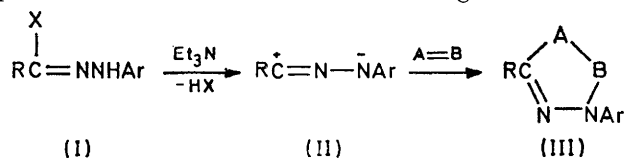


## Fragmentation Paths of Hydrazonyl Halides upon Electron Impact; Simulation of Nitrilimine Formation

By **Peder Wolkoff**, Department of General and Organic Chemistry, University of Copenhagen, The H. C. Ørsted Institute, Universitetsparken 5, DK-2100 Copenhagen, Denmark

The mass spectra of diaromatic hydrazonyl halides with substituents in the *C*- and *N*-aryl rings (Ia—h), and *NN*-disubstituted hydrazonyl chlorides (VI)—(VIII) have been examined and a comparison with chemical behaviour in solution has been attempted. The main reactions of the hydrazonyl halides are expulsion of a halogen radical or dehydrohalogenation to give  $[M - X]^+$  and  $[M - HX]^+$  ions, respectively. The hydrazonyl chlorides derived from 2-, 3-, and 4-nitrophenylhydrazines all show abundant  $[C_7H_5O]^+$  ions which indicate migration of the nitro-group prior to fragmentation. The *NN*-disubstituted hydrazonyl chlorides react by expulsion of a chlorine radical and by cleavage of the hydrazonyl N—N bond to give  $[M - Cl]^+$  and  $[R^1R^2N]^+$  ions, respectively. Hydrogen rearrangement accompanying decomposition also takes place.

HYDRAZONYL halides (I; X = halogen) have been exposed to considerable attention during the last two



decades.<sup>1</sup> They have been used extensively in 1,3-dipolar cycloaddition reactions, where the intermediate

<sup>1</sup> H. Ulrich, 'The Chemistry of Imidoyl Halides,' Plenum Press, New York, 1968.

nitrilimine (II), formed *in situ* by the action of triethylamine, reacts with a dipolarophile (AB) producing a heterocyclic adduct (III).<sup>2</sup>

The kinetics of nitrilimine formation have quite recently been investigated.<sup>3</sup> However, the mass spectral behaviour of hydrazonyl halides upon electron impact has so far not been examined, and this forms the subject of the present paper. Correlation of mass spectral fragmentations of molecular ions with photochemically and

<sup>2</sup> R. Huisgen, *Angew. Chem. Internat. Edn.*, 1963, 2, 565.

<sup>3</sup> A. F. Hegarty, M. P. Cashman, and F. L. Scott, *J.C.S. Perkin II*, 1972, 44.

thermally induced reactions has proven useful in relating and discovering new processes in the three systems;<sup>4</sup> hence a comparison of the unimolecular reactions of the compounds in question in the mass spectrometer to those observed to occur under ordinary solution conditions has been attempted. The study includes diatomic hydrazonyl halides RCXNNHAr (Ia—h; R = aryl) as well as those of type PhCCINNR<sup>1</sup>R<sup>2</sup> (VI)—(VIII), where R<sup>1</sup> and R<sup>2</sup> are methyl and/or phenyl.

*Hydrazonyl Halides of Type RCXNNHAr (Ia—h).*—The hydrazonyl halides of type (I) are listed in Table 1

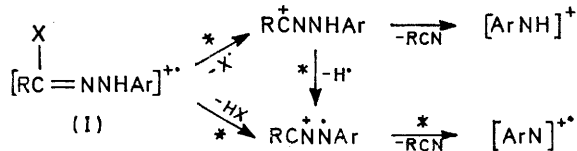
TABLE 1

The principal peaks <sup>a</sup> in the mass spectra (70 eV) of diatomic hydrazonyl halides RC(X)=NNHAr (I) <sup>b</sup>

	R	Ar	M	[M - X]	[M - HX]	[ArCN]	<i>m/e</i> 106	[C <sub>7</sub> H <sub>5</sub> O] <i>m/e</i> 105	[C <sub>7</sub> H <sub>5</sub> N] <i>m/e</i> 104	[ArNH <sub>2</sub> ]	[ArNH]	[ArN]
(Ia)	Ph	Ph	232,230 (17,52)	195 (7.2)	194 (31.8)	103 (7)		(3)	93 (4)	92 (34)	91 (100)	
(Ib)	Ph	Ph <sup>c</sup>	276,274 (26,26)	195 (16.7)	194 (26.4)	103 (9)		(4)	93 (10)	92 (100)	91 (45)	
(Ic)	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	Ph	262,260 (20,55)	225 (13.2)	224 (46.3)	133 (16)			93 (7)	92 (43)	91 (110) <sup>d</sup>	
(Id)	Ph	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	262,260 (13,39)	225 (0.36)	224 (2.35)	103 (9)	(10)	(2)	123 (5)	122 (37)	121 (100)	
(Ie)	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	Ph	277,275 (10,32)	240 (0.55)	239 (2.65)				93 (3)	92 (25)	91 (100) <sup>e</sup>	
(If)	Ph	2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	277,275 (24,67)	240 (2.2)	239 (<0.2)	103 (7)	(9)	(100)	(8)	137 (5)	136 (6) <sup>f</sup>	
(Ig)	Ph	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	277,275 (36,100)	240 (8.0)	239 (40.9)	103 (14)	(7)	(39)	(14)	138 (3)	137 (10)	136 (8) <sup>g</sup>
(Ih)	Ph	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	277,275 (35,100)	240 (6.6)	239 (37.0)	103 (16)	(8)	(46)	(16)	138 (2)	137 (4)	136 (25) <sup>h</sup>

<sup>a</sup> *m/e* (rel. int., average of three independent scans). <sup>b</sup> If not otherwise stated X = Cl. <sup>c</sup> X = Br. <sup>d</sup>  $[M - HCl - CH_3]^+$  209 (10), 103 (7). <sup>e</sup> 103 (3). <sup>f</sup>  $[M - Cl - NO_2]^+$  194 (7), 193 (5), 192 (4), 167 (5), 166 (5), 165 (7). <sup>g</sup>  $[M - HCl - NO]^+$  209 (3),  $[M - Cl - NO_2]^+$  194 (20),  $[M - HCl - NO_2]^+$  193 (29), 192 (5), 166 (4). <sup>h</sup> 209 (5), 194 (18), 193 (18), 192 (7), 165 (3),  $[C_7H_5NO]^+$  145 (17).

together with the principal peaks found in their mass spectra. The molecular ions are abundant though to a lesser extent than the molecular ions are in the spectra of arylhydrazones of aliphatic and aromatic aldehydes and ketones.<sup>5</sup> Expulsion of a halogen radical to give  $[M - X]^+$  ions, and dehydrohalogenation to give  $[M - HX]^+$  ions are the two main reactions of the molecular ions.  $[M - H]^+$  ions are present but only in very low abundance. The  $[M - X]^+$  ions decompose further by loss of hydrogen to produce  $[M - HX]^+$  ions or by elimination of an RCN fragment to give  $[ArNH]^+$  ions, which in the spectrum of the hydrazonyl bromide (Ib) gives rise to the base peak of the spectrum. The  $[M - HX]^+$  ions are possibly structurally analogous to the isomeric ions described recently<sup>6</sup> as the products of the retro-1,3-dipolar cycloaddition reaction of 1,3,4-thiadiazolines. They fragment by elimination of RCN forming  $[ArN]^+$  ions, which give rise to the base peaks in the spectra of (Ia and c—e). The hydrogen involved in



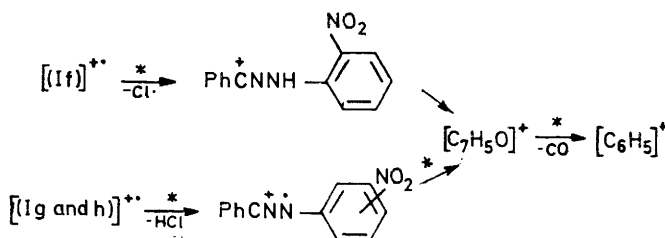
the dehydrohalogenation process was shown to be the hydrazonyl hydrogen, since the *m/e* 195—193 and 93—91 regions in the spectrum of (Ia) were unchanged by replacing the hydrazonyl hydrogen with deuterium. It is

<sup>4</sup> R. C. Dougherty, *Topics Current Chem.*, 1974, **45**, 93; T. W. Bentley and R. A. W. Johnstone, *Adv. Phys. Org. Chem.*, 1968, **8**, 151.

<sup>5</sup> (a) D. Goldsmith and C. Djerassi, *J. Org. Chem.*, 1966, **31**, 3661; (b) W. D. Crow, J. L. Occolowitz, and R. K. Solly, *Austral. J. Chem.*, 1968, **21**, 761; (c) J. Seibl and J. Völlmin, *Org. Mass Spectrometry*, 1968, **1**, 713; (d) F. Benoit and J. L. Holmes, *Canad. J. Chem.*, 1969, **47**, 3611; (e) J. Cable, S. A. Kagal, and J. K. MacLeod, *Org. Mass Spectrometry*, 1972, **6**, 301.

known that the lower primary aliphatic (C<sub>4</sub> and C<sub>5</sub>) halides give abundant  $[M - HX]^+$  ions in a similar 1,3-elimination.<sup>7</sup> Cleavage of the hydrazonyl N—N bond occurs less readily than in the decomposition of phenylhydrazones of aromatic aldehydes and ketones, where daughter ions formed by N—N cleavage carry more than 40% of the total ion current.<sup>5b</sup> The  $[PhNH]^+$  ion in the spectrum of (Ia) was shown in the first field-free region (by metastable defocusing<sup>8</sup>) to arise by decomposition of the  $[M - Cl]^+$  ion (see above) and to a lesser extent from the molecular ion by elimination of (PhCN + Cl).

The mass spectrum of (If; R = Ph, Ar = 2-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) shows significant differences from those of the *meta*- and *para*-isomers (see Table 1). The  $[M - HCl]^+$  ion peak is nearly absent [relative intensity (rel. int.) <0.2%], and *m/e* 105 is the base peak, while in the spectra of (Ig and h) the molecular ions give rise to the base peaks (as generally found for *p*-nitrophenylhydrazones<sup>5c,d</sup>). The *m/e* 105 ion is also very abundant in the spectra of (Ig and h), and



is so for all three compounds found to have the same elemental composition, C<sub>7</sub>H<sub>5</sub>O. This ion is formed, in the spectrum of (If), by decomposition of the  $[M - Cl]^+$  ion (*m/e* 240) and from the molecular ion (as shown by metastable defocusing<sup>8</sup>). In the spectra of (Ig and h) it was shown, both by the presence of the appropriate metastable peak and by metastable defocusing,<sup>8</sup> that this ion was formed by decomposition of the  $[M - HCl]^+$  ions (*m/e* 239) and also from the  $[M - HCl - NO]^+$  ions (*m/e* 209). Formation of the  $[C_7H_5O]^+$  ion in the spectrum of (If) may be readily explained in terms of migration of oxygen to the hydrazonyl carbon atom and subsequent cleavage as described for *o*-nitrophenyl-

<sup>6</sup> P. Wolkoff and S. Hammerum, *Org. Mass Spectrometry*, 1974, **9**, 181.

<sup>7</sup> A. M. Duffield, S. D. Sample, and C. Djerassi, *Chem. Comm.*, 1966, 193.

<sup>8</sup> K. R. Jennings in 'Some Newer Physical Methods in Structural Chemistry,' eds. R. Bonnett and J. G. Davis, United Trade Press, London, 1967, p. 105.

hydrazones by Seibl and Völlmin.<sup>5c</sup> An analogy from solution chemistry has also been found in the dehydrobromination reaction of hydrazone bromides derived from *o*-nitrophenylhydrazines, to form 1-aryloxybenzotriazoles.<sup>9</sup> However, for (Ig and h) migration (possibly isomerisation to the *ortho*-isomer) of the nitro-group in the  $[M - HCl]^{++}$  ions must precede transfer of oxygen for the  $[C_7H_5O]^+$  ions to be formed. The *C*-phenyl group is part of this ion, since there is a clean shift to *m/e* 110 in the spectra of the  $C$ - $[^2H_5]$ phenyl analogues of (Ig and h) [(Ig' and h')].\* Migration of the nitro-group in aromatic systems has (to our knowledge) only been reported in a few special cases; hydroxy-loss from *m*- and *p*-nitrotoluenes and -nitroanilines was found to occur *via* a common ionic intermediate<sup>10</sup> (the *ortho*-isomer). Similarly,  $[M - OH]^+$  ions in the spectra of *m*- and *p*-nitrophenyl(phenyl)methanes<sup>11</sup> may be rationalized in part in terms of an isomerisation to the *ortho*-isomer prior to decomposition. In the spectrum of (Ih) an ion of medium abundance of composition  $C_9H_7NO$  (*m/e* 145)

rings. The dipole ions generated from the molecular ions of hydrazone chlorides with electron-donating substituents in the *N*-aryl group such as (Id) or with electron-attracting groups in the *C*-aryl system [(Ie)] are considerably less abundant (rel. int. 2–3%), than in the unsubstituted case (Ia) (rel. int. 32%). The percentage ion current carried by the dipole ions and (their daughter ions) as given in Table 2 exhibit less variation. This shows that the dehydrohalogenation process is not very dependent on substituents attached to the aromatic rings, but that the relative stability of the dipole ions is. Conversely the kinetic data,<sup>3</sup> show that in solution nitrilimine formation is favoured by electron-donating substituents attached to the hydrazone carbon atom and by electron-withdrawing substituents attached to the *N*-aryl group.<sup>3</sup> The percentage ion current carried by the  $[M - X]^+$  ions, which formally correspond to the hydrazone carbonium ions (IV), and their daughter ions are also given in Table 2. The data demonstrate the well-known fact that bromine [as in (Ib)] is frequently

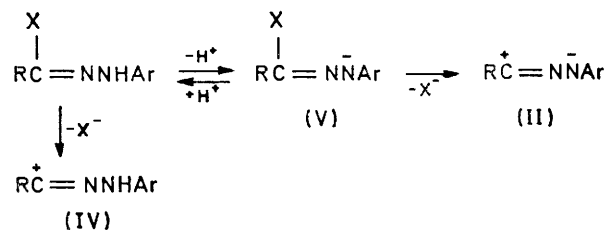
TABLE 2  
Percentage ion current carried by  $[M - HX]^{++}$  ions, and by  $[M - X]^+$  ions

	(Ia)	(Ib)	(Ic)	(Id)	(Ie)	(Ig)	(Ih)
% $\Sigma_{60}$ carried by $[M - HX]^{++}$ , $[M - HX - H]^+$ , $[RCN]^{++}$ , and $[ArN]^{++}$ ions	39.9	22.5	38.5 <sup>a</sup>	35.6	43.1 <sup>b</sup>	24.0 <sup>c,e</sup>	24.3 <sup>c,e</sup>
% $\Sigma_{50}$ carried by $[M - X]^+$ and $[ArH]^+$ ions <sup>e</sup>	8.2	29.5	9.2	9.1	7.6	4.4 <sup>d</sup>	2.6 <sup>d</sup>

<sup>a</sup>  $[M - HCl - CH_3]^+$  is also included. <sup>b</sup> The high ion current is due to the fact that a significant portion of  $[PhN]^{++}$  in this case is also formed from the molecular ion (as seen by metastable defocusing<sup>8</sup>). <sup>c</sup>  $[M - HCl - NO]^{++}$ ,  $[M - HCl - NO_2]^+$ ,  $[C_6H_7NO]^{++}$ ,  $[C_7H_5O]^+$ ,  $[C_7H_6N]^+$ , and  $[C_7H_5N]^{++}$  are also included. <sup>d</sup>  $[M - Cl - NO_2]^{++}$  is also included. <sup>e</sup> Corrected.

was found; a metastable peak and metastable defocusing<sup>8</sup> show that  $[M - HCl]^{++}$  and  $[M - HCl - NO]^{++}$  are the precursor ions. The *C*-phenyl group is incorporated in the *m/e* 145 ion since this shifts to *m/e* 150 in the spectrum of (Ih'), but the formation and structure of this ion are not well understood.

Expulsion of the halogen radical and the dehydrohalogenation process undergone by the molecular ions is reminiscent of the behaviour of hydrazone halides under 'wet' conditions (dioxan-water), where solvolysis produces hydrazone carbonium ions (IV) and (base induced) dehydrohalogenation leads to the nitrilimine (II).<sup>3,†</sup>



The abundance of the  $[M - HCl]^{++}$  ions, which formally correspond to the 1,3-dipole ion (II), is very dependent of the substituents attached to the aromatic

\* A metastable peak in the spectra of both  $[^2H_5]$  compounds confirms the formation of this ion from the  $[M - HCl]^{++}$  ions.

† The thermal decomposition of compound (Ia) at 190 °C has been reported to give small amounts of 2,3,5,6-tetraphenyl-2,5-dihydro-1,2,4-triazine, presumably formed by dimerisation of initially formed (IIa) (M. K. Saxena, N. N. Gudi, and M. V. George, *Tetrahedron*, 1973, **29**, 101).

lost as a bromine radical rather than as part of hydrogen bromide, whereas chlorine is often eliminated as hydrogen chloride.<sup>12</sup>

Intense metastable peaks (rel. int. 0.1–0.3%) corresponding to the hydrogen halide elimination were observed in all spectra. The spectra of (Ia, g, and h) further exhibited metastable peaks corresponding to loss of a chlorine radical from the  $[M - H]^+$  ions; further in the spectrum of (Ic) an intense metastable peak corresponding to expulsion of a chlorine radical from the molecular ion is observed. The overall elimination of hydrogen chloride *via* initial hydrogen loss closely resembles base catalysed nitrilimine formation *via* the reactive anion (V).<sup>3</sup>

*Hydrazone Chlorides of Type*  $PhC(Cl)=NNR^1R^2$  (VI)—(VIII). The principal peaks in the spectra of the hydrazone chlorides (VI)—(VIII), where  $R^1, R^2$  are  $CH_3, CH_3, CH_3, Ph$ , and  $Ph, Ph$ , respectively, are given in Table 3. The molecular ions are abundant and undergo two general types of reaction, expulsion of a chlorine radical to form hydrazone carbonium ions,  $[M - Cl]^+$ , and cleavage of the hydrazone N–N bond to give

<sup>9</sup> I. T. Barnish and M. S. Gibson, *J. Chem. Soc. (C)*, 1968, 8.

<sup>10</sup> T. Keough, J. H. Beynon, R. G. Cooks, C. Chang, and R. H. Shapiro, *Z. Naturforsch.*, 1974, **29a**, 507.

<sup>11</sup> G. E. Robinson, C. B. Thomas, and J. M. Vernon, *J. Chem. Soc. (B)*, 1971, 1273.

<sup>12</sup> D. H. Williams and I. Howe, 'Principles of Organic Mass Spectrometry,' McGraw-Hill, London, 1972, p. 119; D. G. I. Kingston, D. W. Hobrock, M. M. Bursey, and J. T. Bursey, *Chem. Rev.*, 1975, **75**, 693.

$[R^1R^2N]^+$  ions, base peaks of the spectra. The latter ions may fragment further by loss of hydrogen or a hydrogen molecule to give prominent  $[R^1R^2N - H]^+$  and  $[R^1R^2N - H_2]^+$  ions. Also the  $[M - Cl]^+$  ions decompose by fission of the N-N bond to give  $[R^1R^2N]^+$  ions and the very abundant  $[PhCN]^{++}$  ions.

It is interesting to compare these observations to those made for imidoyl halides ( $R^1CXNR^2$ , X = halogen) where the molecular ions for  $R^1, R^2 = \text{aryl, alkyl}$  are of low abundance or absent, while the  $[M - X]^+$  ions give rise to base peaks of the spectra.<sup>13</sup> Recently, the related

hydrogen transfer from one of the methyl groups to the carboxy-part of the ion and subsequent cleavage of the N-N bond (elimination of  $C_2H_5ClN$ ). In the decomposition of (VII) and (VIII) transfer of a hydrogen atom occurs from the C-phenyl group to the hydrazine part of the ions to give abundant  $[R^1R^2NH]^+$  ions,  $m/e$  107 (40%) and 169 (37%), respectively.

#### EXPERIMENTAL

Mass spectra were recorded on an A.E.I. MS 902 mass spectrometer operating at 70 eV. Samples were introduced

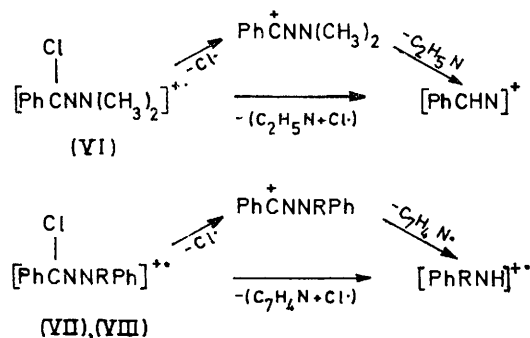
TABLE 3  
The principal peaks <sup>a</sup> in the mass spectra (70 eV) of hydrazonyl chlorides of type  $PhCCl=NNR^1R^2$

Compound	R <sup>1</sup> R <sup>2</sup>		M	[M - Cl]	[M - RCl]	[C <sub>7</sub> H <sub>6</sub> N] m/e 105	[C <sub>8</sub> H <sub>6</sub> N] m/e 104	[PhCN] m/e 103	[R <sup>1</sup> R <sup>2</sup> NH]	[R <sup>1</sup> R <sup>2</sup> N]	[R <sup>1</sup> R <sup>2</sup> N - H]	[R <sup>1</sup> R <sup>2</sup> N - H <sub>2</sub> ]
	R <sup>1</sup>	R <sup>2</sup>										
(VI)	CH <sub>3</sub>	CH <sub>3</sub>	184,182 (23,66)	147 (50)	132 (4)	(4)	(30)	(50)	45 (6)	44 (100)	43 (18)	42 (32)
(VII)	CH <sub>3</sub>	Ph	246,244 (10,30)	209 (10) <sup>b</sup>	194 (2)	(11)	(23)	(90)	107 (40)	106 (100)	m/e 105	m/e 104
(VIII)	Ph	Ph	308,306 (17,49)	271 (12)			(6)	(40)	169 (37)	168 (100)	167 (57)	166 (9)

<sup>a</sup> m/e (rel. int.). <sup>b</sup> [M - HCl], 208 (3).

chloroformamidines  $[R^1NC(X)NR^2R^3]$  were reported also to expel a halogen radical to give  $[M - X]^+$  ions.<sup>14</sup>

Ions corresponding to elimination of  $R^1Cl$  (or  $R^2Cl$ ) from the molecular ions of (VI)—(VIII) are significantly less abundant than the  $[M - HCl]^{++}$  ions of (I). Loss of a methyl radical takes place from the  $[M - Cl]^+$  ions in the spectra of (VI) and (VII) to give the  $[C_8H_8N_2]^{++}$  ion ( $m/e$  132) and the  $m/e$  194 ion, respectively.



R = CH<sub>3</sub>, Ph

The molecular ions and the hydrazonyl carbonium ions ( $[M - Cl]^+$ ) decompose also *via* hydrogen rearrangements to give prominent ions. The abundant  $[C_7H_6N]^+$  ion,  $m/e$  104, in the spectrum of (VI) is formed by a

<sup>13</sup> J. Gal, B. A. Phillips, and R. Smith, *Canad. J. Chem.*, 1973, **51**, 132.

<sup>14</sup> R. Appel, K. Warning, and K.-D. Ziehn, *Chem. Ber.*, 1974, **107**, 698.

<sup>15</sup> P. Wolkoff, *Canad. J. Chem.*, 1975, **53**, 1333.

<sup>16</sup> R. Huisgen, M. Seidel, G. Wallbillich, and H. Knupfer, *Tetrahedron*, 1962, **17**, 3.

by the direct insertion probe, except for (VI) and (VII), which were introduced *via* the glass inlet system. The ion source temperature was 60 (VII) and (VIII), 90 (Id), 100 (Ia and c), 110 (Ib) and (VI), 140 (Ie and g), and 150° (If and h). All reactions (parent ion-daughter ion relationships) discussed have been confirmed either by the presence in the spectra of the appropriate metastable peak or by metastable defocusing.<sup>8</sup> The elemental composition of ions was verified by 'peak matching'.

The hydrazonyl halides were prepared according to literature methods.<sup>15-18</sup> New compounds are *N*-phenyl-*p*-methoxybenzohydrazonyl chloride, m.p. 132—134° (from acetonitrile) (Found: C, 64.5; H, 5.15; N, 10.9.  $C_{14}H_{13}ClN_2O$  requires C, 64.5; H, 5.05; N, 10.75%), and *N*-*p*-methoxyphenylbenzohydrazonyl chloride, m.p. 92—94° (from hexane) (Found: C, 64.45; H, 5.15; N, 10.7%). The *N*-deuteriated [<sup>2</sup>H<sub>1</sub>] analogue of (Ia) was prepared by repeated recrystallizations from 5% D<sub>2</sub>O in acetonitrile. The *C*-[<sup>2</sup>H<sub>5</sub>]phenyl compounds (Ig' and h') were prepared by the procedure given in ref. 15, using [<sup>2</sup>H<sub>5</sub>]benzoyl chloride, which was prepared from [<sup>2</sup>H<sub>5</sub>]benzoic acid and thionyl chloride.<sup>19</sup> [<sup>2</sup>H<sub>5</sub>]Benzoic acid was obtained by oxidation of [<sup>2</sup>H<sub>8</sub>]toluene with KMnO<sub>4</sub>.<sup>20</sup>

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<sup>17</sup> V. V. Kosovtsev, V. N. Christokletov, and A. A. Petrov, *Zhur. obshchei Khim.*, 1971, **41**, 2649.

<sup>18</sup> S. Conde, C. Corral, and R. Madronero, *Tetrahedron*, 1974, **30**, 195.

<sup>19</sup> N. P. Buu-Hoi, N. D. Xuong, A. Beauvillain, and N. V. Bac, *Compt. rend.*, 1962, **255**, 3490.

<sup>20</sup> A. I. Vogel, 'Practical Organic Chemistry,' Longman, London, 3rd edn., 1959, p. 520.