1144. *The Rearrangement of Aromatic* N-*Nitroamines. Part IV.*[1] *The Intramolecularity of the Acid-catalysed Rearrangements of* N-*Nitro-1-naphthylamine and its* N-*Methyl Homologue*

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The acid-catalysed rearrangements of the above-mentioned compounds have been studied at various acidities in the presence of ^{15}N-labelled nitric and nitrous acids. The rearrangement products contained no detectable tracer. These observations, together with the results of experiments with added scavengers, exclude mechanisms involving fission to ionic or radical species followed by intermolecular recombination of the counter-fragments.

THE formation of *C*-nitro-products from the acid-promoted rearrangement of *N*-nitroarylamines is generally considered to be intramolecular,[1-4] but few substrates have been adequately studied over a range of reaction conditions, and in one example an intermolecular component of rearrangement has been claimed.[5] Various methods can give information on this point, but each has its limitations if taken as an isolated criterion.

We have studied the rearrangements of *N*-methyl-*N*-nitro-1-naphthylamine and *N*-nitro-1-naphthylamine, using a combination of methods to enable a decision concerning the intra- or inter-molecularity to be reached. Analogies with previous work[1,5] suggest that intermolecular mechanisms may be especially favoured for these substrates.

RESULTS

Tracer Experiments.—Reactions were carried out in the presence of ^{15}N-labelled nitric and nitrous acids at different acidities. The only rearrangement products were the 2- and 4-nitro-derivatives, and a dinitro-derivative under one set of conditions. These products were isolated, purified, and examined for tracer-uptake by mass spectrometry. Results are in the Table. The error in the abundance measurements was $\pm 0{\cdot}10$ in the units quoted for experiments 1—3, and $\pm 0{\cdot}15$ for experiment 4.

Attempts to simulate the condition of experiment 1 failed for *N*-nitro-1-naphthylamine; rearrangement was negligible but much tar was formed. This seems a characteristic fate if

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[1] Part III, D. V. Banthorpe, E. D. Hughes, and D. L. H. Williams, *J.*, 1964, 5349.
[2] E. D. Hughes and G. T. Jones, *J.*, 1950, 2678.
[3] S. Brownstein, C. A. Bunton, and E. D. Hughes, *J.*, 1958, 4354.
[4] B. A. Geller and L. N. Dubrova, *Zhur. obshchei Khim.*, 1960, **30**, 2646.
[5] W. N. White *et al.*, *Chem. and Ind.*, 1962, 138; *J. Amer. Chem. Soc.*, 1964, **86**, 1517.

Tracer content of rearrangement products

(*a*) *N*-Methyl-*N*-nitro-1-naphthylamine (concn. 0·1M)

Expt.	Solvent	Tracer *	Abundance † isotopically normal 2-isomer	Abundance † isotopically normal 4-isomer	Abundance from rearrangement 2-isomer	Abundance from rearrangement 4-isomer
1	70% H_2SO_4–H_2O (w/w)	0·6N-HNO_3	13·17	13·30	13·24	20·70 ‡
2	85% ,,	0·02N-$NaNO_2$	12·82	12·81	12·82	12·80
3	3·25M aq.$HClO_4$ in 60% dioxan	0·02N-$NaNO_2$	12·85	12·81	12·82	12·90
	(*b*) *N*-Nitro-1-naphthylamine (concn. 0·076M)					
4	70% H_2SO_4–H_2O (w/w)	0·02N-$NaNO_2$	12·14	12·14	11·95	12·37

* The tracer contained 7·9% atoms excess of ^{15}N in all cases. † The abundance is calculated as $(p + 1)\ 100/p$, *i.e.*, the ratio of the ion-currents from the " parent-plus-one " peak and the parent peak in the mass spectrum, expressed as a percentage. The calculated values for the natural abundances in the two substrates are 12·89% and 11·78%, respectively. Deviation of the observed values for the " isotopically normal " substances (which were obtained from a rearrangement carried out in the absence of tracer) from these are due to instrumental fluctuations; but such deviations are constant for each compared pair of values. Such deviations have not been corrected, for they are immaterial when no tracer uptake is observed. ‡ Refers to a dinitro-compound; see text.

primary *N*-nitroarylamines[2, 3] are treated with nitrate ion in strongly acidic media, and is probably due to *N*-nitration and subsequent decomposition. A low concentration of nitrous acid was used in experiments 2—4 in order to minimise any reaction with the substrate; under the actual conditions, this, and nitrosation of the rearrangement products, were shown to be negligible.

In experiment 1 the 2-nitro-isomer was isolated, but also two compounds were obtained which could not be separated chromatographically. Mass-spectrometry indicated a mixture of a mononitro-compound (shown to be the 4-isomer by paper chromatography) and a dinitro-derivative, probably the 2,5-isomer. Only one nitro-group of the latter compound contained tracer (see Experimental section), and the uptake (7·5%) corresponded closely to the ^{15}N abundance in solution (7·9%). Thus, one nitro-group of the dinitro-derivative results from an intramolecular rearrangement and the other derives from labelled nitrate ion in solution (and a small isotope-effect in nitration is perhaps observed).

Experiments 2 and 3 show no detectable tracer uptake, and, although the results obtained from experiment 4 are more erratic, the differences for the results from the tracer experiments are probably not significant when compared with the controls. The analytical method would have detected tracer if more than 2% (expt. 1), 12% (expts. 2 and 3), or 20% (expt. 4) of the reaction leading to either product had been intramolecular. These calculations assume complete equilibration of the fission-group and the added tracer (see Discussion). The mass spectometer used did not possess a double-collector, and these limits are governed by the accuracy of the abundance measurements. However, this shortcoming was counteracted by the location of each peak under very high resolution, before measurement of the ion-current due to it, and thus any contributions to the ion-current by impurities of the same mass number as that of the peak to be measured were completely eliminated.

Cross-nitration Experiments.—The *N*-methyl compound was rearranged in 2·6M-perchloric acid with 60% dioxan–water (w/w) as solvent and in the presence of equimolar amounts of aniline and anisole. Less than 1%, if any, products of cross-nitration, emeraldine-type compounds, or *N*-methyl-1-naphthylamine could be detected by paper chromatography. The topography of the ultraviolet spectra in 95% ethanol–water in the range 350—600 mμ also indicated the absence of these products, and the product proportions (73%, 2 isomer; 27%, 4-isomer; both ±2%) were not changed in the presence of these additives. Similar results were found in 9M-perchloric acid and in 70% (w/w) sulphuric acid–water. In 98% (w/w) sulphuric acid–water, the substrate mainly decomposed to unidentified products, but again no cross-nitration of the above additives could be detected.

Attempted Nitration under Rearrangement Conditions.—*N*-Methyl-1-naphthylamine nitrate was treated with 10·5M- and 7·8M-sulphuric acid, 9·7M-perchloric acid, and 11·9M-hydrochloric acid under conditions of temperature, etc., such as used in the rearrangement of the corresponding N-nitroamine; 1-naphthylamine nitrate was similarly reacted with 18M-, 10M-, and 5M-sulphuric acid. Much tar, but negligible quantities of *C*-nitroamines were obtained in all experiments, although the corresponding acid treatment of the *N*-nitroamines had given over 80% recoveries of these products.

Treatment of *N*-methyl-1-naphthylamine and 1-naphthylamine with sodium nitrite or nitrogen dioxide at various acidities also gave negligible amounts of *C*-nitroamines.

DISCUSSION

Three modes of fission of the protonated substrate could lead to an intermolecular component of reaction. These give the species shown in (a)—(c), which could recombine intermolecularly to form *C*-nitroamines. In addition, the presence of reducing agents could

$$\begin{array}{cccc} \text{Ar–NHR} + \text{NO}_2^{+} & \text{Ar–N}\overset{++}{\text{H}}\text{R} + \text{NO}_2^{-} & \text{Ar–N}\overset{+\bullet}{\text{H}}\text{R} + \text{NO}_2^{\bullet} & \text{Ar–NHR} + \text{N}\dot{\text{O}}_2 \\ \text{(a)} & \text{(b)} & \text{(c)} & \text{(d)} \end{array}$$

lead to the co-existence of species (d). Such possibilities have been previously considered [1,5] and we have given reasons for preferring the route leading to (b).

Our tracer results indicate that the reactions which we studied were either intramolecular or were intermolecular but the nitrating fission-fragment did not equilibrate with the added tracer, *i.e.*, this fragment reacted with its counter-species before it reacted with the solvent or the tracer-carrier. Previously no tracer-uptake into products has been detected using our technique,[1,3] but it has been suggested [5] that equilibration of tracer with all possible fission species did not occur under the conditions used.

If route (a) was employed in our experiments, nitronium ion would have reacted with both the tracer-carriers (mainly NO_3^- in expt. 1 and NO_2^- in expt. 3] and with its aromatic counter-species at the encounter-rate; [6,7] but the former would be present in much greater concentration, especially at the higher acidity. Also, reaction with the solvent would probably occur rather than reaction with the small concentration of free base, despite the much greater reactivity of the latter.[8] Thus any nitro-group introduced intermolecularly at both high and low acidities would have largely originated from N_2O_5, N_2O_4, or $H_2NO_3^+$, and spreading of treacer into the rearrangement products would have resulted. Experiments 2 and 4 would also probably have resulted in tracer uptake if route (a) was utilised, for the nitronium ion would rapidly react with nitrite ion derived from the added tracer-containing material which now would be mainly present as NO^+. The purpose of these two experiments was mainly to give information on the occurrence of route (b).

If route (b) were employed, the freshly generated nitrite ion would immediately be protonated and could scramble with the tracer contained in the nitrite ion of experiment 3. At the higher acidities of expts. 1, 2, and 4, it would react with the tracer-containing entities NO_2^+ and NO^+ rather than its counter-fragment for the reasons described above, or it would be converted into NO^+ or N_2O_3 and again equilibrate with added tracer.

Thus, our experiments rule out routes (a) and (b), but the situation with respect to routes (c) and (d) is less clear. We can not confidently state that nitrogen dioxide would dimerise or react with the solvent and so scramble with the added tracer before reacting with its counter-fragment; although such equilibration is reasonable in view of the low concentration (but high reactivity) of the counter-fragment. The results given under " Cross-nitration experiments " (above) are applicable here, however. Scavengers would probably react with fission products on encounter, and because of their large concentration would remove the latter before recombination to rearrangement products could occur. Thus, the lack of cross-nitration products or other interference with the reaction over the entire acidity range excludes intermolecular processes by routes (a), (c), or (d). Any mechanisms involving nitration of an amine (formed by disproportionation) by a protonated substrate molecule are also excluded.

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[6] N. C. Deno and R. Stein, *J. Amer. Chem. Soc.*, 1956, **78**, 578.

[7] R. P. Bell and E. N. Ramsden, *J.*, 1958, 161.

[8] C. A. Bunton and G. Stedman, *J.*, 1958, 2420, 4357, 4366.

The formation of cross-nitration products in this type of experiment is not unique evidence for intermolecularity.[9] The scavenger could react with the substrate, with an intermediate of an intramolecular rearrangement process, or with fission-products accompanying, but quite unrelated to, the rearrangement. In fact, the substrate has always contained several strongly electron-withdrawing substituents in the reported examples where cross-nitration occurred,[2,10] and these would favour a direct nitration of the scavenger.

In the experiments of the third section of Results, attempts were made to generate the fission products of routes (a) and (d). The lack of rearrangement products is evidence against the occurrence of these routes.

Thus, both our substrates rearrange intramolecularly within the previously stated limits over the whole acidity range studied, a conclusion similar to that drawn for *N*-nitroaniline after less extensive studies [1,3] and for various other *N*-nitroamines on much less compelling evidence.[11] The rearrangement of *N*-methyl-*N*-nitroaniline has been claimed to be partly intermolecular.[5] When ^{15}N-labelled *p*-fluoro-*N*-methyl-*N*-nitroaniline and isotopically normal *N*-methyl-*N*-nitroaniline were rearranged concurrently, the isolated *p*-nitro-*N*-methylaniline was found to contain tracer. The formation of the labelled rearrangement product could have arisen from nitrosation (perhaps by a Fischer–Hepp rearrangement) of the *N*-methylaniline by free nitrous acid and subsequent oxidation (both species were shown to be formed during this rearrangement in contrast to the small quantities with our substrates) rather than by intermolecular processes involving route (c) as was supposed. Alternatively, the labelled product might have been formed intramolecularly by ejection of fluorine (such ejections are well authenticated for halogen-substituted *N*-nitroanilines),[12] or the *p*-fluoro-*N*-methyl-*N*-nitroaniline could have directly nitrated *N*-methylaniline as discussed above. Without further study, this example cannot be firmly claimed as an intermolecular rearrangement progressing through fission fragments of the types considered at the head of this section.

EXPERIMENTAL

Preparations.—Previously described preparations of both substrates [13-15] gave very low yields of impure products. Reaction of the respective amine with potassium alkoxide and ethyl nitrate, a method successful for *N*-nitroaniline,[1] also failed here; when the stronger base butyl-lithium was used [16] good yields of products were obtained.

N-*Methyl*-N-*nitro*-1-*naphthylamine*. *N*-Methyl-1-naphthylamine was prepared from sodium 1-naphthoate and methylamine hydrochloride as previously described for the 2-isomer; [17] yield 48%, b. p. 248°. A solution of this (18·5 g.) in sodium-dried ether (50 ml.) was treated dropwise at −78° under nitrogen with an equimolecular quantity of butyl-lithium in ether during about 30 min., and then ethyl nitrate (10 g.) in ether (50 ml.) was added during 15 min. The mixture was allowed to come to room temperature for 3 hr., and the washed ethereal layer was dried and evaporated, to give a dark paste which was extracted about 10 times with portions (50 ml.) of boiling light petroleum (b. p. 40—60°). When the extract was cooled to −78°, a buff-coloured precipitate of the *N*-nitroamine was thrown down. Yield 60%; decomp. 72—73° on Kofler hot-stage apparatus (lit.,[13] 54—55°) (Found: C, 65·0; H, 5·3; N, 13·8. Calc. for $C_{11}H_{10}N_2O_2$: C, 65·4; H, 5·0; N, 13·9%).

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[9] M. J. S. Dewar in de Mayo, "Molecular Rearrangements," Academic Press, New York, 1963, vol. I, 295.

[10] K. J. P. Orton, *J.*, 1902, **81**, 490, 965; 1905, **87**, 389; 1907, **91**, 146.

[11] K. J. P. Orton and A. E. Bradfield, *J.*, 1929, 915.

[12] K. J. P. Orton and C. Pearson, *J.*, 1908, **93**, 725.

[13] E. Bamberger, *Ber.*, 1922, **55**, 3383.

[14] G. S. Salyamon, I. V. Grachev, and B. A. Porai-Koshits, *Sbornik statei obshchei Khim.*, 1953, **2**, 1315 (*Chem. Abs.*, 1955, **49**, 4554).

[15] E. Bamberger *et al.*, *Ber.*, 1894, **27**, 679; 1920, **53**, 2321; *J. prakt. Chem.*, 1922, **105**, 266.

[16] W. N. White, E. F. Wolfarth, J. R. Klink, J. Kinig, C. Hathaway, and D. Lazdins, *J. Org. Chem.*, 1961, **26**, 4124.

[17] W. J. Hickinbotham, "Reactions of Organic Compounds," 2nd edn., Longmans, London, 1948, p. 300.

N-*Nitro*-1-*naphthylamine*. An ethereal suspension of the lithium salt of *N*-nitro-1-naphthylamine was prepared in a manner analogous to that described above. Ether was evaporated off and the paste was extracted with 20% potassium chloride solution and light petroleum (b.p. 120°), concentrated, the pH adjusted to 7·0, and a two-fold excess of saturated barium chloride solution added to precipitate the barium salt on leaving overnight (65% yield; purity 95% based on elemental analysis). This salt (20 g.) was shaken with a two-fold excess of Amberlite IR-120(Na^+) resin (*ca.* 23 g.) in water (100 ml.) until it dissolved, and the supernatent was evaporated below 30° on a rotary evaporator to give the light yellow *sodium salt* of the *N*-nitroamine (yield based on 1-naphthylamine, 50%), decomp. 120°. Salts of *N*-nitroamines are known to be tenaciously hydrated,[18] and this salt was recovered as a hydrate even after solution in alcohol and reprecipitation with ether [Found: C, 46·5; H, 4·4; N, 10·7; H_2O, 17·0 (by Karl Fischer determination). $C_{10}H_7N_2O_2Na2{\cdot}5H_2O$ requires C, 47·1; H, 4·7; N, 11·0; H_2O, 17·0%]. In additional support of this formulation it was shown that the infrared spectrum exhibited an intense band assigned to a OH vibration, which disappeared and was replaced by an OD vibration when the salt was dissolved in a large excess of deuterium oxide, left to equilibrate for two days, and then recovered. Dehydration was not attempted because of the instability of the compound.

Attempts to prepare *N*-nitro-1-naphthylamine by cautious acidification of a solution of the sodium salt under a variety of conditions, or by treatment with suspensions of Amberlite IRA-120(H^+) or IRC-50(H^+) resins gave tars and rearrangement products. Passage of carbon dioxide through a solution of the barium salt (1 g.) in a mixture of dioxan (50 ml.) and water (2 ml.) for 1 hr., extraction with ether, evaporation, extraction with light petroleum (b. p. 40—60°), and cooling of the extract to −78° gave white crystals of N-*nitro*-1-*naphthylamine* (Found: C, 63·9; H, 4·3. $C_{10}H_8N_2O_2$ requires C, 63·6; H, 5·4%), m. p. 53° (lit.,[13] 124°).* This decomposed to tar within 24 hr., presumably owing to intermolecular proton-transfer catalysing various decompositions in the solid state; the sodium salt was thus used in all experiments.

N-*Methyl*-1-*naphthylamine nitrate*. The amine (5 g.) was dissolved in alcohol-free chloroform (25 ml.), and absolute nitric acid (1·3 g.) was added dropwise at −5°. The precipitate (*ca.* 90% yield) was washed with chloroform and ether and was 95% pure *amine nitrate*, as indicated by elemental analysis. Recrystallisation from chloroform and ethanol mixtures caused decomposition. 1-*Naphthylamine nitrate* was prepared similarly but in a good state of purity (Found: C, 57·6; H, 4·9; N, 13·7. $C_{10}H_{10}N_2O_3$ requires C, 58·3; H, 4·9; N, 13·6%).

Products of Rearrangement.—2-Nitro-*N*-methyl-1-naphthylamine was obtained as a red solid, m. p. 112—113° (lit., 113—114°) (Found: C, 64·8; H, 5·0; N, 13·6. Calc. for $C_{11}H_{10}N_2O_2$: C, 65·3; H, 5·0; N, 13·9%), from chromatography of the rearrangement mixture on alumina (see below). All the nitro-isomers of *N*-methyl-1-naphthylamine have not been characterised, and this compound was identified by conversion into 2-nitro-1-naphthol by refluxing with 10N-potassium hydroxide for 5 hr. 4-Nitro-*N*-methyl-1-naphthylamine was isolated as an orange solid, m. p. 184—185° (lit., 184—185°), and its infrared spectrum was identical with that of the compound synthesised by heating 1-chloro-4-nitronaphthalene [19] with a five-molar excess of methylamine in alcohol in a sealed tube at 140—145° for 5 hr. Attempts to prepare the 2- and 4-nitro-isomers by nitration of the acetyl or benzoyl derivatives of *N*-methyl-1-naphthylamine,[20] by reaction of 1- and 2-nitronaphthalenes with *N*-methylhydroxylamine (in a manner analogous to the known reaction with hydroxylamine [21]), and treatment of 2- or 4-nitro-1-naphthols with ammonia in sealed tubes,[22] gave little or none of the desired products. A reported synthesis [23] of 2-nitro-1-naphthol by reaction of 1-naphthylamine with nitrous fumes could not be repeated. 2-Nitro-1-naphthylamine was isolated similarly from a large-scale product-analysis, m. p. 136—138° (lit., 144°) (Found: C, 63·6; H, 4·6; N, 14·3. Calc. for $C_{10}H_8N_2O_2$: C, 63·8; H, 4·3; N, 14·9%). Its infrared spectrum was identical with that of a specimen prepared by a independent route in 25% yield,[24] which had m. p. 143°. After

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* Bamberger's preparation may well have mainly consisted of rearrangement products.

[18] K. J. P. Orton, *J.*, 1902, **81**, 806.
[19] H. H. Hodgson and J. Walker, *J.*, 1933, 1620.
[20] H. H. Hodgson and J. Walker, *J.*, 1933, 1025; 1934, 180.
[21] C. C. Price and S. Voong, *Org. Synth.*, 1948, **28**, 80.
[22] N. L. Drake, *Org. Reactions*, 1942, **1**, 105.
[23] P. S. Varma and P. V. Krishnamurthy, *Quart. J. Indian Chem. Soc.*, 1926, **3**, 323.
[24] E. R. Ward and B. D. Pearson, *J.*, 1959, 3378.

chromatography on alumina with ether, 4-nitro-1-naphthylamine was similarly obtained, m. p. 195—196° (lit., 196°) and its infrared spectrum was identical with that of an authentic specimen.

Tracer Experiments.—Reaction times of about ½ hr. were taken for experiments involving concentrated acids, and about 24 hr. for the 3M aqueous perchloric acid. The substrate (0·2 g.) in the acid (12 ml.) containing the tracer was rearranged and the solution diluted with ice-water (300 ml.) and neutralised below 10° with 10N-sodium hydroxide. The low temperature was necessary to prevent the formation of nitro-naphthols;[25] the alkali was run slowly down the side of the beaker into the vigorously stirred, cooled solution. Dropwise addition caused local heating and considerable loss of nitroamine. The solution was extracted five times with portions of chloroform (20 ml.), and the dried extract concentrated to about 12 ml. and chromatographed on alumina. For the rearrangements involving *N*-methyl-*N*-nitro-1-naphthylamine the chromatogram was developed with a mixture of 3 parts of ether and 7 parts of benzene; the 2-nitro-compound was eluted first and was recrystallised from light petroleum (b. p. 40—60°), and the 4-nitro-compound and the dinitro-compound (if present) followed. Several minor bands remained on the column.

Samples (*ca.* 1 mg.) of these products were analysed for tracer on an AEI MS9 mass spectrometer. The inlet temperature was 220—260°, and the parent and parent-plus-one peaks were located under high resolution before the ion-currents were measured, in order to prevent interference by any impurities of the same mass number that may have been present. In the study of the mixture of the 4-nitro- and dinitro-compounds, the ion-currents at mass numbers 247, 248, and 249 (P, P + 1, and P + 2) indicated that the composition of the dinitro-derivatives was: $C_{11}H_9NO_4{}^{14}N^{14}N$, 92·6%; $C_{11}H_9NO_4{}^{15}N^{14}N$, 7·4%; $C_{11}H_9NO_4{}^{15}N^{15}N$, 0%.

A similar procedure was adopted with the rearrangement products from *N*-nitro-1-naphthylamine. The reaction was now more complex. A separation of the 2- and 4-nitro-isomers from four or five other products could not be achieved on chromatography with the ether–benzene mixture, and the unresolved bands containing these isomers had to be eluted and rechromatographed with ether and with ethyl acetate, respectively, in order to obtain pure products.

Other Experiments.—The cross-nitration experiments were carried out in the presence of equimolecular quantities of anisole or aniline. The products were separated as previously described and chromatographed on Whatman No. 4 paper which had been soaked in 10% formamide–ethanol for 3 days and then air-dried. The paper was eluted 5 times with ether so that the solvent front advanced about 5 cm. each time, in order to elevate the nitro-compounds to the position of the solvent front and leave tar, etc., on the base line; the paper was then dried and eluted with light petroleum (b. p. 40—60°). Blank experiments showed that this procedure gave a good separation of the rearrangement products and the *o*- and *p*-nitroanilines and nitroanisoles. The latter compounds formed very faint spots, and so the constancy of the products of rearrangement in the presence or absence of anisole was a better criterion for the lack of any cross-nitration than the presence of nitroanisoles on the chromatogram. The *C*-nitro-compounds appeared as yellow spots, any unreacted *N*-nitroamine formed a yellow spot on spraying with dilute acid and alkali in turn, and any *N*-methyl-1-naphthylamine or amine nitrates were detected by diazotisation and coupling.[26] The experiments involving 1-naphthylamine were carried out similarly.

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[26] M. C. Večera, J. Petranek, and J. Gasparič, *Coll. Czech. Chem. Comm.*, 1957, **22**, 1603.