have been observed. The complete absence of this process provides strong evidence for an assumed localized ionization[6] at the nitrogen as the directive force in the fragmentation.

An interesting sidelight in the Ia and Ib spectra is provided by the *m/e* 30 peak of Ia which changes to *m/e* 31 in the deuterio analog. A metastable peak was observed at *m/e* 15.6, with the calculated value of 15.5 being that for a *m/e* 58 to 30 process. The ordinary interpretation of this ($CH_2{=}N^+(CH_3)_2 \rightarrow CH_2{=}N^+H_2$) would predict a shift to *m/e* 32 rather than the observed *m/e* 31. This process will be examined in more detail.

For the second comparison (II *vs.* IV and VI), it is noted[3] that the base peak in the mass spectrum of IV is that resulting from process 1 since we are no longer dealing with a methyl ketone. If this same process held in regard to IIa, the base peak would be expected to appear at *m/e* 98, with a shift to *m/e* 101 in IIb. Examination of Figures 3 and 4 indicates that this is far from being the case, although here this process has not been completely eliminated as in the case of Ia. The base peak of IIa can be assigned to the $CH_2{=}CHCH{=}N^+(CH_3)_2$ ion (*m/e* 84 in IIa and *m/e* 85 in IIb) in complete accordance with observations[5] in the VI systems where no carbonyl is present.

Our results[7] on the photochemistry of Ia and IIa will be reported subsequently. Those interested in making correlations between electron-impact fragmentation and photochemistry have an opportunity, in the meantime, to predict the latter based upon the spectra reported here.

Experimental Section

The mass spectra were taken using an Hitachi Perkin-Elmer RMU-6E mass spectrometer (80 eV, 100°, all-glass inlet).

Dimethylaminoacetone and 2-dimethylaminocyclohexanone were purchased from Aldrich Chemicals and purified by distillation at reduced pressure.

The deuterated analogs were prepared by warming a mixture of ketone and deuterium oxide with a trace of anhydrous sodium carbonate. The ketone was then isolated by extraction with anhydrous ether and the entire procedure was repeated until complete deuteration (as evidenced by mass spectrometry) of all the protons adjacent to the carbonyl was achieved.

Registry No.—Ia, 15364-56-4; Ib, 15364-57-5; IIa, 6970-60-1; IIb, 15364-59-7.

[6] F. W. McLafferty, "Determination of Organic Structures by Physical Methods," F. C. Nachod and W. D. Phillips, Ed., Academic Press Inc., New York, N. Y., 1962, p 93.

[7] F. R. Stermitz and V. P. Muralidharan, unpublished results.

The Preparation of (+)-N-Methyl-1-(1-naphthyl)ethylamine and the Determination of Its Optical Purity by Nuclear Magnetic Resonance[1a]

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Received September 18, 1967

Optically pure 1-(1-naphthyl)ethylamine (**1**) was converted into the optically pure N-methyl derivative (**2**) by methylation of the benzenesulfonamide, followed by cleavage with sodium naphthalene radical anion. It is suggested that this method is a generally useful one for the N-alkylation of optically active amines without loss of optical purity. The optical purities of **1** and **2** were determined by nmr spectroscopic analysis of the O-methylmandelamides. This approach to the estimation of the optical purity of primary and secondary amines appears to have broad applicability.

In connection with other work in progress in these laboratories, it became necessary to prepare optically pure N-methylamines of type $R_1R_2CHNHCH_3$ from the corresponding primary amines, $R_1R_2CHNH_2$. The purpose of the present paper is to describe, through the example of the conversion of (+)-1-(1-naphthyl)ethylamine ("Resoline," **1**) to (+)-N-methyl-1-(1-naphthyl)ethylamine (**2**), a procedure for N-methylation which results in no loss of optical purity and a method for determining the optical purity of primary and secondary amines by nmr spectroscopy which gives accurate estimates and is simple to apply.

One approach to the preparation of **2** involved reduction of the formamide of **1** (**3**) with lithium aluminum hydride[2] in ether. However, reaction for 18 hr afforded only a low yield of the desired product with the recovery of a considerable amount of unreacted starting material.[3] An alternative approach, the methylation of the benzenesulfonamide of **1** (**4**) and subsequent cleavage of the N-methyl derivative (**5**) by commonly reported procedures,[4] was investigated. Attempted cleavage of **5** with cold, concentrated sulfuric acid,[5] 25% aqueous sulfuric acid at reflux,[6] 25% aqueous hydrochloric acid at reflux,[7] or KOH in dimethyl sulfoxide[8] failed to yield the desired product.[9]

[1] (a) This work was supported by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-1188-67; (b) Public Health Service Postdoctoral Fellow, 1966–1967; (c) Public Health Service Predoctoral Fellow, 1964–1966.

[2] J. Ehrlich, *J. Amer. Chem. Soc.*, **70**, 2286 (1948).

[3] The difficulty of the reduction of some monosubstituted amides has been noted previously; *cf.* V. M. Mićović and M. L. Mihailović, *J. Org. Chem.*, **18**, 1190 (1953).

[4] The cleavage of sulfonamides has been discussed by S. Searles and S. Nukina, *Chem. Rev.*, **59**, 1077 (1959).

[5] T. L. Fletcher, M. E. Taylor, and A. W. Dahl, *J. Org. Chem.*, **20**, 1021 (1955). This procedure led to extensive decomposition of the starting material.

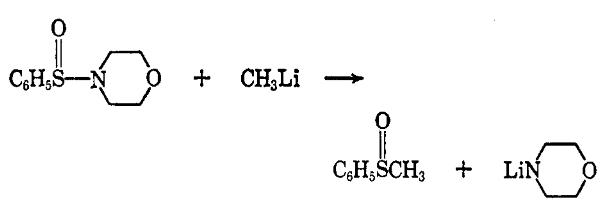
[6] Previous failures to cleave sulfonamides with dilute sulfuric acid (<40%) have been recorded (J. Halberkann, *Ber.*, **54**, 1665 (1921)).

[7] A. Jindra and F. Sipos, *Chem. Listy*, **44**, 235 (1950); *Chem. Abstr.*, **45**, 5569 (1951).

[8] F. C. Chang [*Tetrahedron Lett.*, No. 6, 305 (1964)] has reported the cleavage of toluenesulfonates under similar conditions.

[9] C–N bond cleavage of benzylic sulfonamides has been reported by P. A. Briscoe, F. Challenger, and P. S. Duckworth, *J. Chem. Soc.*, 1755 (1956). The nature of the products (other than recovered starting material) in the present study are unknown.

We recently reported[10] the cleavage of arenesulfinamides with methyllithium as a route to sulfoxides (eq 1), but the anticipated cleavage of **5** under analogous conditions to yield **2** and methyl phenyl sulfone fails to occur.


(1)

The cleavage of sulfonates and sulfonamides with the radical anion of naphthalene has recently been reported.[11] By employing this procedure, we succeeded in cleaving **5** in yields of 75–80%. Since the formation of **4** and the methylation of **4** to **5** are essentially quantitative steps, the over-all yield from **1** to **2** is in the range of 70–80%.

The strongly basic conditions employed in the preparation of **4** and **5**, coupled with the conditions employed in the radical anion cleavage of **5**, might conceivably have led to significant racemization in the course of the conversion of **1** into **2**, by way of abstration of a benzylic α proton.[12] To settle this point, we made use of the nmr method which had been previously applied to the determination of optical purities of alcohols and amines.[13]

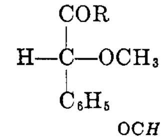
This method depends on the conversion of a mixture of enantiomers ($A_+ + A_-$), using an optically pure reagent, *e.g.*, B_+, into a mixture of diastereomers ($A_+B_+ + A_-B_+$) the ratio of which may be determined by nmr spectroscopy, since, in general, the diastereomers will have similar but distinguishable spectra. The conversion must be carried out in a manner which ensures the equality of the ratios of precursor enantiomers (A_+/A_-) and product diastereomers (A_+B_+/A_-B_+). A reagent previously employed for the determination of the optical purities of alcohols,[14] O-methylmandelyl chloride (**6**), was considered for use with amines. In order to gauge the applicability of the nmr method with the particular reagent under consideration, several amines including **1** and **2** were treated with racemic O-methylmandelyl chloride. In this way mixtures of diastereomers were obtained and their nmr spectra were measured. The use of racemic acid chloride was indicated since an equimolar or nearly equimolar mixture of diastereomers can thus be obtained regardless of the optical purity of the amine used.

In general, when using the nmr method it is advisable to prepare the indicated derivative, here the mandelamides, both from the racemic and from the optically pure reagent, here **6**; if only optically pure acid chloride had been used and no resonance doubling had been observed, it would not have been possible to distinguish between a single diastereomer obtained from reaction with optically pure amine and, given the possibility of accidental coincidence of signals, a mixture of diastereomers obtained from reaction with optically impure amine. Serious errors in interpretation of optical purities may thus be precluded.

The chemical-shift differences of corresponding groups in the resulting mixtures of diastereomeric amides are recorded in Table I. It is seen that in every instance the signals of corresponding protons in the two diastereomeric amides exhibit chemical shift differences of considerable magnitude. The basis was thus laid for the desired determination of optical purity,[13] for if the differences in chemical shift between the diastereotopic[15] O-methyl, C-methyl, methine, and (in the case of **2**) N-methyl groups are large enough and the signals are in a region unencumbered by other resonances, the proportions of the two diastereomers may be determined by integration, each signal affording an independent measure of the diastereomeric ratio.

Table I

Chemical-Shift Differences of Diastereotopic Hydrogens in Some O-Methylmandelamides[a]



$$\begin{array}{c} \mathrm{COR} \\ | \\ \mathrm{H{-}C{-}OCH_3} \\ | \\ \mathrm{C_6H_5} \end{array}$$

R	OCH_3[b]	CH_3OCH[c]	CCH_3[d]
$NHCH(CH_3)(\alpha\text{-}C_{10}H_7)$	3.7	2.8	6.5
$N(CH_3)CH(CH_3)(\alpha\text{-}C_{10}H_7)$[e]	5.2	4.8	4.0
$NHCH(CH_3)C_6H_5$	2.3	2.5	4.0
$NHCH(CH_3)CH_2C_6H_5$	2.3	0.8	4.1

[a] Chemical-shift differences are given in hertz for 60 MHz spectra of approximately 10% solutions in deuteriochloroform. [b] Singlets in the region τ 6.5–6.9. [c] Singlets in the region τ 4.8–5.8. [d] Doublets in the region τ 8.2–9.2 (J = 6.5 Hz). [e] NCH_3 singlets at τ 7.67 and 7.71; $\Delta\nu$ 2.4 Hz.

In order to ascertain that no appreciable racemization occurs in the preparation of the acid chloride (or epimerization in the subsequent reactions), optically pure (−)-menthol was reacted with (A) racemic O-methylmandelyl chloride and (B) acid chloride **6** obtained by reaction of optically pure (−)-(*R*)-O-methylmandelic acid with thionyl chloride. The product of reaction A exhibited doubling of resonance signals, with chemical shift differences of 0.4 Hz for the diastereotopic O-methyl protons and of 2.5 Hz for diastereotopic methoxymethine protons (at τ 5.29 and 5.25), whereas the product of reaction B displayed only one resonance for the methine proton, corresponding to the diastereomer which gives the upfield resonance. In an independent experiment,[16] a sample of (+)-(*S*)-O-methylmandelic acid, $[\alpha]^{23}\text{D}$ +162° (water), was (A) esterified with diazomethane and (B) converted into (*S*)-O-methylmandelyl chloride which was then reacted with methanol. Methyl (*S*)-O-methylmandelate obtained by these two routes had (A) $[\alpha]^{24}\text{D}$ $+91.8 \pm 0.5°$ (acetone) and (B) $[\alpha]^{26}\text{D}$

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(10) J. Jacobus and K. Mislow, *J. Amer. Chem. Soc.*, **89**, 5228 (1967).

(11) W. D. Closson, P. Wriede, and S. Bank, *ibid.*, **88**, 1581 (1966); S. Ji, L. B. Gortler, A. Waring, A. Battisti, S. Bank, W. D. Closson, and P. Wriede, *ibid.*, **89**, 5311 (1967).

(12) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, Chapters 3 and 4.

(13) M. Raban and K. Mislow, *Tetrahedron Lett.*, No. 48, 4249 (1965); M. Raban and K. Mislow in "Topics in Stereochemistry," Vol. 2, N. L. Allinger and E. L. Eliel, Ed., John Wiley and Sons, Inc., New York, N. Y. 1967, p 199. For elegant applications of the method, see H. Gerlach, *Helv. Chim. Acta*, **49**, 2481 (1966), and R. D. Guthrie, W. Meister, and D. J. Cram, *J. Amer. Chem. Soc.*, **89**, 5288 (1967).

(14) M. Raban and K. Mislow, *Tetrahedron Lett.*, No. 33, 3961 (1966).

(15) K. Mislow and M. Raban in "Topics in Stereochemistry," Vol. 1, N. L. Allinger and E. L. Eliel, Ed., John Wiley and Sons, Inc., New York, N. Y., 1967, Chapter 1.

(16) The experiment was performed by Mr. D. J. Sandman.

+90.9 ± 0.9° (acetone) (lit.[17] $[\alpha]^{18}\mathrm{D}$ −96.3° (acetone)).

The method was tested on a sample of partially resolved 1-phenylethylamine, $[\alpha]\mathrm{D}$ +22.6° (methanol), which was converted into the amide by reaction with an excess of optically pure (*R*)-O-methylmandelyl chloride (**6**).[18] Integrated intensities of the O-methyl peaks from 50-cycle sweep width scans indicated a diastereomeric ratio of 90:10, corresponding to an optical purity of 80% in the starting amine. From this, the absolute rotation of 1-phenylethylamine is calculated to be $[\alpha]\mathrm{D}$ 28.3° (methanol), in satisfactory agreement with the reported value[19] of $[\alpha]\mathrm{D}$ 28.5° (methanol).

Reaction of **1** with an excess of optically pure **6** afforded an amide (**7**) whose nmr spectrum consisted of only a single set of signals for the C-methyl, methine, and O-methyl protons, corresponding to the diastereomer which gives the upfield resonance. Reaction of **2** with an excess of optically pure **6** afforded an amide (**8**) whose nmr spectrum consisted of only a single set of signals for the C-methyl, methine, N-methyl, and O-methyl protons, corresponding to the diastereomer which gives the downfield resonance for the first three signals and the upfield resonance for the O-methyl signal. The presence of a single diastereomer in the two O-methylmandelamides demonstrates that **1** and **2** are optically pure within the precision of the nmr measurement and that no racemization takes place in the three-step reaction sequence leading from **1** to **2**.

We believe that the synthesis of **2** from **1** represents a convenient high-yield procedure which is generally useful for the conversion of primary amines of the type $R_1R_2CHNH_2$ to the corresponding N-methyl derivatives without loss of optical purity. The present work further demonstrates the utility of O-methylmandelic acid as an attractive general reagent for the determination of optical purity of amines as well as alcohols by nmr spectroscopy.

Experimental Section[20]

(+)-1-(1-Naphthyl)ethylamine (1) was obtained as "Resoline A" from Crestwood Chemicals, Newport, Tenn., and was purified by distillation and subsequent crystallization of the sulfate salt. The amine had $[\alpha]^{25}\mathrm{D}$ +51° (*c* 2.91, absolute ethanol) (lit.[21] $[\alpha]^{19}\mathrm{D}$ +61.6° (*c* 2.22, ethanol)) and $[\alpha]^{23}\mathrm{D}$ +81.7° (neat) (lit.[21] $[\alpha]^{17}\mathrm{D}$ 82.8° (neat)); the salt had mp 229–232° (lit.[21] mp 230–232°).

(+)-N-[1-(1-Naphthyl)ethyl]formamide (3) was prepared by reaction of **1** with formic acetic anhydride[22] and recrystallized from benzene–petroleum ether (bp 60–70°) to mp 117–118°, $[\alpha]^{25}\mathrm{D}$ +121° (*c* 1.18, ethanol). The nmr spectrum featured a doublet at τ 8.34 (J = 6.5 Hz) assigned to CCH_3 (3 H), a multiplet at 3.83–4.33 (CH_3CH, 1 H), a multiplet at 3.41–3.83 (NH, 1 H), and a singlet at 1.86 (O=CH, 1 H).

Anal. Calcd for $C_{13}H_{13}NO$: C, 78.38; H, 6.57; N, 7.03. Found: C, 78.35; H, 6.65; N, 7.13.

(+)-N-[1-(1-Naphthyl)ethyl]benzenesulfonamide (4) was prepared from **1** in the usual manner:[23] mp 150–151° from acetone; $[\alpha]^{25}\mathrm{D}$ +23° (*c* 0.96, acetone). The nmr spectrum featured a doublet at τ 8.50 (J = 6.5 Hz) assigned to CCH_3 (3 H), a multiplet at 4.33–4.84 (CH_3CH, 1 H), and a multiplet at 2.75–3.08 (NH, 1 H).

Anal. Calcd for $C_{18}H_{17}NO_2S$: C, 69.42; H, 5.50; N, 4.50; S, 10.30. Found: C, 69.46; H, 5.35; N, 4.77; S, 10.56.

(−)-N-Methyl-N-[1-(1-naphthyl)ethyl]benzenesulfonamide (5) was prepared by methylation of **4** in the usual manner;[24] mp 174–176° from acetone; $[\alpha]^{25}\mathrm{D}$ −40° (*c* 1.59, acetone). The nmr spectrum featured a doublet at τ 8.50 (J = 6.5 Hz) assigned to CCH_3 (3 H), a quartet at 3.80 (J = 6.5 Hz) assigned to CH_3CH (1 H), and a singlet at 7.54 (NCH_3, 3 H).

Anal. Calcd for $C_{19}H_{19}NO_2S$: C, 70.13; H, 5.88; N, 4.30; S, 9.85. Found: C, 70.16; H, 5.86; N, 4.52; S, 10.08.

(+)-N-Methyl-1-(1-naphthyl)ethylamine (2).—Following the general procedure of Closson, Wriede, and Bank,[11] 1 equiv of sulfonamide **5** was added to a solution of the radical anion of naphthalene (3.5 equiv) in THF. The reaction mixture was stirred for 1 hr and then quenched with water. The product was isolated by extraction of the reaction mixture with ether, extraction of the ether layer with dilute hydrochloric acid, neutralization of the acid extract with sodium hydroxide, and extraction of the neutral aqueous layer with ether. The ether extract was dried over anhydrous magnesium sulfate, filtered, and the solvent was removed under reduced pressure. Kugelrohr distillation (100° at 0.1 mm) afforded the pure amine (**2**), $[\alpha]^{25}\mathrm{D}$ 74° (*c* 3.885, ethanol). The nmr spectrum featured a doublet at τ 8.57 (J = 6.5 Hz) assigned to CCH_3 (3 H), a quartet at 5.53 (J = 6.5 Hz) assigned to CH_3CH (1 H), and a singlet at 7.66 (NCH_3, 3 H).

Anal. Calcd for $C_{13}H_{15}N$: C, 84.26; H, 8.16; N, 7.56. Found: C, 84.35; H, 8.04; N, 7.80.

Resolution of Mandelic Acid.—*dl*-Mandelic acid (Aldrich) was resolved *via* the (−)-ephedrine salt[25] to give (−)-(*R*)-mandelic acid: mp 130–132.5°; $[\alpha]^{25}\mathrm{D}$ −148.5° (*c* 1.18, water) (lit.[25] mp 133.5°, $[\alpha]^{20}\mathrm{D}$ −156.9° (water)).

(−)-(*R*)-O-Methylmandelic Acid. Method A.—(−)-Mandelic acid was converted into the O-methyl derivative using dimethyl sulfate in base.[26] The crude product was recrystallized from petroleum ether (bp 60–70°) to constant melting point and rotation. The material had mp 65–67°, $[\alpha]^{23}\mathrm{D}$ −161.9°, $[\alpha]^{10.5}\mathrm{D}$ −167.9° (*c* 1.66, water) (lit.[27] mp 63–64°, $[\alpha]^{13.5}\mathrm{D}$ −165.8° (*c* 1.5686, water)).

Method B.—*dl*-O-Methylmandelic acid (Eastman Organic) was resolved *via* the (−)-ephedrine salt[28] ($[\alpha]^{25}\mathrm{D}$ −80° (*c* 1.15, methanol)) to give (−)-(*R*)-O-methylmandelic acid, $[\alpha]^{25}\mathrm{D}$ −164° (*c* 1.47, water).

O-Methylmandelyl Chloride.—O-Methylmandelic acid was refluxed on a steam bath with a five- to tenfold excess of thionyl chloride. Benzene was added and the excess $SOCl_2$ was removed on a rotary evaporator under reduced pressure. The evaporation procedure was repeated three or four times to ensure complete removal of excess thionyl chloride. The slightly yellow acid chloride is satisfactory for use without further purification. If desired, the acid chloride may be distilled (70–75° (0.2 mm), Kugelrohr) to give a colorless liquid.

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(17) A. McKenzie and H. Wren, *J. Chem. Soc.*, 473 (1910).

(18) The ratio of reagents which was employed depends on their state of optical purity and on the purpose to which the reaction is: if optically pure amine is treated with racemic acid chloride, an excess of the amine is employed in order to ensure complete reaction of the acid chloride and to afford a 1:1 mixture of diastereomeric amides; if a sample of amine whose optical purity is to be determined is treated with optically pure acid chloride (**6**), an excess of **6** is employed in order to ensure complete reaction of the amine and to afford a ratio of diastereomeric amides which equals the ratio of enantiomers in the starting amine; if racemic amine is treated with racemic acid chloride, equimolar portions of amine and acid chloride are employed in order to ensure complete reaction of both components and to afford a ratio of diastereomers which is a function of their relative rate constants of formation.

(19) W. Leitke, *Monatsh. Chem.*, **51**, 381 (1929).

(20) Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Nmr spectra were measured on a Varian A-60A spectrometer and refer to approximately 10% solutions in deuteriochloroform, with tetramethylsilane as internal standard.

(21) E. Samuelsson, Thesis, University of Lund, 1923; *Chem. Abstr.*, **18**, 1833 (1924).

(22) C. W. Huffman, *J. Org. Chem.*, **23**, 727 (1958).

(23) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1959, p 103.

(24) W. H. Carothers, C. F. Bickford, and G. J. Hurwitz, *J. Amer. Chem. Soc.*, **49**, 2908 (1927).

(25) R. Roger, *J. Chem. Soc.*, 1544 (1935); R. H. F. Manske and T. B. Johnson, *J. Amer. Chem. Soc.*, **51**, 1909 (1929).

(26) W. Reeve and I. Christoffel, *ibid.*, **72**, 1480 (1950).

(27) A. McKenzie, *J. Chem. Soc.*, **75**, 753 (1899).

(28) D. G. Neilson and D. A. V. Peters, *ibid.*, 1519 (1962). These authors report that (−)-(*R*)-O-methylmandelic acid has $[\alpha]^{20}\mathrm{D}$ −150.7° (*c* 0.574, ethanol). In the present work, the rotation consistently observed by either method A or B was $[\alpha]^{25}\mathrm{D}$ −144° (*c* 1.35, absolute ethanol).

The normal precautions used in handling moisture-sensitive acid chlorides should be exercised. Both racemic and optically pure (**6**) acid chlorides were prepared by this method.

O-Methylmandelamides were prepared by reaction of the appropriate amine in benzene with a solution of O-methylmandelyl chloride in benzene containing an excess of pyridine. The reaction mixture was allowed to stand at room temperature for 30 min and then poured into a separatory funnel containing ether and water. The ether layer was washed successively with dilute aqueous hydrochloric acid, dilute aqueous sodium bicarbonate, and water. The ether layer was dried over anhydrous magnesium sulfate, filtered, and the solvent was removed under reduced pressure to yield the crude mandelamide. The mandelamides thus obtained were sufficiently pure for examination by nmr spectroscopy.[29] Analytical samples were crystallized from benzene–petroleum ether (bp 30–60°) mixtures. Nmr properties of the amides and of menthyl O-methylmandelate (which was prepared in the same manner) are given in Table I and the text.

(−)-N-[1-(1-Naphthyl)ethyl]-O-methylmandelamide (7), prepared from **1** and optically pure (*R*)-O-methylmandelyl chloride (**6**), had mp 132–133°, $[\alpha]^{25}D$ −24° (*c* 1.59, ethanol).

Anal. Calcd for $C_{21}H_{21}NO_2$: C, 78.96; H, 6.63; N, 4.39. Found: C, 78.91; H, 6.55; N, 4.29.

(+)-N-Methyl-N-[1-(1-naphthyl)ethyl]-O-methylmandelamide (8), prepared from **2** and **6**, had mp 93–95°, $[\alpha]^{25}D$ +33° (*c* 0.91, ethanol).

Anal. Calcd for $C_{22}H_{23}NO_2$: C, 79.25; H, 6.96; N, 4.20. Found: C, 79.26; H, 6.85; N, 4.10.

N-[(1-Methyl-2-phenyl)ethyl]-O-methylmandelamide was a diastereomeric mixture (*ca.* 1:1) prepared from racemic amine and racemic O-methylmandelyl chloride and recrystallized three times to mp 59–60°.

Anal. Calcd for $C_{18}H_{21}NO_2$: C, 76.30: H, 7.47; N, 4.94. Found: C, 76.52; H, 7.73; N, 4.66.

N-(1-Phenylethyl)-O-methylmandelamide was a diastereomeric mixture (*ca.* 1:1) prepared from racemic amine and racemic O-methylmandelyl chloride and recrystallized three times to mp 132–137°.

Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.80; H, 7.11; N, 5.20. Found: C, 75.57; H, 7.00; N, 5.26.

Menthyl O-methylmandelate was prepared from an excess of (−)-menthol and racemic O-methylmandelyl chloride. The mixture of diastereomers (*ca.* 1:1) had bp 85° (0.15 mm).

Anal. Calcd for $C_{19}H_{28}O_3$: C, 74.97; H, 9.27. Found: C, 74.74; H, 9.11.

Registry No.—**2,** 15297-33-3 **3,** 15297-34-4; **4,** 15297-35-5; **5,** 15297-36-6 **7,** 15297-37-7 **8,** 15314-01-9; N-[(1-methyl-2-phenyl)ethyl]-O-methylmandelamide, 15297-38-8; N-(1-phenylethyl)-O-methylmandelamide, 17296-90-9; menthyl-O-methylmandilyte, 15296-91-0.

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[29] An nmr spectrum of the crude material should be run prior to any purification in order to ascertain that the ratio of diastereomers is not altered during this procedure.

Carbene Reactions from a Diazomethyltriazole. Contrast with the Isosteric Azide[1]

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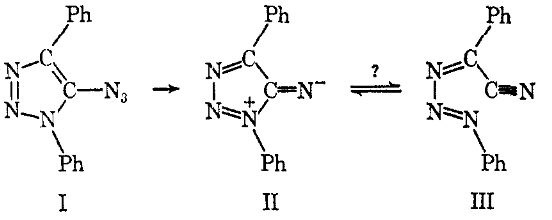
Because 5-azido-1,4-diphenyltriazole loses nitrogen to form an isolable substance that may be an electronically stabilized nitrene, the isosteric diazoalkane was prepared and examined for analogous behavior. No isolable primary decomposition product could be obtained. The crystalline diazo compound lost nitrogen smoothly above 40° without catalysis, attacking the solvent (benzene, cyclohexane, cyclohexene, carbon tetrachloride) to give typical products of carbene insertion or addition in unusually high yields (70%). Decomposition had nearly the same rate in all the hydrocarbon solvents, but was autocatalytic in carbon tetrachloride. The selectivity toward the hydrocarbon solvents was 25:2.1:1 cyclohexene, benzene, and cyclohexane, respectively; the ratio of addition to insertion in reaction with cyclohexene varied from 7.7 to 11. The position isomer, 4-diazomethyl-1,5-diphenyltriazole, lost nitrogen to form a mixture of the corresponding aldazine and the anil of phenyl ethynyl ketone, without detectable attack on any solvent.

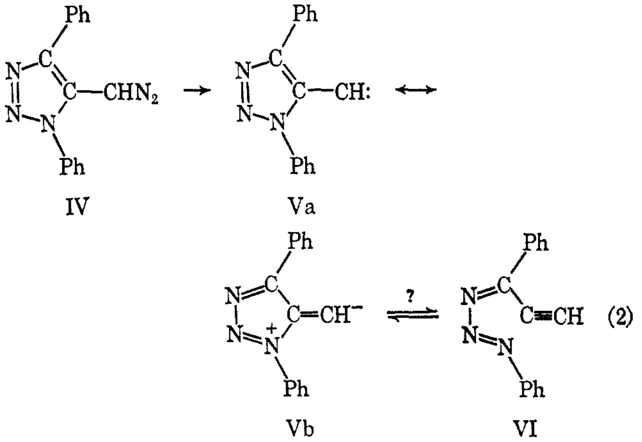
We recently reported[2] on the unusual behavior of an azide, 1,4-diphenyl-5-azidotriazole (I), which loses nitrogen from the azido group at relatively low temperatures and forms a product in which neither rearrangement, cyclization, intermolecular insertion, nor hydrogen abstraction have occurred. The structure of this substance, which might be considered as an electronically stabilized nitrene (imidogen), was narrowed down to two possibilities (II and III); its behavior was most readily accounted for by assuming an active equilibrium between the two in solution (eq 1).



(1)

I II III

The isosteric carbon system, namely, 5-diazomethyl-1,4-diphenyltriazole (IV), became of obvious interest because of the possibility of isolating a substance that might be considered as an electronically stabilized carbene (V) (eq 2), which would bear some analogy to



(2)

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[1] From the Ph.D. Dissertation of J. G. W., Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, p 1620.

[2] P. A. S. Smith, L. O. Krbechek, and W. Resemann, *J. Amer. Chem. Soc.*, **86**, 2025 (1964).