TABLE III

2-METHYLBUTENE-2

255 (0b) (e); 386 (2) (a, e); 443 (2) (a, e); 526 (3) (a, e); 767 (6) (a, b, e); 800 (1b) (a,[a] e); 1052[a] (00) (a, e); 1337 (3) (a, e); 1383 (4) (a, b, e); 1435 (1) (a, e); 1448 (8) (a, e); 1654[a] (000) (e); 1680 (8) (c,[a] d,[a] e); 2732 (2) (a); 2861 (8) (a); 2885 (2) (a); 2919 (20b) (a); 2972 (7) (a); 3026 (1) (a); 3060 (1) (a).

[a] These lines occur on the overexposed plate only.

In the tables, the data are summarized as follows. A weighted average of the Raman shift as determined from plates taken with filtered and unfiltered radiation is followed by a number indicating the relative intensity of the line, and letters indicating the mercury lines by which it was excited. a = 4047 Å., b = 4077 Å., c = 4339 Å., d = 4347 Å., e = 4358 Å. line. The intensity estimated visually is indicated 000 for the lowest, by 10 for very strong, and by 20 for a few exceptionally strong lines. The letter b following an intensity number indicates a broad line.

Summary

The Raman spectrum of synthetic 2-methylbutene-1 has been photographed.

The Raman spectra of the low and the high fractions of the hydrocarbon obtained by the dehydration of tertiary amyl alcohol show the former to be a mixture of 2-methylbutene-1 and 2-methylbutene-2, while the latter is practically pure 2-methylbutene-2.

SOUTH HADLEY, MASS.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

Aliphatic Diazo Compounds. II. Phenyl-alpha-naphthyldiazomethane

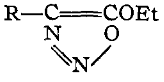
BY GORDON C. HARROLD AND MARTHA G. HEMPHILL WITH FRANCIS EARL RAY

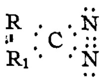
Since Levene and Mikeska[1] first prepared aliphatic diazo esters that seemed to be optically active, a large amount of work has been done in an effort to decide whether an asymmetric carbon atom attached to an amino group retains its asymmetry when the amino group is converted into the diazo derivative. Noyes and Chiles[2] extended and later Lindemann[3] apparently confirmed these results.

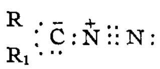
The decomposition of various amino and diazo camphor compounds has been studied also in an attempt to elucidate the structure of the diazo group.[4]

More recently Weissberger[5] has shown that the *p*H of the solution influences the optical activity of the products of decomposition of diazo esters and that these products (hydroxy compounds) were found sufficient to account for *all* the activity previously attributed to the diazo esters. There is a certain similarity between the intermediate compound postulated by Weissberger and that of Noyes and Kendall.[4b] Noyes and Meitzner,[4e] however, point out that in the decomposition of aminolauronic acid a Walden inversion occurs. This means that neither mechanism is adequate to explain the formation of these diazo compounds and their complex decomposition products.

Even if we accept Weissberger's researches as invalidating the conclusions drawn from the previous work on diazo esters, we do not necessarily have to conclude that all aliphatic diazo compounds have the ring structure II. The aliphatic diazo esters are a special class of diazo compounds. It is well known that a carbonyl or ester group contributes greatly to the stability of the diazo grouping.[6] The reason for this may well be ascribed to a tautomeric ring formation involving the nitrogen, oxygen and carbon atoms, I. This compound would be optically inactive, due to the presence of the ethylenic double bond but it would not give any evidence that would enable us to decide between the Curtius, II, and the Angeli–Thiele, III, formulas.[7] (Compare Noyes and Meitzner.[4e])


I


II


III

We have sought, in the present work, a compound which would be without the polar groups

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[1] Levene and Mikeska, *J. Biol. Chem.*, **46**, 592 (1921); **52**, 485 (1922).

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

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

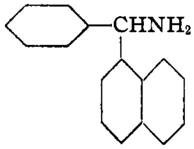
[4] (a) Noyes and Skinner, THIS JOURNAL, **39**, 2692 (1917); (b) Kendall with Noyes, *ibid.*, **48**, 2404 (1926); (c) F. E. Ray, *ibid.*, **52**, 3004 (1930); (d) Heubaum and Noyes, *ibid.*, **52**, 5070 (1930); (e) Noyes and Meitzner, *ibid.*, **54**, 3768 (1932).

[5] Weissberger, *Ber.*, **64B**, 2896 (1931); *ibid.*, **65B**, 265 (1932); *ibid.*, **66**, 559 (1933).

[6] Staudinger, *Ber.*, **37**, 1295 (1904).

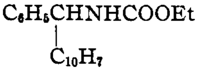
[7] Bradley and Robinson, THIS JOURNAL, **52**, 1558 (1930).

that might lead to ring formation. This we believe we have achieved in phenyl-α-naphthylaminomethane, IV.

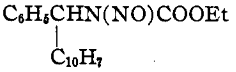


IV

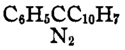
This amine has been prepared and resolved into its optical antipodes by Betti and Poccianti,[8] and Berlingozzi.[9] The active amine was converted into the urethan, V. This was treated with nitrous anhydride and the nitroso derivative, VI, was obtained. Potassium methylate converted this into the diazo compound, VII.


$C_6H_5\underset{C_{10}H_7}{\underset{|}{C}}HNHCOOEt$

V


$C_6H_5\underset{C_{10}H_7}{\underset{|}{C}}HN(NO)COOEt$

VI


$C_6H_5\underset{N_2}{C}C_{10}H_7$

VII

The diazo compound was prepared by dissolving the nitroso derivative, VI, in acetone, cooling to −20° and adding potassium methylate. The solution gradually turned a deep red. It took three to four hours for the color to develop fully. At higher temperatures the color developed more rapidly, but then considerable decomposition occurred and a pure product could not be secured.

When the reaction was completed the acetone solution was poured into ice water, and the pink precipitate collected and dissolved in ligroin.

The ligroin solution of phenyl-α-naphthyl-diazomethane, VII, was deep red with a slight purple cast in reflected light. If protected from moisture and carbon dioxide it was stable at room temperatures for several days. This solution was somewhat active to polarized light but the rotation remained exactly the same after the red diazo compound had been decomposed by heat. The dispersion which was low was also unchanged.

The ligroin was successively evaporated in a stream of dry carbon dioxide-free air, and the solute fractionally crystallized out by cooling in an ether–carbon dioxide bath. The purest material was bright pink in color and showed no rotation. The fractions that showed optical activity retained that exact activity after the diazo compound had been decomposed by heat. The dispersion, also, was unchanged.

The solid diazo compound was not as stable as we had hoped it would be. Decomposition could be observed under the microscope when it was not visible to the unaided eye. In twenty-four hours the compound had decomposed to the extent of 90% as indicated by its nitrogen content.

In the solution, and in those samples of solid that showed activity, the rotatory dispersion was small, though the range observed was limited by the deep color of the diazo compound. No evidence could be obtained of the anomalous dispersion that should characterize an active diazo compound having an absorption band in the visible spectrum.[4b]

Our conclusion is that this diazo compound is optically inactive. It is possible that the instability of the compound in the solid state was an indication of its rapid racemization in solution.[4c] If this is the case a much more stable diazo compound would be required.

Experimental Part

Phenyl α-Naphthyl Ketone.—This compound was prepared according to the method of Grucarevic and Merz.[10] The method of Perrier[11] seems an improvement on this, however.

Phenyl α-Naphthyl Ketoxime.—Betti and Poccianti's[8,12] method was not satisfactory for the preparation of large amounts. The following method gave very good results. Twenty grams of phenyl α-naphthyl ketone was dissolved in 250 cc. of alcohol. Ten grams of hydroxylamine hydrochloride in 20 cc. of water was added, followed by 20 g. of powdered barium carbonate. The mixture was heated at 60–70° for seventy-two hours. It was then filtered and treated with water until turbid. On standing the oxime crystallized out; m. p. 127°, yield 80%.

Phenyl-α-naphthylaminomethane.—The method of Betti and Poccianti[12] was used to prepare this compound. The hydrochloride melts at 275–278°; the acetate at 120° and the free amine at 59°. The acetyl derivative melts at 212–213° and is sparingly soluble in alcohol.

Resolution of Phenyl-α-naphthylaminomethane.—The amine was resolved by Berlingozzi[9] using tartaric acid.

The diastereoisomers did not vary greatly in solubility so that recourse was had to *d*-camphorsulfonic acid. This separated the levo form in a state of purity. 0.2267 g. in 25 cc. of ether in a 2-dm. tube gave α_D −1.03°; $[\alpha]^{22}_D$ −56.8°.

Urethan of Phenyl-α-naphthylaminomethane, V.—Six grams of *l*-amine in 150 cc. of ether, 120 cc. of 5% sodium hydroxide and 6 cc. of ethyl chlorocarbonate were shaken together for twenty minutes. The ether layer was separated, washed with water and dried over sodium sulfate. On evaporation 6.5 g. of product melting at 101–103° was obtained. Recrystallization from alcohol gave 5.0 g.

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(8) Betti and Poccianti, *Gazz. chim. ital.*, **45**, 374 (1915).

(9) Berlingozzi, *ibid.*, **50**, II, 56 (1920).

(10) Grucarevic and Merz, *Ber.*, **6**, 1238 (1873).

(11) Perrier, *Bull. soc. chim.*, [3] **31**, 859 (1904).

(12) Betti and Poccianti, *Gazz. chim. ital.*, **50**, I, 215 (1920).

melting at 125°. $[\alpha]^{20}D$ $-28.0°$, in alcohol. *Anal.* Calcd. for $C_{20}H_{19}O_2N$: C, 78.75; H, 6.23. Found: C, 78.73; H, 6.33.

Nitroso Derivative of the Urethan.—This was prepared by passing dry nitrous anhydride into a suspension of the urethan in ether at $-20°$ for two hours. After standing for thirty minutes the excess gas was removed and the solution poured into water. The nitroso derivative separated and was recrystallized from alcohol; m. p. 87–89° (dec.). An alcoholic solution containing 0.1631 g. in 25 cc. gave in a 2-dm. tube αD $+0.12°$, $[\alpha]^{25}D$ $+9.2°$. *Anal.* Calcd. for $C_{20}H_{18}O_3N_2$: C, 71.83; H, 5.42. Found: C, 72.2; H, 5.8.

Phenyl-α-naphthyl-diazomethane was prepared as previously described. The ligroin solution was evaporated in a stream of dry air free from carbon dioxide until the volume was reduced 25%. The solution was cooled to $-78°$ and filtered. The precipitate was orange colored. This fraction was optically active, as 0.4714 g. in 10 cc. of ether in a 2-dm. tube gave αD $-1.03°$, $[\alpha]^{20}D$ $-9.15°$. It contained 0.002947 g. of nitrogen corresponding to 5.45% of the diazo compound. On recrystallization *l*-phenyl-α-naphthylcarbinol, m. p. 86°, was obtained.[9]

The second fraction was obtained in a similar manner by evaporation of the solution to half the original volume. This material was small in amount, pink in the solid state, and dissolved to give a deep cherry red solution. It melted at 50–54° with vigorous decomposition.

The third fraction separated from the solution that had been evaporated to 25% of its original volume. It was a pink crystalline substance melting at 55–58° with vigorous decomposition. The rotatory dispersion was determined. The material was then heated until the red color had disappeared. This leads to the formation of symmetrical products of decomposition. The rotatory dispersion was again determined and found to be identical with the previous determination. Evidently the diazo compound had no influence on the rotation.

0.0793 g. in 10 cc. of solution in a one-dm. tube gave:

λ	Before heating α	After heating α
486.1	..	−0.19
546.3	..	− .16
577.2	−0.15	− .15
589.3	− .14	− .15
611.4	− .14	..
633.4	− .12	..
656.3	..	− .13

Error ±0.01.

Anal. Calcd. for $C_{17}H_{12}N_2$: N, 11.5. Found: N, 9.34.

The fourth and last fraction was recrystallized from ligroin and gave the purest material melting sharply at 58° with decomposition. The melt was at first a deep red color which became straw colored with the evolution of gas. The solution was optically inactive in red and yellow light. The deep red color of the solution made it impossible to obtain accurate readings at the shorter wave lengths. The pink colored solid was unstable and gave but 1 to 2% diazo nitrogen after standing twenty-four hours. When quickly dried and combusted it gave: *Anal.* Calcd. for $C_{17}H_{12}N_2$: C, 83.7; H, 4.9; N, 11.5. Found: C, 83.5, 83.4; H, 4.6, 4.8; N, 11.2, 11.1.

Summary and Conclusion

Phenyl-α-naphthyldiazomethane has been prepared from *l*-phenyl-α-naphthylaminomethane and found to be optically inactive.

The diazo compound while rather permanent in ligroin solution is only moderately stable in the solid state at room temperature.

Two possibilities, therefore, present themselves: first, the diazo group has a symmetrical structure; second, the compound racemized during the time necessary for its preparation and isolation.[4c]

CINCINNATI, OHIO RECEIVED JANUARY 16, 193

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Structure of Anthracene

BY LOUIS F. FIESER AND WARREN C. LOTHROP

Of the various attempts to account for the special properties of anthracene by means of a special formula, the essentially speculative idea of a reactive para-bond has been found inconsistent[1] with the chemical,[2] electrochemical[3] and optical[4] properties of anthracene derivatives and it has been quite definitely eliminated by the evidence[5] that the carbon atoms of anthracene are practically co-planar and that the distance separating the meso positions is approximately twice the length of any known carbon–carbon linkage.[6] Studies of the magnetic susceptibility[7] of even the most highly reactive of the linear benzologs of the hydrocarbon have shown that the diradical formula postulated by Clar[8] is inadmissible, except perhaps as a reaction phase. Other formulations suggested for anthracene are based upon the fundamental concept of the centric structure of ben-

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[1] Hinsberg, *Ann.*, **319**, 257 (1901).

[2] Clar, *Ber.*, **64**, 2194 (1931).

[3] Fieser and Dietz, THIS JOURNAL, **53**, 1128 (1931).

[4] Goudet, *Helv. Chim. Acta*, **14**, 379 (1931).

[5] Bragg and Bragg, "X-Rays and Crystal Structure," 1924, p. 233; Lonsdale, *Trans. Faraday Soc.*, **25**, 352 (1929).

[6] K. H. Meyer, *Z. angew. Chem.*, **41**, 935 (1928).

[7] E. Müller and I. Müller-Rodloff, *Ann.*, **517**, 134 (1935).

[8] Clar and John, *Ber.*, **62**, 3021 (1929); **63**, 2967 (1930).