

Acknowledgment.—This work was performed under contract with the Office of Naval Research. The n.m.r. spectra were obtained with the assistance of B. J. Nist.

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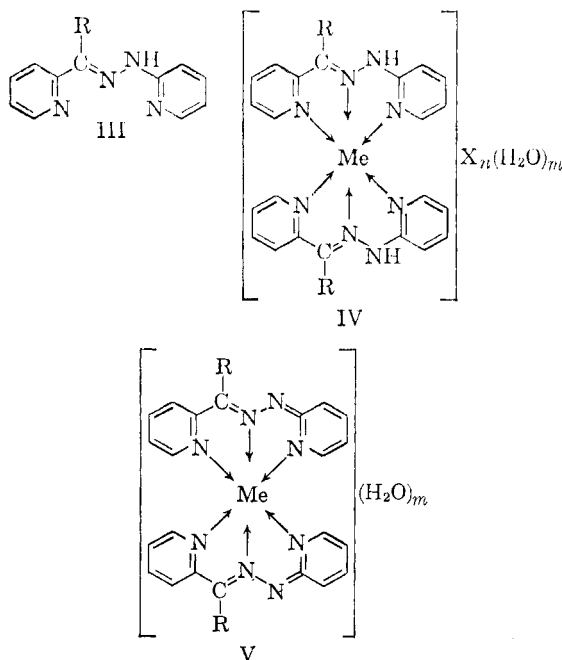
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RECEIVED OCTOBER 14, 1961

NEW AROMATIC-TYPE CHELATE COMPOUNDS

Sir:

We wish to report new aromatic-type oil-soluble very stable chelate compounds which appear to have important potentialities. The hydrazones (I) obtained by interaction of N-heterocyclic hydrazines, similar in type to 2-pyridylhydrazine, with heterocyclic aldehydes and ketones, similar in type of the 2-acyl pyridines, can function as tridentate chelating agents; whilst the osazones (II) derived from such hydrazines and α -dicarbonyl compounds can function as quadridentates.¹ Thus from 1,3-bis-(2'-pyridyl)-1,2-diazaprop-2-ene (III, R = H) the red diamagnetic iron(II) salt IV (R = H, Me = Fe, X = ClO₄, n = 2, m = 2) has been prepared.¹ We now report that addition of alkali to its solution in aqueous ethanol changes the color to green and the green crystalline non-conducting paramagnetic (1.8 B.M. at 18°) complex V (R = H, Me = Fe, m = 1) separates (Calcd. for C₂₂H₁₈N₈Fe·H₂O: C, 56.4; H, 4.3; Fe, 11.9. Found: C, 56.2; H, 4.1; Fe, 12.1). Similar non-conducting complexes from I (R = H) and almost



all of the bivalent transition metals can be prepared readily; for example, the brown nickel(II) complex V (R = H, Me = Ni, m = 1.5. Calcd. for C₂₂H₁₈-

(1) F. Lions and K. V. Martin, *J. Am. Chem. Soc.*, **80**, 3858 (1958).

N₈Ni·1.5H₂O: C, 55.0; H, 4.4; Ni, 23.3. Found: C, 54.8; H, 4.4; Ni, 22.8).

We have prepared very many neutral complexes of similar type from, for example, the 1-pyridylhydrazones, 2-pyrimidylhydrazones and 3-methyl-2-pyrazinyl hydrazones of such aldehydes as 6-methyl-pyridine-2-aldehyde, quinoline-2-aldehyde, isoquinoline-1-aldehyde, isoquinoline-3-aldehyde and quinoline-8-aldehyde, and of such ketones as the series III (R = CH₃ to R = *n*-C₆H₁₃) and metals such as iron, nickel cobalt, cadmium, zinc, manganese, copper—(in fact, almost all of the transition metals). A typical example is the red neutral zinc(II) complex from the α -pyridylhydrazone of 6-methyl-pyridine-2-aldehyde (colorless needles, m.p. 208–210°. Calcd. for C₁₂H₁₂N₄: C, 67.9; H, 5.7; N, 26.4. Found: C, 67.7; H, 5.7; N, 26.8) which crystallized in red needles from benzene-petroleum ether (calcd. for C₂₄H₂₂N₈Zn: C, 59.1; H, 4.6; Zn, 13.4. Found: C, 59.3; H, 4.8; Zn, 13.6).

These intensely colored neutral metal complexes are very soluble in organic solvents such as ether, benzene, carbon tetrachloride, cyclohexanone and the monohydric alcohols. Increasing the chain length of the R group of III markedly increases the solubility of the complexes in saturated hydrocarbon solvents even of low molecular weight. Thus V (R = *n*-C₆H₁₃, Me = Fe, m = 0. Calcd. for C₃₄H₄₂N₈Fe: C, 66.0; H, 6.8; N, 18.1; Fe, 18.1; Fe, 9.0. Found: C, 65.7; H, 6.9; N, 18.2; Fe, 9.2) is best obtained in dark green microcrystals, m.p. 186° from *n*-hexane. Its molecular weight is 618. Similarly V (R = *n*-C₄H₉, Me = Ni, m = 0. Calcd. for C₃₀H₃₄N₈Ni: C, 63.7; H, 6.1; N, 19.8; Ni, 10.4. Found: C, 63.6; H, 6.2; N, 19.7; Ni, 10.5) is obtained in red needles m.p. 249–250° from cyclohexane.

Treatment of the neutral complexes V with acids leads to re-formation of the complex salts IV. Distribution of chelated metal between water and water-immiscible solvents thus depends on hydrogen ion concentration—a property of potential significance in biology (distribution of metal between aqueous media and lipids) metallurgy (extraction of metals from ores) and analytical chemistry.

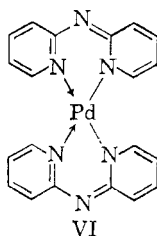
Stability constant determinations show that both the salts IV and the neutral complexes V are very stable. Alcoholic solutions of the chelating agents I can extract transition metals with ease from their EDTA complexes. Some of the neutral complexes V can be sublimed *in vacuo*.

We have prepared similar type neutral complexes from N-heterocyclic hydrazones of simple aldehydes and ketones by removal with alkali of protons from the complex salts they give with transition metal salts when coordinating as bidentates. However, these are not so stable as the tridentate complexes. The osazones II form much more stable neutral complexes, especially with metals like palladium(II) which favor a square planar arrangement.

The molecules of all these multidentate chelating agents possess an acidic hydrogen atom attached to the nitrogen atom of each hydrazine residue proxi-

mal to its heterocyclic nucleus. Coordination of the multidentate with a charged metal ion accentuates the drain on the electrons of each such $>\text{N}-\text{H}$ bond. Hydroxyl ions can then detach such hydrogen atoms as protons, especially if the electrons of the $>\text{N}-\text{H}$ 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 $\text{C}_{20}\text{H}_{16}\text{N}_6\text{Pd}$: 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 $>\text{N}-\text{H}$ bands.



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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), $[\alpha]_D^{25} - 5.0^\circ$ in methanol, was prepared by mild oxidation² of (–)-*trans*-2-methylcyclohexanol, $[\alpha]_D^{25} - 17.8^\circ$ in ether, which was obtained by hydrolysis of the corresponding half phthalate ester, $[\alpha]_D^{25} - 31.4^\circ$.³ Diazomethane ring enlargement under *ex situ* conditions in ether-meth-

anol¹ 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 $[\alpha]_D^{25} - 4.5^\circ$ in methanol, 3-methylcycloheptanone (24%) with $[\alpha]_D^{25} + 17.1^\circ$ 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, $[\alpha]_D^{25} + 18^\circ$ 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 $[\alpha]_{302}^{MeOH} - 282$, peak $[\alpha]_{268}^{MeOH} + 282$; reported⁴ for optically pure (+) epimer; peak $[\alpha]_{305}^{MeOH} + 515$, trough $[\alpha]_{263}^{MeOH} - 565$), (–)-2-methylcycloheptanone (II) to have a negative Cotton effect (trough $[\alpha]_{305}^{MeOH} - 183$, peak $[\alpha]_{265}^{MeOH} + 101$), and (+)-3-methylcycloheptanone (III) to have a positive Cotton effect (peak $[\alpha]_{305}^{MeOH} + 450$, trough $[\alpha]_{270}^{MeOH} - 270$; reported⁵ for material with $[\alpha]_D^{25} - 38^\circ$; trough $[\alpha]_{305}^{MeOH} - 624$, 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 rule⁷ 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-

(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. Muscovitz, W. Klyne and C. Djerassi, *ibid.*, **83**, 4013 (1961).