

# Studies in Stereochemistry. XL. The Unusual Magnitudes of Optical Rotations of Imines of Neopentylamine-1-*d* and Ethylamine-1-*d*<sup>1</sup>

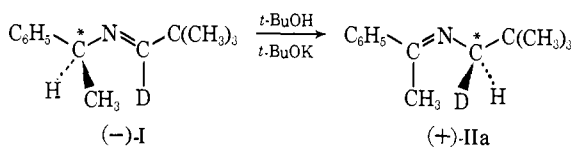
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**Abstract:** The origins of the high magnitudes of rotations of imines of optically pure (+)-(*R*)-neopentylamine-1-*d* and of optically active ethylamine-1-*d* have been investigated. The optical rotatory dispersion curves and ultraviolet spectra are reported of (+)-(*R*)-*N*-(isopropylidene)neopentylamine-1-*d* (IIb), (+)-(*R*)-*N*-(benzhydrylidene)neopentylamine-1-*d* (IIc), (+)-(*R*)-*N*-( $\alpha$ -*t*-butylbenzylidene)neopentylamine-1-*d* (IID), (+)-(*R*)-*N*-( $\alpha$ -methylbenzylidene)neopentylamine-1-*d* (IIa), and (+)-(*R*)-*N*-( $\alpha$ -methylbenzylidene)ethylamine-1-*d* (V). The last compound was prepared by potassium *t*-butoxide catalyzed isomerization of (-)-(*S*)-*N*-(ethylidene-1-*d*)- $\alpha$ -phenylethylamine (IV) in *t*-butyl alcohol at 75°. The first four imines (IIb, IIc, IID, and IIa) gave  $\alpha^{25D}$  (*l* 1 dm, neat) that ranged between a low of 3.77° for IIb and a high of 5.36° for IIa and  $[\phi]^{25}_{\text{max}}$  (hexane) that ranged between a low of 127° (at 322 m $\mu$ ) for IIc and a high of 407° (at 266 m $\mu$ ) for IIb. The fifth imine (V) of undetermined optical purity gave  $[\alpha]^{25D}$  as high as +21.7° (*c* 1, carbon tetrachloride), and a sample with  $[\alpha]^{25D}$  +12° (*c* 0.054, hexane) gave  $[\phi]^{25}_{\text{max}}$  1300° (*c* 0.054, hexane,  $\lambda_{\text{max}}$  259 m $\mu$ ). The rotation of optically pure (+)-(*R*)-neopentylamine-1-*d* is about  $\alpha^{25D}$  +0.25  $\pm$  0.05° (*l* 1 dm, neat), and is potentiated by a factor of about 22 when converted to imine IIa. Similarly, the rotation of (+)-(*S*)-pinacolylamine at the sodium D line and 25° was potentiated by a factor of about 20 when converted to (+)-(*S*)-*N*-( $\alpha$ -methylbenzylidene)pinacolylamine (III). These facts coupled with comparisons between the optical rotatory dispersion and ultraviolet absorption curves of the imines suggest that the Cotton effects observed for the imines are due to transitions of an intrinsically symmetric imine chromophore. The configurational assignment of (+)-neopentylamine-1-*d* as *R* is confirmed and related to that of all new imines. Methyl appears to exceed *t*-butyl in polarizability. When attached to the appropriate chromophores, asymmetric centers whose asymmetry depends on the differences between hydrogen and deuterium can induce sizable rotations at the sodium D line in their molecular hosts.

Recently, (+)-(*R*)-*N*-( $\alpha$ -methylbenzylidene)neopentylamine-1-*d* (IIa),  $\alpha^{25D}$  5.36° (*l* 1 dm, neat), was preliminarily reported<sup>4</sup> as being prepared from the potassium *t*-butoxide catalyzed isomerization of (-)-(*S*)-*N*-



(neopentylidene-1-*d*)- $\alpha$ -phenylethylamine (I) in *t*-butyl alcohol at 75°. The maximum rotation<sup>4,5</sup> of (+)-IIa is  $\alpha^{25D}$  5.40° (*l* 1 dm, neat) and is a very high rotation at the sodium D line for a compound with an asymmetric carbon whose asymmetry is due to the difference between hydrogen and deuterium attached directly to that carbon atom. Hydrolysis of (+)-IIa,  $\alpha^{25D}$  5.36° (*l* 1 dm, neat), yielded (+)-neopentylamine-1-*d* (mixed with ether as shown by vpc),  $\alpha^{25D}$  0.20° (*l* 1 dm, neat), and the rotation of the optically pure amine was about  $\alpha^{25D}$  0.25  $\pm$  0.05° (*l* 1 dm, neat).

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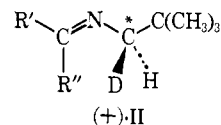
(3) National Science Foundation Science Faculty Fellow at the University of California at Los Angeles, 1967-1968.

(4) R. D. Guthrie, W. Meister, and D. J. Cram, *J. Am. Chem. Soc.*, **89**, 5288 (1967).

(5) R. D. Guthrie, W. Meister, D. A. Jaeger, and D. J. Cram, to be published.

## Results and Discussion

In order to investigate the origin of the abnormally high rotation of (+)-IIa, (+)-(*R*)-*N*-(isopropylidene)neopentylamine-1-*d* (IIb), (+)-(*R*)-*N*-(benzhydrylidene)neopentylamine-1-*d* (IIc), and (+)-(*R*)-*N*-( $\alpha$ -*t*-butylbenzylidene)neopentylamine-1-*d* (IID) were prepared



- (+)-II  
IIa, R' = C<sub>6</sub>H<sub>5</sub>; R'' = CH<sub>3</sub>  
b, R' = CH<sub>3</sub>; R'' = CH<sub>3</sub>  
c, R' = C<sub>6</sub>H<sub>5</sub>; R'' = C<sub>6</sub>H<sub>5</sub>  
d, R' = (CH<sub>3</sub>)<sub>3</sub>C; R'' = C<sub>6</sub>H<sub>5</sub>

by the zinc chloride catalyzed condensation of the appropriate ketone with essentially optically pure (+)-neopentylamine-1-*d* (rotation about  $\alpha^{25D}$  0.25  $\pm$  0.05°; *l* 1 dm, neat). Two additional imines, (+)-(*S*)-*N*-( $\alpha$ -methylbenzylidene)pinacolylamine (III, optically pure)<sup>6</sup> and (+)-(*R*)-*N*-( $\alpha$ -methylbenzylidene)ethylamine-1-*d* (V), also were synthesized. Imine (+)-V of undetermined optical purity was prepared from the potassium *t*-butoxide catalyzed isomerization of optically pure (-)-(*S*)-*N*-(ethylidene-1-*d*)- $\alpha$ -phenylethylamine (IV) in *t*-butyl alcohol at 75°. Reduction of undeuterated IV, *N*-(ethylidene)- $\alpha$ -phenylethylamine, with lithium aluminum hydride yielded *N*-ethyl- $\alpha$ -phenylethylamine.

(6) D. A. Jaeger and D. J. Cram, to be published.

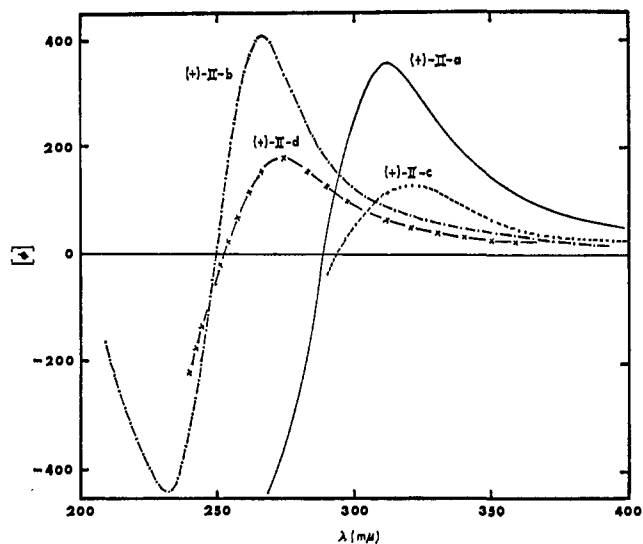


Figure 1. Optical rotatory dispersion curves of (+)-(R)-N-( $\alpha$ -methylbenzylidene)neopentylamine-1-*d* (IIa), —; (+)-(R)-N-(isopropylidene)neopentylamine-1-*d* (IIb), -·-·; (+)-(R)-N-(benzhydrylidene)neopentylamine-1-*d* (IIc), - - - -; and (+)-(R)-N-( $\alpha$ -*t*-butylbenzylidene)neopentylamine-1-*d* (IIId), -x-x-.

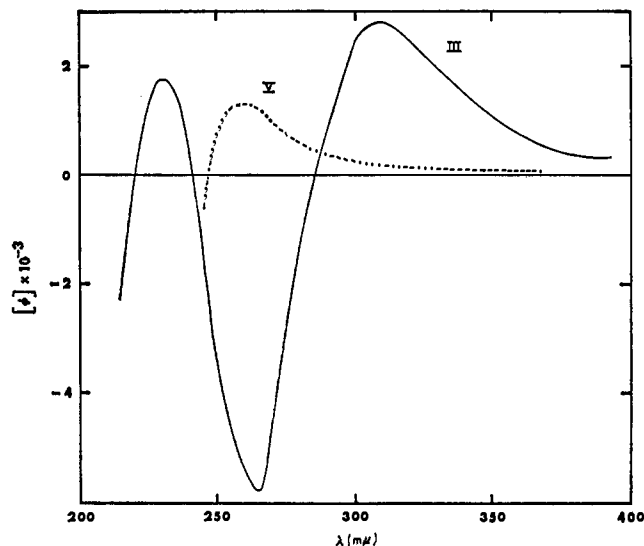
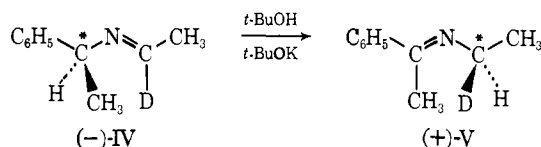


Figure 2. Optical rotatory dispersion curves of (+)-(S)-N-( $\alpha$ -methylbenzylidene)pinacolylamine (III), —; and (+)-(R)-N-( $\alpha$ -methylbenzylidene)ethylamine-1-*d* (V), - - - -.

The optical rotatory dispersion (ORD) and ultraviolet spectra are recorded in Figures 1, 2, and 3, and the important data are summarized in Table I. Imines IIa, III, and V have very similar ultraviolet spectra



with a broad maximum near 240 m $\mu$  ( $\log \epsilon$  4.1–4.5) and a shoulder near 280 m $\mu$  ( $\log \epsilon$  2.6–3.0). The 240-m $\mu$  band is probably due to a  $\pi \rightarrow \pi^*$  transition of the conjugated chromophore and the 280-m $\mu$  shoulder to an  $n \rightarrow \pi^*$  transition. The spectrum of IIb displayed only a shoulder at 243 m $\mu$  ( $\log \epsilon$  2.1). This curve closely resembles that found<sup>7</sup> for azomethine chromophores in totally aliphatic environments. Corresponding absorption bands were assigned to an  $n \rightarrow \pi^*$  transition on the basis of analogy with that of the carbonyl group. The spectrum of IIc displayed multiple bands at 228 m $\mu$  ( $\log \epsilon$  4.5) and 245 m $\mu$  ( $\log \epsilon$  4.5), and a shoulder at 280 m $\mu$  ( $\log \epsilon$  3.6), and the spectrum of IIId displayed multiple bands at 252 m $\mu$  ( $\log \epsilon$  3.2) and 258 m $\mu$  ( $\log \epsilon$  3.1), and a shoulder at 264 m $\mu$  ( $\log \epsilon$  3.0).

The optical rotatory dispersion curve of (+)-IIa exhibited a partial positive Cotton effect with a peak at 312 m $\mu$ ,  $[\phi]^{25}_{\text{max}}$  352°, with  $[\phi]^{25}_{289}$  0°. The increased absorption relative to the small rotations observed prohibited the ORD curve from being determined below about 270 m $\mu$ . Since III differs from IIa only in the substitution of a methyl group for a deuterium, and the ultraviolet spectra of IIa and III are very similar, the shapes of the ORD curves might be expected to closely resemble one another. The ORD curve of (+)-III exhibited multiple Cotton effects with peaks at 310 m $\mu$ ,  $[\phi]^{25}_{\text{max}}$  2790°, and at 230 m $\mu$ ,  $[\phi]^{25}_{\text{max}}$  1810°, and a trough

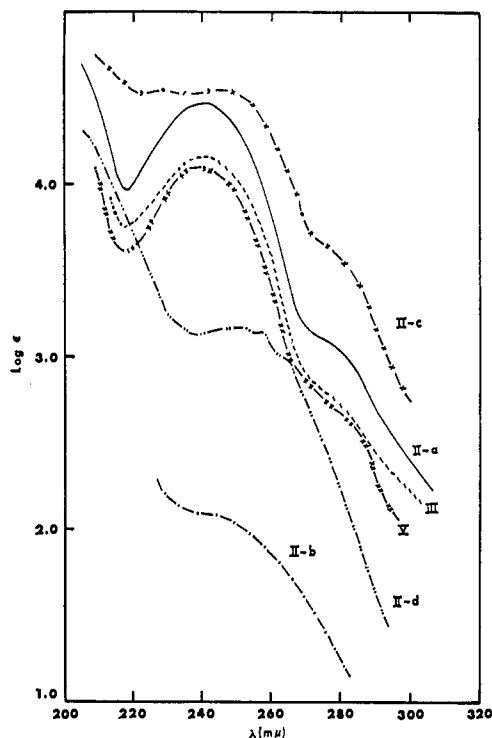


Figure 3. Ultraviolet absorption curves of (+)-(R)-N-( $\alpha$ -methylbenzylidene)neopentylamine-1-*d* (IIa), —; (+)-(R)-N-(isopropylidene)neopentylamine-1-*d* (IIb), -·-·; (+)-(R)-N-(benzhydrylidene)neopentylamine-1-*d* (IIc), -x-x-; (+)-(R)-N-( $\alpha$ -*t*-butylbenzylidene)neopentylamine-1-*d* (IIId), -·-·-·; N-( $\alpha$ -methylbenzylidene)pinacolylamine (III), — — —; and N-( $\alpha$ -methylbenzylidene)ethylamine (V), -x-x-.

at 265 m $\mu$ ,  $[\phi]^{25}_{\text{min}}$  -5780°, with  $[\phi]^{25}_{285}$  0° and  $[\phi]^{25}_{241}$  0°. If the ORD curve of (+)-IIa had been determinable below 270 m $\mu$ , it probably would have continued to resemble that of (+)-III. The Cotton effects centered at 289 m $\mu$  in the ORD curve of (+)-IIa and at 285 m $\mu$  in that of (+)-III probably correspond to the shoulders in the ultraviolet spectra near 280 m $\mu$ . The Cotton effect centered at 241 m $\mu$  in the ORD curve of (+)-III

(7) (a) R. Bonnett, N. J. David, D. Hamlin, and P. Smith, *Chem. Ind. (London)*, 1836 (1963); (b) Z. Badi, R. Bonnett, T. R. Emerson, and W. Klyne, *J. Chem. Soc.*, 4503 (1965).

Table I. Optical Rotatory Dispersion and Ultraviolet Spectral Data for Imines

Imine	$\alpha^{25D^a}$	Cotton effects <sup>b</sup>	Electronic absorptions, $\lambda_{max}^c$
(+)-IIa	5.36	+352 (312), 0 (289)	240 (4.5), 280 sh (3.0)
(+)-IIb	3.77	+407 (266), 0 (250); -444 (231)	243 sh (2.1)
(+)-IIc	4.02	+127 (322), 0 (294)	228 (4.5), 245 (4.5), 280 sh (3.6)
(+)-IId	3.86	+188 (273), 0 (252)	252 (3.2), 258 (3.1), 264 sh (3.0)
(+)-III	86.9 <sup>d</sup>	+2790 (310), 0 (285), -5780 (265), 0 (241), +1810 (230) <sup>e</sup>	241 (4.2), 280 sh (2.7) <sup>e</sup>
(+)-V	12 <sup>f</sup>	+1300 (259), 0 (246)	239 (4.1), 284 sh (2.6) <sup>g</sup>

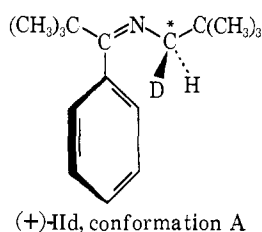
<sup>a</sup> / 1 dm, neat, unless otherwise noted. <sup>b</sup> Described by molecular rotations of peaks and troughs with the corresponding wavelengths in  $m\mu$  in parentheses. The wavelengths of zero molecular rotation are also indicated. Spectra were taken in hexane unless otherwise noted. <sup>c</sup> Wavelengths in  $m\mu$  and  $\log \epsilon$  in parentheses; sh indicates a shoulder. Spectra were taken in hexane unless otherwise noted. <sup>d</sup> *c* 1.21, chloroform. <sup>e</sup> Spectrum taken in cyclohexane. <sup>f</sup> *c* 0.054, hexane. <sup>g</sup> These data are for the undeuterated imine, N-( $\alpha$ -methylbenzylidene)-ethylamine.

corresponds to the absorption maximum at that wavelength.

The ORD curve of (+)-IIb displayed a complete Cotton effect with a peak at 266  $m\mu$ ,  $[\phi]^{25}_{max}$  407°, and a trough at 231  $m\mu$ ,  $[\phi]^{25}_{min}$  -444°, with  $[\phi]^{25}_{250}$  0°. This corresponds well to the Cotton effects of analogous imines<sup>7a</sup> in which the azomethine chromophore is in a totally aliphatic environment.

The ORD curve of (+)-IIc displayed a partial positive Cotton effect with a peak at 322  $m\mu$ ,  $[\phi]^{25}_{max}$  127°, with  $[\phi]^{25}_{294}$  0°, which most likely corresponds to the shoulder in the electronic spectrum near 280  $m\mu$ . Again, increased absorption prohibited measurement of the ORD curve below about 290  $m\mu$ .

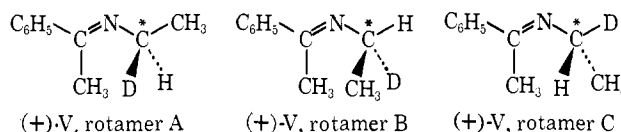
The ORD curve of (+)-IId exhibited a partial Cotton effect with a maximum at 273  $m\mu$ ,  $[\phi]^{25}_{max}$  188°, with  $[\phi]^{25}_{252}$  0°. In general, this curve resembles that of the wholly aliphatic imine, (+)-IIb, a fact compatible with the close similarities of the ultraviolet spectra of IId and IIb. The bulk of the two *t*-butyl groups undoubtedly enforces conformation A on (+)-IId, which in effect decouples the  $\pi$  electrons of the phenyl and imine systems.



The sodium D line rotation of imine (+)-V isolated from the same reaction mixture by preparative vapor phase chromatography varied with retention time, which was controlled by column temperature. The rotations decreased with increasing retention times (decreasing column temperatures), and this suggested that (+)-V was racemized by the column. The highest rotation at the sodium D line obtained for (+)-V was  $[\alpha]^{25D}$  21.7° (*c* 1, carbon tetrachloride). The ORD curve of (+)-V,  $[\alpha]^{25D}$  12° (*c* 0.054, hexane), displayed a partial Cotton effect with a maximum at 259  $m\mu$ ,  $[\phi]^{25}_{max}$  1300°, with  $[\phi]^{25}_{246}$  0°. Imine V differs from IIa only in the substitution of a methyl for a *t*-butyl group, and the ultraviolet spectra of these two imines are very similar. Thus, the general shape and position of the ORD curves of the two substances might be expected to resemble one another. As noted above, the similarity of the ultraviolet curves of IIa and III was ex-

tended to the ORD curves of these two imines in general shape and position. Although the general shapes of the ORD curves of (+)-IIa and (+)-V resemble one another, the general trends of the ORD curve of (+)-V definitely are shifted to longer wavelength relative to those of the ORD curve of (+)-IIa. A possible explanation for this anomaly is as follows.

Imines IIa, IIb, IIc, IId, and III have steric requirements that enforce molecular homogeneity with respect to both *syn-anti* and rotational isomerism. Only the *anti* forms of the rotamers as drawn are sterically feasible. The results of other investigations<sup>8</sup> of *syn-anti* isomerism indicate that V also probably exists solely as the *anti* isomer in solution at room temperature. However, (+)-V (unlike (+)-IIa) is probably an equilibrium mixture of rotamers which differ little in energy, each with its own ORD curve and Cotton effect. Thus, rotamers A, B, and C probably differ little sterically from one another, and therefore the observed ORD curve for (+)-V is really a blend of three ORD curves for each of the three molecular species. The three ORD curves are all expected to differ from one another. Analogy for this explanation is found in the fact that ORD curves of some compounds are temperature dependent,<sup>9</sup> and this has been ascribed to a change in equilibrium concentration of various conformers, each of which possesses its unique ORD contribution.



The potentiation of the rotations of optically active amines and amino acid esters on conversion to their aldimine and ketimine derivatives has been generally observed<sup>10</sup> and may be assumed due to the presence of the azomethine chromophore. For example,<sup>10b</sup> (+)-(*R*)- $\alpha$ -phenylethylamine,  $[\phi]^{25D}$  36° (*c* 2.0, absolute ethanol), and (+)-(*S*)-*sec*-butylamine,  $[\phi]^{25D}$  2° (*c* 2.1, absolute ethanol), on condensation with salicyl-

(8) (a) D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *J. Am. Chem. Soc.*, **88**, 2775 (1966); (b) J. Hine and C. Y. Yeh, *ibid.*, **89**, 2669 (1967).

(9) For example, see (a) C. Djerassi in "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," G. Sznatzke, Ed., Heyden and Son, London, 1967, Chapter 2; (b) P. Crabbé, "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1965, pp 79-83, 138-139.

(10) (a) H. E. Smith, M. E. Warren, Jr., and A. W. Ingersoll, *J. Am. Chem. Soc.*, **84**, 1513 (1962); (b) M. E. Warren, Jr., and H. E. Smith, *ibid.*, **87**, 1757 (1965); (c) H. E. Smith, S. L. Cook, and M. E. Warren, Jr., *J. Org. Chem.*, **29**, 2265 (1964), and references therein.

aldehyde gave (+)-(*S*)-*N*-(salicylidene)- $\alpha$ -phenylethylamine,  $[\phi]^{25D} 424^\circ$  (*c* 1.2, methanol), and (+)-(*S*)-*N*-(salicylidene)-*sec*-butylamine,  $[\phi]^{27D} 104^\circ$  (*c* 1.1, absolute ethanol), respectively. All examples taken together indicate that the rotational potentiation does not depend on any definite structural features of substituents attached to the optically active amine or carbonyl compound.

The increases in rotation on converting optically pure (+)-neopentylamine-1-*d* into imines IIa, IIb, IIc, and IId, and optically active ethylamine-1-*d*<sup>11</sup> into imine V (Table I) represent the most definitive rotational potentiations by the azomethine chromophore. Optically active compounds with asymmetric carbon attached directly to hydrogen and deuterium normally have very small rotations, and Table II lists

**Table II.** Optical Properties of Some Deuterated Compounds

	$[\alpha]_D^a$	$[\phi]_D^b$	Ref
Ethyl-1- <i>d</i> alcohol	0.28	0.13	<i>d</i>
<i>n</i> -Butyl-1- <i>d</i> alcohol	0.45	0.34	<i>e, f</i>
Neopentyl-1- <i>d</i> alcohol	1.15 <sup>c</sup>	3.88	<i>g</i>
Benzyl- $\alpha$ - <i>d</i> alcohol	1.58	1.72	<i>e, f</i>
2-Methylbutane-3- <i>d</i>	0.85	0.62	<i>g</i>
2-Methyl-1-butene-3- <i>d</i>	1.01	0.72	<i>g</i>
1-Phenylethane-1- <i>d</i>	0.76	0.81	<i>f, h</i>
1-Phenylbutane-1- <i>d</i>	1.70	2.30	<i>e, f</i>

<sup>a</sup> All rotations are corrected to one deuterium atom per molecule and represent essentially optically pure materials. Rotations were taken at 17–28°. <sup>b</sup> Molecular rotations,  $[\phi]$ , were calculated as  $[\alpha] \times \text{molecular weight}/100$ . <sup>c</sup> Rotation of the purified acid phthalate (*c* 20, acetone). <sup>d</sup> H. R. Levy, F. A. Loewus, and B. Vennesland, *J. Am. Chem. Soc.*, **79**, 2949 (1957). <sup>e</sup> V. E. Althouse, D. M. Feigl, W. A. Sanderson, and H. S. Mosher, *ibid.*, **88**, 3595 (1966). <sup>f</sup> A. Streitwieser, Jr., J. R. Wolfe, Jr., and W. D. Schaeffer, *Tetrahedron*, **6**, 338 (1959). <sup>g</sup> W. A. Sanderson and H. S. Mosher, *J. Am. Chem. Soc.*, **88**, 4185 (1966). <sup>h</sup> E. L. Eliel, *ibid.*, **71**, 3970 (1949).

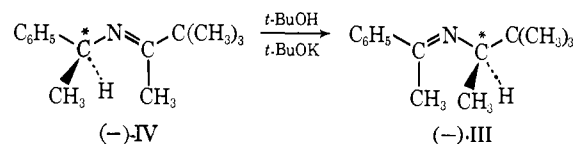
the examples of maximum rotation. The rotation of (+)-neopentylamine-1-*d* was increased by a factor of about 22 at the sodium D line on conversion to its *N*-( $\alpha$ -methylbenzylidene) derivative. About the same factor ( $\sim 20$ ) was observed at the sodium D line<sup>6</sup> on conversion of (+)-pinacolylamine to its *N*-( $\alpha$ -methylbenzylidene) derivative. Therefore, the rotation of IIa is no higher than expected on the basis of rotational comparisons of analogous compounds, and the high rotation is clearly due to the azomethine chromophore.

Complete Cotton effects in the ORD curves of compounds with centers asymmetric due to the difference between hydrogen and deuterium have not been reported previously. The ORD curve of (+)-IIb presents the first example. Streitwieser<sup>12a</sup> found only plain ORD curves for a number of such asymmetric compounds, but Verbit<sup>12b</sup> and Englard, *et al.*,<sup>12c</sup> observed small partial Cotton effects for (+)-(*R*)-1-butyl-1-*d* acetate and succinic-2-*d* acid, respectively. Djerassi and Tursch<sup>13</sup> found no Cotton effect or even a perceptible rotation in the ORD curve of optically active 3-deuteriocyclopentanone, although the molecular am-

plitude of the Cotton effect of (+)-3-methylcyclopentanone<sup>14</sup> exceeded 8700°. Possibly, optically pure 2-deuteriocyclopentanone and its imine derivatives would exhibit high rotations and observable Cotton effects. The Cotton effects of imines IIa, IIb, IIc, IId, and V are assigned to transitions of the inherently symmetric azomethine chromophore asymmetrically perturbed by the center which owes its asymmetry to the difference between hydrogen and deuterium. The molecular amplitudes of the Cotton effects of structurally similar imines<sup>7a</sup> and of imine III suggest that the azomethine chromophores in these imines and those derived from (+)-neopentylamine-1-*d* and optically active ethylamine-1-*d* are not inherently dissymmetric. In the imine series derived from (+)-neopentylamine-1-*d* (IIa, IIb, IIc, and IId) the steric requirements of the groups attached to the azomethine chromophore vary over a wide range. Any asymmetric twisting about the double bond due to steric interactions would result in an inherently dissymmetric chromophore. Should such an effect be present, the different members of the series should exhibit widely different molecular amplitudes for their Cotton effects. Inspection of their ORD curves (Figures 1 and 2) indicates that these amplitudes apparently are of the same order of magnitude. Furthermore, the rotations of imines (+)-IIa, (+)-IIb, (+)-IIc, and (+)-IId at the sodium D line are very similar. Thus, such an effect appears to be absent or trivial.

The *R* configuration was assigned<sup>4</sup> to (+)-neopentylamine-1-*d* on the basis of Brewster's rules<sup>15</sup> and on the assumption that the methyl and *t*-butyl groups have similar polarizabilities relative to the amino group. The absolute configurations of (+)-(*S*)-pinacolylamine<sup>16</sup> and (+)-(*S*)-pinacolyl alcohol<sup>17</sup> and Brewster's rules<sup>15</sup> allow the ranking of methyl and *t*-butyl group polarizabilities and verify the assumption<sup>4</sup> that methyl and *t*-butyl groups have similar polarizabilities relative to the amino group. The configurations of these latter compounds are predicted with Brewster's rules if the polarizability of the methyl group is greater than that of the *t*-butyl group, and both are greater than the polarizabilities of the amino and hydroxyl groups. All of these considerations strongly support the absolute configurational assignments of imines (+)-IIa, (+)-IIb, (+)-IIc, and (+)-IId.<sup>18</sup>

Further confirmation for the configurational assignment has been adduced by chemical data. Thus, (–)-(*R*)-*N*-( $\alpha$ -methylbenzylidene)pinacolylamine (III) was prepared<sup>6</sup> by the potassium *t*-butoxide catalyzed isomerization of (–)-(*S*)-*N*-( $\alpha$ -methylneopentylidene)- $\alpha$ -phenylethylamine (VI) which was, in turn, prepared



from (–)-(*S*)- $\alpha$ -phenylethylamine.<sup>19</sup> The absolute con-

(11) The rotation of optically pure ethylamine-1-*d* is not known but is estimated to be low on a number of grounds (*e.g.*, see Table II).

(12) (a) A. Streitwieser, Jr., L. Verbit, and S. Andreades, *J. Org. Chem.*, **30**, 2078 (1965); (b) L. Verbit, *J. Am. Chem. Soc.*, **89**, 167 (1967); (c) S. Englard, J. S. Britten, and I. Listowsky, *J. Biol. Chem.*, **242**, 2255 (1967).

(13) C. Djerassi and B. Tursch, *J. Am. Chem. Soc.*, **83**, 4609 (1961).

(14) C. Djerassi and G. W. Krakower, *ibid.*, **81**, 237 (1959).

(15) (a) J. H. Brewster, *ibid.*, **81**, 5475 (1959); (b) J. H. Brewster, *Tetrahedron Letters*, No. 20, 23 (1959).

(16) H. Pracejus and S. Winter, *Chem. Ber.*, **97**, 3173 (1964).

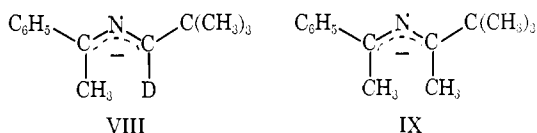
(17) P. G. Stevens, *J. Am. Chem. Soc.*, **55**, 4238 (1933).

(18) H. S. Mosher has made the same configurational assignment based on independent data; private communication.

(19) W. Leithe, *Chem. Ber.*, **64**, 2827 (1931).

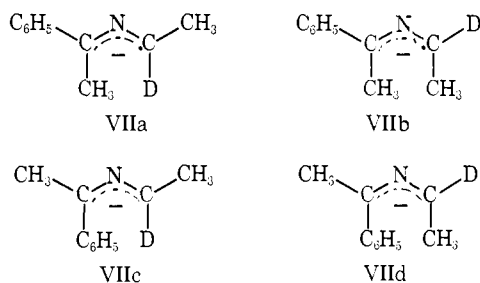
figuration of (–)-III is also known since (–)-(*R*)-pinacolylamine<sup>18</sup> is produced on hydrolysis. Therefore, the absolute configurations of both (–)-VI and (–)-III are known, and with the imines as drawn in their sterically enforced conformations, the isomerization can be described as having proceeded with over-all retention of configuration. Imine IIa differs from III only in the substitution of a deuterium for a methyl group. By analogy with the VI → III transformation, (–)-(*S*)-I (prepared from (–)-(*S*)- $\alpha$ -phenylethylamine) undoubtedly isomerized with over-all retention of configuration in the same solvent–base system to yield (+)-IIa as indicated.

The same analogy predicts that (–)-(*S*)-IV, in the same solvent–base system, also isomerized with over-all retention of configuration to yield (+)-V as indicated. However, the prediction is based on the assumption that the intermediate azaallylic carbanion (VII) in the IV → V isomerization has a geometry similar to intermediates VIII and IX in the I → II and VI → III



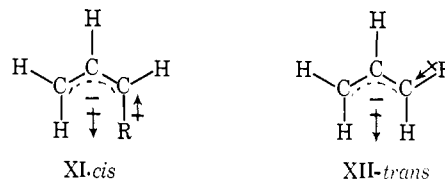
isomerizations, respectively. The bulk of the *t*-butyl group and the tendency of the phenyl group to maintain maximal  $\pi$ -electron overlap with the azaallylic system enforce the conformations of VIII and IX as indicated, with these two groups in the *anti* positions. The highly stereospecific isomerization of (–)-I → (+)-IIa is envisioned<sup>5</sup> as proceeding by abstraction of a proton from (–)-I to yield anion VIII solvated by *t*-butyl alcohol and a potassium ion only on that side from which the proton was abstracted (below the plane of the paper). Collapse of this asymmetrically solvated anion VIII to product yields (+)-IIa, which was described above as the product of over-all retention. With asymmetrically solvated IX as an intermediate, an analogous mechanism was invoked<sup>6</sup> in the explanation of the highly stereospecific isomerization of (–)-VI → (–)-III. Again in anion IX, the phenyl and the *t*-butyl groups undoubtedly enforce the conformation drawn.

The most stable conformation of anion VII, the intermediate in the (–)-IV → (+)-V isomerization, is open to question. Four possible conformations can be drawn: VIIa, VIIb, VIIc, and VIId. Anions VIIc and VIId are considered unlikely because steric



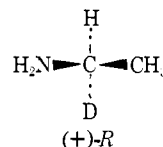
interactions of the phenyl group with deuterium (VIIc) and with the methyl group (VIId) prevent the aromatic ring from attaining maximum  $\pi$ -electron overlap with the azaallylic system. In conformations VIIa and

VIIb, coplanarity of the ring and double bond is sterically feasible. The methyl–deuterium steric interaction (VIIa) is less than a methyl–methyl interaction (VIIb), and on the basis of steric effects alone anion VIIa should be the most stable intermediate anion. However, Schriesheim, Bank, and Whiting<sup>20</sup> have suggested that in some aliphatic allylic anions the *cis* conformation (XI) is more stable than the *trans* conformation (XII) due to the interaction of the allylic  $\pi$ -system dipole with that of the alkyl substituent. An



analogous dipole effect might operate in anion VII, and as a result, VIIb might be more stable relative to VIIa than expected on only steric grounds.

Imine (+)-V, produced from the isomerization of (–)-IV, was assigned the *R* configuration principally on the assumption that (+)-N-( $\alpha$ -methylbenzylidene)-ethylamine-1-*d* would yield (+)-ethylamine-1-*d* on hydrolysis and on Brewster's rules.<sup>15</sup> The assumption is supported by the fact that (+)-neopentylamine-1-*d* yielded only dextrorotatory imines, (+)-IIa, (+)-IIb, (+)-IIc, and (+)-II-*d*. Also, (+)-pinacolylamine yielded (–)-III, and (–)- $\alpha$ -phenylethylamine yielded (–)-I, (–)-IV, and (–)-VI. In all cases except for (–)-VI a rotational potentiation of the same sign was observed. Brewster's rules<sup>15</sup> predict the *R* configuration as indicated for (+)-ethylamine-1-*d*. This



assignment is made even though the ORD curve of (+)-V does not resemble that of (+)-IIa as much as was expected. Finally, the assignment of the *R* configuration to (+)-ethylamine-1-*d* and (+)-V indicates that anion VIIa is the major intermediate in the isomerization of (–)-IV → (+)-V. Thus, steric effects in the azaallylic anion appear to dominate over dipole–dipole effects. The stereospecificity of the isomerization is unknown.

## Experimental Section

**General.** All melting and boiling points are uncorrected. Optical rotations were measured on a Perkin-Elmer Model 141 polarimeter with a 1-dm cell. Optical rotatory dispersion curves (ORD) were recorded on a Cary 60 spectropolarimeter, and the ultraviolet spectra on a Cary 14 spectrometer with 1-cm, 1-mm, and 0.1-mm cells. Infrared spectra were recorded on a Beckman IR-5 machine, and solvent was carbon tetrachloride. Nuclear magnetic resonance spectra (nmr) were recorded on a Varian A-60 instrument with about 1% added tetramethylsilane.

**Vapor Phase Chromatography (vpc).** Analytical and Preparative. Analytical and preparative separations were carried out on two columns: column A, 20 ft  $\times$   $\frac{3}{8}$  in. aluminum column packed

(20) (a) S. Bank, A. Schriesheim, and C. A. Rowe, Jr., *J. Am. Chem. Soc.*, **87**, 3244 (1965); (b) S. Bank, *ibid.*, **87**, 3245 (1965); (c) M. D. Carr, J. R. P. Clarke, and M. E. Whiting, *Proc. Chem. Soc.*, 333 (1963), and references therein.

with 30% SE-30 on 40–60 mesh Firebrick; column B, 10 ft  $\times$   $\frac{3}{8}$  in. aluminum column packed with 25% SE-30 on 40–60 mesh Firebrick. Both columns were installed in an Aerograph Autoprep Model A-700. The flow rate of helium carrier gas was ca. 200 cc/min. In preparative work material was collected in standard Autoprep collectors unless stated otherwise. Approximate retention times in minutes on column A were as follows: ether, 3.5 (110–120°); (+)-neopentylamine-1-*d*, 7 (110–120°); N-(isopropylidene)neopentylamine, 35 (75–80°); N-(benzhydrylidene)neopentylamine, 34 (250–270°); N-( $\alpha$ -*t*-butylbenzylidene)neopentylamine, 17 (225–240°). Retention times in minutes on column B were as follows:  $\alpha$ -phenylethylamine, 18 (125°) and 10 (160°); (–)-N-(ethylidene-1-*d*)- $\alpha$ -phenylethylamine, 30 (125°) and 14 (160°); (+)-(*R*)-( $\alpha$ -methylbenzylidene)ethylamine-1-*d*, 60 (125°) and 28 (160°).

(+)-Neopentylamine-1-*d*. To a solution of 6.0 g (32 mmol) of (+)-(*R*)-N-( $\alpha$ -methylbenzylidene)neopentylamine-1-*d* (IIa),  $\alpha^{25D}$  5.36° (*l* 1 dm, neat), in 100 ml of acetone was added 5 ml of concentrated hydrochloric acid. The mixture was refluxed for 0.5 hr, and the acetone was removed by distillation through a Vigreux column. The concentrated solution was evaporated under vacuum (0.05 mm), and 10 ml of acetone was added to the residue. The solution was refluxed and cooled to 0°, and two crops of crystals were collected. The combined crops were sublimed at 160° (0.05 mm) to yield 3.47 g (89%) of (*R*)-neopentylamine-1-*d* hydrochloride, mp 298–299° (sealed tube). The hydrochloride was dissolved in 20 ml of water, 25 ml of ether was added, and the mixture was treated with 15% sodium hydroxide solution. The aqueous layer was separated and extracted with two 25-ml portions of ether, and the combined ether layers were washed with saturated sodium chloride solution and dried. The solution was fractionally distilled through a Vigreux column to yield 1.48 g (54%) of (+)-neopentylamine-1-*d*,  $\alpha^{25D}$  0.20° (*l* 1 dm, neat), bp 80–81°. Analysis by vpc (column A, 110–120°) showed ether as a small impurity, and the rotation of amine free of ether was estimated to be about  $\alpha^{25D}$  0.25  $\pm$  0.05° (*l* 1 dm, neat).

N-(Isopropylidene)neopentylamine. Neopentylamine was prepared as follows. To a slurry of 6.2 g (0.17 mol) of lithium aluminum hydride in 100 ml of anhydrous ether was added 12.0 g (0.15 mol) of trimethylacetone. The mixture was stirred overnight and then hydrolyzed with 6.2 ml of water. After the addition of 6.2 ml of 15% sodium hydroxide solution and 19 ml of water, the ether layer was separated, dried, and fractionally distilled through a Vigreux column to yield 8.9 g (70%) of neopentylamine, bp 80–81°.

In a round-bottomed flask were placed 500 mg (5.7 mmol) of neopentylamine, 2.0 ml of acetone dried over molecular sieves, 5.0 ml of anhydrous benzene, and  $\sim$ 100 mg of freshly fused zinc chloride. The mixture was refluxed for 1 hr before and after the addition of  $\sim$ 100 mg of anhydrous magnesium sulfate. The precipitate was filtered, and the filtrate was concentrated by distillation of the volatile components through a Vigreux column. The product was isolated from the crude mixture by preparative vpc (column A, 75–80°) and flash distillation at about 60° (15 mm) to yield 208 mg (29%) of N-(isopropylidene)neopentylamine,  $n^{25D}$  1.4190. *Anal.* Calcd for  $C_8H_{17}N$ : C, 75.52; H, 13.47. Found: C, 75.70; H, 13.53.

The infrared spectrum of this material gave a band at 6.05  $\mu$  (C=N stretch). The nmr spectrum taken in deuteriochloroform exhibited a singlet at  $\tau$  7.04 (methylene protons, 1.9), two singlets at  $\tau$  8.00 and 8.21 (isopropylidene methyl protons, 2.8 each), and a singlet at  $\tau$  9.07 (*t*-butyl methyl protons, 9.4).

(+)-(*R*)-N-(Isopropylidene)neopentylamine-1-*d* (IIb). This imine was prepared from (+)-(*R*)-neopentylamine-1-*d*,  $\alpha^{25D}$  0.25  $\pm$  0.05° (*l* 1 dm, neat), using the above procedure for racemic material. From 330 mg of amine was obtained 145 mg (30%) of (+)-IIb,  $\alpha^{25D}$  3.77° (*l* 1 dm, neat),  $n^{25D}$  1.4193. The optical rotatory dispersion and ultraviolet spectra were measured in hexane,  $5.2 \times 10^{-3}$  M.

N-(Benzhydrylidene)neopentylamine. In a round-bottomed flask were placed 500 mg (5.7 mmol) of neopentylamine, 1.3 g (7.0 mmol) of benzophenone, 5 ml of anhydrous benzene, and  $\sim$ 100 mg of freshly fused zinc chloride. The flask was fitted to a Soxhlet extractor containing anhydrous magnesium sulfate, and the mixture was refluxed for 48 hr with the magnesium sulfate being renewed after 24 hr. The reaction mixture was then filtered through anhydrous magnesium sulfate and concentrated under reduced pressure. The product was isolated from the crude mixture by preparative vpc (column A, 250–270°) with collection in a spiral collector filled with glass helices. A flash distillation (0.1 mm) yielded 360 mg (24%),

of N-(benzhydrylidene)neopentylamine,  $n^{25D}$  1.5585. *Anal.* Calcd for  $C_{18}H_{21}N$ : C, 86.01; H, 8.42. Found: C, 86.16; H, 8.30. The infrared spectrum of this material gave a band at 6.15  $\mu$  (C=N stretch). The nmr spectrum taken in deuteriochloroform exhibited a multiplet at  $\tau$  2.21–3.02 (aromatic protons, 10.3), a singlet at  $\tau$  6.88 (methylene protons, 1.8), and a singlet at  $\tau$  9.03 (*t*-butyl methyl protons, 8.9).

(+)-(*R*)-N-(Benzhydrylidene)neopentylamine-1-*d* (IIc). This imine was prepared from (+)-(*R*)-neopentylamine-1-*d*,  $\alpha^{25D}$  0.25  $\pm$  0.05° (*l* 1 dm, neat), by the above procedure for N-(benzhydrylidene)neopentylamine. From 500 mg of amine was obtained 700 mg (47%) of (+)-IIc,  $\alpha^{25D}$  4.02° (*l* 1 dm, neat),  $n^{25D}$  1.5584. The optical rotatory dispersion and ultraviolet spectra were measured in hexane,  $4.9 \times 10^{-2}$  and  $3.7 \times 10^{-5}$  M, respectively.

N-( $\alpha$ -*t*-Butylbenzylidene)neopentylamine. Pivalophenone was prepared as follows. The Grignard reagent of bromobenzene was prepared in the usual manner from 12.5 g (0.5 g-atom) of magnesium turnings, 78 g (0.5 mol) of bromobenzene, and 50 ml of anhydrous ether. To the Grignard solution was added a solution of 42.0 g (0.5 mol) of trimethylacetone in 150 ml of anhydrous ether. The mixture was refluxed for 1 hr, cooled, and hydrolyzed with 90 ml of concentrated ammonium chloride solution. The ether layer was then separated, dried, and evaporated to leave a residue which was fractionally distilled to yield 54.2 g (67%) of pivalophenone, bp 51° (0.7 mm),  $n^{25D}$  1.510 (lit.<sup>21</sup>  $n^{16D}$  1.508).

Using the procedure for the preparation of N-(benzhydrylidene)neopentylamine, 500 mg (5.7 mmol) of neopentylamine, 1.0 g (6.2 mmol) of pivalophenone, and  $\sim$ 100 mg of freshly fused zinc chloride in 5.0 ml of anhydrous benzene yielded 400 mg (30%) of N-( $\alpha$ -*t*-butylbenzylidene)neopentylamine,  $n^{25D}$  1.4852, after preparative vpc (column A, 225–240°) and flash distillation (0.1 mm). The ketimine crystallized at  $-72^\circ$ , mp 36–38°. *Anal.* Calcd for  $C_{18}H_{23}N$ : C, 83.05; H, 10.89. Found: C, 83.22; H, 10.90. The infrared spectrum of this material gave a band at 6.10  $\mu$  (C=N stretch). The nmr spectrum taken in deuteriochloroform exhibited a multiplet at  $\tau$  2.52–2.80 (aromatic protons, 3.1), a multiplet at  $\tau$  2.93–3.19 (aromatic protons, 2.0), a singlet at  $\tau$  7.31 (methylene protons, 2.0), and two singlets at  $\tau$  8.85 and 9.13 (*t*-butyl methyl protons, 9.1 and 9.0, respectively).

(+)-(*R*)-N-( $\alpha$ -*t*-Butylbenzylidene)neopentylamine-1-*d* (IIId). This imine was prepared from (+)-(*R*)-neopentylamine,  $\alpha^{25D}$  0.25  $\pm$  0.05° (*l* 1 dm, neat), by the above procedure for N-( $\alpha$ -*t*-butylbenzylidene)neopentylamine. From 500 mg of amine was obtained 179 mg (13%) of (+)-IIId,  $\alpha^{25D}$  3.86° (*l* 1 dm, neat),  $n^{25D}$  1.4854. The ketimine crystallized at  $-72^\circ$ , mp 36–37°, and mmp 36–37° with N-( $\alpha$ -*t*-butylbenzylidene)neopentylamine prepared above. The optical rotatory dispersion and ultraviolet spectra were measured in hexane,  $3.2 \times 10^{-2}$  and  $1.2 \times 10^{-4}$  M, respectively.

Acetaldehyde-1-*d* from 2-Methyl-1,3-dithiane-2-*d*. The preparation of 2-methyl-1,3-dithiane was patterned after that for 2-phenyl-1,3-dithiane.<sup>22</sup> For 5 min hydrogen chloride was bubbled slowly through an ice bath cooled solution of 35 g (0.32 mol) of 1,3-propanedithiol and 14 g (0.38 mol) of acetaldehyde in 35 ml of chloroform. The solution immediately became cloudy and was dried by the addition of anhydrous calcium sulfate (Drierite). After 1 hr the reaction mixture was evaporated under reduced pressure, and the residue was distilled to yield 25 g (58%) of 2-methyl-1,3-dithiane, bp 42–45° (0.4 mm).

To a solution of 25 g (0.18 mol) of 2-methyl-1,3-dithiane in 800 ml of anhydrous tetrahydrofuran at  $-50^\circ$  under nitrogen was added slowly 125 ml of *n*-butyllithium in hexane (1.6 M). After 1 hr the solution was warmed to 0° during 1 hr, and 5 g of deuterium oxide ( $>99.8\%$  D) was added slowly. The reaction mixture was warmed to room temperature, and 4 l. of 0.05 M hydrochloric acid was added. Tetrahydrofuran was removed under reduced pressure, and the remaining aqueous solution was extracted with a total of 800 ml of 1:1 (v/v) dichloromethane–pentane. The extracts were dried over magnesium sulfate and evaporated, and the residue was distilled to yield 19 g (76%) of 2-methyl-1,3-dithiane-2-*d*, bp 47–50° (0.6 mm).

To a suspension of 80 g of cadmium carbonate and 70 g of mercuric chloride in 250 ml of dimethyl sulfoxide<sup>23</sup> and 10 ml of water was added 15 g of 2-methyl-1,3-dithiane-2-*d*. After 18 hr at room

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(22) D. Seebach, B. W. Erickson, and G. Singh, *J. Org. Chem.*, **31**, 4303 (1966).

(23) A. G. Brook, J. M. Duff, P. F. Jones, and N. R. Davis, *J. Am. Chem. Soc.*, **89**, 431 (1967). The use of dimethyl sulfoxide unnecessarily complicates the separation. The more usual aqueous alcoholic solvent would be adequate and more easily handled.

temperature the mixture was heated to 100°, and the volatile components were collected at -78°. The nmr spectrum of the odiferous distillate taken in carbon tetrachloride exhibited two singlets at  $\tau$  7.88 and 7.95, indicative of acetaldehyde-1-*d* and dimethyl sulfide. The solution was used for the preparation of (-)-IV without further purification.

**Acetaldehyde-1-*d* from Ethyl Alcohol-1,1-*d*<sub>2</sub>.** To an ice bath cooled solution of 200 g (1.55 mol) of 1-octanol in 100 ml of benzene was added 145 g (1.85 mol) of acetyl chloride. After vigorous hydrogen chloride evolution ceased, the reaction mixture was washed with sodium bicarbonate solution, dried, and evaporated under reduced pressure. The residue was distilled to yield 246 g (92%) of 1-octyl acetate, bp 43–44° (0.3 mm). This material was reduced with sodium and acetic acid-*O-d*, using the procedure of Hauser<sup>24</sup> with the modifications of Streitwieser.<sup>25</sup> From 74 g (0.43 mol) of 1-octyl acetate was obtained 12.8 g (63%) of ethyl alcohol-1,1-*d*<sub>2</sub>, bp 78–79°. The nmr spectrum of this material taken in carbon tetrachloride exhibited a broad singlet at  $\tau$  8.83 (methyl protons).

The chromic acid oxidation of ethyl alcohol-1,1-*d*<sub>2</sub> to acetaldehyde-1-*d* followed the standard procedure.<sup>26</sup> From 12.0 g (0.25 mol) of alcohol, 7.8 g (68%) of acetaldehyde-1-*d* was collected at -78°. The nmr spectrum in carbon tetrachloride showed a sharp singlet at  $\tau$  7.89 (methyl protons).

**(-)-(S)-N-(Ethylidene-1-*d*)- $\alpha$ -phenylethylamine (IV).** To 3.0 g (0.025 mol) of (-)- $\alpha$ -phenylethylamine,  $\alpha^{25D} -37.38^\circ$  (*l* 1 dm, neat),<sup>27</sup> held at -10°, was added 1.2 g (0.027 mol) of acetaldehyde-1-*d* at -10°, in several portions. Anhydrous calcium sulfate (Drierite) was added, and after standing overnight at -10°, the reaction mixture was decanted with the aid of anhydrous pentane. Solvent was removed at -10° under reduced pressure to leave 4.0 g of (-)-(S)-N-(ethylidene-1-*d*)- $\alpha$ -phenylethylamine,  $[\alpha]^{25D} -50.3^\circ$  (*c* 4.11, hexane), which was used without further purification. The nmr spectrum taken in carbon tetrachloride exhibited a multiplet at  $\tau$  2.62–3.05 (aromatic protons, 5.1), a symmetrical quartet centered at  $\tau$  5.88,  $J = 6.5$  cps (benzylic proton, 0.92), a singlet at  $\tau$  8.19 (ethylidene methyl protons, 2.7), and a doublet at  $\tau$  8.62,  $J = 6.5$  cps (benzylic methyl protons, 3.2). This material was subject to hydrolysis and disproportionation, and attempts to purify it only led to more impurities.

Undeuterated imine, N-(ethylidene)- $\alpha$ -phenylethylamine, was prepared from  $\alpha$ -phenylethylamine and acetaldehyde in an analogous manner and reduced as follows. To 1.3 g of lithium aluminum hydride in 50 ml of anhydrous ether was added 8.0 g of N-(ethylidene)- $\alpha$ -phenylethylamine. The mixture was refluxed for 5 hr and cooled, and 1.3 ml of water, 1.3 ml of 15% aqueous sodium hydroxide, and 4 ml of water were added successively. The ether solution was decanted from the white solid, dried over calcium sulfate, and concentrated under reduced pressure. The residue was fractionally distilled to yield 4.4 g (55%) of N-ethyl- $\alpha$ -phenylethylamine, bp 41–43° (0.1 mm). *Anal.* Calcd for C<sub>10</sub>H<sub>13</sub>N: C,

80.48; H, 10.13. Found: C, 80.65; H, 10.16. The nmr spectrum of this material taken in carbon tetrachloride displayed a multiplet at  $\tau$  2.55–3.00 (aromatic protons, 5.2), two symmetrical quartets centered at  $\tau$  6.34,  $J = 6.5$  cps, and at  $\tau$  7.57,  $J = 7$  cps (benzylic and methylene protons, 0.90 and 1.8, respectively), and a closely spaced series containing a doublet centered at  $\tau$  8.75,  $J = 6.5$  cps, and a triplet centered at  $\tau$  9.01,  $J = 7$  cps, overlapping with a singlet centered at about  $\tau$  9.00 (benzyl methyl, N-ethyl methyl, and nitrogen protons, respectively, total 7.1).

**N-( $\alpha$ -Methylbenzylidene)ethylamine.** This imine was previously prepared<sup>28</sup> by the acetic acid catalyzed condensation of acetophenone with ethylamine. To an ice bath cooled solution of 12.0 g (0.10 mol) of acetophenone and 3.0 g (0.016 mol) of titanium tetrachloride in 25 ml of anhydrous benzene was added 12.0 g (0.27 mol) of ethylamine in 10 ml of anhydrous benzene. The mixture was stirred at 0° for 1 hr and filtered to remove the white solid present. The filtrate was distilled to yield 8.2 g (56%) of N-( $\alpha$ -methylbenzylidene)ethylamine, bp 49–52° (0.2 mm). Analysis of this material by vpc (column B) showed a trace of acetophenone, and an nmr spectrum (carbon tetrachloride) of material purified by preparative vpc (column B) showed two complex multiplets at  $\tau$  2.12–2.47 and at 2.63–3.00 (aromatic protons, 1.8 and 3.1, respectively), a quartet centered at  $\tau$  6.58,  $J = 7$  cps (methylene protons, 2.0), a singlet at  $\tau$  7.90 (benzylic methyl protons, 3.0), and a triplet centered at  $\tau$  8.72 (N-ethyl methyl protons, 3.0). The ultraviolet spectrum was taken in hexane,  $1.05 \times 10^{-4}$  M. This imine was used throughout to calibrate the vpc retention times (column B) of (+)-V at different temperatures.

**Isomerization of (-)-(S)-N-(Ethylidene-1-*d*)- $\alpha$ -phenylethylamine (IV) to (+)-(R)-N-( $\alpha$ -Methylbenzylidene)ethylamine-1-*d* (V).** To 30 ml of *t*-butyl alcohol *ca.* 0.43 M in potassium *t*-butoxide was added 1.0 g (0.0068 mol) of (-)-N-(ethylidene-1-*d*)- $\alpha$ -phenylethylamine,  $[\alpha]^{25D} -50.3^\circ$  (*c* 4.11, hexane). After 12 hr at 75° the reaction mixture was dark and contained some finely divided powder. The mixture was frozen, and all the solvent and volatile solute was sublimed at 0° (0.2 mm) into a receiver at -78°. The dark red residue was extracted with dry pentane, and evaporation of the extracts left only a dark film which was discarded. The sublimate was concentrated by resublimation at -30 to -40° (0.2 mm), and the concentrated mixture was analyzed and preparatively separated by vpc (column B, 125–175°). Analysis indicated less than 5%  $\alpha$ -phenylethylamine, *ca.* 40% (+)-V, and the remainder (-)-IV. Imine (-)-IV collected from vpc (column B, 125°) gave rotation  $[\alpha]^{25D} -51^\circ$  (*c* 0.47, hexane). The specific rotation of (+)-V in hexane appeared to be partially dependent on retention time, which varied with oven temperature: 125°,  $[\alpha]^{25D} \sim 0^\circ$  (*c* 0.44); 145°,  $[\alpha]^{25D} 3.8^\circ$  (*c* 0.92); 160°,  $[\alpha]^{25D} 11^\circ$  (*c* 0.55); 165°,  $[\alpha]^{25D} 9.0^\circ$  (*c* 0.51).

In another run, 1.5 g (0.010 mol) of (-)-IV prepared from (-)- $\alpha$ -phenylethylamine,  $\alpha^{25D} -35^\circ$  (*l* 1 dm, neat), was isomerized in 60 ml of *t*-butyl alcohol *ca.* 0.43 M in potassium *t*-butoxide for 45 hr. Imine (+)-V, collected by vpc (column B, 170°), showed rotation  $[\alpha]^{25D} 21.7^\circ$  (*c* 1, carbon tetrachloride). The optical rotatory dispersion curve of (+)-V,  $[\alpha]^{25D} 12^\circ$  (*c* 0.054, hexane), was measured in hexane,  $3.6 \times 10^{-3}$  M.

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(25) A. Streitwieser, Jr., and W. D. Schaeffer, *ibid.*, **78**, 5597 (1956).

(26) C. D. Hurd and R. N. Meinert, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p 341.

(27) W. Theilacker and H. S. Winkler, *Chem. Ber.*, **87**, 690 (1954).