Stereochemistry of Bimolecular Displacement in Azavinyl Systems: Crystal and Molecular Structure of *N*-(2,4-Dinitrophenyl)-*N*-methylpivalohydrazonyl Bromide

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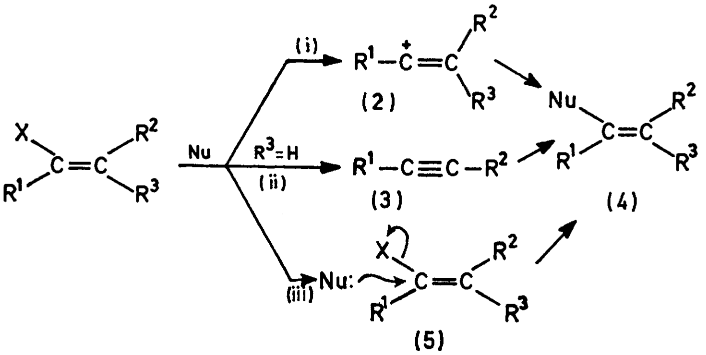
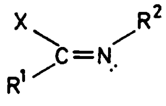
Crystal structure determination and n.m.r. measurements show that hydrazonyl halides have the *Z* configuration [(6); X = Br, R^1 = Bu^t, R^2 = $N(Me)C_6H_3(NO_2)_2$; X = Cl, R^1 = Ph, and R^2 = N(Me)Ph, $N(Me)C_6H_4NO_2$, and $N(Me)C_6H_3(NO_2)_2$]. Reaction of the halides with methoxide ion in methanol or in methanol–dioxan is bimolecular and under these conditions the sole products formed are the *Z*-isomers (6; X = MeO), although in general the *E* isomers (7; X = MeO) are thermodynamically more stable. This observed retention of configuration at sp^2 carbon is discussed. Crystals of the title compound are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions a = 7.35(5), b = 8.06(6), c = 25.60(10) Å, β = 95.0(1)°. The structure was determined by the heavy-atom method from visually estimated data and refined by full-matrix least-squares techniques to R 0.104 for 526 unique reflections.

Nucleophilic substitution at sp^2 hybridized carbon in vinyl halides has been the subject of much interest in recent years.[1-4] The possibility of *cis–trans* isomerism of substituted ethylenes offers substrates of known configuration, thereby raising the interesting question as to whether configuration is retained or inverted during substitution. Three general mechanisms (see Scheme 1) have been identified for the displacement of halide ion (X^-) from vinyl halides (1) by a nucleophile (Nu): (i) a vinyl cation pathway which is now well established; it is characterised by pH independence, high solvent-sensitivity, and rearranged products;[5] (ii) an elimination addition mechanism which requires a β hydrogen in the substrate; and (iii) addition–elimination which involves reaction of the nucleophile at the vinylic bond; the timing of bond formation (Nu–C) and bond breaking (C–X) can clearly vary through a wide spectrum in this mechanism and (5) can be either a transition state (when bond formation and bond breaking are synchronous) or an intermediate.[6,7] A variety of stereochemical behaviour is shown by vinyl systems, even within a group of compounds which share a common mechanism.[1-4] We have begun a detailed examination of the corresponding aza-systems where one of the carbons is replaced by a substituted nitrogen;[8] we are particularly interested in the effect of the lone pair of electrons now present on the atom adjacent to the carbon in determining the stereochemistry of the substitution process.

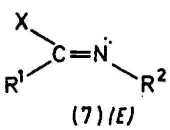


Scheme 1

Unlike vinyl systems, the ionization pathway [analogous to (i)] dominates the chemistry of imidoyl halides, owing to the stabilization of the carbonium ion formed by the adjacent lone pair (the ion is therefore more properly termed a 'nitrilium ion'). We have previously shown[9] that the product is formed stereospecifically by this pathway, only the material in which the nucleophile and lone pair on nitrogen are *trans* being isolated (although this may not be the thermodynamically more stable isomer). In this paper we have examined the bimolecular pathway for (6), a process which usually



(6)(*Z*)



(7)(*E*)

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[1] Z. Rappoport and A. Topol, *J.C.S. Perkin II*, 1975, 863, and other papers in this series.

[2] G. Modena, *Accounts Chem. Res.*, 1971, **4**, 73.

[3] S. I. Miller and P. K. Yonan, *J. Amer. Chem. Soc.*, 1957, **79**, 5931.

[4] G. Marchese, F. Meso, and G. Modena, *J. Chem. Soc.* (*B*), 1969, 290.

[5] Z. Rappoport, *Adv. Phys. Org. Chem.*, 1969, **7**, 1.

[6] S. Patai and Z. Rappoport, in 'The Chemistry of Alkenes,' ed. S. Patai, Interscience, New York, 1964, ch. 8.

[7] Z. Rappoport and Y. Apeloig, *J. Amer. Chem. Soc.*, 1975, **97**, 821.

[8] For a preliminary account, see M. T. McCormack and A. F. Hegarty, *Tetrahedron Letters*, 1976, 395.

[9] M. T. McCormack and A. F. Hegarty, *J.C.S. Perkin II*, 1976, 1701.

leads to predominant retention of configuration (although there are exceptions [10]) in vinyl systems.[1-4]

RESULTS AND DISCUSSION

Because of the ease with which inversion of configuration occurs at nitrogen, it was important to use substrates (and substitution products) in which this isomerisation route is slowed. We have used substrates (6) in which R^2 is NR_2, a feature which is known to slow inversion to such a degree that the materials are configurationally stable at room temperature.[11] Two methods were used to assign configuration:

(*a*) *Crystal Structure of* N-(2,4-*Dinitrophenyl*)-N-*methylpivalohydrazonoyl Bromide.*—The molecular structure and atom numbering system of this compound are shown in Figure 1. The following features are of particular interest. The bromo-group is *trans* to the lone pair on the adjacent nitrogen, *i.e.* the configuration is as in (6) (X = Br) rather than (7). The *o*-NO_2 group is adjacent to the lone pair on N(1) and is twisted out of coplanarity with the aryl ring by 47°; the *p*-NO_2 group is not coplanar with the ring either, but the angle of twist (20°) is smaller. The five atoms [C(1), C(2), Br, N(1), N(2)] about the carbon–nitrogen bond are essentially coplanar. The aryl ring intersects this plane at 54° which can be largely attributed to steric interaction between N(1) and the *o*-NO_2 group. However because of the extended configuration, nucleophilic attack at C(1) perpendicular to the plane of the carbon nitrogen double bond is not expected to be especially hindered by the bulky dinitrophenyl group.

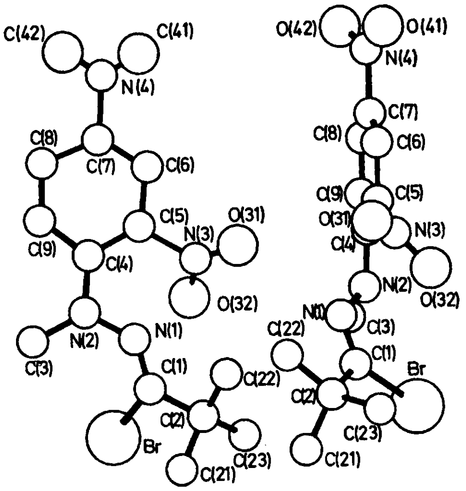

FIGURE 1 Structure and atom numbering scheme for (6) [R^1 = Bu^t, X = Br, R^2 = N(Me)—$C_6H_3(NO_2)_2$]; the two projections are at 95° to one another

(*b*) *Hydrazonyl Chlorides.*—We have previously reported [9] that the relative chemical shifts of the *N*-Me and *O*-Me protons of the *E* and *Z* isomers [(6) and (7); X = OMe, R^2 = N(Me)Ar] are significantly different, owing to the shielding effects of the *C*-aryl ring (R^1 = aryl). The *N*-Me protons in configurationally similar alkyl hydrazonates [(6), (7); X = MeO, R^2 = N(Me)Ar] and hydrazonyl chlorides [(6), (7); X = Cl, R^2 = N(Me)Ar] should experience the same chemical environment. On this basis all the hydrazonyl chlorides studied [R^1 = Ph, R^2 = N(Me)Ar] have the *Z* configuration. As an example, for (6) with R^1 = Ph, R^2 = $N(Me)C_6H_3(NO_2)_2$, the chemical shift (δ) for the NMe group is 3.19 (in chlorobenzene as solvent, 3.49 in $CDCl_3$) when X = Cl, while when X = OMe, the corresponding δ values for the *Z* and *E* isomers are 3.15 (3.41 in $CDCl_3$) and 2.55 (2.90 in $CDCl_3$) respectively. Because of the absence of a *C*-aryl group in the hydrazonyl bromide whose structure was determined by *X*-ray crystallography [(6); X = Br, R^1 = Bu^t, R^2 = $N(Me)C_6H_3(NO_2)_2$], this method could not be applied directly. In fact the *N*-Me signal for the *E* and *Z* isomers of the hydrazonates (6) and (7) [X = OMe, R^1 = Bu^t, R^2 = $N(Me)C_6H_3(NO_2)_2$] are identical (δ 2.80) in chloroform. In chlorobenzene as solvent, however, the *N*-Me signals are different for the hydrazonates (3.22 and 3.05 p.p.m.). In this solvent the *Z* bromide [6; X = Br, R^1 = Me_3C, R^2 = $N(Me)C_6H_3(NO_2)_2$] has the *N*-Me signal at δ 3.25 p.p.m., so the methyl hydrazonate with the similar *N*-Me resonance (3.22 p.p.m.) was assigned the *Z* configuration. Similar structural assignments based on chemical shifts in aromatic and non-aromatic solvents have previously been reported.[12,13]

An attempt was also made to confirm the structures of the chlorides by use of the lanthanoid-shift reagent, $Eu(fod)_3$,[14] since complex formation with the lone pair on nitrogen in (6) and (7) should alter the chemical shifts of groups in R^1 (and possibly R^2). However, in all cases the observed alterations were small. Thus when added (in a ratio of 0.8 : 1.0) to (*E*)-methyl *N*-(2,4-dinitrophenyl)-*N*-methylbenzohydrazonate [(7); X = OMe, R^1 = Ph, R^2 = $N(Me)C_6H_3(NO_2)_2$] there was a downfield displacement of the *O*-Me (0.12 p.p.m.) and *N*-Me (0.09 p.p.m.) signals. In the *Z* isomer (6) complex formation should occur *trans* to the X group; consistent with this was the observation that the addition of equimolar quantities of $Eu(fod)_3$ left the position of the *O*-Me resonance unchanged. The small shifts which we have observed may be due to poor complex formation with the imino-nitrogen due both to its low basicity [15] and to steric hindrance towards approach to this site (see crystal structure in Figure 1).

Dipole moment data has also been used to determine the structure of configurationally stable imine systems,

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[10] R. H. Summerville and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1972, **94**, 3629; T. C. Clarke, D. R. Kelsey, and R. G. Bergman, *ibid.*, p. 3626.

[11] A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem. Internat. Edn.*, 1970, **9**, 400; H. O. Kalinowski, H. Kessler, D. Leibfritz, and A. Pfeffer, *Chem. Ber.*, 1973, **106**, 1023.

[12] J. Bjorgo, D. R. Boyd, C. G. Watson, and W. B. Jennings, *J.C.S. Perkin II*, 1974, 757.

[13] C. G. McCarty, in 'The Chemistry of the Carbon–Nitrogen Double Bond,' ed. S. Patai, Wiley–Interscience, New York, 1970.

[14] R. V. Ammon and R. D. Fischer, *Angew. Chem. Internat. Edn.*, 1972, **11**, 695.

[15] A. de Savignac, A Lattes, and M. Bon, *Org. Magn. Resonance*, 1974, **6**, 528.

such as oxime ethers.[16-18] However, owing to free rotations about the N–N and N–C (aryl) bonds, several conformations are possible for both the *E* and *Z* isomers. Moreover, the unsymmetrical 2,4-dinitrophenyl group presented a further complication since the dipole moment of this group would depend on the orientation of the aryl ring relative to the C=N plane. Theoretical calculations even with the more symmetrical (*E*)- and (*Z*)-*N*-(*p*-nitrophenyl)-*N*-methylbenzohydrazonyl chlorides [(6) and (7); X = Cl, R^1 = Ph, $R^2 = 4\text{-}NO_2C_6H_4$], gave the same dipole moment (6.7 D) for both isomers when the 'extended' configuration analogous to that shown by the bromide (Figure 1) is assumed; when the *N*-Me and *N*-$C_6H_4NO_2$ group positions are reversed, then the calculated dipole moments are 2.2 and 4.9 D for the *Z* and *E* isomers. A previous determination[19] of the configuration of *NN*-diphenylbenzohydrazonyl chloride by dipole-moment measurements has favoured the *Z* form (X = Cl, R^1 = Ph; $R^2 = NPh_2$), as in the present work.

Attempts were made to effect equilibration between the *Z* and *E* forms of the various hydrazonyl bromides and chlorides investigated either by heating, treatment with acid, or on irradiation (conditions known to favour equilibration among simple imine isomers).[20] However, no evidence (n.m.r. and t.l.c.) was observed for the presence of *E* isomers.

Kinetic Studies.—Because of the facility with which imidoyl halide substrates undergo S_N1-type reaction,[21] S_N2-type displacements could only be observed with good nucleophiles and in solvents of low dielectric constant. Moreover, since even small concentrations of base induce an E_1cB type elimination in mono-substituted hydrazonoyl halides[22] [*e.g.* (6) or (7) with R^2 = NHAr], the study was limited to substrates where this mode of reaction was inhibited by *NN*-disubstitution.

With methoxide ion as nucleophile in methanol, the rate of displacement of chloride from (6) [X = Cl, R^1 = Ph, $R^2 = N(Me)C_6H_3(NO_2)_2$] was proportional to methoxide ion concentration at 25 °C (see Figure 2 for a typical example). Similar bimolecular behaviour was shown under these conditons by (6) [X = Cl, R^1 = Ph, $R^2 = N(Me)C_6H_4NO_2$]. With the hydrazonyl bromide, because of the better leaving-group involved, unimolecular solvolysis occurred even in methanol in the presence of 0.5M-methoxide ion. However, bimolecular reaction was observed for (6) [X = Br, $R^1 = Bu^t$, $R^2 = N(Me)C_6H_3(NO_2)_2$] over the concentration range $[MeO^-]$ = 0.20—0.5M in methanol–dioxan (*a*) 1 : 4 at 25 °C, and (*b*) 1 : 9 at 45 °C (the higher temperature being used because of the low solubility of the substrate in solvent mixtures with low methanol content).

Product Analysis.—Having established conditions under which bimolecular reaction with methoxide ion occurred, the configurations of the products formed were then examined. In each case the (*Z*)-hydrazonyl halide gave the corresponding (*Z*)-methyl hydrazonate exclusively. The absence of the *E* isomer was indicated by n.m.r. analysis and confirmed by t.l.c.; control experiments indicated that >5% of the *E* isomer would have been detected by these techniques. Methoxide catalysed *Z*/*E* isomerisation of the inital hydrazonyl halide (noted in some cases for hydroximoyl halides[23]) was also absent, as shown by the presence of only two materials [the (*Z*)-halide and methyl hydrazonate] at all times during the course of the reaction. The possibility that the (*Z*)-methyl hydrazonates are merely the most stable products (which might indicate that the observed products represent thermodynamic rather than kinetic control) was ruled out by the observation that on heating in methanol (in the presence or absence of methoxide ion) *Z*/*E* equilibration of the hydrazonates took place; the time-independent equilibrium ratios (*Z*/*E* hydrazonate) varied from 80 : 20 to 22 : 78 for the products under study. Clearly these ratios are distinctly different from those observed (exclusive *Z* isomer formation) under kinetic control.

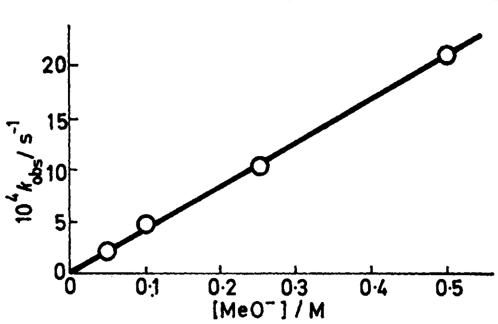

FIGURE 2 Plot of the observed rate of reaction of (6) [X = Cl, R^1 = Ph, $R^2 = -N(Me)C_6H_3(NO_2)_2$] in methanol at 25 °C *vs.* methoxide-ion concentration

Mechanism.—The dependence on methoxide-ion concentration eliminates the unimolecular mechanism previously described. A synchronous displacement of X^- by MeO^- is also unlikely for two reasons. (*a*) The element effect (k_{Br}/k_{Cl}) of the leaving group is small [we have measured a value of 0.2 for reaction of (6) with X = Br, $R^1 = Bu^t$, $R^2 = N(Me)C_6H_3(NO_2)_2$ and with X = Cl, R^1 = Ph, $R^2 = N(Me)C_6H_3(NO_2)_2$ in 1 : 4 methanol–dioxan at 25 °C]; in the extreme cases when unimolecular ionization precedes bond formation and of addition–elimination when bond formation precedes bond fission, element effect values k_{Br}/k_{Cl} in the region of 50 and 1 respectively have been reported.[24,25] Although the compounds compared in the present instance did not

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[16] J. E. Johnson, E. A. Nalley, Y. K. Kunz, and J. R. Springfield, *J. Org. Chem.*, 1976, **41**, 252.

[17] A. Battaglia, A. Dondoni, and O. Exner, *J.C.S. Perkin II*, 1972, 1911.

[18] O. Exner, V. Jehlicka, A. Dondoni, and A. C. Boiceili, *J.C.S. Perkin II*, 1974, 567.

[19] B. I. Buzykin, S. A. Flegonotov, and Yu. P. Kitaev, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1974, 2030; *Chem. Abs.*, 1975, **82**, 30870.

[20] A. Padwa and F. Albrecht, *J. Org. Chem.*, 1974, **39**, 2361.

[21] A. F. Hegarty, J. D. Cronin, and F. L. Scott, *J.C.S. Perkin II*, 1975, 429.

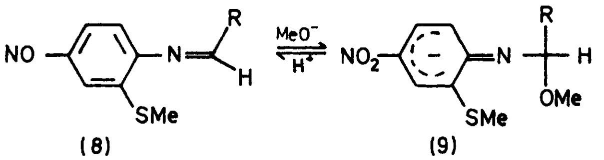
[22] A. F. Hegarty, M. P. Cashman, and F. L. Scott, *J.C.S. Perkin II*, 1972, 44.

[23] J. E. Johnson, E. A. Nalley, and C. Weidig, *J. Amer. Chem. Soc.*, 1973, **95**, 2051.

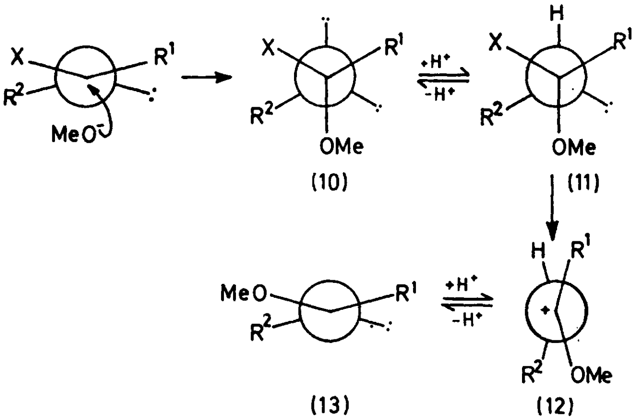
[24] Z. Rappoport and A. Gal, *J. Org. Chem.*, 1972, **37**, 1174.

[25] R. Ta-Shma and Z. Rappoport, *J.C.S. Perkin II*, in the press

carry exactly the same substituents any synchronous C–Br bond fission would be facilitated by the more bulky t-butyl group, leading to a larger k_{Br}/k_{Cl} effect than observed. (*b*) Recent work by Bartoli and co-workers [26] has described the isolation of relatively stable adducts of methoxide ion and imines such as (8) in dimethyl sulphoxide. The adducts (9) on reaction with a proton donor regenerate the inital imine and do not appear to undergo C–N bond-fission (as also noted for MeOH adducts to benzylideneaniline in MeCN [27]). Such adducts are analogous to the possible intermediates formed from hydrazonoyl halides.



An addition–elimination mechanism which accounts for the observed retention of configuration is presented in Scheme 2. Addition of the nucleophile perpendicular to the plane of the C=N bond gives the intermediate (10) which undergoes rapid proton-exchange from the solvent. Without further C–N bond rotation the intermediate is now in the correct conformation to allow antiperiplanar elimination of X^- to give (12) and thus the observed product (13). The leaving ability of Cl^- and Br^- are such that unimolecular expulsion to give the stabilized iminium ion should be rapid (indeed examples * are known); the elimination is thus not the exact reversal of the addition step. If protonation occurs on the other site on nitrogen (and this might be facilitated by prior hydrogen-bonding of the solvent to the lone pair on the starting imine) then proton-removal would be required for *anti*-elimination of X^- (without further nitrogen inversion or C–N bond rotation). The conformation (11) (independent of the position of protonation of nitrogen) also minimises interactions between the bulky R^1 and R^2 groups (which are thought to be among the most important factors in determining the stereochemistry of substitution at vinylic carbon); [5] the formation of the inverted product would involve proximate R^1 and R^2 groups in the transition state.



Scheme 2

The only previous data available in the stereochemistry of bimolecular reactions in azavinyl systems involves reaction of MeO^- on (*E*)- and (*Z*)-hydroxamoyl chlorides [(6) and (7); X = Cl, R^2 = *O*-alkyl],[23] which apparently led to inversion (or predominant inversion) of configuration. However, the configurational assignments of the starting chlorides [16] [(6) and (7); X = Cl, R^2 = *O*-alkyl] has recently been reversed.[29] On this basis data for the hydroxamoyl chlorides [23] and hydrazonyl chlorides and bromides (present work; see also ref. 8) are in agreement: the *Z* isomers give complete retention of configuration. The formation of both *E* and *Z* isomers [23,29] (with the *E* isomer predominating) on reaction of the (*E*)-chloride (7; X = Cl, R^2 = *O*-alkyl) with methoxide ion is now also explicable since the tetrahedral intermediate [analogous to (11)] which is formed in this case must undergo C–N bond rotation (or nitrogen inversion) to permit antiperiplanar elimination of chloride ion.

EXPERIMENTAL

Ultraviolet spectra and reaction rates were measured by use of Perkin-Elmer 124A or Unicam SP 800B spectrophotometers. A Perkin-Elmer R20A was used for n.m.r. spectra with tetramethylsilane as internal standard and deuteriochloroform as solvent, unless otherwise stated. Methanol and dioxan were AnalaR grade and used without further purification. *N*-(2,4-Dinitrophenyl)-*N*-methylbenzohydrazonyl chloride. *N*-(4-nitrophenyl)-*N*-methylbenzohydrazonyl chloride, and the corresponding (*Z*)- and (*E*)-methyl *N*-(2,4-dinitrophenyl- and 4-nitrophenyl)-*N*-methylbenzohydrazonates were available from a previous study.[9]

(Z)-Methyl N-*(2,4-Dinitrophenyl)*-N-*methylpivalohydrazonate* [6; X = MeO; R^1 = Bu^t; R^2 = $N(Me)C_6H_3(NO_2)_2$]. *N*-(2,4-Dinitrophenyl)-*N*-methylpivalohydrazonoyl bromide (1.0 g) was dissolved in methanol (300 ml) containing 1.0M-sodium methoxide and stirred at room temperature for 45 min. On addition of water the *methyl hydrazonate* precipitated (in quantitative yield), m.p. 110 °C, R_F = 0.50 [silica gel; 2 : 3 chloroform–light petroleum (b.p. 60—80 °C) as eluant] (Found: C, 50.5; H, 5.9; N, 18.4. $C_{13}H_{18}N_4O_5$ requires C, 50.3; H, 5.8; N, 18.1%). The corresponding (*E*)-pivalohydrazonate was prepared by thermal rearrangement of the *Z* isomer to an equilibrium mixture containing 20% of the *E* isomer in chlorobenzene at 130 °C. The isomers were separated by dry column chromatography on silica gel (activity III/30 mm; eluant as before). The *(E)-hydrazonate* had m.p. 93 °C and R_F = 0.65 (under conditions already detailed) (Found: C, 50.4; H, 5.6; N, 18.2. $C_{13}H_{18}N_4O_5$ requires C, 50.3; H, 5.8; N, 18.1%).

Crystal Structure of N-*(2,4-Dinitrophenyl)*-N-*methylpivalohydrazonyl Bromide*.—Crystals of the hydrazonyl bromide were prepared by diffusing low b.p. light petroleum (<40 °C) into a solution of the hydrazonoyl bromide (20 mg) dissolved in 1 : 1 acetone–hexane (10 ml) in an enclosed space.

Crystal Data.—$C_{12}H_{15}BrN_4O_4$, *M* = 359.18. Monoclinic,

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* *E.g.* α-halides (R_2NCH_2X) exist in the solid state as crystalline salts $R_2N^+ : CH_2X^-$.[28]

[26] G. Bartoli, F. Ciminale, and P. E. Todesco, *J.C.S. Perkin II*, 1975, 1472.

[27] Y. Ogata and A. Kawasaki, *J. Org. Chem.*, 1974, **39**, 1058.

[28] H. Bohme, L. Koch, and E. Kohler, *Chem. Ber.*, 1962, **95**, 1849.

[29] J. E. Johnson, personal communication.

$a = 7.35(5)$, $b = 8.06(6)$, $c = 25.60(10)$ Å, $\beta = 95.0(1)°$, $U = 1\,516.57$ Å^3 $F(000) = 728$. Cu-K_α radiation, $\lambda = 1.5418$ Å; μ(Cu-K_α) = 36.59 cm^{-1}. D_m not determined (because of the high solubility of the hydrazonoyl bromide in most organic solvents) and, in the absence of further information Z was taken to be 4. Space group $P2_1/c$ (C_{2h}, No. 14) from systematic absences: $h0l$ for l odd, and $0k0$, for k odd.

TABLE 1

Atomic co-ordinates for non-hydrogen atoms, with estimated standard deviations in parentheses, isotropic and anisotropic thermal parameters (Å^3 × 10^4), and calculated atomic co-ordinates for hydrogen atoms of (*Z*)-*N*-(2,4-dinitrophenyl)-*N*-methylpivalohydrazonyl bromide.

	x/a	y/b	z/c	U/Å^2
Br	0.619 6(8)	0.641 1(9)	0.303 5(2)	*
O(31)	0.714 7(40)	0.008 0(39)	0.479 5(12)	*
O(32)	0.540 0(37)	0.867 8(37)	0.426 5(10)	*
O(41)	0.638 4(43)	0.731 1(40)	0.652 0(11)	*
O(42)	0.769 4(33)	0.508 7(38)	0.659 9(11)	*
C(1)	0.802 7(43)	0.746 0(44)	0.351 2(12)	30(10)
C(2)	0.886 3(48)	0.902 8(47)	0.327 8(13)	45(11)
C(3)	0.809 8(47)	0.408 2(46)	0.394 7(13)	45(11)
C(4)	0.735 1(48)	0.577 6(48)	0.470 3(14)	39(11)
C(5)	0.696 1(54)	0.722 9(53)	0.496 3(17)	53(13)
C(6)	0.681 3(46)	0.748 4(51)	0.550 7(15)	47(12)
C(7)	0.701 6(49)	0.605 6(52)	0.576 0(14)	51(12)
C(8)	0.734 6(48)	0.440 6(50)	0.555 1(14)	48(12)
C(21)	0.990 9(61)	0.843 9(61)	0.279 8(16)	91(16)
C(21)	0.227(50)	0.981 6(53)	0.370 6(15)	67(14)
C(23)	0.735 6(50)	0.331(48)	0.306 0(14)	53(12)
N(1)	0.837 6(34)	0.705 9(31)	0.396 8(12)	21(7)
N(2)	0.748 4(40)	0.565 2(40)	0.418 8(11)	49(9)
N(3)	0.647 7(48)	0.886 0(49)	0.464 7(14)	42(10)
N(4)	0.695 5(52)	0.618 1(59)	0.634 1(15)	58(12)
HC(3)	0.746 4	0.305 9	0.413 4	
HC(3)	0.956 4	0.393 7	0.399 3	
HC(3)	0.763 7	0.409 9	0.353 5	
HC(6)	0.657 1	0.866 9	0.568 6	
HC(8)	0.747 7	0.332 2	0.579 9	
HC(9)	0.768 6	0.316 2	0.482 5	
HC(21)	1.052 9	0.948 8	0.262 0	
HC(21)	0.894 6	0.785 3	0.251 3	
HC(21)	1.095 6	0.755 9	0.293 1	
HC(22)	0.002 5	0.933 0	0.331 3	
HC(22)	0.009 7	1.114 6	0.369 9	
HC(22)	−0.067 2	0.926 6	0.395 5	
HC(23)	0.747 4	0.069 9	0.265 8	
HC(23)	0.601 2	−0.017 4	0.309 5	
HC(23)	0.837 4	−0.059 9	0.317 2	

* U-values are the coefficients of the anisotropic temperature factor expression $\exp(U_{11}h^2 + U_{22}k^2 + U_{33}l^2 + 2U_{12}hk + 2U_{13}hl + 2U_{23}kl)$ with parameters

	U_{11}	U_{22}	U_{33}
Br	89(5)	118(5)	83(3)
O(31)	100(27)	47(22)	89(24)
O(32)	41(19)	82(22)	55(16)
O(41)	99(27)	62(23)	75(22)
O(42)	37(20)	87(23)	98(25)

	U_{12}	U_{23}	U_{13}
Br	−47(4)	−5(4)	−10(3)
O(31)	−19(19)	−13(19)	8(2)
O(32)	22(18)	4(19)	25(2)
O(41)	14(22)	9(20)	14(2)
O(42)	25(18)	74(23)	18(2)

Six layers ($h0$—$5l$) of equi-inclination Weissenberg data (Cu-K_α radiation) were collected for intensity measurements from a crystalline needle mounted about the b axis. The crystal was remounted about the a axis and three layers (0—$2kl$) collected for cross-reference. The integrated intensities were estimated visually and corrected for Lorentz and polarisation effects but not for absorption. A total of 795 reflections were estimated which yielded 526 unique reflections.

TABLE 2

Bond lengths (Å) with estimated standard deviation in parentheses (6) [X = Br, R^1 = Bu^t, R^2 = N(Me)-$C_6H_3(NO_2)_2$]

Br–C(1)	1.93(3)	C(5)–C(6)	1.42(5)
C(1)–C(2)	1.55(5)	C(6)–C(7)	1.32(5)
C(2)–C(21)	1.58(5)	C(7)–C(8)	1.46(5)
C(2)–C(22)	1.58(5)	C(8)–C(9)	1.40(4)
C(2)–C(23)	1.59(5)	C(5)–N(3)	1.57(5)
C(1)–N(1)	1.22(3)	C(7)–N(4)	1.50(5)
N(1)–N(2)	1.41(3)	N(3)–O(31)	1.15(4)
N(2)–C(3)	1.47(4)	N(3)–O(32)	1.21(3)
N(2)–C(4)	1.35(4)	N(4)–O(41)	1.12(4)
C(4)–C(5)	1.39(5)	N(4)–O(42)	1.20(4)
C(4)–C(9)	1.39(5)		

TABLE 3

Bond angles (°) with estimated standard deviations in parentheses for (6) [X = Br, R^1 = Bu^t, R^2 = N(Me)-$C_6H_3(NO_2)_2$]

Br–C(1)–C(2)	113.0(2.1)	C(4)–C(5)–C(6)	128.9(4.0)
Br–C(1)–N(1)	124.6(2.7)	C(4)–C(5)–N(3)	120.5(3.5)
C(2)–C(1)–N(1)	122.0(3.1)	N(3)–C(5)–C(6)	110.5(3.6)
C(1)–C(2)–C(21)	107.0(3.1)	C(5)–C(6)–C(7)	112.3(3.6)
C(1)–C(2)–C(22)	108.6(2.8)	C(6)–C(7)–C(8)	128.9(3.5)
C(1)–C(2)–C(23)	112.8(2.9)	C(6)–C(7)–N(4)	114.6(3.9)
C(21)–C(2)–C(22)	109.0(3.1)	C(8)–C(7)–N(4)	116.5(3.8)
C(21)–C(2)–C(23)	107.2(2.8)	C(7)–C(8)–C(9)	115.1(3.7)
C(22)–C(2)–C(23)	112.0(3.1)	C(8)–C(9)–C(4)	121.4(3.8)
C(1)–N(1)–N(2)	122.3(2.8)	C(5)–N(3)–O(31)	118.4(3.6)
N(1)–N(2)–C(2)	113.2(2.4)	C(5)–N(3)–O(32)	114.7(3.7)
N(1)–N(2)–C(4)	114.9(3.1)	O(31)–N(3)–O(32)	126.9(3.9)
C(3)–N(2)–C(4)	122.2(3.2)	C(7)–N(4)–O(41)	120.5(4.6)
N(2)–C(4)–C(5)	125.4(3.8)	C(7)–N(4)–O(42)	116.5(4.2)
N(2)–C(4)–C(9)	118.7(3.6)	O(41)–N(4)–O(42)	122.7(4.1)
C(5)–C(4)–C(9)	115.8(3.3)		

TABLE 4

The equations of some relevant mean planes, given in the form $lx + my + nz = p$; deviations (Å × 10^3) of the most relevant atoms from the planes given in square brackets

Plane (1): Br, C(1), C(2), N(1), N(2)

$$0.720\,2x + 0.584\,5y + 0.363\,8z = 2.494\,0$$

[Br 13.4, C(1) −55.3, C(2) 19.4, N(1) 18.4, N(2) 4.0]

Plane (2): C(4)—(9)

$$0.984\,4x + 0.161\,2y + 0.069\,8z = 6.834\,0$$

[C(4) 26.1, C(5) −22.1, C(6) 3.2, C(7) 9.9, C(8) −3.9, C(9) 13.2]

Plane (3): N(3), O(31), O(32)

$$-0.753\,4x + 0.145\,0y + 0.641\,3z = 4.817\,1$$

Plane (4): N(4), O(41), O(42)

$$0.877\,2x + 0.477\,0y - 0.053\,8z = 6.019\,8$$

Interplane angles (°): (1)–(2) 54, (2)–(3) 47.3, (2)–(4) 20.5.

Values for the atomic scattering factors were taken from ref. 30. Calculations were carried out by use of the programs SHELX and XANADU [31] on an IBM 370/135 computer. Figure 1 was drawn by use of the PLUTO [32] program. The structure was solved by the standard heavy-atom technique, followed by difference-Fourier synthesis phased on an increasing number of atom positions.

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[30] 'International Tables for *X*-Ray Crystallography,' vol. IV, Kynoch Press, Birmingham, 1974.

[31] SHELX and XANADU programs for IBM 370/1350 by G. M. Sheldrick, University Chemical Laboratory, Cambridge.

[32] PLUTO, program by G. S. Motherwell, University Chemical Laboratory, Cambridge.

Full-matrix least-square refinement of positional and isotropic temperature factors of all non-hydrogen atoms and overall scale factor followed by refinement of the interlayer scale factors gave R 0.169. At this stage the isotropic temperature factors of the bromine and oxygen atoms were set anisotropic and the positions of the hydrogen atoms calculated geometrically and floated on the adjacent carbon atom assuming C–H 1.08 Å and a fixed temperature factor of 0.07; a final refinement produced R 0.104. Final atomic co-ordinates and thermal parameters, together with their estimated standard deviations, are given in Table 1. Table 2 lists final bond distances, and Table 3 bond angles. Table 4 reports some relevant mean planes.* Figure 1 illustrates the molecular structure and atom numbering system used.

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* Final observed and calculated structure factors are listed in Supplementary Publication No. SUP. 21985 (4 pp., 1 microfiche). See Notice to Authors No. 7, in *J.C.S. Perkin II*, 1976, Index issue.