

Acetyl Derivatives.—These derivatives were obtained by heating the appropriate phenolisatins with acetic anhydride at 130–135° for two hours.

TABLE I

Oxindole	Formula	M. p., °C.	Nitrogen, %		Iodine, %	
			Calcd.	Found	Calcd.	Found
A. 1-Acetyl-3,3-bis-(4'-acetoxyphe-nyl)-5-iodo-	$C_{26}H_{20}O_6NI$	169–170 ^{oa}	2.46	2.51, 2.47	22.31	22.13
B. 3,3-Bis-(4'-acetoxyphe-nyl)-5,7-di-iodo-	$C_{24}H_{17}O_6NI_2$	256–257 ^{ob}	2.29	2.09, 2.18	38.89	38.93
C. 1-Acetyl-3,3-bis-(3', 5'-di-iodo-4'-acetoxyphe-nyl)-	$C_{26}H_{17}O_6NI_4$	267–268 ^{oc}	1.47	1.31, 1.34	53.64	53.99
D. 1-Acetyl-3,3-bis-(3', 5'-di-iodo-4'-acetoxyphe-nyl)-5-iodo-	$C_{26}H_{16}O_6NI_5$	272–273 ^{od}	1.30	1.24, 1.19	59.17	59.07
E. 3,3-Bis-(3', 5'-di-iodo-4'-acetoxyphe-nyl)-5,7-di-iodo-	$C_{24}H_{13}O_6NI_6$	255–256 ^{oe}	1.21	1.11, 1.25	65.86	66.04

^a Colorless prisms from glacial acetic acid. ^b Colorless plates from glacial acetic acid. ^c Colorless prisms from acetic anhydride. ^d Colorless prisms from acetic anhy-
dride. ^e Colorless plates from acetic anhydride.

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Summary

Several iodinated derivatives of phenolisatin have been prepared.

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

OPTICALLY ACTIVE DIAZO COMPOUNDS. VI. DIAZOCAMPHOR

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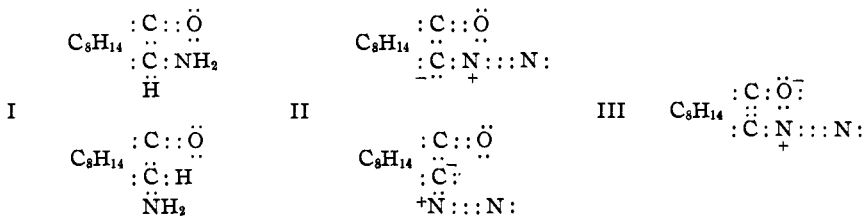
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This is a continuation of a study of the question whether diazo compounds of the type, $R: \overset{\cdot\cdot}{C}: N:: N:$, may occur in optically active forms.¹

Some of the previous investigations have not been satisfactory because the instability of some of the diazo compounds has prevented their isolation in a state of sufficient purity to demonstrate conclusively that the small rotations observed were not due to optically active impurities. The fact that in many of them the diazo group was attached to a carbon atom adjacent to a carbonyl group, may also have been an important factor (see below).

¹ Fifth paper, W. A. Noyes and Ulrich Heubaum, *THIS JOURNAL*, **52**, 5070 (1930). Further references will be found in that paper.

Diazocamphor (II) has been prepared by Schiff² by the action of nitrous



acid on an aminocamphor (I) which had not been resolved into active constituents. The compound is reported as comparatively stable and its study seemed to be of especial interest for our purposes. The same diazocamphor was obtained from each of the stereomeric aminocamphors. This excludes the formulas (II), which represent optically active forms. Formula (III) seems possible.

Experimental Part

Resolution of Amino-*d*-camphor.—*d*-Camphor was converted into isonitroso-*d*-camphor by treatment with ethyl nitrite in the presence of sodium.³ The mixture of α - and β -oxime obtained was reduced with zinc and alkali according to Duden and Pritzkow.⁴ The freshly distilled aminocamphor was converted into the neutral oxalate by addition of an equivalent of oxalic acid. The properties of the salt agreed with those given by Duden and Pritzkow for the acid oxalate. We found the acid salt much more easily soluble. The melting point of the neutral salt prepared from the unresolved aminocamphor was 135°.

Anal. (micro-Dumas). Calcd. for the neutral salt, N, 6.6; for the acid salt, N, 5.5. Found: N, 6.56.

The first crop of crystals consisted mostly of the low rotating oxalate and gave a constant rotation after three or four crystallizations. This salt was converted into the benzoate and further crystallized, but the amine recovered from the oxalate and benzoate showed no difference in rotation.

It may be remarked that as amino-*d*-camphor has two asymmetric carbon atoms besides the one connected with the amino group, the use of an optically active acid is not necessary for its resolution.

The mother liquor from the first crystallizations contained the high rotating oxalate still in mixture with the low rotating salt. The solution was evaporated under diminished pressure, to avoid decomposition by long boiling. The separated crystals were filtered off from time to time and crystallizations, with constantly increasing rotations, were obtained in this way. The last fractions were recrystallized to constancy.

Amino-*d*-camphor 1. $[\alpha]_D +17.5^\circ$ in alcohol ($p = 1.6492$). Oxalate: m. p. 212°. $[\alpha]_D +8.49^\circ$; 8.22° in water ($p = 1.4520$; 1.4908). Amino-*d*-camphor 2. $[\alpha]_D 55.5^\circ$ in alcohol ($p = 1.6700$). Oxalate: m. p. 203°; $[\alpha]_D 43.3^\circ$; 43.7° in water ($p = 1.3588$; 0.6456).

Preparation of Diazocamphor.—Attempts to prepare diazocamphor by the method of von Pechmann were without success. The urethan, which we obtained from aminocamphor and ethyl chlorocarbonate by means of the Schotten-Baumann reaction,

² Schiff, *Ber.*, **14**, 1375 (1881); Angeli, *ibid.*, **26**, 1715 (1893).

³ Claisen and Manasse, *Ann.*, **274**, 73 (1893).

⁴ Duden and Pritzkow, *Ber.* **32**, 1539 (1899).

could be converted into a rather unstable nitroso derivative, which on treatment with sodium methylate at low temperatures gave the yellow solution of diazocamphor. Every attempt to free the solution from alkali resulted in a rapid evolution of nitrogen. We therefore reverted to the method already employed by Schiff and by Angeli.²

The oxalate of the aminocamphor obtained by the resolution was suspended in an ice-cold solution of sodium nitrite and placed in a separatory funnel with some petroleum ether. The calculated amount of dilute acetic acid was added while shaking. The yellow solution of diazocamphor in the petroleum ether was separated and then washed with water. The diazocamphor separated on cooling to -80° and was recrystallized by dissolving in petroleum ether at room temperature and subsequent cooling until the melting point was 74° . Such preparations were proved by combustion to be pure and were used exclusively for the determination of the rotation.

Anal. Calcd.: N, 15.76. Found: N, 15.7.

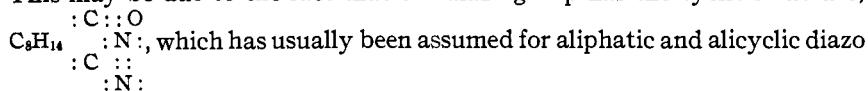
The measurements were made with a sensitive Schmidt and Haensch half-shade polarimeter with a monochromater. The source of light was a 1000-watt lamp and the readings were taken with the usual precautions. Ether was used as a solvent.

SPECIFIC ROTATION OF DIAZO-*d*-CAMPHOR

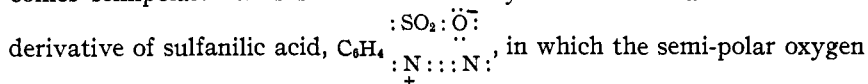
λ	From aminocamphor 1			From aminocamphor 2	
	0.8306	0.4012	0.6856	0.3984	0.8290 g/100 cc.
620	87.6	87.4	87.6	86.9	...
589	100.1	99.6	99.7	100.3	100.0
565	107.7	110.0	108.1	109.1	108.7
545	116.1	115.7	115.9	115.0	115.7
510	119.1	121.2	120.6	119.4	120.5

Discussion

These results demonstrate that the carbon atom attached to the diazo group has lost the asymmetry characteristic of the same carbon atom in the two aminocamphors from which the diazocamphor was prepared. This may be due to the fact that the diazo group has the cyclic structure,



Another explanation is that it has the structure (III) given at the beginning of the paper. In this formula the carbon atom bearing the diazo group is represented as forming a double covalence with the adjacent carbon atom, while the oxygen atom of the carbonyl group becomes semipolar. This structure is closely related to that of the diazo



atom of the sulfonic ion balances the positive ammonium ion of the diazonium group.

Weissberger and Haase⁵ and Weissberger and Bach have recently prepared a crystalline, optically inactive, diazo compound from *d*-amino-succinic ester and have shown that a diazo compound prepared by the

⁵ Weissberger and Haase, *Ber.*, **64**, 2896 (1931); Weissberger and Bach, *ibid.*, **65**, 285 (1932).

formulas indicate. There is a Walden inversion and the ethoxy group takes the place of the unshared electrons of the diazo compound, these electrons shifting to the place of the diazo group to receive the hydrogen ion from the alcohol.⁹ It may be objected that this indicates a cyclic arrangement for the nitrogen atoms of the diazo group, but such a structure will not account for the asymmetry of the carbon atom which is retained in this and in many other decompositions of active amino compounds by nitrous acid.

Noyes and Coss also demonstrated that the compound described by Noyes and Taveau is a ketazine, the bis-hydrazone of camphonic acid, $(C_2H_5OCOC_3H_{14}=N-)_2$, and obtained very definite indications that a diazo compound is an intermediate step in the formation of the ketazine. Kendall and Noyes¹⁰ succeeded in preparing the intermediate diazo compound in a crystalline form and showed that it decomposes almost quantitatively to give the ketazine. This demonstrates that the diazo compound is an intermediate step in the formation of the ketazine from the nitroso derivative. Kendall and Noyes also prepared a crystalline diazo compound from the *trans*-aminolauronic acid, which differs from the *cis*-aminolauronic acid only in the asymmetry of the carbon atom to which the amino group is attached. These compounds were so unstable that it was impossible to show any difference in their optical rotations.

Ray¹¹ has prepared these two diazo compounds from the *cis*- and *trans*-aminolauronic esters and has shown that their decomposition gives, in part at least, the same decomposition products which were obtained by Noyes and Skinner⁹ and by Skinner¹² by treatment of the esters with nitrous acid. This demonstrates that the two diazo compounds are different and that the carbon atoms to which they are attached are asymmetric. It also gives almost conclusive evidence that when an aliphatic or alicyclic amine is decomposed by treatment with nitrous acid the first step in the process is the formation of a diazo compound, which retains the asymmetry of the amine.

Noyes and Heubaum¹ have prepared diazo compounds from the two bornylamines. These showed apparent differences in their rotary dispersion curves and one gave a dextrorotatory bornyl chloride and the other a levorotatory chloride.

Gibson¹³ has been unable to resolve trisulfonylmethanes of the type, $\begin{array}{c} \text{XO}_2\text{S} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{YO}_2\text{S} \end{array} \begin{array}{c} \text{SO}_2\text{Z} \\ \diagdown \\ \text{H} \end{array}$, in which the hydrogen is capable of ionization, leaving

⁹ Noyes and Potter, *THIS JOURNAL*, **34**, 1067 (1912); Noyes and Skinner, *ibid.*, **39**, 2692 (1917).

¹⁰ Kendall and Noyes, *ibid.*, **48**, 2404 (1926).

¹¹ Ray, *ibid.*, **52**, 3004 (1930).

¹² Skinner, *ibid.*, **45**, 1498 (1923).

¹³ Gibson, *J. Chem. Soc.*, 2637 (1931).

a negative carbon atom, with two unshared electrons, a condition similar to that supposed above for the aliphatic diazo compounds. Gibson suggests that ionization may have rendered the activity too fugitive to be observed. This indicates that active compounds of this type are difficult to isolate but, in the light of the evidence given above, is not conclusive against the possibility of such structures.

Summary

1. Amino-*d*-camphor, which had not previously been resolved, has been separated into two amines with specific rotations $[\alpha]_D$ 17.5 and 55.5°, respectively.

2. The diazocamphors prepared from the two amines were proved to be identical.

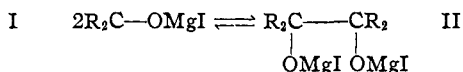
3. The theoretical aspect of this fact is discussed.

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COMMUNICATIONS TO THE EDITOR

THE MECHANISM OF THE PINACOL SYNTHESIS BY THE SYSTEM $Mg + MgI_2$ Sir:

In a recent paper [THIS JOURNAL, **54**, 2112 (1932)] Bachmann criticizes adversely the arguments brought by Bergmann and Schuchardt [*Ann.*, **487**, 225 (1931)] in favor of their interpretation of the reduction of aromatic ketones by $Mg + MgI_2$. In the considerations advanced by Bachmann, there are two erroneous assumptions to which I intend to draw attention. In the first place, it is impossible to ascribe to the equation



more than only a formal meaning, because the ketyls—and the left-hand compound belongs, to all appearances, to the ketyls—are practically monomeric, as was pointed out by Schlenk and Thal [*Ber.*, **46**, 2840 (1913)]. In contrast to Bachmann's opinion, we are far from denying that the iodomagnesium pinacolate (II) is capable of dissociation into radicals, but we may almost deny that it is capable of existence in its dimeric form. It is very probable that molecules of the formula I can be formed, for instance by the action of a Grignard reagent on a pinacol, and come in equilibrium with the five-membered compound (III), but as it is impossible to obtain pinacols from the sodio-ketyls, we shall not make the "MgI-ketyls" responsible for the formation of the pinacols. In the paper criticized by Bachmann it was assumed, therefore, that the five-membered ring compound III is formed and, on hydrolysis, yields the pinacols.