[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

OPTICALLY ACTIVE DIAZO COMPOUNDS. DIAZOCAMPHANE

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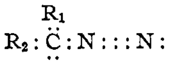
RECEIVED OCTOBER 23, 1930 PUBLISHED DECEMBER 18, 1930

The question whether or not a carbon atom which is attached to a diazo group might cause optical activity has been the subject of a great number of investigations during the last ten years.

On the one hand the results of the investigations of Levene and Mileska[1] in 1921 and of Noyes and Chiles[2] in 1922 imply an asymmetry of a carbon atom which is bound to diazo nitrogen. These investigators prepared the diethyl-α-diazo-succinate in which the only possible asymmetric carbon atom is connected to a diazo group and they found the compound to possess a small optical rotatory power. This fact has recently been confirmed by H. Lindemann[3] and his co-workers. The straight-chain formula established by Angeli and Thiele[4] and modified by Noyes[5] according to the octet theory explains the asymmetry of the carbon atom (A). In this formula the carbon atom represents a center of asymmetry since it is bound to three different substituents and possesses one electric charge.


$R_2:\overset{R_1}{\underset{\cdot\cdot}{\ddot{C}}}:N:::N:$

(A)

On the other hand, some qualities of the diazo compounds seem to justify the ring structure rather than the open-chain formula.[6]

This work has been undertaken in order to get further evidence of the behavior of alicyclic diazo compounds. Diazocamphane (B) contains, besides the carbon atom which is connected with the diazo group, the two asymmetric carbon atoms of the camphor. It, therefore, can be expected to exist in four optically active modifications which give two pairs of optical antipodes and two pairs of stereoisomers. The *d*-camphor consequently furnishes two stereoisomeric diazo compounds and in the same way two stereoisomeric amines or chlorides.[7]

The diazocamphane $C_9H_{16}{=}C{=}N_2$ has been prepared in ethereal solu-

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[1] Levene and Mileska, *J. Biol. Chem.*, **45**, 592 (1921); **52**, 485 (1922).

[2] Chiles with Noyes, THIS JOURNAL, **44**, 1798 (1922).

[3] H. Lindemann, Wolter and Groger, *Ber.*, **63**, 702 (1930).

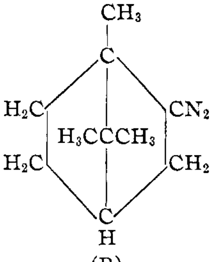
[4] A. Angeli, *Atti accad. Lincei*, [V] **32**, i, 443 (1923). J. Thiele, *Ber.*, **44**, 2522 (1911).

[5] Kendall with Noyes, THIS JOURNAL, **48**, 2404 (1926). Staudinger [*Helv. Chim. Acta*, **5**, 75 (1922)], by a study of the addition of phosphines to diazo compounds, also found the open-chain formula to be more probable.

[6] See, for instance, Sidgwick, *J. Chem. Soc.*, 1108 (1929), and Lindemann and Thiele, *Ber.*, **61**, 1529 (1928).

[7] Only one of the bornyl chlorides derived from the *d*-camphor, the dextrorotatory bornyl chloride, has been known until now. Studying the reaction of the diazocamphanes with hydrochloric acid, we have prepared very small amounts of the corresponding stereoisomeric levorotatory form.

tion from the normal and the neo-bornylamines, both of which are formed by the reduction of *d*-camphor-oxime and represent stereoisomers. The ethereal solution of both of the diazocamphanes is deeply red colored and extremely unstable. Even below 0° the compounds decompose with the evolution of nitrogen and the formation of the inactive polycyclic hydrocarbon, tricyclene. This reaction proves the old assumption that the diazocamphane is temporarily formed as an intermediate product in the preparation of tricyclene by the oxidation of camphor-hydrazone with mercuric oxide.[8]

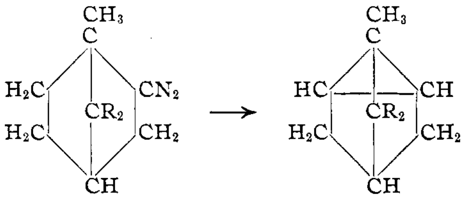


(B)

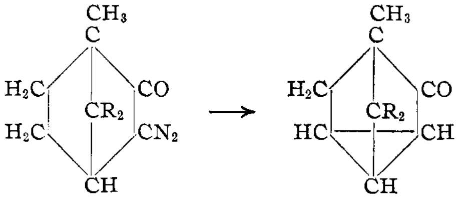
$$C_9H_{16}:C:NNH_2 + HgO \longrightarrow C_9H_{16}:C:N_2 \longrightarrow C_{10}H_{16} + N_2$$

Furthermore, the diazocamphane is very sensitive to hydrogen ions. Even carbon dioxide favors its decomposition.

Tricyclene was found to be the only product of the spontaneous decomposition of the diazocamphane. No nitrogen-containing compounds such as ketazides or bis-hydrazones have been observed. This decomposition is analogous to that of the diazocamphor



Diazocamphane ⟶ Tricyclene (α-pericyclocamphane)



Diazocamphor ⟶ β-Pericyclocamphanone

When cooled to a temperature of a carbon dioxide–acetone mixture, the compound could be kept without appreciable decomposition for several days.

Attempts to crystallize the diazocamphane from its solution failed because of its instability.

The specific rotations of both of the diazocamphanes are very high, ranging between about +60 and +450°.

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[8] Friedländer, "Fortschritte der Teerfarbenfabrikation," German Patent 353,933 (1922). Because of the instability of the diazocamphane it is impossible to prepare it by this reaction. Staudinger, *Ber.*, **53,** 1106 (1920).

For determining the concentration of the diazo solutions, the gasometric method was used. The diazo compound was decomposed by dilute sulfuric acid and the volume of nitrogen evolved was measured. In some cases the two diazo compounds have been compared colorimetrically. The readings of the rotation were taken at about −5°, at which temperature the compound decomposes very slowly. On account of the relatively great inaccuracy of this method in connection with the instability of the diazo compound, the values for the specific rotation vary considerably. The average values of the specific rotation of the diazocamphanes for light of different wave lengths are given in Table I.

TABLE I

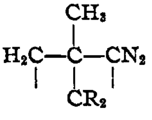
SPECIFIC ROTATION OF NORMAL DIAZOCAMPHANE

λ	615	603	592	584	572
[α]	179	164	196	350	420
λ	568	557	547	538	530
[α]	411	411	339	286	71

SPECIFIC ROTATION OF NEO-DIAZOCAMPHANE

λ	645	635	602	592	585
[α]	170	238	279	275	320
λ	578	572	567	558	
[α]	455	466	420	398	

The dispersion curve of each of the diazo compounds shows its highest value in the light green part of the spectrum, beginning with a λ of about 5750 Å., and then goes down very rapidly in yellow and blue light. The anomaly of the dispersion curve in this part of the spectrum is caused by an absorption band which is located at about λ5650 Å. (Cotton effect)[9] (Fig. 1). This absorption band is undoubtedly due to the diazo group. It possesses a strong vicinal effect upon the substituents of the one asymmetric carbon atom of the original camphor (C), thus increasing its asymmetry and causing the extremely high rotation.[10] Similar effects have been observed with other alicyclic diazo compounds, *e. g.*, the methyl γ-diazocamphonanate of Noyes and Kendall.[5]



$$\mathrm{H_2C}-\underset{\underset{\mathrm{CR_2}}{|}}{\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{C}}}-\mathrm{CN_2}$$

(C)

While the study of the single values of the specific rotation did not seem to give satisfactory evidence concerning a difference of the two diazo compounds, a consideration of the whole dispersion curves seemed to be more successful. The curve obtained from the normal compound rises very rapidly toward the green and then shows a rather slow inflection near the maximum. The curve from the neo-compound rises very rapidly, too, but then shows a very strong inflection near the maximum (Fig. 1).

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[9] Cotton, *Ann. chim. phys.*, [7] **8,** 347 (1896).

[10] W. Kuhn, *Ber.*, **63,** 200 (1930).

The curves plotted from the original observations, as shown in Fig. 2, bring out the differences between the two compounds more clearly. In these curves the inaccuracies of the volumetric determinations of the quantities present are eliminated. Two different solutions were used for each compound. It will be seen that the shapes of the two curves for the normal compound are alike and are different from the shapes of the two curves for the neo compound.

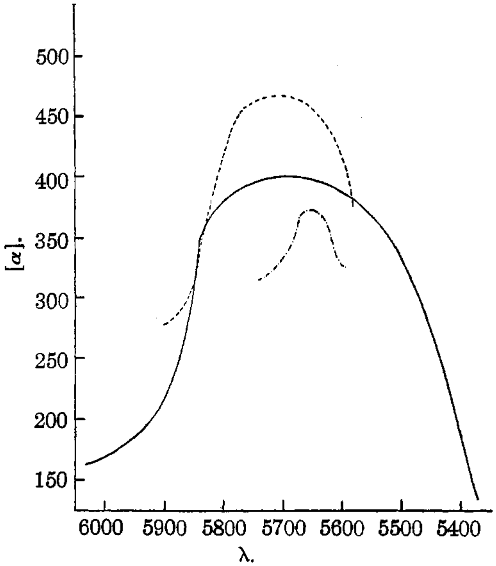


Fig. 1.—Rotatory dispersion of normal and neo-diazocamphane: ———, normal diazocamphane; - - - - - - -, neo-diazocamphane; –·–·–·–, absorption curve.

Another evidence showing a difference of the two diazocamphanes was obtained in studying their decomposition products. A rather concentrated ethereal solution of diazocamphane decomposes with ethereal hydrochloric acid forming tricyclene and small amounts of bornyl chloride. The bornyl chloride obtained from the normal diazocamphane was levorotatory, having a specific rotation of $[\alpha]_D$ $-33.2°$ in ether. It thus represents the stereoisomer of the ordinary

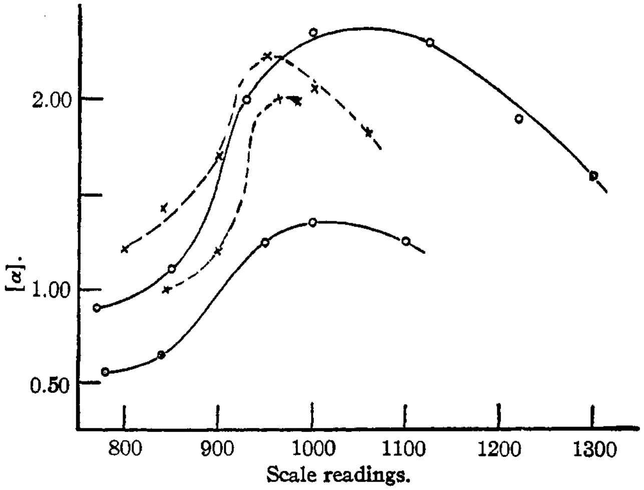
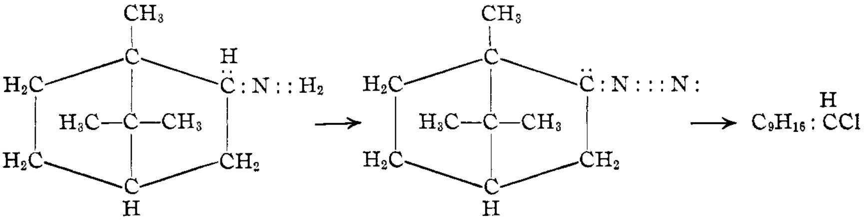


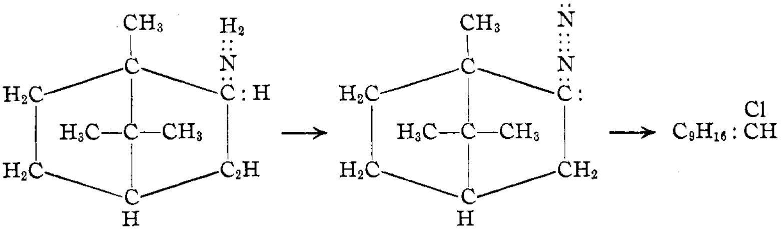
Fig. 2.—Observed rotations of normal and neo-diazocamphane: ———, normal; — — — —, neo.

dextrorotatory bornyl chloride. The neo-diazocamphane decomposed under the same conditions with the formation of a very small amount of bornyl chloride, the specific rotation of which we have been unable to determine but it was found to be dextrorotatory.

The fact that the two diazo compounds give different decomposition products and that their dispersion curves have different shapes indicates that their structure must be different. Their behavior might be explained by the following diagrams.

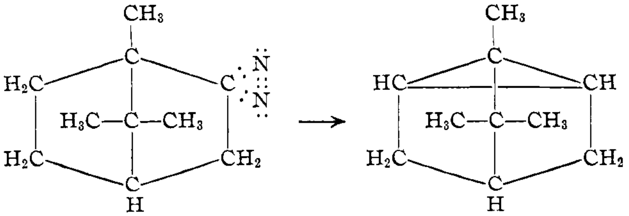


Normal bornylamine ⟶ Normal diazocamphane ⟶ Normal bornyl chloride



Neo-bornylamine ⟶ Neo-diazocamphane ⟶ Neo-bornyl chloride

On the other hand, the formation of tricyclene from both diazo compounds indicates that they may have the same structure, in part. This can be explained by the cyclo form



Cyclo-diazocamphane Tricyclene

The loss of a molecule of nitrogen from this cyclo form would leave a bivalent carbon atom bearing two electrons. This would be followed by the transfer of a hydrogen ion from the CH_2 group to these two electrons and the formation of the bridge across the ring.

The fact that mainly tricyclene and only very little bornyl chloride is formed in each case indicates that the diazocamphane consists mostly of the cyclic form, which is in equilibrium with the chain form.

This idea has recently been suggested by Lindemann,[3] while Sidgwick[6] has advocated the cyclic formula. Further evidence for the existence of optically active chain forms has very recently been secured by Ray[11] through his study of the decomposition of the two methyldiazocamphonanates obtained from the methyl esters of the *cis* and *trans* aminocamphonanic acids.

Experimental Part

Normal bornylamine, $C_{10}H_{17}NH_2$ and neo-bornylamine are formed by the reduction of camphor-oxime with sodium and amyl alcohol.[12] Normal bornylamine is formed chiefly and was separated from the mixture by fractional crystallization of the chlorides from water. The hydrochloride of the normal amine is much less soluble in water than that of the neo-base. The rotation of 1.36 g. of normal bornylamine hydrochloride in 100 cc. of absolute alcohol was $[\alpha]_D$ +22.6°. The melting point of the free amine was found to be 162.5–163° and its rotation in absolute alcohol $[\alpha]_D$ +45.9°. These values are in close agreement with those obtained by Forster.

Since the bornylamine, being a very strong base, forms a stable nitrite with nitrous acid it is impossible to obtain the diazocamphane by treating the primary amine with N_2O_3. We therefore used the method indicated by v. Pechmann,[13] that of treating the nitroso derivative of an acyl amine with alkali.

N,N′-Dibornylurea, $(C_{10}H_{17}NH)_2CO$, has been obtained by treating an ethereal solution of normal bornylamine cooled to −15° with an equivalent amount of phosgene dissolved in toluene. After evaporating the ether and toluene the residue was purified by recrystallization from aqueous alcohol.[14] The urea sublimes in long needles without melting. In this method the theoretical yield is only 50% since one-half of the amine is converted into the hydrochloride. It can easily be prepared, however, when using diphenylcarbonate, giving a yield of practically 100%.[15]

Mononitroso normal bornylurea has been prepared by passing carefully dried N_2O_3 into the ethereal solution of the urea cooled to −15° until it is colored green and keeping the solution at this temperature for about two hours. The solution is washed first with water and then twice with an ice cold solution of sodium bicarbonate. It is dried by freezing out the water at −80° and filtering off the ice. After evaporating the ether the nitroso compound crystallizes in yellow needles which are quite stable at 0° when kept over phosphorus pentoxide. The compound gives a positive Liebermann test for the nitroso group.

Anal. Subs., 0.3205: N_2, 31.6 cc. (24°, 752 mm.). Calcd. for $C_{10}H_{17}NH—CO(NO)NC_{10}H_{17}$: N, 11.63. Found: N, 11.5.

The crystals melt between 73 and 75° with decomposition. The nitroso compound is readily soluble in ether and alcohol. It slowly decomposes at room temperature, changing back into the urea. With sodium hydroxide or sodium methylate the yellow ether solution turns red, forming the diazo compound according to the equation

$$C_{10}H_{17}N(NO)CONHC_{10}H_{17} \xrightarrow{KOH} C_9H_{16}{=}C{=}N_2 + CO_2 + C_{10}H_{17}NH_2$$

This equation shows that only 50% of the amine applied can be converted into the diazo

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[11] F. E. Ray, THIS JOURNAL, **52,** 3004 (1930).

[12] Forster, *J. Chem. Soc.*, **73,** 386 (1889).

[13] Von Pechmann, *Ber.*, **27,** 1888 (1894).

[14] Neville and Pickard, *J. Chem. Soc.*, **65,** 687 (1894).

[15] Heubaum, THIS JOURNAL, **52,** 2149 (1930).

compound, which means a considerable loss of the raw material. Furthermore, the diazo solution is contaminated by bornylamine, which can hardly be separated. We therefore found the urethane derivative of the bornylamine more useful for the preparation of the diazo compound since all of the amine is turned into the diazo compound. The diazo solution obtained in this way does not contain any contaminating by-products

$$C_{10}H_{17}N(NO)COOC_2H_5 \xrightarrow{KOH} C_9H_{16}{=}C{=}N_2 + CO_2 + C_2H_5OH$$

Normal bornyl urethane has been obtained by the action of an excess of chloroethyl carbonate on normal bornylamine, which was suspended in aqueous potassium hydroxide at 0°. The product was then extracted with ether and purified by recrystallization from aqueous alcohol. All of the amine was thus converted into the urethane. The urethane melted sharply at 93° (Neville and Pickard found 89°)[14] and gave a specific rotation of $[\alpha]_D$ −10.9° in absolute alcohol and $[\alpha]_D$ +3.1° in absolute ether (Neville and Pickard found $[\alpha]_D$ +6.43 in chloroform). The urethane has also most easily been prepared by warming equivalent amounts of the amine and phenylethyl carbonate on the water-bath, only the phenoxy radical being substituted by the amine.[15]

Nitroso normal bornylurethane was obtained in the same way as the nitroso urea. The yellow crystals are more unstable at room temperature than those of the corresponding nitroso urea, turning back into the urethane (m. p. 93°). The compound gives a positive Liebermann test and a specific rotation of $[\alpha]_D$ +11° in ethereal solution. It is very sensitive to hydrogen ions and that is probably why Forster[16] failed to obtain it.

Normal Diazocamphane.—The dry solution of the nitroso urethane in ether was cooled to −20° and then a 2% solution of sodium methylate in methyl alcohol was added. The yellow color of the solution slowly changed to red. After standing for thirty minutes at −20° the diazo solution was washed with water to remove the sodium hydroxide and the methyl alcohol and then dried by cooling to −80°. No nitrogen evolution was observed at that temperature. The solution was analyzed by passing a measured volume (5–10 cc.) into a flask which contained dilute sulfuric acid and ether at exactly 0° and which was connected with a eudiometer. The volume of nitrogen evolved was corrected for temperature and the vapor pressures of ether and water; 6.1 cc. of diazo solution gave 7.1 cc. of nitrogen at 23° and 747 mm. This corresponds to a concentration of 0.56%. This solution had a rotation of +2.0° for λ5840 Å. which gives a specific rotation of $[\alpha]_{5840}$ +350°. A Schmidt and Haensch Universal Polarimeter was used and a 1000-watt lamp as a source of light. The light was sent through a spectroscope to obtain light of the wave length desired. On account of the high absorption, especially of the green light, by the diazo compound, exact readings were very difficult to obtain in this part of the spectrum.

Neo-bornylamine.—The separation of the pure neo-bornylamine from the mixture of the two amines was rather difficult and has been carried out in two different ways. One method indicated by Forster[17] consists in converting the amines into the oxamides and recrystallization from ethyl acetate, petroleum ether and absolute alcohol, the neo-bornyl oxamide being much less soluble in those solvents. We obtained a small quantity of the neo-bornyl oxamide in this way. The melting point was 184° and $[\alpha]_D$ −60.1°, both values in close agreement with those obtained by Forster. This method of separation, however, can only be applied to mixtures which contain 60% or more of the neo-amine. Attempts to deal with mixtures containing equal amounts of the two isomers led to the isolation of a compound which melts at 100° (the "normal-oxamide" melts at 140°) and gives a mixture of the two amines on saponification. This compound has

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[16] Forster, *J. Chem. Soc.*, **85**, 1193 (1904).

[17] Forster, *ibid.*, **77**, 1152 (1900).

already been described by Forster. The analysis points to the empirical formula of the bornyloxamide. It represents very probably the neo-bornyl-normal-bornyl-oxamide.

Attempts to prepare the diazo compound directly from the oxamide failed since it was impossible to obtain a nitroso derivative of the oxamide.

Since this method of separation is not very satisfactory, we carried out more successfully the method indicated by Pope and Read,[18] using *d*-oxymethylene-camphor. The *d*-oxymethylene-camphor was prepared by the method described by Bishop, Claisen and Sinclair[19] and then treated with the corresponding quantity of the mixture of the amines which were dissolved in 50% acetic acid. The normal-bornylamine-oxymethylene-camphor is almost insoluble in petroleum ether and acetone, and remains after extracting the mixture with either one of these solvents. It can be purified by crystallization from alcohol and then gives a specific rotation of $[\alpha]_D$ +380° (Pope and Read found +330°). As much as possible of the normal compound was separated in this way from the mixture. The mother liquors then contained the almost pure neo-compound. After evaporating the mother liquors, the residue was dissolved in alcohol and decomposed with bromine, bornylamine hydrochloride and bromo-oxymethylene-camphor being formed. For further purification the amine then was converted into the oxamide.

Neo-bornylurethane.—The pure neo-bornyloxamide thus obtained was saponified with alcoholic potash and the amine converted into the urethane, using chloro-ethyl-carbonate. The neo-bornylurethane melted at 37° and gave a specific rotation of $[\alpha]_D$ −28.0° in absolute alcohol and of $[\alpha]_D$ −31.2° in absolute ether (Neville and Pickard found m. p. 36° and $[\alpha]_D$ −9.6° in benzene).

Nitroso neo-bornylurethane was obtained in the same way as the corresponding normal nitroso compound. Its specific rotation was $[\alpha]_D$ −18.5° in ethereal solution. In other respects it shows the same properties as the normal nitroso compound.

Comparison of Normal and Neo-diazocamphanes.—A solution of neo-diazocamphane in ether which had been obtained in the same way as the normal diazocamphane was compared colorimetrically with a normal diazo solution which had a concentration of 0.34%. The tubes of the colorimeter were cooled with carbon dioxide and acetone. According to the readings the concentration of the normal solution was to the concentration of the neo solution as 21 to 27. The neo solution, therefore, contained 0.44% of diazocamphane, and had a rotation of α +2.03°, which for λ5720 Å. gives a specific rotation $[\alpha]_{5720}$ +466°, while the normal solution gave a specific rotation of $[\alpha]_{5720}$ +420° in light of the same wave length.

Exact readings of the rotation in the green and blue light were rather difficult to obtain because of the high absorption in this part of the spectrum. The dispersion curves for the specific rotation of the normal diazo compound as obtained in two different samples show rather high discrepancies, because of the inaccuracy of the gasometric method.

The measurements of the absorption could be carried out only rather roughly since it was impossible to obtain accurate values because of the instability of the compound. At about λ5650 Å., however, an absorption band has been found.

The decomposition of the diazo compounds with ethereal hydrochloric acid has been carried out at −25° and the bornyl chloride separated from the tricyclene by fractional distillation *in vacuo;* 0.2192 g. of the bornyl chloride obtained from the normal diazocamphane dissolved in 5 cc. of absolute ether gave a rotation of α −4.2°. $[\alpha]_D$, therefore, is −33.2°. The amount of the dextrorotatory bornyl chloride prepared

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[18] Pope and Read, *J. Chem. Soc.*, **103**, 455 (1913).

[19] Bishop, Claisen and Sinclair, *Ann.*, **281**, 328 (1894).

from the neo-diazocamphane was so small that it was impossible to determine its specific rotation.

Summary

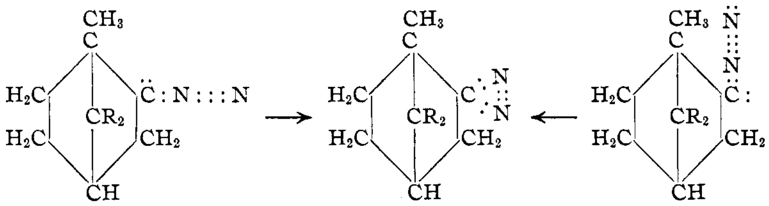
1. Diazocamphane has been prepared in ethereal solution from the nitroso urethanes of two stereoisomeric bornylamines with sodium methylate at −20°.

2. Its specific rotation varies between +60 and +450 in different parts of the spectrum.

3. The anomaly of the rotation in the green light is due to an absorption band located at about 5650 Å., caused by the $=CN_2$ group.

4. The shapes of the dispersion curves of the diazo camphanes prepared from the normal- and neo-bornylamine are different, thus indicating a difference in structure of the diazo compounds concerned.

5. Studying the decomposition of the diazocamphanes with hydrochloric acid, a new levorotatory bornyl chloride of $[\alpha]_D$ −33.2° has been prepared from the normal diazocamphane. The neo-diazocamphane gave small amounts of a dextrorotatory bornyl chloride. Both diazo compounds, however, give mainly the same decomposition product, namely, the inactive polycyclic hydrocarbon tricyclene, which indicates that they have partly the same structure. Their behavior is explained by the following formulas



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