane (14 mmol) in ether (25 cm^3) was added to triethyl phosphite (26 mmol) in ether (25 cm^3). After 36 h at 18 °C, evaporation gave a residue (5.9 g) which on distillation gave triethyl phosphate (2.00 g, 94%) (i.r. identical with that of an authentic specimen), b.p. 92 °C/12 mmHg, containing hydrobromic acid (80%). Hydrocyanic acid (66%) was trapped as before and estimated with a cyanide sensitive electrode).

(*c*) *With potassium iodide.* Potassium iodide (29 mmol) in methanol (55 cm^3) was added dropwise at 20 °C to bromonitromethane (28 mmol) in methanol (25 cm^3). After 36 h, titration against thiosulphate showed the formation of iodine (65%). Potassium bromide (1.6 g) was filtered off. This material showed a positive nitrite reaction (azo-dye formation) but titration with $Ce(SO_4)_2$ showed it to be present in negligible quantity. The filtrate was added to aniline (12 mmol) and sodium hydrogen carbonate (25 mmol) in methanol (50 cm^3). After 12 h at 18 °C, addition of water and extraction gave a residue (2.2 g) which on flash chromatography gave 4-iodoaniline (0.52 g, 30%), m.p. and mixed m.p. 61 °C (i.r. spectrum identical with that of an authentic specimen), obtained (53% yield) from iodine under the same conditions.

(*d*) *With thiourea.* Thiourea (10 mmol) in water (25 cm^3) and concentrated nitric acid (1.5 cm^3) was treated with bromonitromethane (5 mmol) dropwise at 0 °C. After 12 h, filtration and washing of the residue with water and ethanol gave formamidine disulphide dinitrate (0.67 g, 48%), m.p. and mixed m.p. 115 °C (lit.,[41] m.p. 110 °C) and i.r. spectrum identical with an authentic specimen prepared by permanganate oxidation of thiourea.

(*e*) *With dimethyl sulphide.* Bromonitromethane (14 mmol), acetonitrile (4 cm^3), and dimethyl sulphide (2 cm^3) were kept in a sealed tube at 50 °C for 4 days. Addition of ether (100 cm^3) gave a precipitate of trimethylsulphonium bromide (1.36 g, 62%), m.p. and mixed m.p. 177 °C (from methanol–di-isopropyl ether) and distillation of the filtrates gave first recovered bromonitromethane (30%), b.p. 58/12 mmHg, and then methyl nitromethyl sulphide. This fraction was contaminated with bromonitromethane and was treated with an ethanolic solution of sodium methanethiolate. Addition of the mixture to acetate buffer gave the pure *nitro-sulphide* (0.96 g, 68%), b.p. 62 °C/12 mmHg, n^{26}_D 1.4874; δ 2.4 (s) and 5.25 (s) in the ratio 3:2; δ_C 16.63 and 136.0 (Found: C, 22.6; H, 4.3; N, 13.0. $C_2H_5NO_2S$ requires C, 22.4; H, 4.6; N, 13.0%).

Similar treatment of 2-methylthiopropanenitrile with bromonitromethane at 120 °C for 5 days gave no reaction.

(*f*) *With sodium borohydride.* Bromonitromethane (2 g) was added to sodium borohydride (0.52 g) in ethanol (20 cm^3). Vigorous effervescence occurred immediately and after 1 h, addition of ether (50 cm^3) precipitated the sodium salt of bromonitromethane (1.7 g, 74%), i.r. spectrum identical with that of an authentic sample.

Non-Reactions with Bromonitromethane.—(*a*) *With benzaldehyde.* Treatment of benzaldehyde (28 mmol) with bromonitromethane (28 mmol) in ethanol (25 cm^3) and a catalytic amount of methylammonium chloride and sodium carbonate at reflux for 4 days showed no reaction (t.l.c.). Similar reactions with butylamine, dimethylamine, and trimethylamine gave no reaction.

(*b*) *With propenenitrile.* Addition of one drop of triethylamine to a solution of bromonitromethane (9.2 mmol) and pentenenitrile (9.2 mmol) in $CDCl_3$ (3 cm^3) gave no ^1H n.m.r. spectral change over 7 days. Use of sodium ethoxide and solvent DMSO likewise gave no evidence of addition.

Attempted Trapping of Nitrocarbene.—Butyl-lithium (1.6 M) in hexane (9 cm^3, 13 mmol) was added to bromonitromethane (14 mmol) in dry THF (75 cm^3) containing cyclohexene (10 cm^3) at −70 °C. After 30 min at −70 °C, the solution was warmed to 20 °C. After 2 h, addition of the mixture to acetate buffer and extraction gave recovered bromonitromethane (35%) but no evidence of any product derived from cyclohexene.

Non-Reactions.—(*a*) *Sodium nitromethane with benzonitrile.* Nitromethane (29 mmol) was added to an ethanolic solution of sodium ethoxide [prepared from ethanol (50 cm^3) and sodium (0.6 g, 26 mmol)] at 0 °C. After 10 min, benzonitrile (29 mmol) was added and the mixture was kept for 2 h at 0 °C and then for 15 h at 20 °C; addition to water and extraction with ether (3 × 50 cm^3) gave recovered benzonitrile (73%).

(*b*) *Sodium nitromethane with disulphides.* Diphenyl disulphide (1.6 g) was added to an ethanolic solution of sodium nitromethanide [from nitromethane (0.47 g) and sodium (0.18 g) in ethanol (50 cm^3)] at 0 °C. After 2 h at 0 °C and 15 h at 20 °C, dilution with water and extraction gave recovered disulphide (94%) (m.p. and mixed m.p.).

Bis-*o*-nitrodiphenyl disulphide was recovered (100%) by similar treatment.

(*c*) *Benzenethiolate with phenylthionitromethane.* Phenylthionitromethane (6.9 mmol) in ethanol (15 cm^3) was added to a solution prepared from sodium (0.16 g, 6.9 mmol) and thiophenol (6.90 mmol) in ethanol (15 cm^3), at 15 °C. After 4 h, filtration gave sodium phenylthionitromethanide (0.84 g) and removal of solvent gave a residue which on treatment with ether precipitated a further crop (0.31 g) of sodium phenylthionitromethanide. The salt was identified by addition to acetate buffer and extraction (CH_2Cl_2), giving the nitro sulphide in 97% yield.

(*d*) *Benzenesulphinate ion with diphenyl disulphide.* Diphenyl disulphide (6.8 mmol) and sodium benzenesulphinate (6.8 mmol) in ethanol (30 cm^3) were kept for 4 days at 20 °C. Addition to water (100 cm^3) and extraction gave recovered diphenyl disulphide (98%), m.p. 58 °C raised to 60 °C (from methanol), alone or mixed with an authentic specimen.

Reaction of Bromonitromethane with Tributylborane.—2,6-Di-t-butylphenol (30 mmol) in dry THF (50 cm^3) was refluxed with potassium (25 mg-atom) for 1 h. Tributylborane (28 cm^3 of a 1M-solution in THF) was added to the solution at 0 °C, followed by dropwise addition, after 30 min, of a solution of bromonitromethane (28 mmol) in dry THF (25 cm^3). Reaction was followed by g.l.c. on SE30 with N_2 carrier gas and octan-1-ol as external standard. After 2 h, 64% of reaction had occurred and there was no further change after 14 h. Ethanol (50 cm^3) was added and, after evaporation, the residue was added to dichloromethane (100 cm^3). Filtration and evaporation gave a residue which on distillation gave 1-nitropentane (1.7 g, 57%), b.p. 54 °C/12 mmHg, n^{20}_D 1.4180 (lit.,[42] b.p. 57 °C/12 mmHg, n^{25}_D 1.4161), i.r. and ^1H n.m.r. spectra identical with those of an authentic specimen.

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References

1 D. E. Carrington, K. Clarke, and R. M. Scrowston, *J. Chem. Soc. C*, 1971, 390.
2 L. Rene, S. Risse, P. Demerseman, R. Royer, and R. Cavier, *Eur. J. Med. Chem.—Chim. Ther.*, 1979, **14**, 223.
3 J. Einhorn, P. Demerseman, L. Rene, R. Royer, and P. Cavier, *Eur. J. Med. Chem.—Chim. Ther.*, 1983, **18**, 79.
4 J.-P. Buisson, G. Lamotte, and P. Demerseman, *Eur. J. Med. Chem.—Chim. Ther.*, 1983, **18**, 169.
5 R. Royer, and J.-P. Buisson, *Eur. J. Med. Chem.—Chim. Ther.*, 1980, **15**, 275.
6 R. Royer, J.-P. Buisson, and L. Rene, *Bull. Soc. Chim. Fr.*, 1972, 4158.
7 W. Ried and L. Kaiser, *Synthesis*, 1976, 120.
8 W. Ried and L. Kaiser, *Justus Liebigs Ann. Chem.*, 1976, 395.
9 R. Laliberte, H. Warwick, and G. Medawar, *Can. J. Chem.*, 1968, **46**, 3643.
10 J. E. Beck and J. A. Yahner, *J. Org. Chem.*, 1974, **39**, 3440.
11 F. Benedetti, D. R. Marshall, C. J. M. Stirling, and J. L. Leng, *J. Chem. Soc. Chem. Commun.*, 1982, 918.
12 R. P. Redman, P. J. Thomas, and C. J. M. Stirling, *J. Chem. Soc., Perkin Trans. 2*, 1978, 1135.
13 N. Kornblum, *Angew. Chem., Int. Edn. Engl.*, 1975, **14**, 734.
14 W. R. Bowman, and G. D. Richardson, *J. Chem. Soc., Perkin Trans. 1*, 1980, 1407.
15 For references see ref. 14.
16 W. R. Bowman, D. Rakshit, and M. D. Valmas, *J. Chem. Soc., Perkin Trans. 1*, 1984, 2325.
17 W. R. Bowman, personal communication.
18 N. S. Zefirov, and D. I. Makhonkov, *Chem. Rev.*, 1982, **82**, 615.
19 G. A. Jones, C. J. M. Stirling, and N. G. Bromby, *J. Chem. Soc., Perkin Trans 2*, 1983, 385.
20 C. J. M. Stirling, *J. Chem. Soc.*, 1957, 3597.
21 C. D. Beadle, W. R. Bowman, and J. Prousek, *Tetrahedron Lett.*, 1984, **25**, 4979.
22 C. T. Goralski and T. C. Klingler, U.S.P. 4 053 633 (*Chem. Abstr.*, 1978, **88**, P 6552v).
23 A. E. Arbuzov, B. A. Arbuzov, and B. P. Lugovkin, *Bull. Acad. Sci. U.R.S.S. Classe Sci. Chim.*, 1947, 535 (*Chem. Abstr.*, 1948, **42**, 1886).
24 'Comprehensive Organic Chemistry,' eds. D. H. R. Barton and W. D. Ollis, Pergamon, Oxford, 1979, section 10.3.2.3.
25 S. Trippett, B. J. Walker, and H. Hofmann, *J. Chem. Soc.*, 1965, 7140.
26 F. G. Bordwell and J. E. Bartmess, *J. Org. Chem.*, 1978, **43**, 3101.
27 H. C. Brown, N. Nanbui, and M. M. Rogic, *J. Am. Chem. Soc.*, 1969, **91**, 6854.
28 A. Pelter and K. Smith, in 'Comprehensive Organic Chemistry,' eds. D. H. R. Barton and W. D. Ollis, Pergamon, Oxford, 1979, vol. 3, Section 14.3.4.3.
29 A. Pelter and K. Smith, in 'Comprehensive Organic Chemistry,' eds. D. H. R. Barton and W. D. Ollis, Pergamon, Oxford, 1979, vol. 2, Section 7.2.1.
30 Y. Takahashi, M. Tokuda, M. Itoh, and A. Suzuki, *Synthesis*, 1976, 616.
31 J. J. Zeilstra and J. B. F. N. Engberts, *J. Org. Chem.*, 1974, **39**, 3215.
32 N. Kharasch and J. L. Cameron, *J. Am. Chem. Soc.*, 1951, **73**, 3864.
33 H. Slagh, U.S.P. 2 632 776 (*Chem. Abstr.*, 1954, **48**, 1412).
34 C. D. Hurd and M. E. Nilson, *J. Org. Chem.*, 1955, **20**, 927.
35 L. Bauer and T. L. Walsh, *J. Org. Chem.*, 1961, **26**, 1443.
36 D. E. Carrington, K. Clark, and R. M. Scrowston, *J. Chem. Soc. C*, 1971, 3903.
37 G. Van Zyl, C. J. Bredeweg, R. H. Rynbrandt, and D. C. Neckers, *Can. J. Chem.*, 1966, **44**, 2283.
38 J. J. Zeilstra and J. B. F. N. Engberts, *Recl. Trav. Chim. Pays-Bas.*, 1974, 11.
39 A. C. Poshkus, J. E. Herweh, and F. A. Magnotta, *J. Org. Chem.*, 1963, **28**, 2766.
40 S. Trippett and D. Walker, *J. Chem. Soc.*, 1960, 2976.
41 E. A. Werner, *J. Chem. Soc.*, 1912, **101**, 2166.
42 N. Kornblum, B. Taub, and H. E. Ungarde, *J. Am. Chem. Soc.*, 1954, **76**, 3209.

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