194. *Nitramines and Nitramides. Part X.* The Formation of Alkyl Cations during Acid-catalysed Decomposition : Evidence from* (+)-sec.-*Butylnitramine and* O-*Methyl*-N-neo*pentylnitramine.*

By PETER BRUCK, I. N. DENTON, and ALEX. H. LAMBERTON.

(+)-*sec.*-Butylnitramine has been prepared : on decomposition in aqueous mineral acids the optical activity was almost wholly destroyed. A similar decomposition of *O*-methyl-*N*-*neo*pentylnitramine, in the presence of an oxidising agent, yielded a solution from which acetone—an oxidation product of *tert.*-pentyl alcohol—was isolated as the 2 : 4-dinitrophenylhydrazone.

The resolution of *sec.*-butylamine is improved.

IN earlier papers [1,2] of this series the production of alkyl cations during acid-catalysed decomposition of primary nitramines, and of *ON*-dialkylnitramines, has been postulated mainly on the evidence of the formation of alkyl chlorides. Whilst formation of alkyl chlorides shows that at least some alkyl cations have been produced, non-formation of the chlorides does not disprove production of the cations. Two factors are involved in the formation of RCl from $R{\cdot}NH{\cdot}NO_2$: the production of R^+, and its behaviour in its natal environment. It was therefore decided to apply standard methods for the recognition of alkyl cations to the decomposition of two suitable nitramines. In both cases the results were positive, though by the test of halide formation *sec.*-butylnitramine and *O*-methyl-*N*-*neo*pentylnitramine had given little or no indication of ion formation.

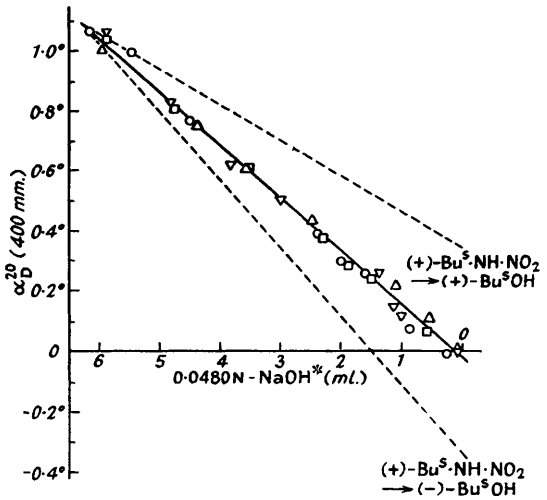
When (+)-*sec.*-butylnitramine was heated in dilute hydrochloric or sulphuric acid the observed rotation fell and, within experimental error, the fall in rotation and the fall in acidity (due to the removal of $Bu^s{\cdot}NH{\cdot}NO_2$) were concurrent. The final values of observed rotation were close to zero, with a slight bias (confirmed by a later experiment) in favour

* Part IX, *J.*, 1955, 3997.

[1] Barrott, Denton, and Lamberton, *J.*, 1953, 1998.
[2] Bruck and Lamberton, *J.*, 1955, 3997.

of negative rotation. The results are best exhibited graphically: the Figure shows a plot of observed rotations against volumes of standard alkali. The broken lines indicate the rotations which would have resulted from the conversion of active *sec.*-butylnitramine into active forms of *sec.*-butyl alcohol, and control experiments have shown that racemisation and volatilisation of *sec.*-butyl alcohol would be unlikely to give a loss of more than 0·03° (runs I—III) or 0·10° (run IV) in optical activity. In a recent paper [3] oxygen exchange and racemisation of *sec.*-butyl alcohol have been correlated on the basis of the incipient formation of a carbonium ion, which reacts with a water molecule before the shielding influence of the original oxygen atom has been withdrawn. Though the nitramine decomposition is presumably similar in some respects, it differs in that the remainder of the molecule has apparently little shielding effect upon the butyl cation.

Relation between rotation and acidity during decomposition of (+)-sec.-*butylnitramine at* 84°.



△ *Run* I: 592 *mg. of nitramine and* 50 *ml. of* 0·1027M-HCl.
▽ *Run* II: 595 *mg. of nitramine and* 50 *ml. of* 0·1027M-HCl.
□ *Run* III: 594 *mg. of nitramine and* 50 *ml. of* 0·099M-H_2SO_4.
○ *Run* IV: 593 *mg. of nitramine and* 50 *ml. of* 0·01M-H_2SO_4.

* The volume of sodium hydroxide is the excess in titre of a 3 ml. aliquot portion over the titre (of 3 ml.) of the acid used to make up the solution. (As the presence of decomposition products must very slightly lower the concentration of the acid, the final value, at complete decomposition, can be negative on this scale—if the solution has not been concentrated by evaporation. The final values were expected to be between zero and −0·1 ml.; and the lines have been drawn to terminate at −0·05 ml.)

The *neo*pentyl cation, if formed in the decomposition of *O*-methyl-*N*-*neo*pentylnitramine, will rearrange and yield *tert.*-pentyl alcohol by reaction with water. To distinguish *tert.*-pentyl alcohol from *neo*pentyl alcohol in dilute aqueous solution would be difficult: instead, *O*-methyl-*N*-*neo*pentylnitramine was decomposed by 20% sulphuric acid in the presence of dichromate as an oxidising agent. After removal of the excess of oxidant, acetone was isolated as the 2 : 4-dinitrophenylhydrazone. Acetone is a known product of the dichromate oxidation of *tert.*-pentyl alcohol,[4] whilst oxidation of *neo*pentyl alcohol yields trimethylacetaldehyde, trimethylacetic acid, and methyl *iso*propyl ketone.[5] The methylbutenes ($Me_2C{:}CHMe$ and $CH_2{:}CEtMe$) derived from the rearranged cation could act as sources of acetone and of other carbonyl compounds, but not of those materials typical of the oxidation of *neo*pentyl alcohol.

[3] Bunton, Konasiewicz, and Llewellyn, *J.*, 1955, 604.
[4] Wischnegradski, *Annalen*, 1878, **190**, 355.
[5] Samec, *ibid.*, 1907, **351**, 256; Daniloff and Danilova, *Ber.*, 1926, **59**, 377; Conant, Webb, and Mendum, *J. Amer. Chem. Soc.*, 1929, **51**, 1246; Takagi and Sakaguti, *J. Pharm Soc. Japan*, 1938, **58**, 701.

Experimental

Resolution of sec.-*Butylamine*: *Method of Polarimetric Control.*—Like previous workers [6,7,8] we employed the amine hydrogen tartrates. To use the amine economically, we first removed some (+)-amine (+)-tartrate, then set the slightly lævorotatory residual amine free by treatment of the mother-liquors with sodium hydroxide, and used (−)-tartaric acid to obtain the (−)(−)-salt. When this had been removed, the amine was again liberated, and a second batch of (+)(+)-salt prepared. This procedure was facilitated by polarimetric control, which cannot be direct, since the diastereoisomers from one form of tartaric acid differ only slightly (see below) in rotation. A sample (0·2 g.) of a crop containing the (+)- and (−)-amine in unknown proportions was shaken with 2N-sodium hydroxide (5 ml.) and benzoyl chloride (0·3 ml.). Excess of benzoyl chloride was removed by twice warming the suspension until the crude benzoyl derivative melted, and shaking until solidification occurred. The mixed (+)- and (−)-benzoyl derivatives were extracted with ether (2 × 5 ml.); and the extract was washed with water (3 × 2 ml.), dried (Na_2SO_4), filtered by gravity through a (fluted) hardened filter paper, and evaporated (on the steam-bath, and finally in a vacuum-desiccator), to yield *ca.* 100 mg. of mixed benzamides. Simple precautions were taken to exclude dust. The resolution, which requires about four crystallisations from weights of water rather less than those of the salts, is complete when the benzoyl derivative so produced has $[\alpha]_D^{18-22}$ +31·0° ± 0·2° (*c* 4—5 in EtOH). Repeated crystallisation of a larger sample of the derivative from toluene yielded needles of constant m. p. (95°) and rotation ($[\alpha]_D^{19}$ +31·0°, *c* 4·81 in EtOH): Pope and Gibson [9] gave m. p. 92° and $[\alpha]_D^{20}$ +30·7° (*c* 1·00 in EtOH).

Alcohol may be used to wash the crops, but was an unsatisfactory solvent for crystallisation: the degree of resolution was poor. A few, and unsuccessful, attempts were made to use the pure (+)(+)- and (−)(−)-salts to seed solutions containing both forms of acid and amine. We found passage through a column of " Zeo-karb 225 " to be a convenient method of preparing (−)-tartaric acid from sodium ammonium (−)-tartrate, or of recovering (−)-tartaric acid from solutions of disodium (−)-tartrate in aqueous sodium hydroxide.

The active amines were distilled, through a short column, from samples of the pure salts treated with an excess of 40% sodium hydroxide. After drying with solid potassium hydroxide, but without further distillation, these had d_4^{20} 0·731, $[\alpha]_D^{20}$ +7·48°; and d_4^{19} 0·728, $[\alpha]_D^{19}$ −7·64°. Thomé [6] gave d_4^{20} 0·724, $[\alpha]_D^{20}$ +7·44°, whilst Leithe [8] gave $[\alpha]_D^{15}$ +7·80°.

Diastereoisomeric Salts of sec.-*Butylamine with* (+)-*Tartaric Acid.*—(+)-*sec.*-Butylammonium hydrogen (+)-tartrate crystallised from water as slender prisms of the monohydrate, m. p. 96°, $[\alpha]_D^{21}$ +16·8° (*c* 2·8 or 4·8 in H_2O) (Found: C, 40·2, 39·9; H, 7·8, 7·7. Calc. for $C_8H_{17}O_6N,H_2O$: C, 39·8; H, 7·9%). The water of hydration was retained for 18 hr. over potassium hydroxide at 15 mm., but the anhydrous salt was obtained as plates, m. p. 139—140°, $[\alpha]_D^{21}$ +18·1° (*c* 10·8 in H_2O), on crystallisation from alcohol and drying, finally over phosphoric oxide at 80°/0·1 mm. (Found: C, 43·5; H, 7·7. Calc. for $C_8H_{17}O_6N$: C, 43·0; H, 7·6%). Thomé [6] gave analyses of the monohydrate, but no m. p.; Leithe [8] gave m. p. (98—99° and 146—147°) but no analyses.

The more soluble (−)-*sec.*-butylammonium hydrogen (+)-tartrate was prepared from the pure (−)-amine and tartaric acid. Crystallisation from water yielded material of indeterminate constitution, but the *monohydrate* was obtained as needles by crystallisation from ethanol–water (4 : 1 by vol.) and 7 days' exposure to the atmosphere. The material had m. p. 85°, $[\alpha]_D^{21}$ +17·8° (*c* 2·8 in H_2O) (Found: C, 40·1; H, 7·9. $C_8H_{17}O_6N,H_2O$ requires C, 39·8; H, 7·9%). The *anhydrous salt*, obtained by crystallisation from ethanol and drying, finally over phosphoric oxide at 80°/0·1 mm., had m. p. 138—139°, $[\alpha]_D^{20}$ +19·8° (*c* 9·9 in H_2O) (Found: C, 43·0; H, 7·3. $C_8H_{17}O_6N$ requires C, 43·0; H, 7·6%).

The rotations and m. p.s of the anhydrous salts are subject to some uncertainty, as water is rapidly absorbed from the atmosphere. The rotations of the monohydrates were determined in a 400 mm. polarimeter tube.

(+)-sec.-*Butylnitramine.*—The amine was converted into the nitramine by standard methods.[10,11] The intermediate (+)-*sec.*-butylurethane had d_4^{21} 0·945, $[\alpha]_D^{21}$ +19·3°, whilst the intermediate (+)-*sec.*-butylnitrourethane had d_4^{19} 1·098 and $[\alpha]_D^{19}$ +10·2°. (+)-sec.-*Butylnitramine*, b. p. 101°/10 mm. (Found: C, 40·9; H, 8·7. $C_4H_{10}O_2N_2$ requires C, 40·7; H, 8·5%),

[6] Thomé, *Ber.*, 1903, **36**, 582.
[7] Fleury-Larsonneau, *Bull. Soc. chim. France*, 1939, **6**, 1576.
[8] Leithe, *Ber.*, 1930, **63**, 804.
[9] Pope and Gibson, *J.*, 1912, **101**, 1706.
[10] Denton and Lamberton, *J.*, 1955, 1655.
[11] Curry and Mason, *J. Amer. Chem. Soc.*, 1951, **73**, 5042.

had α_D (100 mm.) +45·1°, 44·9°, and 44·6° at, respectively, 18°, 19°, and 20°, d_4^{20} 1·061, and $[\alpha]_D^{20}$ +42·1°. The following rotations were observed in solution: $[\alpha]_D^{21}$ +28° (*c* 0·47 in H_2O), +40° (*c* 4·1 in EtOH), $[\alpha]_D^{20}$ +35° (*c* 4·2 in $CHCl_3$), +39° (*c* 3·6 in Ph·NO_2), $[\alpha]_D^{21}$ +49° (*c* 0·44 in 0·0915M-NaOH, equiv. to Na salt in 0·042M-NaOH). The solution of the sodium salt had unchanged rotation after 2 weeks at room temperature.

Determination of Alkyl Chloride formed by Decomposition in 1·0M-*Hydrochloric Acid.*—The method has been reported.[2] In two experiments, (±)-*sec.*-butylnitramine showed halide formation of 3·0, 3·8% by acidimetry, and 2·8, 3·9% by determination of chloride ion. *O*-Methyl-*N*-*neo*pentylnitramine gave no indication of halide formation.[2]

Decomposition of (+)-sec.-*Butylnitramine.*—The solutions (see Figure for compositions) were heated, under a ground-glass reflux condenser, in a 100 ml. flask immersed to the neck in the thermostat. At suitable intervals the flask was removed and the contents were cooled rapidly to 20°; the rotation was observed in a 400 mm. tube, and the acidity found by titration of a 3 ml. sample. The polarimetric solution was returned to the flask, and heating re-commenced. The sample of nitramine used was of 78% optical purity, having α_D^{18} (100 mm.) +35·1°. The rate of decomposition was in agreement with earlier measurements[10] of greater precision; half-life times were about 95 min. for runs I—III, and 12 hr. for run IV. Final observations were made after, respectively, *ca.* 24 hr., 1023 min., 1146 min., and 90 hr. of heating. At these (final) times the residual nitramine should be negligible, but the alkali titres were higher than expected. These discrepancies, which may have arisen from evaporation, or other causes, were in all cases less than 0·3 ml., and it has been thought best to make no attempt at " correction " : the Figure is based simply on the observed values. The end-points of the broken lines are uncertain to perhaps ±0·03°; their calculation involves the optical purity of the nitramine, also the rotation (in dilute acid) and optical purity of the *sec.*-butyl alcohol prepared by us; curiously, no value of the rotation of (+)-*sec.*-butyl alcohol in water appears to exist in the literature. We found that a sample of 93·4% optical purity[12] [dried by distillation from barium oxide : α_D^{20} +10·21° (100 mm.)] had $[\alpha]_D^{20}$ +13·5° (*c* 2·61 or 0·75 in H_2O, or 0·75 in 0·11M-HCl). From this, the rotation of the pure (+)-isomer is $[\alpha]_D^{20}$ +14·5° in dilute aqueous solutions.

Racemisation of sec.-*Butyl Alcohol.*—The results of Bunton *et al.*,[3] and our own experiments in sealed tubes, show that racemisation of the alcohol could not cause significant loss of optical activity during the decomposition of *sec.*-butylnitramine. A more likely source of error would be volatilisation of the alcohol. A sample of 70—75% optical purity was prepared,[13] and solutions (of similar molarity to those of the nitramine) were treated as described for the decomposition of *sec.*-butylnitramine. A slow loss of activity, due to volatilisation and racemisation, was observed; and the results, expressed as the time for the loss of half the activity, were between 150 and 300 hr. for hydrochloric acid (0·11 or 0·002M), or for sulphuric acid (0·10 or 0·01M). In the decomposition of *sec.*-butylnitramine the rate of volatilisation may increase on account of the evolution of nitrous oxide, but we believe the figures we have given (0·03° for 24 hr., and 0·1° for 90 hr.) to be a generous estimate of the losses which could thus result; and also, if the changes in rotation shown in the Figure were due to volatilisation or racemisation, it seems most unlikely that they would be—as in fact they are—related linearly to the changes in acid titre.

Confirmatory Experiments in Sealed Tubes.—A sample of pure (+)-*sec.*-butylnitramine (236·8 mg., 2·01 mmole) was made up to 20 ml. with 0·110M-hydrochloric acid, and heated in a sealed tube for 16 hr. at 86—88°. The residual nitramine, by acidimetry, was less than 1%. The observed rotations, α_D^{23} (400 mm.), were initially +1·265° and finally −0·025°. The reality of the small negative rotation was confirmed by distillation of the residual solution available (16—17 ml.) through a short column. A first fraction of rather less than 1 ml. was collected, and found to have α_D^{22} (100 mm.) −0·11°. Quantitative production of (−)-*sec.*-butyl alcohol would have given a rotation of about −0·43° in the 400 mm. tube, compared with the observed value of −0·025°. A sample of partially resolved *sec.*-butyl alcohol (143·8 mg., 1·94 mmole) was made up to 20 ml. with the same acid, and heated similarly and simultaneously in the same furnace. The rotation, α_D^{23} (400 mm.), was practically unaltered (+0·34° ⟶ +0·325°). A second sample of alcohol (141·1 mg.), made up to 20 ml. with the same acid, gave rotations of +0·32° and +0·31° before and after heating at 86—90° for 17 hr. Samples of the alcohol in, respectively, 0·110M-hydrochloric acid and 0·01M-sulphuric acid were heated simultaneously for 87 hr. at 86—90° : the rotations, α_D^{21-22} (400 mm.) changed only from +0·31° to +0·30°, and from +0·34°

[12] Pickard and Kenyon, *J.*, 1913, **103**, 1941.
[13] Ingersoll, " Organic Reactions," Wiley and Sons, New York, 1944, Vol. II, p. 403.

to +0·33°. These changes cannot be considered of quantitative significance, but show that the rate of racemisation is very small.

Decomposition of O-*Methyl*-N-neo*pentylnitramine in an Oxidising Medium.*—*O*-Methyl-*N*-*neo*pentylnitramine (0·21 g.) was heated under reflux for 2 hr. on the steam-bath with 0·5N-potassium dichromate (40 ml.) and concentrated sulphuric acid (5 ml.). After cooling, the excess of oxidant was removed by the addition of sodium sulphite (2 g.); the resultant solution was added to a saturated aqueous solution of 2 : 4-dinitrophenylhydrazine hydrochloride (50 ml.), and the whole set aside overnight at 0°. If sodium sulphite was not added, oxidation of the hydrazine gave 2 : 4-dinitrophenol. Acetone 2 : 4-dinitrophenylhydrazone (250 mg., crude) was collected and identified, after two crystallisations from acetic acid–water, by m. p. (124°) and mixed m. p. (Found : C, 45·2; H, 4·3. Calc. for $C_9H_{10}O_4N_4$: C, 45·4; H, 4·2%). The m. p. was depressed to 90° by mixture with the 2 : 4-dinitrophenylhydrazone of methyl *iso*propyl ketone (m. p. 120°).

We thank the Department of Scientific and Industrial Research for a Maintenance Grant (to P. B.) and the Chemical Society for a grant from the Research Fund.

STAVELEY CHEMICAL LABORATORIES,
THE UNIVERSITY, SHEFFIELD, 10.

[*Received, October 25th*, 1955.]