in the eight-membered ring.[6] This leaves *cis-trans*-1,5-cycloöctadiene as the only possible structure for the labile diene. The fact that the enantiomeric methohydroxides lead to enantiomeric *cis-trans*-1,5-cycloöctadienes shows that the asymmetry characteristic of the bases is preserved in the transition states leading to the olefins. This is the first case in which a cyclic *trans* olefin has been shown to be asymmetric. The rigid structure of the ring and the non-bonded hydrogen interactions prevent rotation of the *trans*-CH═CH— unit with respect to the rest of the ring, which would result in racemization.

(6) R. B. Turner and W. R. Meador, *J. Am. Chem. Soc.*, **79**, 4133 (1957).

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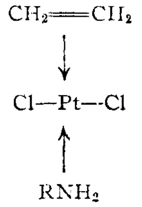
RECEIVED JUNE 25, 1962

RESOLUTION OF *trans*-CYCLOÖCTENE; CONFIRMATION OF THE ASYMMETRY OF *cis-trans*-1,5-CYCLOÖCTADIENE[1]

Sir:

Optically active stereoisomers of *trans*-cycloalkenes should be capable of existence provided the ring is sufficiently small to preclude rotation of the —CR═CR— unit relative to the rest of the molecule. This expectation has been realized by partial resolution of *trans*-cycloöctene.

Complexes with square planar geometry (formula I) can be prepared from "ethylene platinous chloride" [1,3-diethylene-2,4-dichloro-μ-dichlorodiplatinum(II)], or Zeise's acid [$H(PtC_2H_4Cl_3)$] derived from it, and an amine such as *p*-toluidine.[2]



$$\begin{array}{c} CH_2{=\!=}CH_2 \\ \downarrow \\ Cl{-}Pt{-}Cl \\ \uparrow \\ RNH_2 \end{array} \qquad I$$

Displacement of ethylene by other olefins in platinum(II) complexes is well known,[3] and one case involving an olefin amine platinum(II) complex has been reported.[4]

The method of resolution was to prepare a complex using optically active (+)-1-phenyl-2-aminopropane ("Dexedrine," dex) (I, where R is $C_6H_5CH_2{}^*CH(CH_3)$—) and then to displace the ethylene by *trans*-cycloöctene, forming *trans*-dichloro-*trans*-cycloöctene "Dexedrine" platinum-(II) (II). If *trans*-cycloöctene is capable of existence in optically active forms, this complex II would constitute a mixture of diastereomers.

The reaction of $H(PtC_2H_4Cl_3)$ with "Dexedrine" led to the complex I, $C_2H_4PtCl_2$dex, m.p. 120–121°, $[\alpha]^{28}$D +20.5° (*c* 2.5, methylene chloride). (*Anal.* Calcd. for $C_{11}H_{17}NPtCl_2$: C, 30.76; H, 3.99; N, 3.27; Pt, 45.74. Found: C, 30.54; H, 4.00; N, 3.31; Pt, 45.74.)

Reaction of *trans*-cycloöctene[5] with I in methylene chloride[6] gave the expected complex C_8H_{14}-$PtCl_2$dex, II. Fractional crystallization from hexane at −20° gave as the least soluble material IIa, a viscous oil at room temperature (crystalline at −20°), $[\alpha]^{28}$D +24° (*c* 2.5, methylene chloride); and as the most soluble material IIb, a viscous oil also crystalline at lower temperatures, $[\alpha]^{28}$D +4° (*c* 2.5, methylene chloride). (*Anal.* Calcd. for $C_{17}H_{27}NPtCl_2$: C, 39.91; H, 5.32; N, 2.75; Pt, 38.17. Found for IIa: C, 39.90; H, 5.26; N, 2.82; Pt, 38.04. Found for IIb: C, 40.28; H, 5.41; N, 3.03; Pt, 37.95.)

The olefin and amine were liberated by shaking a solution of each complex (IIa and IIb) in methylene chloride with 10% aqueous potassium cyanide solution. The methylene chloride solutions were washed with water, 5% hydrochloric acid (to remove the amine), 5% sodium bicarbonate and water. After drying over sodium sulfate, the solvent was evaporated at room temperature and the residues were distilled, yielding *trans*-cycloöctene, identified by comparison of infrared spectra with the spectrum of an authentic sample. From IIa the *trans*-cycloöctene had $[\alpha]^{28}$D −21° (*c* 2, pentane); from IIb $[\alpha]^{28}$D +18.5° (*c* 2, pentane).[7] Each sample was hydrogenated over prereduced platinum oxide in acetic acid to optically inactive cycloöctane (m.p. 11°) with the uptake of 95% of the theoretical amount of hydrogen.

Application of the same method to *cis-trans*-1,5-cycloöctadiene also resulted in partial resolution, confirming the asymmetry of the molecule (*cf.* the preceding communication). Reaction of *cis-trans*-1,5-cycloöctadiene with I gave a complex (III), $C_8H_{12}Pt_2Cl_4dex_2$, which was fractionally crystallized from benzene–cyclohexane yielding as the most soluble material IIIa, m.p. 106–108° (after further recrystallization from carbon tetrachloride), $[\alpha]^{28}$D +55.2° (*c* 2.5, methylene chloride); and as the least soluble material IIIb, m.p. 155–157°, $[\alpha]^{28}$D −18.3° (*c* 2.5, methylene chloride). (*Anal.* Calcd. for $C_{26}H_{38}N_2Pt_2Cl_4$: C, 34.28; H, 4.20; N, 3.08; Pt, 42.87. Found for IIIa: C, 34.42; H, 4.05; N, 2.75; Pt, 43.22. Found for IIIb: C, 34.10; H, 4.33; N, 3.06; Pt, 42.46.) Treatment of IIIa and IIIb in the manner described for IIa and IIb gave samples of *cis-trans*-1,5-cycloöctadiene, identified by comparison of infrared spectra with the spectrum of an authentic sample. The diene from IIIa had $[\alpha]^{28}$D −26° (*c* 1.3, pentane); the diene from IIIb had $[\alpha]^{28}$D +34° (*c* 1.2, pentane).

This method of resolution should be general for olefins forming sufficiently stable pi complexes with platinum. It is being extended to other cyclic olefins with molecular asymmetry, and rates

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[1] Presented at the Carl S. Marvel Honorary Symposium, Tucson, Arizona, December 28, 1961.

[2] J. Chatt, *J. Chem. Soc.*, 3340 (1949).

[3] J. S. Anderson, *ibid.*, 971 (1934).

[4] A. H. Gelman, *Compt. rend. Acad. Sci. URSS*, **32**, 347 (1941).

[5] A. C. Cope, R. A. Pike and C. F. Spencer, *J. Am. Chem. Soc.*, **75**, 3212 (1953).

[6] For one of many similar examples see J. R. Joy and M. Orchin, *ibid.*, **81**, 305, 310 (1959).

[7] NOTE ADDED IN PROOF.—(−)-*trans*-Cycloöctene completely resolved through the tomplex $C_8H_{14}PtCl_2C_6H_5CH(NH_2)CH_3$ has $[\alpha]^{29}$D −411° (*c* 0.27, methylene chloride) (A. C. Cope and T. V. Van Auken, unpublished results).

of racemization relative to ring size are being determined.

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MASS SPECTRA OF ORGANIC MOLECULES. II.[1] AMINO ACIDS[2]

Sir:

In our efforts to extend the applicability of mass spectrometry to organic molecules of extremely low volatility, we have been able to determine the mass spectra of amino acids without prior conversion to more volatile derivatives required for our earlier work.[1,3] Using the same technique which had made it possible to obtain mass spectra of nucleosides,[4] volatilization of the sample directly into the ion source and close to the ionizing electron beam gave excellent spectra of free amino acids and even their hydrochlorides.[5]

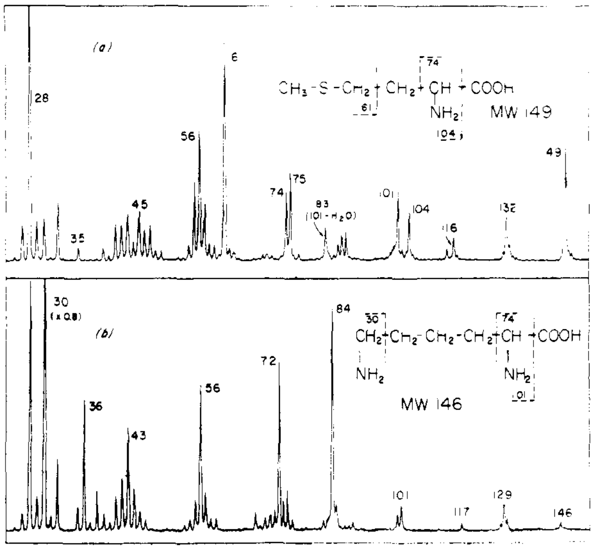
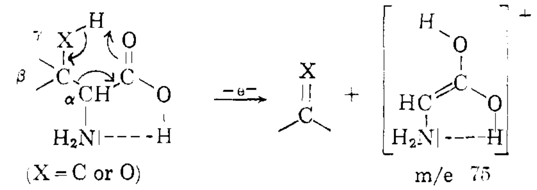


Fig. 1.—Reproductions of mass spectra of amino acids: (a) methionine; (b) lysine monohydrochloride (mass 28 and 32 due to air; mass 30 in (b) 1.25 × as abundant as shown).

These spectra[6] (determined with samples ranging from 0.25–10 μg.) were quite similar to those of the corresponding ethyl esters,[1] indicating that free amino acids exist in the gas phase as the undissociated amino carboxylic acids or possibly hydrogen-bonded forms thereof. It will, therefore, suffice to discuss only those peaks not present as such in the mass spectra of the amino acid ethyl esters.

The lack of the ester group leads to a shift of 28 mass units in peaks due to the elimination of a group other than the acid moiety (*e.g.*, m/e 102 in ethyl esters *vs.* m/e 74 in the acids). There seem to be only two new modes of fragmentation: First, there is always found a peak of significant intensity at m/e 45 corresponding to the carboxyl group while the corresponding one at m/e 73 in ethyl esters is absent. This we attribute to the stability of a positively charged carboxyl fragment ($O{=}C{=}O^+{-}H$) which is equivalent to a protonated carbon dioxide molecule while the corresponding carbethoxy ion of mass 73 ($O{=}C{=}O^+{-}C_2H_5$) is energetically less favored.

The second difference is found in the presence of a peak at m/e 75 in the spectra of a number of amino acids, namely, all those containing a hydrogen atom in a γ-position. This rearrangement is well known[7] for fatty acids and their esters, but is not observed in α-amino esters, because of the availability of the free electron pair on nitrogen.[1] In the free acids hydrogen bonding seems to decrease this effect, thus favoring this rearrangement which is very sensitive to the electron density at the atom attached to C_α.[8]



The mass spectrum of methionine (Fig. 1a) illustrates the similarity to that of the ester.[1] The peaks at mass 74, 101, 132, and 149 (mol. wt.) are those which occur 28 mass units higher in the ethyl ester. Fragments of mass 75, 57, and 45 correspond to the additional fragmentation modes discussed above; (m/e 75 is only partly due to CH_3-S-CH_2-CH_2^+, as evidenced by deuteration experiments).

It is thus possible to interpret the mass spectra of free amino acids based on the behavior of amino esters under electron impact as discussed previously.[1] Glutamic acid appears to dehydrate to pyroglutamic acid prior to sublimation, but hydroxyamino acids vaporize without decomposition.

The fragmentation processes discussed here and earlier[1] are corroborated by the mass spectra of N^{15}-labeled amino acids and of N,O-perdeuterio derivatives which can easily be obtained.[9]

Even salts are amenable to this technique if both the corresponding base and acid are sufficiently volatile and thermally stable at the

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(1) Paper I: K. Biemann, J. Seibl and F. Gapp, *J. Am. Chem. Soc.*, **83**, 3795 (1961).

(2) This investigation was supported by a grant from the National Aeronautics and Space Administration (NsG 211-62). We wish to thank Mr. M. Munroe for invaluable help with the instrumentation.

(3) K. Biemann, J. Seibl and F. Gapp, *Biochem. Biophys. Res. Communs.*, **1**, 307 (1959).

(4) K. Biemann and J. A. McCloskey, *J. Am. Chem. Soc.*, **84**, 2005 (1962).

(5) W. L. Baun and D. W. Fischer [*Anal. Chem.*, **34**, 294 (1962)] reported the introduction of free amino acids into a spark source mass spectrometer. Our spectrum of lysine hydrochloride (Fig. 1b) indicates that the much more gentle conditions of sublimation of the sample at relatively low temperatures into an electron beam of 70 ev. as contrasted to sparking at high frequency with 100 Kv. lead to spectra which are much more characteristic of the original molecule.

(6) For experimental conditions see footnote 6 in reference 4. Samples were vaporized at temperatures between 80° and 200°.

(7) F. W. McLafferty, *Anal. Chem.*, **31**, 82 (1959).

(8) For a detailed discussion of the interpretation of mass spectra see K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chap. 3.

(9) For experimental details see footnote 9 in reference 4.