ing of the cyclic intermediate in S–O transfer had to be estimated by more indirect methods. Isotopic exchange experiments provide one of the few tools for evaluation of partitioning in intermolecular reactions. Demonstration of general base catalysis for S–N transfer and a knowledge of reaction rates of fast proton transfer reactions permit evaluation of the absolute rate constants in this system. In the O–N transfer system, general base catalysis presumably occurs only at high *p*H where intermolecular reaction effects would be competitive with intramolecular transfer.

Finally, the question of retention or inversion of configuration in acyl transfer reactions has received considerable attention.[14] The mechanism proposed here involves retention of configuration. In S → N, N → S, O → S and O → N transfer reactions, inversion of configuration would yield different products than assumed here. The identical equilibrium results obtained by starting with more than one of the reactants in the thiazoline[5] or oxazoline[13] systems would seem to rule out any kind of inversion mechanism for these systems. In S → O and N → O transfer both mechanisms would yield the same products in aqueous solutions, but a retention mechanism is favored by analogy with the other similar transfer reactions considered here.

Acknowledgment.—This research was supported by grants from the National Science Foundation and the National Institutes of Health.

---

[14] For instance, L. H. Welsh, *ibid.*, **71**, 3500 (1949); G. E. McCasland, *ibid.*, **73**, 2295 (1951); E. E. van Tamelen, *ibid.*, **73**, 5773 (1951); G. Fodor and J. Kiss, *J. Chem. Soc.*, 1589 (1952); S. Winstein and R. Boschan, *J. Am. Chem. Soc.*, **72**, 4669 (1950).

COMMUNICATIONS TO THE EDITOR

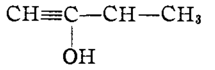
THE ABSOLUTE CONFIGURATION OF PENTADIENDIOIC ACID

Sir:

In the past two years the absolute configurations of two allenic compounds have been deduced by mechanistic correlation with their optically active non-allenic progenitors. Jones, Loder, and Whiting[1] related the allenic aldehyde I to but-3-yn-2-ol (II) of known absolute configuration, and the tentative assignment of Eliel[2] of configuration to III based on Brewster's rules[3] permits the establishment of a similar relationship between that compound and its transformation product IV.[4]

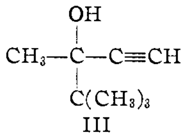
$CH_3CH{=}C{=}CHC(CH_3)_2CHO$

I



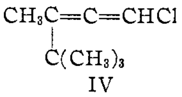
$\mathrm{CH{\equiv}C{-}\underset{\displaystyle OH}{CH}{-}CH_3}$

II



$\mathrm{CH_3{-}\overset{\displaystyle OH}{\underset{\displaystyle C(CH_3)_3}{C}}{-}C{\equiv}CH}$

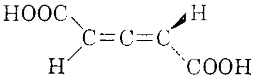
III



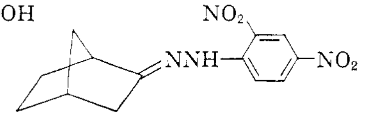
$\mathrm{CH_3\underset{\displaystyle C(CH_3)_3}{C}{=}C{=}CHCl}$

IV

An alternative approach[5] to this problem of allene absolute configuration would be the preparation of an active allene of unknown stereochemistry followed by its transformation into an active compound possessing asymmetric carbon. The absolute geometry of this latter material could then be determined by any of a number of now conventional techniques.[6,7,8] To this end we have partially resolved pentadiendioic (glutinic) acid (V) and converted it into optically active norcamphordinitrophenylhydrazone (VI). The configuration of VI was established by comparison with a sample prepared from optically active norcamphor, the absolute stereochemistry of which was determined recently by Berson.[9] On the basis of the arguments and transformations outlined below (+)glutinic acid is assigned the absolute configuration shown (V). All reactions and proofs of structure were first carried out with racemic compounds, and then the appropriate steps repeated with optically active material.



V



VI

The Diels–Alder reaction between glutinic acid and cyclopentadiene gave an adduct in over 90% yield, as previously reported.[10] We have separated this by fractional crystallization into approximately equal amounts of two isomeric compounds, one melting 205–207°,[11] and the other 245–246°.[11]

---

[1] E. R. H. Jones, J. D. Loder, and M. C. Whiting, *Proc. Chem. Soc.*, 180 (1960).

[2] E. L. Eliel, *Tetrahedron Letters*, No. 8, 16 (1960).

[3] J. H. Brewster, *J. Am. Chem. Soc.*, **81**, 5475 (1959).

[4] S. R. Landor and R. Taylor-Smith, *Proc. Chem. Soc.*, 154 (1959).

[5] *Cf.* D. W. Dicker, D. Phil. Thesis, Oxford, 1957.

[6] C. Djerassi, "Optical Rotatory Dispersion, Ch. 10, McGraw-Hill Book Co., New York, N. Y., 1960.

[7] V. Prelog, *Bull. Soc. Chim. France*, 987 (1956).

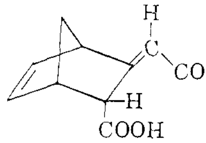
[8] J. A. Mills and W. Klyne, Ch. 5 in "Progress in Stereochemistry," Vol. 1 (ed. W. Klyne), Butterworths, London, 1954.

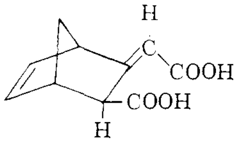
[9] Prof. Jerome Berson of the University of Southern California was very kind to provide a copy of his paper prior to publication as well as a sample of resolved norcamphor. It is a pleasure to record here our appreciation of his willing and valuable aid. J. A. Berson, J. S. Walia, A. Remanick, S. Suzuki, P. Reynolds-Warnhoff, and D. Willner, *J. Amer. Chem. Soc.*, **83**, 3986 (1961).

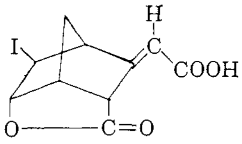
[10] E. R. H. Jones, G. H. Mansfield, and M. C. Whiting, *J. Chem. Soc.*, 4073 (1956).

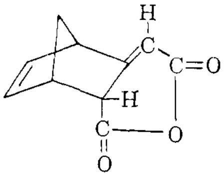
[11] Satisfactory elementary analysis for carbon and hydrogen was obtained for this compound.

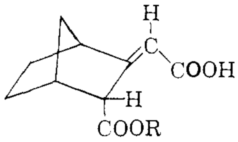
Since the lower melting compound (VII) yielded an iodolactone[11] (IX, infrared split lactone carbonyl band 5.54, 5.58 μ; acid carbonyl band 5.89 μ; double bond 6.01 μ) on treatment with iodine and sodium bicarbonate,[12] the carboxyl participating in this reaction must possess the *endo* configuration shown. Further, the stereochemistry of the α,β-unsaturated acid grouping must be as indicated, since treatment of the diacid with warm acetic anhydride gave a monomeric anhydride[11] (X, infrared carbonyl bands 5.54, 5.71 μ). The anhydride was hydrolyzed back to VII in good yield by warming with aqueous dioxane. These facts and consideration of the reaction sequence leading to VI serve to establish structure VII for the lower melting adduct. Although we have done little work with the higher melting Diels–Alder product, we may say that it probably has structure VIII, since its reaction with iodine and bicarbonate gives no iodolactone, but treatment with acetic anhydride does afford X.[13]


VII


VIII


IX

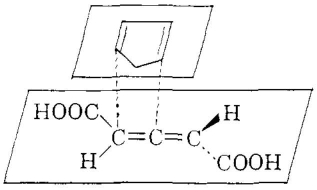

X


XI, R = H
XII, R = CH_3

Adduct VII absorbed one mole of hydrogen rapidly in methanol over palladium on carbon to furnish the dihydrodiacid XI[11] (one vinyl proton in n.m.r. spectrum), which then was esterified with diazomethane to XII.[11] This ester was successively ozonized at $-60°$, treated with potassium iodide–acetic acid,[14] and hydrolyzed and decarboxylated with hot concentrated hydrochloric acid.[15] The resulting crude product was converted directly into norcamphor dinitrophenylhydrazone (VI),[16] the identity of which was confirmed by comparison with an authentic sample.

To obtain optically active material a sample of glutinic acid was resolved partially with brucine; the dextrorotatory allene ($[\alpha]_D$ 2.4°) thus obtained condensed with cyclopentadiene to give optically active VII. The dinitrophenylhydrazone formed on degradation of this adduct was found to be dextrorotatory ($[\alpha]_D$ 2.2°).

Now, Berson's work[9] has demonstrated the absolute configuration implied in VI for (+)norcamphor itself, and the dinitrophenylhydrazone prepared from his ketone is also dextrorotatory. We can, therefore, assign structure VI in the absolute sense to the material formed on degradation of VII and accept the absolute stereochemistry of structure VII for the original optically active adduct. This requires in turn that (+)pentadiendioic acid have the absolute configuration shown in V. (The steric relationship between V and VII is depicted in XIII.) We may note finally that VII is the adduct predicted by the Alder–Stein rules[10,17] in conjunction with simple steric considerations. Formation of either of the possible, unobserved adducts (alternative *cis–trans* isomer of the α,β-unsaturated acid) would require approach of cyclopentadiene to V directly over a carboxyl group rather than a hydrogen atom (*cf.* XIII).


XIII

---

[12] (a) E. E. van Tamelen and M. Shamma, *J. Am. Chem. Soc.*, **76**, 2315 (1954); (b) C. S. Rondestvedt, Jr., and C. D. Ver Nooy, *ibid.*, **77**, 4878 (1955).

[13] The epimerization implied in the transformation of both VII and VIII to X requires no comment, as X is a glutaconic anhydride. As might be expected (ref. 10), the compound does appear to exist in the form written; its solution infrared spectrum shows no trace of hydroxyl absorption.

[14] P. S. Bailey, *Chem. Ber.*, **88**, 795 (1955).

[15] L. Ruzicka, *Helv. Chim. Acta*, **3**, 748 (1920).

[16] K. Alder, H. K. Schäfer, H. Esser, H. Krieger, and R. Reubke, *Ann.*, **593**, 23 (1955).

[17] K. Alder and G. Stein, *Ann.*, **514**, 1 (1934); *Angew. Chem.*, **50**, 510 (1937).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA
WILLIAM C. AGOSTA

RECEIVED JULY 24, 1961

ROTATORY DISPERSION STUDIES OF COORDINATION COMPOUNDS. I. ABSORPTION SPECTRA AND ELLIPTICITY OF OPTICALLY ACTIVE DIHEDRAL COBALT(III) COMPLEXES

Sir:

From a study of the rotatory dispersion in the visible absorption bands of the $[Co(en)_3]^{3+}$ dihedral complex ion, Moffitt[1] suggested that the rotational strengths of the $^1A_{1g} \rightarrow {}^1T_{1g}$ inverse transition could be attributed to an admixture of the 4p with the 3d orbitals due to the trigonal component associated with the system. However, Sugano[2] has shown, from symmetry arguments alone, that Moffitt's first order theory cannot account for the rotational strengths and has suggested that different mechanisms operate for rotations and visible absorption. Sugano's symmetry arguments are applicable to strictly dihedral systems but for slightly distorted dihedral systems, which include most of the optically active cobalt(III) complexes, the argument cannot be applied precisely. We wish to point out some experimental evidence in support of Sugano's argument that a different

---

[1] W. Moffitt, *J. Chem. Phys.*, **25**, 1189 (1956).

[2] S. Sugano, *ibid.*, **33**, 1883 (1960).