Cyclic Meso-ionic Compounds. Part XII.[1] Synthesis, Spectroscopic Properties, and Chemistry of 1,3,4-Oxadiazolium-2-aminides

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Representatives of a new class of meso-ionic heterocycles which are derivatives (II) of 1,3,4-oxadiazolium-2-aminide have been prepared. Their physical properties and chemical reactions are compared with those of the isomeric derivatives (I) of 1,3,4-triazolium-2-olate.

1,3,4-TRIAZOLIUM-2-OLATES (I) have been prepared by the reaction of phosgene with *N*-aminobenzamidines (III) or by base-catalysed cyclodehydration of the semicarbazide derivatives (IV).[2,3] The 1,4-diphenyl derivative (Ia) has been prepared by 1,3-dipolar cycloaddition of phenyl isocyanate to *N*-phenylsydnone (V).[4] The 1,3,4-triazolium-2-olates (I) are stable, colourless, crystalline compounds which have been fully characterised.[3] The isomeric 1,3,4-oxadiazolium-2-aminides (II) have not been previously reported. In continuation of our studies on isomeric pairs of meso-ionic systems of the general types (VI) and (VII), we have synthesised derivatives of the 1,3,4-oxadiazolium-2-aminides (II)[5] and have compared their physical and chemical properties with those of the isomers (I).

In the preceding papers, we have shown that meso-ionic aminides of the types (VI; $X = NR^3$, $Y = NR^4$)[1] and (VI; $X = S$, $Y = NR^3$)[6] can be prepared by condensation of isocyanide dichlorides with the hydrazine derivatives (III) and (VIII), respectively. The corresponding synthesis of the 1,3,4-oxadiazolium-2-aminides (II) by condensation of an *N*-acylhydrazine (IX) with an isocyanide dichloride has now been examined. When phenyl isocyanide dichloride was added dropwise to a solution of *N*-benzoyl-*N*-methylhydrazine[7] (IX; $R^1 = Me$, $R^2 = Ph$) in benzene, an exothermic reaction took place giving 2-anilino-4-methyl-5-phenyl-1,3,4-oxadiazolium chloride (Xb). The 1,3,4-oxadiazolium chlorides (Xc—e) were similarly obtained as colourless, crystalline compounds. Their i.r. spectra show N–H absorption at 2700—2800 cm^{-1} and a band at 1660 cm^{-1} which can be attributed to C=N stretching. The n.m.r. spectra are consistent with structure (X).

The transformation of 1,3,4-oxadiazolium chlorides (X) into 1,3,4-oxadiazolium-2-aminides (II) by various bases was examined, but the best reagent was found to be diazomethane. A suspension of 2-anilino-4-methyl-5-phenyl-1,3,4-oxadiazolium chloride (Xb) in dichloromethane was treated dropwise with a solution of diazomethane in ether. Nitrogen was liberated and an orange colour developed. The orange solution was concentrated at room temperature; addition of dry carbon tetrachloride then gave the yellow 4-methyl-5-phenyl-1,3,4-oxadiazolium-2-anilide (IIb). Compounds (IIc and d) were similarly prepared. The extreme sensitivity of the 1,3,4-oxadiazolium-2-aminides (II) to water demands the use of rigorously anhydrous conditions. For comparison, the 1,3,4-triazolium-2-olates (Ib), (Id), and (Ie) were prepared by cyclodehydration of the appropriate semicarbazide (IV) with sodium ethoxide in boiling ethanol at reflux remperature.

The i.r. spectra of the 1,3,4-oxadiazolium-2-aminides (II) show a strong absorption in the region 1630—1670 cm^{-1}, which can be attributed to exocyclic C=N stretching. This is at higher wavenumber than the corresponding absorption of the 1,3,4-triazolium-2-aminides (VI; $X = NR^3$, $Y = NR^4$) (1550—1560 cm^{-1})[1] and the 1,3,4-thiadiazolium-2-aminides (VI; $X = S$, $Y = NR^3$) (1550—1580 cm^{-1}).[5] The oxadiazolium-2-aminides (II) show no sign of N–H or carbodi-imide absorption. The i.r. spectra of the isomeric 1,3,4-triazolium-2-olates (I) show a strong absorption in the region 1660—1680 cm^{-1}, corresponding to exocyclic C=O stretching.

The dipole moment of the 1,3,4-oxadiazolium-2-aminide (IIb) (7·56 D) in benzene solution has been

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[1] Part XI, W. D. Ollis and C. A. Ramsden, preceding paper.

[2] M. Busch and S. Schneider, *J. prakt. Chem.*, 1903, **67**, 263; M. Busch and R. Ruppenthal, *Ber.*, 1910, **43**, 3008.

[3] K. T. Potts, S. K. Roy, and D. P. Jones, *J. Heterocyclic Chem.*, 1965, **2**, 105; *J. Org. Chem.*, 1967, **32**, 2245.

[4] H. Kato, S. Sato, and M. Ohta, *Tetrahedron Letters*, 1967, 4261.

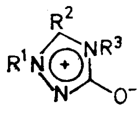
[5] W. D. Ollis and C. A. Ramsden, *Chem. Comm.*, 1971, 1223.

[6] Part X, W. D. Ollis and C. A. Ramsden, *J.C.S. Perkin I*, 1974, 633.

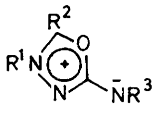
[7] Part IX, A. R. McCarthy, W. D. Ollis, and C. A. Ramsden, *J.C.S. Perkin I*, 1974, 627.

measured,[8] and is in excellent agreement with the meso-ionic structure (II).

The n.m.r. spectra of pairs of isomers of the types (I) and (II) are similar but distinct. Thus, the chemical shifts of the *N*-methyl singlet in the 1,3,4-triazolium-2-olate (Ib) (τ 6·33) and the 1,3,4-oxadiazolium-2-aminide (IIb) (τ 6·06) are different. Similarly, the splitting patterns associated with the ten aromatic protons of the two compounds (Ib) and (IIb) are distinct. U.v. spectra of the isomers (I) and (II) are similar to those of other meso-ionic systems with the general structures (VI) and (VII).[1,6,7]



(I)



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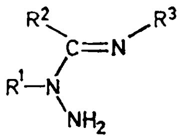

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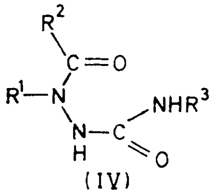
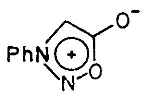
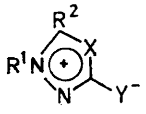


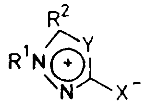
(IV)



(V)



(VI)



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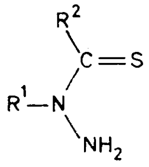
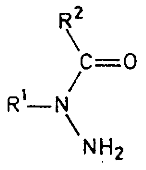
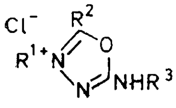


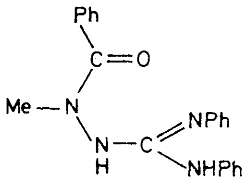
(VIII)



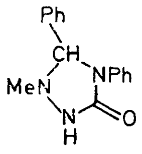
(IX)



(X)



(XI)



(XII)

In formulae (I)—(IV), and (X):

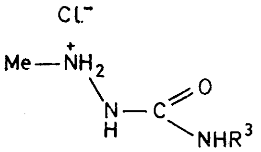
- a; $R^1 = R^3 = Ph$, $R^2 = H$
- b; $R^1 = Me$, $R^2 = R^3 = Ph$
- c; $R^1 = Me$, $R^2 = Ph$, $R^3 = p\text{-}ClC_6H_4$
- d; $R^1 = Me$, $R^2 = Ph$, $R^3 = p\text{-}MeC_6H_4$
- e; $R^1 = R^3 = Me$, $R^2 = Ph$

The mass spectra of the 1,3,4-triazolium-2-olates (I) and the 1,3,4-oxadiazolium-2-aminides (II) are quite different. Both systems give a molecular ion, but the triazole isomers (I) show the fragment ion $R^2C\equiv\overset{+}{N}R^3$, whereas the oxadiazole isomers (II) give the fragment ion $R^2C\equiv\overset{+}{O}$. This clearly distinguishes between the two skeletons (I) and (II).[9] The mass spectra of the 1,3,4-oxadiazolium-2-aminides (II) are very similar to those of the 1,3,4-oxadiazolium chlorides (X).

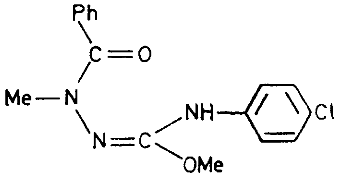
The 1,3,4-oxadiazolium-2-aminide (IIb) reacts with aniline to give the guanidine derivative (XI). This reaction is analogous to the reaction of diphenylisosydnone (VI; $R^1 = R^2 = Ph$, $X = Y = O$) with aniline to give the semicarbazide (IV; $R^1 = R^2 = R^3 = Ph$).[10] The formation of the guanidine (XI) is good chemical evidence for the meso-ionic structure (IIb).

We have found that the 1,3,4-triazolium-2-olate (Ib) can be reduced with lithium aluminium hydride in hot dioxan to the 1,3,4-triazolidine (XII), which shows a strong carbonyl absorption at 1720 cm^{-1}. The structure (XII) is fully supported by the n.m.r. and mass spectra.

No method of interconverting the meso-ionic systems (I) and (II) has been discovered.[1,6,7]

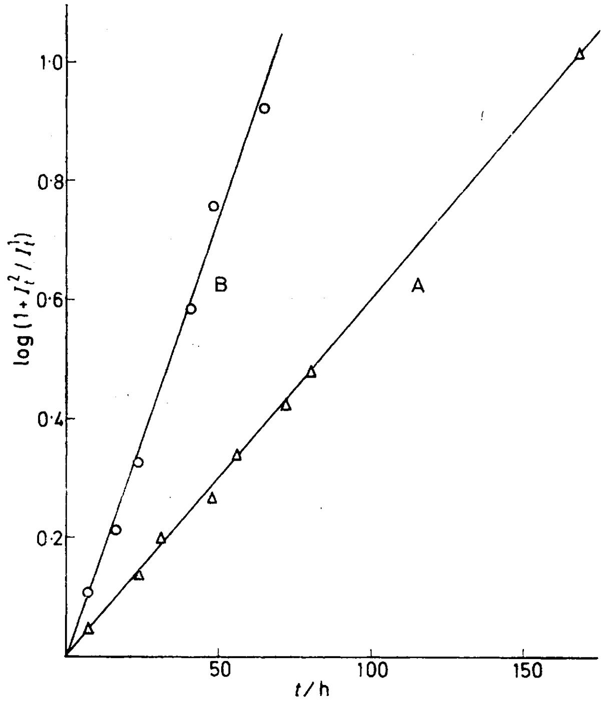


(XIII)



(XIV)

The 1,3,4-oxadiazolium chlorides (Xb and d) react with methanol at room temperature to give the semicarbazide hydrochlorides (XIII; R^3 = Ph or *p*-tolyl). The reaction (Xd) ⟶ (XIII; R^3 = *p*-tolyl) in [$^2H_4$]-methanol at room temperature has been monitored by n.m.r. spectroscopy; it was observed to proceed in quantitative yield and shows pseudo-first-order kinetics



The pseudo-first-order dependence of the rates of the reactions (Xd) ⟶ (XII; R^3 = *p*-tolyl) (A) and (Xc) ⟶ [$^2H_3$]-(XIV) (B) in [$^2H_4$]methanol at 20°

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[8] W. D. Ollis, C. A. Ramsden, and L. E. Sutton, forthcoming publication.

[9] Part XIII, W. D. Ollis and C. A. Ramsden, *J.C.S. Perkin I*, 1974, 645.

[10] M. Hashimoto and M. Ohta, *Bull. Chem. Soc. Japan*, 1961, **34**, 668.

(Figure; plot A) (at 20° $t_{\frac{1}{2}}$ 1·81 × 10^4 s, k 3·83 × 10^{-5} s^{-1}). However, a different result was obtained when 2-*p*-chloroanilino-4-methyl-5-phenyl-1,3,4-oxadiazolium chloride (Xc) was treated with methanol at room temperature. In this case, the product was compound (XIV). This reaction (Xc) ⟶ (XIV) has been monitored similarly in [$^2H_4$]methanol; it proceeds in quantitative yield and also shows pseudo-first-order kinetics (Figure; plot B) (at 20° $t_{\frac{1}{2}}$ 7·47 × 10^3 s, k 9·28 × 10^{-5} s^{-1}).

EXPERIMENTAL

General experimental directions are given in Part VIII.[11]

1,3,4-*Oxadiazolium Chlorides* (X).—Phenyl isocyanide dichloride[6] (2·3 g) was added dropwise to a solution of *N*-benzoyl-*N*-methylhydrazine[7] (2·0 g) in dry benzene (10 ml). An exothermic reaction occurred and after further gentle heating (45 min) under reflux, the mixture was cooled. The crystalline solid was collected, washed with ether, and recrystallised from chloroform–ether and then from ethanol–ether giving 2-*anilino*-4-*methyl*-5-*phenyl*-1,3,4-*oxadiazolium chloride* (Xb) (0·73 g, 19%), needles, m.p. 175° (Found: C, 62·9; H, 5·1; Cl, 12·2; N, 14·6. $C_{15}H_{14}ClN_3O$ requires C, 62·6; H, 4·9; Cl, 12·3; N, 14·6%); $\lambda_{max.}$ 244 and 311 nm (ε 20,200 and 9700); $\nu_{max.}$ 1660 cm^{-1}; τ ($CDCl_3$–$CF_3{\cdot}CO_2H$) 2·0—3·0 (m, 10 aromatic H) and 5·82 (s, NMe); *m/e* 251 ($M^{\cdot+}$ − HCl).

The following compounds were similarly prepared from *N*-benzoyl-*N*-methylhydrazine[7] (1·0 g) and an equimolar amount of the appropriate isocyanide dichloride[6] with benzene (10 ml) as solvent: 4-*methyl*-2-*methylamino*-5-*phenyl*-1,3,4-*oxadiazolium chloride* (Xe) (0·53 g, 35%), crystals, m.p. 175°, from ethanol–ether (Found: C, 52·9; H, 5·3; Cl, 16·0; N, 18·4. $C_{10}H_{12}ClN_3O$ requires C, 53·2; H, 5·3; Cl, 15·7; N, 18·6%); $\lambda_{max.}$ 235 and 296 nm (ε 6700 and 12,000); $\nu_{max.}$ (KBr) 1620 and 1675 cm^{-1}; *m/e* 189 ($M^{\cdot+}$ − HCl); 2-p-*chloroanilino*-4-*methyl*-5-*phenyl*-1,3,4-*oxadiazolium chloride* (Xc) (0·54 g, 25%), needles, m.p. 170—171° (from chloroform–ether and then from ethanol–ether) (Found: C, 56·1; H, 4·1; Cl, 21·8; N, 12·8. $C_{15}H_{13}Cl_2N_3O$ requires C, 55·9; H, 4·1; Cl, 22·05; N, 13·0%); $\nu_{max.}$ 1660 cm^{-1}; τ ($CDCl_3$–$CF_3{\cdot}CO_2H$) 2·0—3·0 (m, 9 aromatic H) and 5·75 (s, NMe); 4-*methyl*-5-*phenyl*-2-p-*tolylamino*-1,3,4-*oxadiazolium chloride* (Xd) (0·28 g, 14%), needles, m.p. 172—174° (from chloroform–ether and then from ethanol–ether); $\nu_{max.}$ 1660 cm^{-1}; τ ($CDCl_3$–$CF_3{\cdot}CO_2H$) 2·0—3·0 (m, 9 aromatic H), 5·76 (s, NMe), and 7·65 (s, Me); *m/e* 265 ($M^{\cdot+}$ − HCl).

1,3,4-*Oxadiazolium*-2-*aminides* (II).—2-Anilino-4-methyl-5-phenyl-1,3,4-oxadiazolium chloride (Xb) (0·5 g) was suspended in dry dichloromethane maintained at 0°. Diazomethane in ether was then added dropwise and the solution immediately turned deep orange, nitrogen being evolved. When the reaction was complete, the solution was filtered and the filtrate was concentrated under diminished pressure at room temperature. Dry carbon tetrachloride was added dropwise, and the yellow crystals which separated were rapidly collected. Recrystallisation from dichloromethane–carbon tetrachloride gave 4-*methyl*-5-*phenyl*-1,3,4-*oxadiazolium*-2-*anilide* (IIb) (0·08 g, 18%), bright yellow platelets, m.p. 123—125° (Found: C, 71·9; H, 5·3; N, 16·5%; M^+, 251·1058. $C_{15}H_{13}N_3O$ requires C, 71·7; H, 5·2; N, 16·7%; *M*, 251·1059); $\lambda_{max.}$ (CH_2Cl_2) 250 and 324 nm (ε 22,800 and 6300); $\nu_{max.}$ (CH_2Cl_2) 1640 cm^{-1}; τ 2·1—2·7 (m, 10 aromatic H) and 6·06 (s, NMe).

The following compounds were similarly prepared from the corresponding 1,3,4-oxadiazolium chloride (X) (0·5 g): 4-*methyl*-5-*phenyl*-1,3,4-*oxadiazolium*-2-p-*chloroanilide* (IIc) (0·05 g, 11%), yellow prisms, m.p. 130—132° (from dichloromethane–carbon tetrachloride) [Found: M^+ 285·0678 (^{35}Cl). $C_{15}H_{12}ClN_3O$ requires *M*, 285·0669 (^{35}Cl)]; $\lambda_{max.}$ (CH_2Cl_2) 254 and 327 nm (ε 22,800 and 6900); $\nu_{max.}$ (CH_2Cl_2) 1575, 1600, and 1630 cm^{-1}; τ 2·34 (s, C_6H_5), 2·75 (m, C_6H_4), and 6·08 (s, NMe); 4-*methyl*-5-*phenyl*-1,3,4-*oxadiazolium*-2-p-*toluidide* (IId), (0·07 g, 16%), yellow needles, m.p. 136—137° (from dichloromethane–carbon tetrachloride) (Found: M^+, 265·1207. $C_{16}H_{15}N_3O$ requires *M*, 265·1215); $\lambda_{max.}$ (CH_2Cl_2) 250 and 329 nm (ε 9550 and 2300); $\nu_{max.}$ (CH_2Cl_2) 1595 and 1640 cm^{-1}; τ 2·2—3·0 (m, 9 aromatic H), 6·06 (s, NMe), and 7·71 (s, Me).

1-*Acylsemicarbazides* (IV).—*N*-Benzoyl-*M*-methylhydrazine[7] (5·0 g) in ethanol (40 ml) was stirred at 0° (15 min) after a solution of phenyl isocyanate (5·0 g) in ethanol (10 ml) had been added. The mixture was kept at room temperature overnight, and the crystalline solid was collected. Crystallisation from ethanol yielded 1-benzoyl-1-methyl-4-phenylsemicarbazide (IVb) (6·4 g, 71%), needles, m.p. 173—174° (lit.,[3] 171—172°); $\nu_{max.}$ 1640 and 1720 cm^{-1}; τ ($CDCl_3$–$CF_3{\cdot}CO_2H$) 2·51 (s, C_6H_5), 2·73 (s, C_6H_5), and 6·65 (s, NMe).

The following derivatives were similarly prepared: 1-*benzoyl*-4-p-*chlorophenyl*-1-*methylsemicarbazide* (IVc) (1·36 g, 66%), needles, m.p. 175—176° (from ethanol) [Found: C, 59·4; H, 4·8; Cl, 11·4; N, 13·75%; M^+, 303 (^{35}Cl). $C_{15}H_{14}ClN_3O_2$ requires C, 59·3; H, 4·6; Cl, 11·7; N, 13·8%; *M*, 303 (^{35}Cl)]; τ ($CDCl_3$–$CF_3{\cdot}CO_2H$) 2·49 (s, C_6H_5), 2·75 (s, C_6H_4), and 6·58 (s, NMe); 1-*benzoyl*-1-*methyl*-4-p-*tolylsemicarbazide* (IVd) (1·23 g, 65%), needles, m.p. 177—178° (from ethanol) (Found: C, 67·75; H, 6·1; N, 14·65%; M^+, 293. $C_{16}H_{17}N_3O_2$ requires C, 67·85; H, 6·0; N, 14·8%; *M*, 283); τ ($CDCl_3$–$CF_3{\cdot}CO_2H$) 2·53 (s, C_6H_5), 2·88 (s, C_6H_4), 6·64 (s, NMe), and 7·66 (s, Me).

1,3,4-*Triazolium*-2-*olates* (I).—Sodium metal (0·5 g) was dissolved in absolute ethanol (50 ml) and 1-benzoyl-1-methyl-4-phenylsemicarbazide (IVb) (2·0 g) was added. The solution was then heated (2 h) under reflux and the ethanol was evaporated off. Addition of water, extraction with chloroform, evaporation, and recrystallisation of the residue from ethanol yielded 4-*methyl*-1,5-*diphenyl*-1,3,4-*triazolium*-2-*olate* (Ib) (1·03 g, 55%), cubes, m.p. 242—243° (Found: C, 71·9; H, 5·15; N, 16·9%; M^+, 251. $C_{15}H_{13}N_3O$ requires C, 71·7; H, 5·2; N, 16·7%; *M*, 251); $\lambda_{max.}$ 207 and 279 nm (ε 20,400 and 6600); $\nu_{max.}$ 1650—1670 cm^{-1}; τ 2·52 (s, C_6H_5), 2·66 (s, C_6H_5), and 6·33 (s, NMe).

Similarly prepared was 4-*methyl*-5-*phenyl*-1-p-*tolyl*-1,3,4-*triazolium*-2-*olate* (Id) (0·48 g, 51%), prisms, m.p. 190° (Found: C, 72·3; H, 5·7; N, 15·8%; M^+, 265. $C_{16}H_{15}N_3O$ requires C, 72·5; H, 5·7; N, 15·85%; *M*, 265); $\nu_{max.}$ 1617 cm^{-1}; τ 2·51 (s, C_6H_5), 2·82 (s, C_6H_4), 6·29 (s, NMe), and 7·67 (s, Me).

Reaction of 4-*Methyl*-5-*phenyl*-1,3,4-*oxadiazolium*-2-*anilide* (IIb) *with Aniline*.—Compound (IIb) (0·4 g) in dichloromethane (15 ml) was gently heated (15 min) under reflux with aniline (0·6 g). The orange colouration faded and after evaporation the residual oil was crystallised from ethanol yielding N″-(N-*methylbenzamido*)-NN′-*diphenylguanidine* (XI) (0·36 g, 65%), needles, m.p. 185° (Found: C, 73·0; H, 5·8; N, 16·0%; M^+, 344. $C_{21}H_{20}N_4O$ requires

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[11] Part VIII, A. R. McCarthy, W. D. Ollis, and C. A. Ramsden, *J.C.S. Perkin I*, 1974, 624.

C, 73·2; H, 5·8; N, 16·3%; *M*, 344); $\nu_{max.}$ (KBr) 1595, 1615, and 1675 cm^{-1}; τ ($CDCl_3$–$CF_3{\cdot}CO_2H$) 2·4—3·1 (m, 15 aromatic H) and 6·58 (s, NMe).

Reduction of 4-*Methyl*-1,5-*diphenyl*-1,3,4-*triazolium*-2-*olate* (Ib).—Compound (Ib) (1·0 g) was stirred under reflux with dry dioxan (25 ml) and lithium aluminium hydride (0·1 g) was added. After 15 min, the solution was cooled and the excess of lithium aluminium hydride was destroyed by careful addition of water (25 ml). Addition of 2N-sodium hydroxide, extraction with chloroform, evaporation, and crystallisation from chloroform–ether gave 4-*methyl*-1,5-*diphenyl*-1,3,4-*triazolidin*-2-*one* (XII) (0·60 g, 60%), prisms, m.p. 163—165° (Found: C, 71·4; H, 5·8; N, 16·65%; M^+, 253. $C_{15}H_{15}N_3O$ requires C, 71·15; H, 5·9; N, 16·6%; *M*, 253); $\lambda_{max.}$ 245 nm (ε 12,650); $\nu_{max.}$ 1720 cm^{-1}; τ 2·61 (m, 10 aromatic H), 3·21br (s, NH), 4·53 (s, CH), and 7·25 (s, Me).

Reaction of 2-*Anilino*-4-*methyl*-5-*phenyl*-1,3,4-*oxadiazolium Chloride* (Xb) *with Methanol*.—A solution of compound (Xb) (0·5 g) in methanol (10 ml) was maintained at room temperature (5 days). Concentration of the solution, addition of ether, and crystallisation of the precipitate from methanol–ether yielded 1-*methyl*-4-*phenylsemicarbazide hydrochloride* (0·18 g, 64%), flakes, m.p. 148—149° (Found: C, 47·6; H, 5·95; Cl, 17·55; N, 20·6. $C_8H_{12}ClN_3O$ requires C, 47·6; H, 6·0; Cl, 17·6; N, 20·8%); $\nu_{max.}$ (KBr) 1710 cm^{-1}; *m/e* 165 ($M^{\cdot+}$ – HCl).

In the same way, 4-methyl-5-phenyl-2-*p*-tolylamino-1,3,4-oxadiazolium chloride (Xd) (0·5 g) reacted with methanol giving 1-*methyl*-4-p-*tolylsemicarbazide hydrochloride* (0·17 g, 57%), flakes, m.p. 148—150° (from methanol–ether) (Found: C, 50·1; H, 6·5; Cl, 16·2; N, 19·25. $C_9H_{14}ClN_3O$ requires C, 50·1; H, 6·5; Cl, 16·5; N, 19·5%); $\nu_{max.}$ (KBr) 1710 cm^{-1}; τ ($CDCl_3$–$CF_3{\cdot}CO_2H$) 2·83 (s, C_6H_4), 6·90 (s, NMe), and 7·70 (s, Me); *m/e* 179 ($M^{\cdot+}$ – HCl).

Reaction of 2-p-*Chloroanilino*-4-*methyl*-5-*phenyl*-1,3,4-*oxadiazolium Chloride* (Xc) *with Methanol*.—A solution of compound (Xc) (0·5 g) in methanol (15 ml) was kept at room temperature (5 days). After concentration, ether was added and the precipitate was recrystallised from methanol–ether yielding N′-[p-*chloroanilino*(*methoxy*)-*methylene*]-N-*methylbenzohydrazide* (XIV) (0·27 g, 55%), needles, m.p. 183—184° (Found: [*M* – MeOH]$^+$, 285·0668. $C_{15}H_{12}ClN_3O$ requires [*M* – MeOH], 285·0669); $\nu_{max.}$ (KBr) 1710, 1660, 1620, and 1545 cm^{-1}; τ ($CDCl_3$–$CF_3{\cdot}CO_2H$) 2·0—3·0 (m, aromatic H), 6·58 (s, OMe), and 6·82 (s, NMe).

Kinetic Studies of the Reaction of 1,3,4-*Oxadiazolium Chlorides* (X) *with* [$^2H_4$]*Methanol*.—The reactions were carried out in [$^2H_4$]methanol solution in an n.m.r. tube at 20°, and the n.m.r. spectrum of the mixture was determined after various time intervals. The relative proportions of precursor and product after time *t* were estimated by integration of the *N*-methyl signals of the precursor and the product.

(*a*) 4-Methyl-5-phenyl-2-*p*-tolylamino-1,3,4-oxadiazolium chloride (Xd) reacted with [$^2H_4$]methanol to give 1-methyl-4-*p*-tolylsemicarbazide hydrochloride (XIII; R^3 = *p*-tolyl). I^1_t is the relative intensity of the *N*-methyl signal of (Xd) (τ 5·73) after time *t*; I^2_t is the relative intensity of the *N*-methyl signal of (XIII; R^3 = *p*-tolyl) (τ 6·98) after time *t*. The graph of log $(1 + I^2_t/I^1_t)$ against *t* (Figure; plot A) is a straight line, indicating pseudo-first-order kinetics.

(*b*) 2-*p*-Chloroanilino-4-methyl-5-phenyl-1,3,4-oxadiazolium chloride (Xc) reacted with [$^2H_4$]methanol to give the hydrazide [$^2H_3$]-(XIV). I^1_t is the relative intensity of the *N*-methyl signal of (Xc) (τ 5·73): I^2_t is the relative intensity of the *N*-methyl signal of [$^2H_3$]-(XIV) (τ 6·97). The graph of log $(1 + I^2_t/I^1_t)$ against *t* (Figure; plot B) is a straight line, indicating pseudo-first-order kinetics.

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