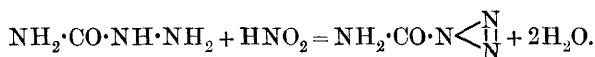


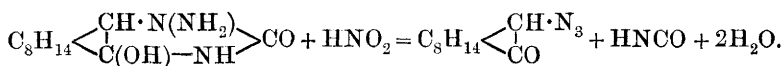
LXXXV.—*Studies in the Camphane Series. Part XX.*
Camphorylazoimide.

By MARTIN ONSLOW FORSTER and HANS EDUARD FIERZ.

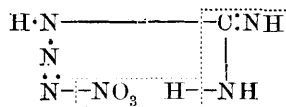
By their investigation of semicarbazide, Thiele and Stange showed (*Ber.*, 1894, **27**, 31, and *Annalen*, 1894, **283**, 1) that a solution of the hydrochloride, when treated with sodium nitrite, yields carbaminoazoimide,



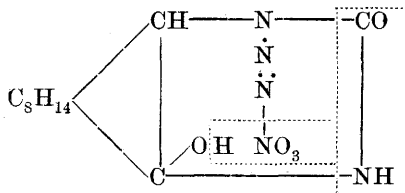
In view of the tertiary character of the nitrogen atom to which the amino-group in camphoryl- ψ -semicarbazide is attached (compare this vol., p. 722), the possibility of obtaining camphorylazoimide by the action of nitrous acid appeared somewhat remote. Nevertheless, we find that sodium nitrite, when added to an aqueous solution of camphoryl- ψ -semicarbazide nitrate, causes the immediate precipitation of camphorylazoimide, owing to simultaneous elimination of cyanic acid:



In seeking for the explanation of this change, it is necessary to recall the behaviour of diazoguanidine nitrate, which has been shown by Thiele (*Annalen*, 1892, **270**, 1) to yield cyanamide and azoimide under the influence of alkalis:

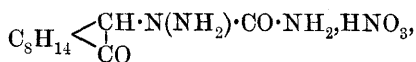


It is not unlikely that the action of nitrous acid on camphoryl- ψ -semicarbazide nitrate involves the momentary production of a diazo-derivative, from which camphorylazoimide would arise by eliminating nitric and cyanic acids :



Attempts to isolate this compound, which would correspond to the extraordinarily stable diazoguanidine nitrate, have not been successful.

The alternative explanation which suggests itself is not supported by facts. It might be supposed that when concentrated nitric acid acts on acetone camphoryl- ψ -semicarbazone, the salt produced is the nitrate of normal camphorylsemicarbazide,

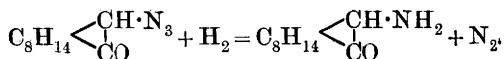


corresponding to Rupe's camphorylcarbamide, because we have already shown that whilst alkalis transform the last-named substance into camphoryl- ψ -carbamide, the converse change is brought about by acids. If the same relationship connected the semicarbazides, the nitrate obtained from acetone camphoryl- ψ -semicarbazone should yield with aldehydes a series of semicarbazones distinct from those described in our previous communication (this vol., p. 727), all of which were prepared from the acetic acid solution of freshly reduced camphorylnitroso- ψ -carbamide. This, however, is not the case. A specimen of benzylidene camphoryl- ψ -semicarbazone has been prepared from benzaldehyde and camphoryl- ψ -semicarbazide nitrate, and found to be identical with the substance already described (*loc. cit.*).

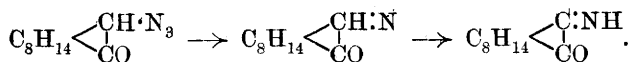
Although readily fusible, camphorylazoimide crystallises with unusual ease; its behaviour when superheated resembles that of phenylazoimide and its *p*-nitro-derivative, energetic decomposition taking place without actual detonation. An unusual feature is its failure to yield hydrazoic acid with alkalis or acids, but it must be remembered that whilst the acylazoimides readily yield hydrazoic acid on hydrolysis, phenylazoimide resists the action of acids and alkalis, yielding diazoimide only when converted into the *p*-nitro-derivative; with this in mind, we have tried to prepare substituted camphorylazoimides, hitherto without success. Moreover, the substance under discussion represents a type of azoimide distinct from that of hippurylazoimide, phenylazoimide, benzylazoimide, and the recently described

methylazoimide (Dimroth and Wislicenus, *Ber.*, 1905, **38**, 1573), attachment of the azoic nucleus in camphorylazoimide occurring at a carbon atom which forms the unit of a fully hydrogenated cycloid instead of an open chain or a benzene ring.

In other respects, however, the behaviour of camphorylazoimide agrees with that of other nitrides. Reduction with zinc and acetic acid gives rise to aminocamphor, and a solution of stannous chloride in hydrochloric acid liberates two-thirds of the azoic nitrogen, as in the case of carbaminoazoimide (Thiele and Stange, *Annalen*, 1894, **283**, 1):

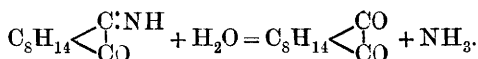


The same proportion of nitrogen is eliminated when alcoholic alkalis act on the substance, the product consisting of a new compound, α -iminocamphor:



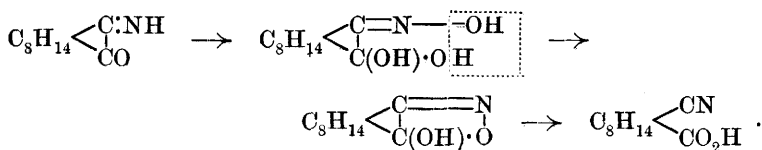
This curious change, which takes place quantitatively, recalls the behaviour of benzylazoimide towards acids, Curtius and Darapsky having shown (*J. pr. Chem.*, 1901, ii, **63**, 428) that among other products benzaldehyde and ammonia are formed, doubtless arising from the intermediate imino-compound, $\text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{NH}$.

It will be observed that α -iminocamphor is the monoimine of camphorquinone, and, as would be foreseen from the recent work of Willstätter, Eugen Meyer, and Pfannenstiel (*Ber.*, 1904, **37**, 1494 and 4605), the solid substance is highly unstable. A few minutes after being spread on porous earthenware it undergoes spontaneous change, which takes place suddenly if the material is pressed together in a compact mass; at the same time, white fumes are evolved, and considerable rise of temperature occurs. α -Iminocamphor is indifferent towards alkalis, but is readily soluble in dilute acids, which resolve it quantitatively into camphorquinone and ammonia:



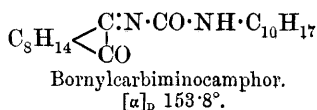
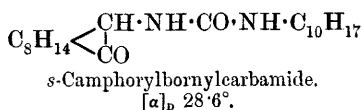
It was expected that hydrogen peroxide would transform imino-camphor into *isonitrosocamphor*, Haase and Wolffenstein having shown (*Ber.*, 1904, **37**, 3228) that the product from piperidine and hydrogen peroxide, previously regarded as δ -aminovaleraldehyde, consists of piperidine oxide, $\text{C}_5\text{H}_{10}\text{N} \cdot \text{OH}$ or $\text{C}_5\text{H}_{10}\text{NH} \cdot \text{O}$, but although the empirical result in both cases is the same, namely, addition of an oxygen atom, α -camphornitrilic acid is produced instead of *isonitroso-*

camphor. We suspect this change to depend on the intermediate formation of the *pseudo*-modification of *isonitrosocamphor*,

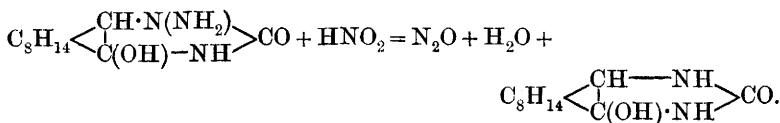


Attempts to isolate this compound in the form of its colourless benzoyl derivative have been unsuccessful.

Although α -iminocamphor is so extremely prone to change, it may be arrested in the form of a stable carbamide by adding the calculated amount of bornylcarbimide to a solution of the freshly-prepared substance in light petroleum. The derivative thus obtained can be recrystallised and heated considerably above 100° without undergoing alteration, but hot dilute acids resolve it into camphorquinone and bornylcarbamide. It is interesting to compare the specific rotatory power of the new compound with that of camphorylborylcarbamide (this vol., p. 120), from which it differs only by the possession of one double linkage :

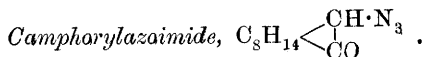


It remains to be mentioned that although camphorylazoimide is precipitated on adding sodium nitrite to an aqueous solution of camphoryl- ψ -semicarbazide nitrate, the action takes a different course when the acetate is the salt employed ; in presence of a slight excess of acetic acid, nitrous oxide is liberated and crystals of camphoryl- ψ -carbamide separate :



Thiele also (*loc. cit.*) observed that aminoguanidine nitrate behaved differently from the acetate towards sodium nitrite, but the liberation of nitrous acid was not recorded.

EXPERIMENTAL.



Thirty-five grams of camphoryl- ψ -semicarbazide nitrate were dissolved in 200 c.c. of water, and, the solution having been cooled with ice, 8 grams of sodium nitrite crystals were added in small quantities. Turbidity was developed immediately, but no evolution of gas occurred at the outset. When, roughly, one-half the nitrite had been added, a white, crystalline precipitate was formed, and the transparent, gummy mass which had previously accumulated began to harden; simultaneously, the pungent odour of cyanic acid became perceptible, and towards the end of the reaction disengagement of this gas became quite brisk. After an hour, the substance was filtered and dried, the yield being 90 per cent. of the theoretical amount; the neutralised filtrate, when concentrated on the water-bath, developed the vivid blue coloration with cobalt nitrate in acetic acid which is characteristic of cyanates.

Camphorylazoimide crystallises from alcohol in transparent, hexagonal prisms, which usually become aggregated in lustrous plates; it melts at 67° , and when heated in a dry tube decomposes suddenly without exploding. If protected from light, the freshly crystallised substance retains its lustre indefinitely, but a few minutes' exposure to sunlight renders the crystals dull and opaque.

0.1830 gave 0.4163 CO_2 and 0.1334 H_2O . $C = 62.04$; $H = 8.10$.

0.1574 „ 29.9 c.c. of nitrogen at 20° and 762 mm. $N = 21.79$.

$C_{10}H_{15}ON_3$ requires $C = 62.17$; $H = 7.77$; $N = 21.76$ per cent.

The substance is readily volatile in steam, the vapour having a pleasant camphor-like odour; it does not reduce Fehling's solution or ammoniacal silver oxide, and bromine appears to have no substituting action. It is moderately soluble in boiling water and in cold absolute alcohol, dissolving freely in ethyl acetate, acetone, and light petroleum. Determinations of rotatory power were carried out in a 2-dcm. tube, 25 c.c. of solvent being employed in each case.

0.2608 gram in benzene gave $\alpha_D - 7^\circ 20'$, whence $[\alpha]_D - 351.5^\circ$.

0.2602 „ in absolute alcohol gave $\alpha_D - 5^\circ 55'$, whence $[\alpha]_D - 284.2^\circ$.

0.2610 „ in acetone gave $\alpha_D - 5^\circ 50'$, whence $[\alpha]_D - 279.4^\circ$.

0.2589 „ in chloroform gave $\alpha_D - 5^\circ 6'$, whence $[\alpha]_D - 246.2^\circ$.

All attempts to obtain azoimide from the camphoryl derivative have been fruitless. The substance was treated with boiling 20 per cent.

sulphuric acid under a reflux condenser, to the upper end of which were attached bulbs containing aqueous sodium hydroxide; there was no trace of sodium nitride after one hour, and 50 per cent. sulphuric acid merely charred the material without eliminating hydrazoic acid. In neither case was there any sign of camphorquinone, but this substance is quickly formed when camphorylazoimide is heated with dilute aqueous sodium hydroxide; hydrazoic acid cannot be detected in the alkaline liquid, however. Equally unsuccessful were experiments in which the compound was heated in sealed tubes with aqueous and alcoholic solutions of silver nitrate; in both cases, silver was deposited, unaccompanied by silver nitride.

Reduction with Zinc and Acetic Acid.—Three grams of the azoimide were dissolved in 30 c.c. of glacial acetic acid and treated with 5 grams of zinc dust; after 12 hours, the liquid was heated on the water-bath, filtered, and treated with excess of potassium hydroxide, which precipitated aminocamphor. The base was identified by conversion into camphorylcarbamide, which was then transformed into the characteristic carbimide.

Action of Stannous Chloride.—Camphorylazoimide is not much more soluble in hydrochloric acid than in water, but on adding stannous chloride, minute bubbles of gas appear, effervescence continuing during a considerable period if the liquid remains at the ordinary temperature; ultimately the substance dissolves completely, forming a colourless solution. Using weighed quantities, it is found that two thirds of the total nitrogen is liberated in the change.

0.2477 gave 31.9 c.c. of nitrogen at 25° and 773 mm. $N = 14.64$.

$C_{10}H_{15}ON_3$ requires $2/3N = 14.51$ per cent.

In order to identify the other product, 3 grams of the azoimide suspended in 20 c.c. of concentrated hydrochloric acid were treated with 5 grams of stannous chloride. The oily base liberated by excess of potassium hydroxide was extracted with ether, dried with solid potash, and precipitated in the form of carbonate, which was then transformed into Rupe's camphorylcarbamide, and finally into the carbimide.

Action of Concentrated Sulphuric Acid.—When the azoimide is dropped into concentrated sulphuric acid, a very violent change takes place, nitrogen being set free suddenly, with considerable rise of temperature, whilst the acid solution remains clear, but does not become yellow. On repeating the experiment with weighed quantities in a closed vessel communicating with a nitrometer, the proportion of nitrogen evolved was found to be the same as when stannous chloride acts on the substance,

0.2328 gave 28.6 c.c. of nitrogen at 22° and 770 mm. $N = 14.10$.

$C_{10}H_{15}ON_3$ requires $2/3N = 14.51$ per cent.

We have not identified the other products.

α-Iminocamphor (Camphorquinonemonoimine), $C_8H_{14} \begin{matrix} \text{C:NH} \\ \diagup \quad \diagdown \\ \text{CO} \end{matrix}$.

When aqueous potassium hydroxide is added to an alcoholic solution of camphorylazoimide, a vigorous action takes place accompanied by brisk effervescence; if the colourless liquid is evaporated, it becomes pale yellow, and dilution precipitates an oil which quickly solidifies. This product is soluble in hot water, and dissolves freely in cold alcohol; it does not reduce Fehling's solution or ammoniacal silver oxide, but the aqueous solution becomes yellow immediately on adding a few drops of dilute sulphuric acid, the development of colour being rapidly followed by the formation of a bulky precipitate of camphorquinone, the filtrate from which contains ammonium sulphate. Complete removal of nitrogen from camphorylazoimide can be effected, therefore, in two stages, each of which is reached quantitatively. A tube containing a weighed amount was enclosed in a wide-mouthed bottle placed in communication with a nitrometer filled with water; on tilting the bottle, which contained alcoholic potassium hydroxide, the volume of gas produced could be measured.

0.3045 gave 39.6 c.c. of nitrogen at 23° and 762 mm. $N = 14.62$.

0.3357 „ 43.3 c.c. „ „ 23° „ 762 mm. $N = 14.50$.

$C_{10}H_{15}ON_3$ requires $2/3N = 14.51$ per cent.

In order to estimate the nitrogen removed during the second stage of the decomposition, a weighed quantity of camphorylazoimide was dissolved in ether and allowed to float on a few c.c. of a 50 per cent. aqueous solution of pure sodium hydroxide in a small separating funnel; on adding a few drops of absolute alcohol, a vigorous action ensued, and when this had subsided the alkali was removed. The ethereal solution of iminocamphor was agitated with dilute hydrochloric acid, becoming bright yellow in consequence. On evaporating the acid solution, a residue of ammonium chloride was obtained, and from this the platinichloride was prepared as usual.

0.5213 gram azoimide gave 0.2380 Pt. $N = 6.58$.

0.3472 „ „ „ 0.1689 Pt. $N = 7.01$.

$C_{10}H_{15}ON_3$ requires $1/3N = 7.25$ per cent.

The ethereal solution deposited camphorquinone on evaporation.

Although these experiments leave but little doubt regarding the identity of the product from camphorylazoimide and alcoholic alkali,

α -iminocamphor is so unstable, and so sensitive to the action of acids and of air, that it is not possible to obtain it in purified form. The compound can be isolated by dissolving 2 or 3 grams of camphorylazoimide in pure ether, adding 50 per cent. aqueous potassium hydroxide, and then sufficient absolute alcohol to begin the action; when gas is no longer evolved, the colourless ethereal solution is decanted through a dry filter and quickly evaporated. On adding water to the oily residue, α -iminocamphor is obtained as a crystalline paste, which quickly dries on porous earthenware; it is then only very pale yellow, and easily crumbled, but soon becomes bright yellow and cohesive. No definite melting point can be recorded; a freshly prepared specimen, almost free from colour, melted at 50–60°, and it has been generally noticed that the bright yellow substance into which it changes melts at 120–130°. One specimen was analysed immediately after isolation, and subsequently at intervals of one day and two days, with the following results:

0·1804 gave 0·4554 CO₂ and 0·1528 H₂O. C = 68·84; H = 9·41.

0·1553 „ 0·3883 CO₂ „ 0·1295 H₂O. C = 68·19; H = 9·26.

0·1782 „ 0·4300 CO₂ „ 0·1443 H₂O. C = 66·94; H = 9·26.

C₁₀H₁₅ON requires C = 72·72; H = 9·02 per cent.

C₁₀H₁₅O₂N „ C = 66·30; H = 8·28 „ „

The spontaneous change, therefore, appears to involve addition of oxygen, and although the bright yellow colour of the product suggests the formation of camphorquinone, an intensely yellow specimen which had remained during 8 days in a desiccator containing calcium chloride and potassium hydroxide gave an amount of nitrogen corresponding to 7·74 per cent. (C₁₀H₁₅O₂N requires N = 7·73 per cent.).

On adding ethereal ferric chloride to a freshly prepared solution of iminocamphor, a brown coloration is developed, followed almost immediately by a brown precipitate of ferric hydroxide mixed with camphorquinone.

The specific rotatory power of α -iminocamphor was determined by dissolving a weighed quantity of camphorylazoimide in light petroleum, allowing the solution to float on 50 per cent. potassium hydroxide, and adding 2 drops of absolute alcohol, evolution of nitrogen continuing during one hour; when this had ceased, the alkali was removed, and the filtered petroleum, which was practically colourless, diluted to a measured volume. Thus iminocamphor from 0·7984 gram of camphorylazoimide, dissolved in 50 c.c. of light petroleum, gave α_D 2°30' in a 2-dm. tube, whence $[\alpha]_D$ 91·5°. One attempt to determine the specific rotatory power of the freshly isolated α -iminocamphor failed because the substance became hot and emitted white fumes while on the balance-pan; on another occasion, 0·4154 gram dissolved in

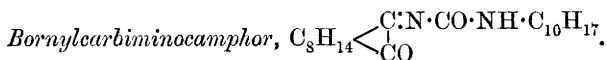
25 c.c. of absolute alcohol gave α_D $2^\circ 35'$ in a 2-dcm. tube, whence $[\alpha]_D$ 77.8° .

Action of Hydrogen Peroxide.—A neutral solution of hydrogen peroxide was agitated with an ethereal solution of α -iminocamphor; rise of temperature took place, but no development of colour occurred. On removing the ethereal portion and evaporating the solvent, α -camphornitrilic acid was obtained; it melted at 148° , and did not depress the melting point of a specimen prepared from isonitrosocamphor.

0.1737 gave 0.4221 CO_2 and 0.1355 H_2O . C = 66.26; H = 8.66.

$\text{C}_{10}\text{H}_{15}\text{O}_2\text{N}$ requires C = 66.29; H = 8.28 per cent.

It was hoped that the intermediate stage in this curious change might be recognised by drawing air through a suspension of iminocamphor in water during several days. On filtering the bright yellow product at the end of one week, the liquid was found to be indifferent towards Fehling's solution and ammoniacal silver oxide, giving ammonia with alkali; the yellow solid still contained 4 per cent. of nitrogen, but it has not been possible to obtain from it the "colourless benzoyl derivative of isonitrosocamphor."



Two grams of camphorylazoimide were dissolved in 30 c.c. of light petroleum and the solution allowed to float on concentrated aqueous potassium hydroxide; conversion into α -iminocamphor having been effected in the manner described, the filtered petroleum solution was treated with 1.8 grams of bornylcarbinide and transferred to a desiccator. No alteration in the temperature or appearance of the solution was noticeable, but within one hour, minute white needles appeared, accumulating during 12 hours until 3.2 grams were obtained. After being washed with petroleum, the substance melted at 205° , becoming bright yellow at about 190° .

0.1319 gave 0.3534 CO_2 and 0.1144 H_2O . C = 73.07; H = 9.63.

0.1868 „ 13.8 c.c. of nitrogen at 24° and 765 mm. N = 8.34.

$\text{C}_{21}\text{H}_{32}\text{O}_2\text{N}_2$ requires C = 73.25; H = 9.30; N = 8.14 per cent.

The following determinations of rotatory power were carried out in a 2-dcm. tube, 25 c.c. of the solvent being employed in each case.

0.3332 gram in chloroform gave α_D $4^\circ 6'$, whence $[\alpha]_D$ 153.8° .

0.2988 „ benzene „ α_D $3^\circ 9'$, „ $[\alpha]_D$ 131.8° .

0.3513 „ acetone „ α_D $3^\circ 24'$, „ $[\alpha]_D$ 121.0° .

0.2318 „ alcohol „ α_D $2^\circ 1'$, „ $[\alpha]_D$ 108.7° .

The substance dissolves readily in the foregoing liquids, more sparingly in boiling light petroleum, from which it crystallises in silky needles, whilst hot concentrated alcoholic solutions deposit lustrous prisms which have a faint yellow colour; it transmits yellow light, and the solutions in organic media are bright yellow. On adding a few drops of dilute sulphuric acid to an alcoholic solution, the yellow colour disappears, being restored in a more intense shade on boiling the liquid, from which camphorquinone separates on cooling.

Action of Nitrous Acid on Camphoryl- ψ -semicarbazide in Acetic Acid.

The slightly acid solution of camphoryl- ψ -semicarbazide obtained by reducing the nitroso- ψ -carbamide with zinc and acetic acid effervesced slowly when treated with sodium nitrite, and a white, crystalline precipitate separated; this was filtered and recrystallised from boiling water, which deposited lustrous, white needles, melting and evolving gas at 194° , and yielding the nitroso-compound already described (this vol., p. 116). The temperature is 6° higher than that recorded as the melting point of the ψ -carbamide, doubtless owing to a trace of the normal modification in specimens previously obtained. In fact, the difficulty of completely transforming the *pseudo*-carbamide into the isomeride is greater than we thought at first; so much so, that the apparent production of camphorylcarbimide by the action of hot water on camphorylnitroso- ψ -carbamide must now be recognised as due to traces of the normal carbamide in the material submitted to the action of nitrous acid.

It has not been difficult to identify the gaseous product as nitrous oxide, and in order to ascertain whether the action proceeds quantitatively on the lines indicated by the equation already given, the gas obtainable from 10 c.c. of solution was measured, and the *pseudo*-semicarbazide present in the same volume of liquid was determined by weighing in a Gooch crucible the semicarbazone precipitated by benzaldehyde.

10 c.c. gave 0.3970 gram of semicarbazone. Available N = 1.78 grams per litre.

10 c.c. gave 32.4 c.c. of nitrous oxide at 24° and 762 mm.

Available N = 1.82 grams per litre.

These results are in sufficiently close agreement to show that all the available nitrogen is removed in the form of nitrous oxide.

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