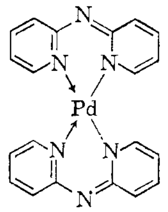
mal to its heterocyclic nucleus. Coordination of the multidentate with a charged metal ion accentuates the drain on the electrons of each such >N—H bond. Hydroxyl ions can then detach such hydrogen atoms as protons, especially if the electrons of the >N–H bond can be re-distributed into a resonating ring system of aromatic type. The formula V represents one canonical form of such an aromatic species. Aromatic compounds of type V with molecules containing two planar resonating systems at right angles to each other, linked through a common metal atom, are unusual (*cf.*, however, the beryllium derivatives of β-dicarbonyl compounds). The quadridentate complexes from the osazones II are formally similar to compounds of porphyrin type.

Finally, in support of our views concerning the structures of these compounds, we report the preparation of the orange, benzene-soluble, neutral palladium (II) complex VI (calcd. for $C_{20}H_{16}N_6Pd$: C, 53.8; H, 3.6; N, 18.8; Pd, 23.8. Found: C, 54.2; H, 3.8; N, 18.8; Pd, 24.4) by treatment of the corresponding bis-(2,2′-dipyridylamine)-palladium(II) perchlorate with alkali. The infrared spectrum of VI completely lacks >N–H bands.



VI

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RECEIVED APRIL 5, 1962

RING ENLARGEMENTS. VIII. THE STEREOCHEMICAL COURSE OF THE DIAZOALKANE-CARBONYL REACTION

Sir:

The interaction of diazomethane with aldehydes and ketones to form homologous carbonyl compounds falls in the class of 1,2-rearrangement reactions and, on the basis of existing evidence, has been thought to be of nucleophilic type.[1] The stereochemical fate of the migrating group has not been adequately tested, however, and it is with this point that the present communication is concerned.

Optically active 2-methylcyclohexanone (I), $[\alpha]^{25}\text{D}$ $-5.0°$ in methanol, was prepared by mild oxidation[2] of (−)-*trans*-2-methylcyclohexanol, $[\alpha]^{25}\text{D}$ $-17.8°$ in ether, which was obtained by hydrolysis of the corresponding half phthalate ester, $[\alpha]^{25}\text{D}$ $-31.4°$.[3] Diazomethane ring enlargement under *ex situ* conditions in ether–methanol[1] yielded a mixture which was distilled and then separated on a preparative scale vapor phase chromatographic column (1.3 × 25 cm., packed with fire brick containing Dow-Corning no. 710 silicone oil) into recovered starting material (19%), 2-methylcycloheptanone (21%) with $[\alpha]^{25}\text{D}$ $-4.5°$ in methanol, 3-methylcycloheptanone (24%) with $[\alpha]^{25}\text{D}$ $+17.1°$ in methanol, methylcyclooctanones and oxides (36%). The assignment of structure to the separated methylcycloheptanones was based on infrared spectral data, on a comparison of their reactivities to sodium bisulfite (3-methylcycloheptanone more reactive) and on a comparison of their propensities to undergo base-catalyzed racemization (2-methylcycloheptanone racemized completely upon standing for *ca.* 3 hr. in a 0.01 *M* solution of sodium methoxide in methanol; 3-methylcycloheptanone upon similar treatment showed no tendency to racemize and, in fact, increased slightly in rotation due to the racemization of a small amount of (−)-2-methylcycloheptanone present as a contaminant). Further purification of 3-methylcycloheptanone was achieved through conversion to the semicarbazone, from which the parent ketone was regenerated, $[\alpha]^{25}\text{D}$ $+18°$ in methanol.

The optical changes occurring during diazomethane ring enlargement were checked in the enantiomeric series and found to follow the same pattern. Thus, starting with (+)-2-methylcyclohexanone, the products were (+)-2-methylcycloheptanone and (−)-3-methylcycloheptanone. It should be noted, however, that the specific rotations of (+)II and (−)III were somewhat higher in this series, possibly indicating that racemization of I prior to ring enlargement occurs to a varying extent in these reactions.

Optical rotatory dispersion measurements showed (−)-2-methylcyclohexanone (I) to have a negative Cotton effect (trough $[\alpha]^{\text{MeOH}}_{302}$ -282, peak $[\alpha]^{\text{MeOH}}_{268}$ $+282$; reported[4] for optically pure (+) epimer; peak $[\alpha]^{\text{MeOH}}_{305}$ $+515$, trough $[\alpha]^{\text{MeOH}}_{263}$ -565), (−)-2-methylcycloheptanone (II) to have a negative Cotton effect (trough $[\alpha]^{\text{MeOH}}_{305}$ -183, peak $[\alpha]^{\text{MeOH}}_{265}$ $+101$), and (+)-3-methylcycloheptanone (III) to have a positive Cotton effect (peak $[\alpha]^{\text{MeOH}}_{305}$ $+450$, trough $[\alpha]^{\text{MeOH}}_{270}$ -270: reported[5] for material with $[\alpha]^{25}\text{D}$ $-38°$; trough $[\alpha]^{\text{MeOH}}_{305}$ -624, peak not reported).

The diazomethane ring enlargement of (+)-3-methylcyclohexanone (V), the absolute configuration of which has been established by conversion to (−)-α-methylglutaric acid,[6] must proceed with retention of configuration and yields (−)-3-methylcycloheptanone (III). Employing the octant rule[7] and assuming that the major contribution to the Cotton effect in 2-methylcyclohexanone arises from the chair conformation in which the methyl group is attached by an axial bond, the absolute configuration for (−)-2-methylcyclohex-

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[1] C. D. Gutsche, "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 364.

[2] H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **83**, 2952 (1961), have described a method employing chromic acid in ether solution at room temperature.

[3] G. A. C. Gough, H. Hunter and J. Kenyon, *J. Chem. Soc.*, **129**, 2052 (1926).

[4] C. Beard, C. Djerassi, T. Elliott and R. C. C. Tao, *J. Am. Chem. Soc.*, **84**, 874 (1962).

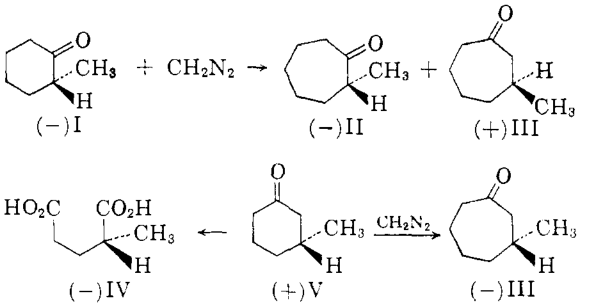
[5] C. Djerassi and G. W. Krakower, *ibid.*, **81**, 237 (1959).

[6] A. Fredga, *Arkiv. Kemi. Mineral Geol.*, **24A**, No. 32 (1947); E. J. Eisenbraun and S. M. McElvain, *J. Am. Chem. Soc.*, **77**, 3383 (1955)

[7] W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne and C. Djerassi, *ibid.*, **83**, 4013 (1961).

anone is established as (−) I, a conclusion also reached by Djerassi and co-workers.[4] The (−)-2-methylcycloheptanone (II) obtained from the ring enlargement of (−)-2-methylcyclohexanone should retain the absolute configuration of the starting ketone. In this connection it is interesting to note that although the sign of rotation and Cotton effect change in going from the cyclohexanone to cycloheptanone in the 3-substituted series,[5] this is not the case in the 2-substituted series.

If the configurational assignments to (−)-α-methylglutaric acid and the series of compounds which have been related to it are correct, and if the octant rule accurately predicts the configuration of 2-methylcyclohexanones, the inexorable conclusion is that the diazomethane ring enlargement of I to III proceeds with inversion of configuration. This seems inadmissible, however, on the basis of the generally-accepted mechanism which puts it in the class of nucleophilic 1,2-rearrangements (which in all known cases proceed with retention of configuration of the migrating group[8]), on the basis of other published observations (*e.g.*, diazomethane ring enlargement of *cis*-α-decalone yields *cis*-β-hexahydrobenzosuberone[9]), and in view of the fact that the ring enlargement of I *via* the Demjanow-Tiffeneau method (conversion of the ketone to the cyanohydrin, reduction of the cyanohydrin to the amino alcohol, and treatment of the amino alcohol with nitrous acid) follows the same steric course; *e.g.*, 2-methylcyclohexanone with $[\alpha]^{25}\text{D}$ +5.5° yielded 2-methylcycloheptanone with $[\alpha]^{25}\text{D}$ +29° and 3-methylcycloheptanone with $[\alpha]^{25}\text{D}$ −27°. It is hoped that experiments directed to the establishment of the absolute configuration of the 2-methylcyclohexanones by chemical interrelations will provide an answer to these contradictions.



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(8) D. J. Cram, "Steric Effects in Organic Chemistry," ed. by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 249.

(9) C. D. Gutshe and H. H. Peter, *J. Am. Chem. Soc.*, **77**, 5971 (1955).

A REVISED MODEL FOR AMMONIA SOLUTIONS OF ALKALI METALS

Sir:

It is well established that, in extremely dilute solutions of alkali metals in liquid ammonia, the metal is completely dissociated into ammoniated metal ions and ammoniated electrons. Each ammoniated electron is believed to exist in a large spherical cavity in the solvent and to be stabilized by the orientation of the ammonia dipoles on the periphery of the cavity. The decrease in the equivalent electrical conductance of these solutions as the concentration is increased to about 0.05 *M* indicates that ion pairing or assembly into larger aggregates takes place. The decrease of the molar paramagnetic susceptibility of the solutions with increasing concentration indicates that the ammoniated electrons associate to form species containing electron pairs. Both of these effects may be reproduced by assuming appropriate constants for these equilibria

$$M^+ + e^- = M$$

$$2M^+ + 2e^- = M_2$$

At −33° these equilibria shift in the vicinity of 0.01 *M* and the associated species predominate at higher concentrations.

It has been proposed by Becker, Lindquist, and Alder[1] that the monomer, M, consists of an ammoniated M^+ ion with the electron located in an expanded orbital on the protons of the coördinated ammonia molecules. Likewise, it has been proposed that the dimer, M_2, consists of two ammoniated M^+ ions held together by a pair of electrons in a bonding molecular orbital located principally between the two ions. These descriptions of the monomer and dimer are inconsistent with certain properties, in part newly measured, of alkali metal–ammonia solutions which are summarized below. We propose a revised description of the monomer and dimer species which more adequately accounts for all the properties of the solutions.

(1) The absorption spectra of sodium–ammonia solutions which are less concentrated than 0.03 *M* follow Beer's law within an experimental uncertainty of ± 2–5% at all wave lengths between 4000 and 25,000 Å. In fact, Beer's law is obeyed with similar precision for wave lengths between 4000 Å. and the absorption maximum (15,000 Å.) for concentrations at least as high as 0.1 *M*.[2] There is no indication of a separate absorption band near 6700 Å. Such a band has been observed in amines by Fowles, McGregor and Symons[3] and was attributed to a diamagnetic species. We have been unable to substantiate the claimed[4] appearance of shoulders at 6700 and 8000 Å. in the absorption spectra of ammonia solutions of sodium and sodium iodide. Thus the three species e^-, Na, and Na_2 have almost identical absorption spectra.

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(1) E. Becker, R. H. Lindquist and B. J. Alder, *J. Chem. Phys.*, **25**, 971 (1956).

(2) M. Gold and W. L. Jolly, unpublished data.

(3) G. W. A. Fowles, W. R. McGregor and M. C. R. Symons, *J. Chem. Soc.*, 3329 (1957).

(4) H. C. Clark, A. Horsfield and M. C. R. Symons, *ibid.*, 2478 (1959).