

314. Pyrolysis of Organic Azides: A Mechanistic Study.

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A kinetic examination of the thermal decomposition of phenyl, *p*-methoxyphenyl, and cyclohexyl azides in different media has revealed that there are two distinct mechanistic paths; product studies support the kinetic data. In inert media the process with the higher activation energy has small entropy requirements and is unimolecular, leading to the production of free $R-\dot{N}$ intermediates. That with the lower activation energy has large entropy requirements and occurs in those cases where intermediate triazoline formation and concerted decomposition are possible. Free $R-\dot{N}$ intermediates can abstract hydrogen homolytically from each other or from solvent molecules.

STUDIES of azide decomposition¹ have revealed that there are reactions of several types and these have been classified by Smolinsky² into those in which an intermediate, $R-\dot{N}$, behaves as a diradical, and those in which it exhibits electrophilic properties analogous to those of carbenes. There are several examples (*e.g.*, formation of carbazoles from 2-azido-biphenyls³) in which the action of the intermediate may be of either type, or in which loss of nitrogen is so concerted with ring closure that no discrete intermediate is involved, whilst other reactions (*e.g.*, that between phenyl azide and styrene⁴) involve the formation of an intermediate, isolable, triazoline.

Interest has been taken in this Laboratory in the type of chemical reactivity associated with free radicals of nitrogen, $R_2\dot{N}$; it was felt that the combined evidence of kinetic and product studies of azide decompositions in which the occurrence of concerted reactions was precluded might reveal the nature of radical behaviour in "univalent nitrogen" compounds, $R-\dot{N}$. We have therefore examined the thermal decomposition of phenyl, *p*-methoxyphenyl, and cyclohexyl azides in various solvents. Except for the reactions in indene, which may pass through a triazoline adduct, the kinetic evidence indicates that a species, RN , is first formed, which later undergoes a series of fast reactions such that a complex mixture of products results.

Kinetic Results.—Pyrolysis of azides in the media listed in Table I proceeded, in general, with approximately quantitative evolution of nitrogen and with good first-order rates which were estimated graphically. In decalin an enhanced initial rate was observed for phenyl azide and all the reactions in styrene were complex. The results presented are in most cases average values from duplicate experiments. In ethyl benzoate and cumene the rates of decomposition were shown to be independent of azide concentration over a five-fold range.

The results fall into classes of fast, intermediate, and slow rates, which distinction is further justified by the nature of the products. Thus, azo-compounds and amines result from the slow decompositions in inert media. A complete absence of azo-compounds and production of a single main compound involving the medium characterises reactions in indene. Those cases deemed intermediate in rate yield a mixture of complex products, but no azo-compounds.

The variation of rate with temperature was studied with ethyl benzoate and indene, these being convenient examples of inert and reactive media, respectively. Cyclohexyl azide decomposed at an appreciable rate in inert solvents only at elevated temperatures.

¹ Boyer and Canter, *Chem. Rev.*, 1954, **54**, 35.² Smolinsky, *J. Amer. Chem. Soc.*, 1961, **83**, 2489.³ Smith, Hall, and Carter, *J. Amer. Chem. Soc.* 139th Meeting, Abs., p. 42-O; Smith and Hall, unpublished work.⁴ Wolff, *Annalen*, 1912, **394**, 23, 59.

Solvent	Phenyl	Azide <i>p</i> -Methoxyphenyl	Cyclohexyl
Paraffin (Nujol)	0.66		
Tetralin	0.56		
Cumene	0.69	6.9	
Tetrachloroethylene	0.54		
Decalin	0.72 ^a	8.4	
Benzophenone		8.9	
Et benzoate	0.78	9.1	3.8 ^c
Benzene	1.00 ^b		
Cyclohexane	1.32 ^b		
Aniline	1.41		
Benzyl alcohol		20.0	
Diphenylmethanol		24.3	
<i>trans</i> -Stilbene		45	
Indene	150	166	8.7
Styrene		Fast ^a	

	80·0°	111·3°	117·9°	132·6°	139·3°
Phenyl azide in: Et benzoate	—	—	—	0·78	—
indene	—	26	53	150	185
p-Methoxyphenyl azide in: Et benzoate	—	0·60	1·65	9·1	17·3
indene	(3·3) ^a	33 (32) ^a	69	166	235
Cyclohexyl azide in: Et benzoate			(0·21) ^b		(3·8) ^c
indene		0·80		8·7	

	Medium	Phenyl azide	<i>p</i> -Methoxyphenyl azide	Cyclohexyl azide
Et benzoate: $\Delta E_{\text{Arr.}}$ (kcal./mole) ^a		(39.0) ^c	38.5	47.5
ΔS^\ddagger (cal./deg. mole) ^d ...		(18.7) ^c	19.6	32.2 ^b
Indene: $\Delta E_{\text{Arr.}}$ ^a		23.6	23.2	34.6
ΔS^\ddagger ^d		-4.6	-4.9	17.4

Product Studies.—Phenyl azide decomposes on pyrolysis* in inert solvents to give azobenzene, hydrazobenzene, and aniline together with smaller amounts of benzidine. Our results are in accord with Bertho's observations⁷ although the yield of aniline was found to be much increased. A single product seemed to result from reaction with indene, although it proved unstable and was not characterised; no azo-compounds resulted in this case.

⁷ Bertho, *Ber.*, 1924, 57, 1138.

TABLE 4.

Product yields (per mole of azide consumed).

Phenyl azide in:	Azobenzene	Hydrazobenzene	Aniline
decalin	0.025	0.008	0.79
tetralin			0.63
cumene			0.75
<i>p</i> -Methoxyphenyl azide in:	Azo-cpd. (I)	Phenazine (II)	<i>p</i> -Anisidine
cumene (bicumyl 0.20)	0.15	0.03	0.43
Et benzoate	0.10	0.02	

These products are superficially explained by an azene intermediate, $\text{MeO}\cdot\text{C}_6\text{H}_4\text{-}\dot{\text{N}}\text{:}$, which can either abstract hydrogen from the solvent to yield *p*-anisidine, or can attack another azide molecule to give the observed products which include small amounts of more complex materials with ultraviolet absorption in the benzenoid region and a weaker broad absorption at long wavelength. Although the latter have not been characterised they seem to bear structural relationship to the observed known products (Table 5) (they may

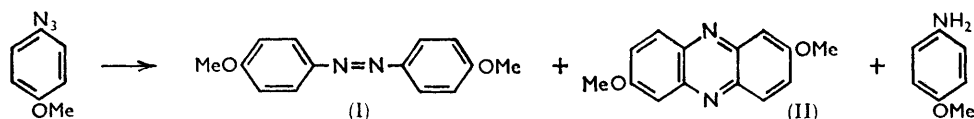


TABLE 5.

Ultraviolet absorption spectra of pyrolysis products of *p*-methoxyphenyl azide.

Product	Yield (%) (in cumene)	$\lambda_{\text{max.}}$ ($E_{1\text{cm.}}^{1\%}$) (in EtOH)
(I)	30	241 (650), 353 (1180), 430 (78)
(II)	6	263 (3750), 344 (141), 410 (368), 422 (392)
M. p. 172—175°	3	266 (244) 473 (92)
M. p. 190—200°	12	265 (525) 553 (136)

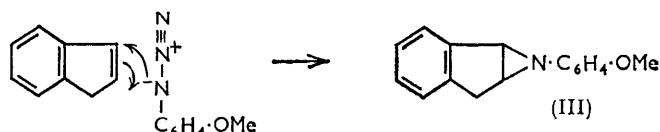
be azine dyes). Together with these products the pyrolysis of *p*-methoxyphenyl azide in cumene yields bicumyl by hydrogen abstraction. The yield of bicumyl accounts for only half of the hydrogen required to form *p*-anisidine; no α -methylstyrene is isolated and the hypothesis that the remaining hydrogen is furnished by *p*-methoxyphenyl azide molecules is supported quantitatively by the yield of coloured products, for, if each molecule of azide which is attacked provides a whole molecule of hydrogen, the measured hydrogen balance would account for their nature.*

Discussion.—The kinetic results indicate that the organic azides can undergo thermal decompositions of two types, (a) slow, with the production of azo-compounds and (b) fast, without azo-compound formation. The former is evidently a unimolecular reaction, $\text{R}\cdot\text{N}_3 \rightarrow \text{R}\cdot\text{N} + \text{N}_2$, whilst the latter may possibly involve triazoline formation or a cyclic transition state structurally similar thereto.

In their fast reactions in styrene and indene, phenyl and *p*-methoxyphenyl azide decompose at almost the same rate, though in the inert solvents the rates differ by a factor of ten. A triazoline intermediate has been isolated⁴ after reaction of phenyl azide and styrene and when further heated this loses nitrogen. In contrast we find that for the decomposition of *p*-methoxyphenyl azide in indene the rate of disappearance of azide from the system is the same as the rate of evolution of nitrogen and we were not able to isolate any intermediate. We suggest, therefore, that this decomposition involves a concerted elimination of nitrogen, giving the aziridine (III). Table 3 indicates that this type of concerted reaction requires 15–20 kcal./mole less activation energy than does the formation of a free $\text{R}\cdot\text{N}\cdot$ intermediate. Also, as would be expected, the entropy requirements

* Hydrogen balance: 0.43 mole of *p*-anisidine requires 0.86 H atom; 0.40 H atom is provided by the solvent in forming bicumyl, 0.06 results from the formation of 0.03 mole of 2,7-dimethoxyphenazine, and the remaining 0.40 is abstracted from the 0.20 mole of azide accounted for by unknown coloured products.

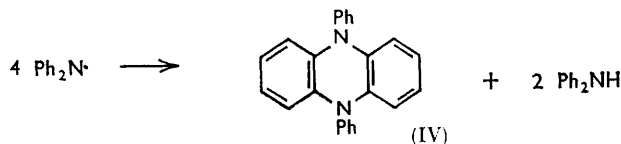
of the highly ordered transition state are much more demanding than those involved in the separation of molecular nitrogen by the unimolecular decomposition of an azide molecule. Supporting evidence comes from the work of Smith and Hall³ on the decomposition of



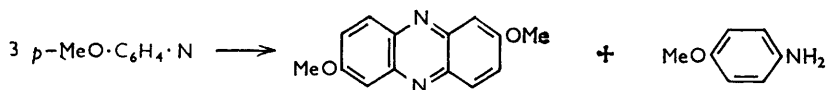
phenyl azide in decalin, for, as Table 3 shows, their figures accord with ours for both the activation energy and the entropy of the slow decomposition. Again their values for the entropies and enthalpies of activation for the decomposition of 2-azidobiphenyls are comparable with our values for azide decomposition in indene. Similarly the entropies of activation given by Saunders and Ware⁸ for the thermal rearrangement of triarylmethyl azides indicate that a considerably ordered transition state is involved, in agreement with these authors' conclusion of aryl participation in the loss of nitrogen.

From the foregoing evidence we suggest that information concerning the nature and chemical reactivity of "univalent nitrogen" intermediates, $R\dot{N}$, should be sought only from studies of slow unimolecular decomposition of organic azides. The present indication is that these intermediates act rather non-specifically in the following ways.

(a) *Hydrogen abstraction.* In a medium prone to lose hydrogen atoms by free-radical attack, *e.g.*, cumene or benzyl alcohol, the type of reaction $R\dot{N} + H-R' \longrightarrow RNH + \cdot R'$ evidently occurs. There is no evidence that $R-\dot{N}:$ will abstract molecular hydrogen, *i.e.*, $R-\dot{N}: + H_2R'' \longrightarrow NH_2R + R''\cdot$; thus decomposition of phenyl azide in cumene gives no α -methylstyrene, and in decalin only a small amount of octalin was detected. $R-\dot{N}:$ also attacks aromatic hydrogen, though perhaps less easily than aliphatic hydrogen, for the isolation of a small percentage of 2,7-dimethoxyphenazine from *p*-methoxyphenyl azide merits comment. Wieland and Fressel⁹ showed that diphenylnitrogen radicals, $Ph_2\dot{N}$, slowly disproportionate, giving diphenylamine and a dark product which, from analytical data alone, they thought was 5,10-dihydro-5,10-diphenylphenazine (IV). The



nature of the latter substance, however, requires reinvestigation, for Waters and Watson¹⁰ have shown that 5,10-dihydrophenazine derivatives are colourless, and Gilman and Dietrich¹¹ have prepared compound (IV) by an unequivocal route and have shown that it is quite different in nature from Wieland's product. Nevertheless Wieland's demonstration that diphenyl radicals abstract hydrogen from aromatic nuclei is significant in relation to the present work which shows that the reaction is one route of stabilisation of the $R-\dot{N}:$ intermediate.



The reactions of $R_2\dot{N}$ and $R-\dot{N}:$ show in both cases one consistent type of chemical reactivity associated with the electron-deficient nitrogen atom. Again homolytic hydrogen

⁸ Saunders and Ware, *J. Amer. Chem. Soc.*, 1958, **80**, 3328.

⁹ Wieland and Fressel, *Annalen*, 1912, **392**, 133.

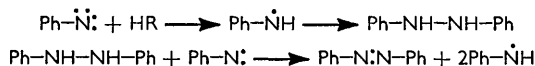
¹⁰ Waters and Watson, *J.*, 1959, 2085.

¹¹ Gilman and Dietrich, *J. Amer. Chem. Soc.*, 1957, **79**, 6178.

abstraction from solvent molecules, commented on above, has also been shown, by Cowley and Waters,¹² to be a typical property of dimethylnitrogen radicals $\text{Me}_2\dot{\text{N}}\cdot$.

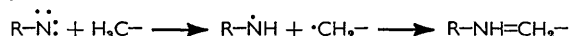
Other free-radical reactions of $\text{R}-\dot{\text{N}}\cdot$ have been described by Heacock and Edmison¹³ who have studied the decomposition of benzenesulphonyl azide and its catalysis of vinylic polymerisation.

(b) *Formation of azo-compounds.* The reaction, $2\text{R}-\dot{\text{N}}\cdot \longrightarrow \text{R}\cdot\text{N}=\text{N}\cdot\text{R}$ appears so obvious a route for the stabilisation of $\text{R}-\dot{\text{N}}\cdot$ intermediates that the small yield of azo-compounds isolated from both phenyl and *p*-methoxyphenyl azide, in comparison with the much higher yields of amines, NH_2R , in the inert solvents decalin and ethyl benzoate (Table 4) is a significant feature of our work. We suggest that the evidence of section (a) above indicates that the $\text{R}-\dot{\text{N}}\cdot$ intermediates, instead of combining directly with each other, nearly all abstract a hydrogen atom from a solvent molecule or from each other, and that both the azo-compound and the complex coloured products result from reactions of $\text{RNH}\cdot$ radicals, *e.g.*:



The hydrazobenzene isolated from the decomposition of phenyl azide is thus visualised as a precursor of the azobenzene, whilst the coloured products may be allied to those complex substances which have been isolated by many workers on homolytic oxidation of aromatic amines.

(c) *Insertion reactions.* These have not been encountered in the present work, but evidently are favoured (50% product yield) if the C-H bond of a methyl group is spatially oriented near the developing $\text{R}-\dot{\text{N}}\cdot$ intermediate of a decomposing azide.¹⁴ They can be viewed as concerted processes involving bond homolysis:



in which the adjacent pair of univalent radicals combines without becoming true "free" radicals.

In contrast to these reactions, which appear to be homolytic in type, there is little evidence that $\text{R}-\dot{\text{N}}\cdot$ intermediates undergo electrophilic substitution or insertion reactions similar to those exhibited by carbenes. The formation of an aziridine from indene is evidently a concerted reaction, whilst the decomposition of *p*-methoxyphenyl azide in *trans*-stilbene (Table 1), which might have led to specificity studies, is again too fast to involve a free $\text{R}-\dot{\text{N}}\cdot$ intermediate.

We therefore concur both with Smolinsky and with Heacock and Edmison that $\text{R}-\dot{\text{N}}\cdot$ intermediates have the chemical characteristics of biradicals with two unpaired electrons.

EXPERIMENTAL

M. p.s were determined on a Kofler block and are corrected.

Materials.—The media employed in pyrolyses were prepared by fractional distillation of commercial products. Cumene was treated with concentrated sulphuric acid before being washed and distilled. Samples of decalin and tetralin were shown to be pure by spectroscopic and vapour-phase chromatographic examination.

Phenyl azide¹⁵ was purified by steam distillation followed by fractionation from a still-pot at $30-35^\circ/10^{-2}$ mm.; it had ν_{max} (in CS_2) 2083 cm^{-1} (ϵ 166).

p-Methoxyphenyl azide was prepared from *p*-anisidine in 51% yield by procedure A of Smith and Brown.^{16a} The product separated as an oil which was extracted with ether, washed

¹² Cowley and Waters, *J.*, 1961, 1228.

¹³ Heacock and Edmison, *J. Amer. Chem. Soc.*, 1960, **82**, 3460.

¹⁴ Smolinsky, *J. Amer. Chem. Soc.*, 1960, **82**, 4717; Barton and Morgan, *Proc. Chem. Soc.*, 1961, 206.

¹⁵ Lindsay and Allen, *Org. Synth.*, Coll. Vol. III, p. 710.

¹⁶ Smith and Brown, *J. Amer. Chem. Soc.*, 1951, **73**, (a) 2438, (b) 2435.

with aqueous sodium carbonate and water, dried (Na_2SO_4), and evaporated, yielding a yellow solid. Recrystallisation from ether-ethanol gave pale yellow plates, m. p. 34–36°, ν_{max} (in CS_2) 2092 cm^{-1} (ϵ 162) (Rupe and von Majewski¹⁷ give m. p. 36°).

Cyclohexyl azide was prepared from cyclohexyl bromide in 53% yield by a method similar to that by which phenethyl azide was obtained.^{16b} The mixture was extracted with ether, and the extract dried (Na_2SO_4) and evaporated. From the residue a colourless oil was obtained by distillation at 20°/10⁻² mm., having n_D^{24} 1.4662 (Boyer *et al.*¹⁸ give n_D^{25} 1.4690).

Samples of azides in various degassed media were pyrolysed in a solvent-jacketed Pyrex tube attached to a nitrometer; a "Teflon" sleeve formed an efficient seal at the hot joint of the tube. Corrections for small portions of the system not at the solvent-jacket temperature were estimated from control experiments. The tendency for material to distil out of the reaction tube was shown to be insignificant by the accuracy of the first-order rate plots. Decompositions above the b. p. of some media were carried out in evacuated break-seal ampoules which were eventually broken into a vacuum-line for nitrogen estimation.

Pyrolysis Products.—Complete product studies were attempted for the decomposition of *p*-methoxyphenyl azide. In assessment of product yields the azide consumed was assumed to be equivalent to the amount of nitrogen evolved; * attempts to estimate azide concentration from the infrared absorption intensity in the region of 2090 cm^{-1} were shown by control experiments to be less accurate except in the slowest reactions. Yields of the corresponding amines were determined by titration of the initial pyrolysed products with 0.01N-perchloric acid in glacial acetic acid with Crystal Violet as indicator. Where actual isolation was carried out the yields of amine agreed closely with the titration values.

Pyrolyses of *p*-methoxyphenyl azide. (a) In cumene. A solution of *p*-methoxyphenyl azide (236 mg.) in cumene (4.21 g.) was heated in the absence of air at 132° for 26 hr. Infrared estimation of the product in cumene revealed the presence of bicumyl (31.5 mg.); 16 mg. of this material were isolated as a sublimate on evaporation of the pyrolysis product. It had m. p. 116–117° and did not depress the melting point of an authentic sample, m. p. 115–116°, prepared by pyrolysis of *t*-butyl peracetate in cumene (Kharasch and Urry¹⁹ give 115°).

The residue obtained on evaporation was passed in benzene down a column of alumina, giving an initial orange band from which 4,4'-dimethoxyazobenzene (I) was isolated as orange needles (57 mg., 30%) (from methanol), m. p. 165–166° (Found: C, 69.2; H, 6.2; N, 11.4. Calc. for $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_2$: C, 69.4; H, 5.8; N, 11.6%), λ_{max} (in EtOH) 241, 353, and 430 $\text{m}\mu$ (ϵ 15,600, 28,500, and 1880). An olive-green band, eluted with benzene-ether, gave 2,7-dimethoxyphenazine (II) (13 mg., 6%), m. p. 250–251°, pale yellow needles from methanol (Found: N, 11.4. Calc. for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_2$: N, 11.5%), λ_{max} (in EtOH) 263, 344, 410, and 422 $\text{m}\mu$ (ϵ 91,000, 7400, 9000, and 9600). This product showed no depression of m. p. on admixture with an authentic sample, m. p. 250–251°, prepared by the method of Yoshioka²⁰ who gives m. p. 246°. Smaller amounts of several coloured products were eluted from the column but none of these was characterised. In particular a red solid was obtained (7 mg.), having m. p. 172–175°, λ_{max} (in EtOH) 266 and 473 $\text{m}\mu$ ($E_{1\text{cm}}^{1\%}$ 244 and 92). The last fraction to leave the column required elution with 1 : 49 methanol-ether; it was *p*-anisidine (85 mg., 43%), m. p. and mixed m. p. 56°. A purple band remained strongly attached at the top of the column; by Soxhlet extraction with methanol a blue solid resulted (27 mg.), having m. p. 190–200°, λ_{max} (in EtOH) 265 and 553 $\text{m}\mu$ ($E_{1\text{cm}}^{1\%}$ 525 and 136).

(b) In ethyl benzoate. The azide (1.03 g.) in ethyl benzoate (6.16 g.) was heated in the absence of air at 132° for 20 hr. The mixture was evaporated at 100°/10⁻² mm. and the residue chromatographed in benzene solution. First to be eluted was an orange band, giving 4,4'-dimethoxyazobenzene (163 mg., 20%), as orange needles, m. p. 164–165°; then ether removed 2,7-dimethoxyphenazine (38 mg., 4%), m. p. 250°. Several other coloured bands gave products similar to those observed in experiment (a).

(c) In benzyl alcohol. The azide (195 mg.) in benzyl alcohol (5.71 g.) was heated in the absence of air at 132° for 5 hr. The product was steam-distilled and the distillate treated

* Thermal decomposition in indene produced a 91–96% yield of nitrogen from phenyl azide, and 95–100% from *p*-methoxyphenyl azide (cf. Smith and Hall²).

¹⁷ Rupe and von Majewski, *Ber.*, 1900, **33**, 3405.

¹⁸ Boyer, Canter, Hamer, and Putney, *J. Amer. Chem. Soc.*, 1956, **78**, 325.

¹⁹ Kharasch and Urry, *J. Org. Chem.*, 1945, **10**, 401.

²⁰ Yoshioka, *Pharm. Bull. Japan*, 1953, **1**, 66.

with Brady's reagent under controlled conditions, giving benzaldehyde 2,4-dinitrophenylhydrazone (187 mg., 50%), m. p. 237°. Chromatographic examination of the residue from steam-distillation gave only unstable oils.

(d) In indene. A solution of *p*-methoxyphenyl azide (1.89 g.) in indene (5 ml.) was heated at 130° for 2 hr. The product was evaporated at 100°/10⁻² mm.; the residue, when triturated with ether, gave a white solid (1.55 g.) which by sublimation gave needles of 1,1a,7,7a-tetrahydro-1-*p*-methoxyphenylindano[1,2-*b*]aziridine (III) (1.36 g., 45%), m. p. 147—148° (Found: C, 80.9, 80.9; H, 6.2, 6.4; N, 6.3, 6.3%; *M*, 251. C₁₆H₁₅NO requires C, 81.0; H, 6.4; N, 5.9%; *M*, 237), λ_{max} (in EtOH) 238 and 290 mμ (ε 15,000 and 1850), ν_{max} (in CS₂) 2850s, 1950w, 1370m, 1240m, 1114s, 930m, 830m, and 740m cm.⁻¹. Nuclear magnetic resonance spectrum: tetramethylsilane was added to a solution of the compound in chloroform; τ 6.88 p.p.m. (4 aliphatic protons), 6.23 (3 MeO), 3.12 (4 Ph); the phenyl-protons of the indenyl ring were obscured by solvent.

The compound (III) (60 mg.) was treated with 50% hydrochloric acid (10 ml.) at 95° for 3 hr. The neutral and the basic fraction were separated, giving *p*-anisidine (20 mg., 65%), m. p. and mixed m. p. 59°, and indan-2-one (10 mg., 31%), m. p. 58° alone or mixed with a sample prepared as described by Pfeiffer²¹ [m. p. 56—57°, λ_{max} (in EtOH) 268 and 275 mμ (ε 1190 and 1320), ν_{max} (in CCl₄) 1740 cm.⁻¹].

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²¹ Pfeiffer, *J. prakt. Chem.*, 1941, **158**, 315.