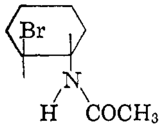
principally *trans*-dibromocyclohexane and cyclohexene bromohydrin.[12,13]

The most characteristic features of the infrared spectrum are the strong bands at 6.2 and 7.85 μ, assigned, respectively, to the C=N[14] and C–O–C groupings. The nmr absorptions centered at τ 4.96, 5.87, 7.6, and 8.34 contain, respectively, one, one, three, and eight protons. That the addition to the double bond is *trans*[15] was determined by preparation of the adduct of cyclohexene-3,3,6,6-d_4.[16] The AB quartet shown for this compound has $J = 9.0$ Hz. Comparison of this latter spectrum with that previously[16] recorded for cyclohexene-3,3-6,6-d_4 bromohydrin indicates that H_A is at τ 4.96 and H_B at τ 5.87.



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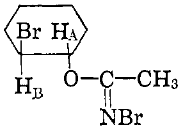

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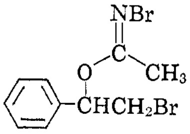

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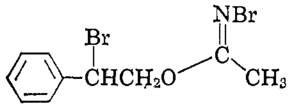

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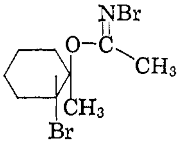

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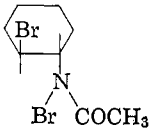

6

The adduct prepared analogously from tetramethylethylene[17,18] had mp 40–41°. The styrene adduct[17] was shown to have structure **3** rather than **4** by comparison of its nmr spectrum with that of styrene bromohydrin (styrene + HOBr) and its derived acetate. The adduct from 1-methylcyclohexene[17] was similarly assigned structure **5**.

The observations made so far indicate that the Wohl reaction must be reinterpreted in terms of a process in which bromine and N-bromoacetimidyl fragments add successively to a double bond. Although the initial stages of the reaction involving only the NBA are undoubtedly radical in nature,[19] the actual addition to the double bond need not be. Homolysis of NBA (eq 2) must be followed by rapid exchange (eq 3 or 4) which generates an N-bromoacetimidyl radical. Step 4 would be followed rapidly by steps 5[20] and then 6, the latter being necessary to account for the absence of unsaturated bromides or dibromoolefins as *primary* products.[12,13] The sequences 4, 5, 6 and 2, 3, 7 each lead to N,N-dibromoacetamide (NDBA), a compound mentioned only once[21] in the chemical literature. Interestingly, NDBA undergoes rapid addition to cyclohexene in the dark to produce **2** and the isomeric N-bromo amide **6**, mp 76°.[17] The brominating properties of NDBA, its role in NBA reactions, and the question of whether the addition to the double bond is ionic or radical are being investigated further.

$$CH_3CONHBr \longrightarrow CH_3CONH + Br \tag{2}$$

$$CH_3CONH + CH_3CONHBr \longrightarrow CH_3CONH_2 + CH_3CONBr \tag{3}$$

$$Br + CH_3CONHBr \longrightarrow HBr + CH_3CONBr \tag{4}$$

$$HBr + CH_3CONHBr \longrightarrow Br_2 + CH_3CONH_2 \tag{5}$$

$$Br_2 + CH_3CONBr \longrightarrow Br + CH_3CONBr_2 \tag{6}$$

$$CH_3CONBr + CH_3CONHBr \longrightarrow CH_3CONBr_2 + CH_3CONH \tag{7}$$

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June 30, 1967

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[12] Both of these products are the result of *intramolecular* rearrangements (S. Wolfe and D. V. C. Awang, to be published).

[13] 3-Bromocyclohexene is not a product of the thermal decomposition of **2** but *is* formed in low yield when **2** is pyrolyzed in the presence of excess cyclohexene. The fate of the imido moiety in the pyrolysis has not yet been established.

[14] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1962, pp 267–270.

[15] The geometry of the >C=NBr grouping was not established.

[16] S. Wolfe and P. G. C. Campbell, *Can. J. Chem.*, **43**, 1184 (1965).

[17] Satisfactory analytical and spectral data were obtained.

[18] The same compound was obtained using the conditions reported by Wohl.[3a]

[19] Bromine is produced when a solution of NBA in carbon tetrachloride is refluxed in the absence of an olefin. If the volatile material is slowly swept out of the system and the solvent removed when there is no further bromine evolution, the residue is found to consist of acetamide.

[20] P. Goldfinger, P. A. Gosselain, and R. H. Martin, *Nature*, **168**, 30 (1951).

[21] A. W. Hoffmann, *Ber.*, **15**, 407 (1882).

1,3-Asymmetric Induction in a Transamination Reaction[1]

Sir:

We have observed that when optically pure, deuterated imine (−)-(*S*)-I-*d* is isomerized by heating in *t*-butyl alcohol–potassium *t*-butoxide, the product is essentially optically pure (+)-(*R*)-II-*d*. The only other nonenzymatic and stereospecific 1,3-proton transfers of which we are aware involve tertiary amines as catalysts and indenes as substrates.[2]

Reduction of pivalonitrile with lithium aluminum deuteride[3] gave deuterated pivalaldehyde, which with α-phenylethylamine, $\alpha^{25}\text{D}$ −38.18° (neat, l = 1 dm),[4] was converted to imine (−)-(*S*)-I-*d*,[5] $\alpha^{25}\text{D}$ −42.48° (neat, l = 1 dm), 99.6% of one atom of deuterium/molecule (combustion and falling drop). This material (17.0 g) was heated at 75° for 78 hr in a 0.45 *M* solution of potassium *t*-butoxide to give a mixture of imines separated by preparative vpc on a 30% silicone gum column at 180° (20 ft × 3/8 in.) with helium as carrier gas. Starting material, (−)-(*S*)-I-*d*, 4.8 g (28%), $\alpha^{25}\text{D}$ −40.5° (neat, l = 1 dm), was recovered, retention time 25 min, and product, (+)-(*R*)-II-*d*, 8.7 g (54%), $\alpha^{25}\text{D}$ +5.24° (neat, l = 1 dm), retention time 41 min, was obtained. In eight runs with reaction times that varied between 10 and 126 hr (10% II, 90% I to 87% II, 13% I) $\alpha^{25}\text{D}$ (neat, l = 1 dm) varied from 5.62 to 5.16°.

A sample of (+)-(*R*)-II-*d* (2.9 g), $\alpha^{25}\text{D}$ +5.36° (neat, l = 1 dm), was hydrolyzed with concentrated hydrochloric acid in acetone to give neopentylamine-α-*d* hydrochloride (82%), mp 300–301° (evacuated tube), which was treated with 40% sodium hydroxide to give

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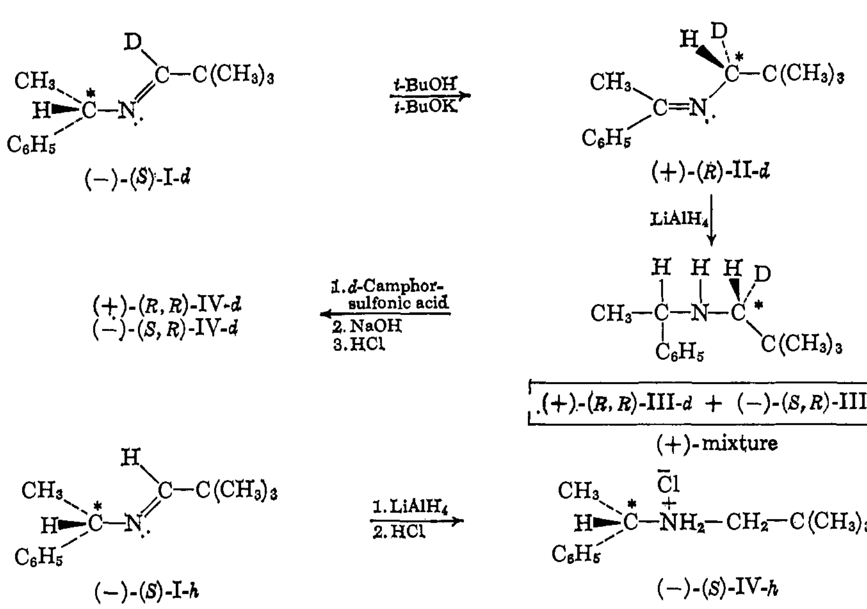
[1] This research was supported in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research Grant No. AF-AFOSR-124-65, and by the U. S. Army Research Office, Durham. The authors express their thanks.

[2] L. Ohlsson, I. Wallmark, and G. Bergson, *Acta Chem. Scand.*, **20**, 750 (1966).

[3] H. C. Brown and C. P. Gary, *J. Am. Chem. Soc.*, **86**, 1085 (1964).

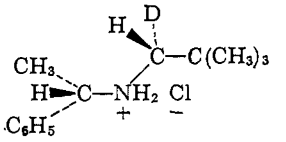
[4] W. Theilhacker and H. G. Winkler, *Chem. Ber.*, **87**, 690 (1954).

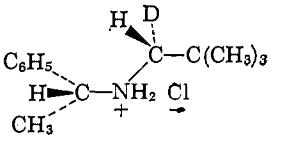
[5] All new compounds reported here gave carbon and hydrogen analyses within 0.3% of theory.



0.9 g of neopentylamine-α-*d* (mixed with ether as shown by vpc analysis), $\alpha^{25}\text{D}$ +0.20° (neat, l = 1 dm). This material was converted with acetophenone back to 0.71 g of (+)-(*R*)-II-*d*, $\alpha^{24}\text{D}$ +5.40° (neat, l = 1 dm), 99.2% of one atom of D/molecule (combustion and falling drop). Based on Brewster's rules[6] and the assumption that methyl and *t*-butyl groups have similar polarizabilities relative to the amino group, (+)-neopentylamine-α-*d* must have the *R* configuration formulated in the series of derivatives. The optical rotatory dispersion curves and high rotation of (+)-(*R*)-II-*d* will be discussed in a future communication. Because of the difficulty in removing solvent, the maximum rotation of neopentylamine-α-*d* has not been obtained accurately, but is probably about $\alpha^{25}\text{D}$ +0.30° (neat, l = 1 dm).

Maximum rotation of (−)-(*S*)-IV-*h*, $[\alpha]^{25}\text{D}$ −22.8° (*c* 3.0, H_2O), was determined by its preparation from optically pure (−)-(*S*)-I-*h*, $\alpha^{25}\text{D}$ −42.45° (neat, l = 1 dm). When reduced with lithium aluminum hydride, 7.4 g of (+)-(*R*)-II-*d* gave 5.7 g of a mixture of (+)-(*R*,*R*)-III-*d* and (−)-(*S*,*R*)-III-*d*, which gave $\alpha^{25}\text{D}$ +1.51° (neat, l = 1 dm), 98–100% of one atom of D/molecule by mass spectral method. The diastereomers (4.8 g) were separated with *d*-camphorsulfonic acid in water. The hydrochloride, (+)-(*R*,*R*)-IV-*d*, was brought to maximum rotation, $[\alpha]^{25}\text{D}$ +23.0° (*c* 2.7, H_2O), 0.25 g, and (−)-(*S*,*R*)-IV-*d* to 90% of maximum rotation, $[\alpha]^{25}\text{D}$ −20.6° (*c* 2.1, H_2O), 0.050 g. A 10% by weight in D_2O of a diastereomeric mixture of IV-*d* (configurationally homogeneous at methylene) exhibited in its nmr spectrum two singlets (intensities of 1.00 and 1.00) for its methylene protons at τ 7.02 and 6.80 (external standard of tetramethylsilane), these peaks being separated by a substantial base line. A nmr spectrum of (+)-(*R*,*R*)-IV-*d*, 10% by weight in D_2O, gave a singlet at τ 6.80, assumed intensity 1.00, and remnants of a singlet at τ 7.02, relative intensity 0.02 (a time-averaging computer was used). Addition of 2, 6, and 10% racemic IV-*d* in three experiments increased the intensity of the band at τ 7.02 to 0.03, 0.06, and 0.08, respectively. A nmr spectrum of (−)-(*S*,*R*)-IV-*d* (90% maximum rotation), 10% by weight in D_2O, gave a singlet at τ 7.02, assumed intensity 1.00, and a singlet at τ 6.80, relative intensity 0.07. These data demonstrate that imine (+)-(*R*)-II-*d* was about 98% pure (2% of (−)-(*S*)-II-*d*).


(−)-(*S*,*R*)-IV-*d*


(+)-(*R*,*R*)-IV-*d*

The 4.8 g of recovered starting material possessed a rotation 95.3% of maximum. Calculations based on first-order one-point rate constants for isomerization and racemization indicate that about 99% of (+)-(*R*)-II-*d* and 1% of (−)-(*S*)-II-*d* would have been formed had the reaction been 100% stereospecific. Thus, the potassium *t*-butoxide catalyzed proton transfer in this transamination reaction was essentially completely stereospecific.

Similar transformations in which deuterium rather than protium was transferred have been carried out in potassium *t*-butoxide–*t*-butyl alcohol-O-*d* to give similar results. For example, when (−)-(*S*)-I deuterated in the benzyl position was 41% isomerized in deuterated solvent, recovered starting material was 8% racemized and (−)-(*S*)-II-*d* was produced, $\alpha^{25}\text{D}$ −4.60° (neat, l = 1 dm). Similarly, nondeuterated (−)-(*S*)-I was partially isomerized in deuterated solvent, and benzyl-deuterated (−)-(*S*)-I was partially isomerized in protonated solvent, but in each case isotopic exchange of starting material occurred faster than isomerization of starting material, and isomerized products possessed low rotations.

Careful kinetic studies were made of isomerizations of a variety of the above labeled imines in several solvents, and the pseudo-first-order rate constants for isomerization, k_i (corrected for the slow return of product to starting material), were determined. Additional independent one-point rate constants were determined for isotopic exchange of starting material (both combinations of deuterated and nondeuterated substrate and solvent), k_e, and for racemization of starting material (both combinations of deuterated and nondeuterated substrate and solvent), k_α. From these

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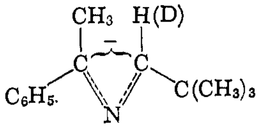
[6] J. H. Brewster, *Tetrahedron Letters*, 20, 23 (1959).

rate constants a number of interesting rate ratios and values were determined: $(k_e/k_\alpha)_{OD}{}^{CH} \sim 28$; $(k_e/k_\alpha)_{OH}{}^{CD} \sim 34$; $(k_i{}^H/k_i{}^D)_{OH} = 3.3$; ratio of rate of collapse of azaallylic anion to starting material to that to product, 4.9–6.0; intramolecularity when proton is transferred in deuterated solvent, ~13%; intramolecularity when deuterium is transferred in protonated solvent, ~13%.

These data provide the following interesting conclusions. (1) The proton transfer in this base-catalyzed transamination is essentially completely stereospecific and involves only a single face of an azaallylic anion. (2) This result could only have been obtained had the reaction occurred essentially exclusively through one of the four possible azaallylic anions, undoubtedly the one least strained (A). (3) Collapse of azaallylic anion favors starting material over product, although the product is the more thermodynamically stable isomer. (4) Starting material undergoes isotopic exchange with high retention. (5) While a proton or deuteron is being transferred, extensive isotopic exchange with solvent occurs. (6) Stereospecificity in this proton transfer does not depend on intramolecularity. (7) In spite of the fact that isotopic exchange of starting material occurs faster than isomerization, a substantial kinetic isotope effect for isomerization is observed. (8) This method provides a useful means of preparing optically active deuterated primary amines.



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[7] NATO Postdoctoral Fellow at University of California at Los Angeles, 1965–1967, sponsored by Deutscher Akademischer Austauschdienst, Bad Godesberg, Germany.

Protonation of Monohomocyclooctatraene Dianion[1,2]

Sir:

Reactions of the aromatic ten-π-electron cyclooctatetraene dianion[3a] as a nucleophile[3b] are both interesting and useful. Similar interest attaches to the chemistry of the homoaromatic counterpart of cyclooctatetraene dianion, namely monohomocyclooctatetraene dianion (I). The latter species was recently reported,[4a] and we now describe the first information on its chemical behavior, specifically its behavior on protonation with methanol.

A priori, assuming stepwise protonation of I, it is not easy to predict whether the first protonation should lead to monocyclic anions, such as IIa–d, or to bicyclic ones containing a cyclopropane ring (III).[5] It is also not clear to what extent the initial protonation would be governed by relative charge densities at C_1–C_8 or by relative stabilities of the monoanions. Further, in a product of diprotonation of I containing a cyclopropane ring it would not be clear without a labeling study whether the cyclopropane methylene group in the final product is the same as the original methylene group of the homocyclooctatetraene (IV) from which the dianion I was derived. For this and other reasons, the 9,9-dideuterio dianion I-D, generated from IV-D,[4a,b] was also quenched in MeOH, and the protio-I was protonated with MeOD.

The potassium salt of I was generated as before[4a] by allowing a solution of *ca.* 25 mg of monohomocyclooctatetraene IV in *ca.* 1.5 ml of 1,2-dimethoxyethane (DME) to stand at −80° over a mirror of excess K. The reaction mixture was prepared in one leg of a two-legged vacuum line apparatus equipped with a small side arm into which some of the solution could be diverted for the detection of an esr signal. Complete conversion of IV to the dianion was checked by the absence of such a signal for the monohomocyclooctatetraene anion radical.[4b,c] A 1-ml quantity of anhydrous MeOH was degassed on the vacuum line and then distilled under vacuum into the DME anion solution which had been transferred to the other leg of the apparatus and thus was no longer in contact with the excess K mirror but was still at −80°. Addition of the MeOH produced an immediate color change from deep orange-brown to a light straw yellow with essentially no further change as the solution was allowed to come to room temperature. Only one main product[6] was detected by vpc and this, obtained in over 85% yield, was collected by preparative vpc. The retention time of the product was identical with that of bicyclo[6.1.0]octa-2,4-diene[7a–e] (V) and its infrared, nmr, and ultraviolet spectra were identical with those of authentic material (Table I).

When the dianion I-D from IV-9,9-D_2 was quenched with MeOH the final product was pure V-9,9-D_2 with infrared, nmr, ultraviolet, and mass spectra identical with those of authentic material prepared from 1,3,5-cyclooctatriene and CD_2I_2. When CH_3OD was employed in the quench of the protio dianion I the bicyclooctadiene product contained two D atoms as judged by the mass spectrum, and the nmr spectrum showed that

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[1] (a) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research; (b) research supported in part by the National Science Foundation.

[2] Reported in part by S. Winstein, Special Publication No. 21, The Chemical Society, London, 1967, p 5.

[3] (a) T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784 (1960); (b) *e.g.*, T. J. Katz and P. J. Garratt, *ibid.*, **86**, 4876, 5194 (1964); W. R. Roth, *Ann.*, **671**, 25 (1964); D. A. Bak and K. Conrow, *J. Org. Chem.*, **31**, 3958 (1966).

[4] (a) M. Ogliaruso, R. Rieke, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 4731 (1966); (b) R. Rieke, M. Ogliaruso, R. McClung, and S. Winstein, *ibid.*, **88**, 4729 (1966); (c) T. J. Katz and C. Talcott, *ibid.*, **88**, 4732 (1966).

[5] Monocyclic anions IIa–d may be visualized as arising from 1-, 3-, 4-, and 2-protonation, respectively. Bicyclic anions may be visualized as arising from monocyclic ones, IIIa and IIIb from IIb, IIIc and IIId from IIc, and IIIe and IIIf from IId. Alternatively, bicyclic anions IIIa, IIIc, and IIIe may be visualized as arising directly from protonation of I.

[6] Two very small additional vpc peaks were observed, but these were shown to arise in blank experiments involving all manipulations except inclusion of hydrocarbon IV.

[7] (a) P. Radlick and S. Winstein, *J. Am. Chem. Soc.*, **85**, 344 (1963); (b) D. S. Glass, J. Zirner, and S. Winstein, *Proc. Chem. Soc.*, 276 (1963); (c) W. R. Roth, *Ann.*, **671**, 10 (1964); (d) P. Radlick, Ph.D. Thesis, University of California at Los Angeles, 1964; (e) J. Zirner, unpublished work; (e) D. Glass, Ph.D. Thesis, University of California at Los Angeles, 1966; (f) J. W. H. Watthey and S. Winstein, *J. Am. Chem. Soc.*, **85**, 3715 (1963); D. S. Glass, J. W. H. Watthey, and S. Winstein, *Tetrahedron Letters*, 377 (1965).