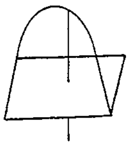
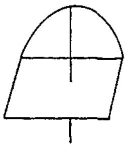
raphy into three stereoisomers. A good deal of discussion in the literature, summarized by Schetty[1] and Pfitzner,[2] is concerned with the stereochemistry of metal complex dyes. Schetty's[3] work indicates that *o,o'*-dihydroxyazo dyes with chromium and cobalt form 2:1 octahedral complexes in which the dyes occupy three *mer* positions on the metal (III) rather than the *fac* positions (IV).



III



IV

The 1:1 chrome dye II, Inochrome Pink N (Francolor), CI 1876, was converted to the sulfonyl chloride with phosgene in methylene chloride and dimethylformamide. The crude sulfonyl chloride was allowed to react with a large excess of piperidine and drowned in water. The product, a mixture of the piperidide and the starting dye, was dissolved in hot dimethylformamide and 2,5-pentanedione. The products of this reaction were obtained by precipitating in water, filtering, and drying. Chromatography was on Woelm alumina, activity grade I, packed in acetone and washed with benzene. The crude dye was applied and eluted with methylene chloride, giving one fraction; elution with acetone gave a second fraction; and finally elution with 10% methanol in acetone gave a third fraction. No other material could be eluted with pure methanol. The three fractions had identical visible, ultraviolet, and infrared spectra; their X-ray powder diagrams, however, were significantly different from each other. *Anal.* (of one of the chromatographic fractions) for $C_{30}H_{32}CrN_5O_7S$: Calcd: C, 54.7; H, 4.9; Cr, 7.9; N, 10.6; S, 4.9. Found: C, 53.7; H, 5.1; Cr, 8.0; N, 10.9; S, 4.8. The electronic spectrum showed λ_{max} (log ϵ) 256 (4.50), 348 (4.11), 524 (4.33), and 556 mμ (4.34). Dye I is a crystalline substance stable to alkali but less stable to acid.

If the dye formed a complex of structure III, the introduction of the bidentate ligand 2,5-pentanedione could lead to only one isomer (*dl* pair). On the other hand, structure IV leads to three isomers (*dl* pairs). The isolation of three isomers forces us to conclude that the dye I must exist in the *fac* structure IV. It is likely that Inochrome Pink N also exists in the *fac* structure because its visible spectrum is very similar to that of I.[4]

Schetty has shown that 2:1 complexes of *o*-hydroxy-*o'*-carboxyazo dyes may exist in either the *fac* ("sandwich") or *mer* ("Drew-Pfitzner") form depending on the structures of the dyes or the manner in which they were prepared.[4,5] Bearing this in mind, and noting that our 1:1 complex of an *o,o'*-dihydroxyazo dye exists in the *fac* form rather than the *mer* form predicted by Schetty's generalization, we believe that complexes of *o,o'*-dihydroxyazo dyes are capable of existence in either the *fac* or *mer* form.

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Received September 15, 1965

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[1] G. Schetty, *J. Soc. Dyers Colourists*, **71**, 705 (1955).

[2] H. Pfitzner, *Angew. Chem.*, **62**, 242 (1950).

[3] G. Schetty, *Helv. Chim. Acta*, **45**, 1095 (1962).

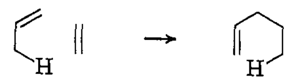
[4] G. Schetty, *ibid.*, **47**, 921 (1964).

[5] G. Schetty, *ibid.*, **46**, 1132 (1963).

A Preference for Endoid Addition in the Ene Synthesis[1]

Sir:

The ene synthesis or "indirect substitutive addition"[2] (eq 1) is structurally related to the Diels-Alder reaction (eq 2) in that formation of the adduct is accompanied by obligatory movement of a double bond in the ene or diene.[3] Although the question of *endo vs. exo* stereochemistry in the Diels-Alder reaction has been studied extensively,[5] the present paper reports the first solutions of the corresponding problem for the ene synthesis.



(1)

(2)

A benzene solution of *cis*-2-butene and maleic anhydride heated at 225° for 8 hr gives a 20-30% yield of the diastereomeric 3-(1-butenyl)succinic anhydrides in the ratio 15-20% Ia and 80-85% Ib. The observed ratio is essentially the kinetically controlled one, since the product mixture at lower conversion (1 hr at 225°, 6% total yield) also has the composition 15% Ia:85% Ib. With *trans*-2-butene, although the selectivity is lower (57% Ia:43% Ib) the stereochemical direction of the reaction is qualitatively preserved, since the major diastereomer (Ia) in the *trans* series is the minor one in the *cis*. The two 2-butenes do not interconvert significantly under the reaction conditions.

The 1-butene-maleic anhydride adduct 4-(2-butenyl)-succinic anhydride (III)) is present in no more than trace quantities in the 2-butene-maleic anhydride product mixture. Similarly, the 3-butenylsuccinic anhydrides (Ia and Ib) are at most minor components of the 1-butene-maleic anhydride adduct. The virtual absence of cross-products excludes a radical-chain mechanism with initiation by allylic hydrogen abstraction for ene syntheses with 1- or 2-butene.

Fractional crystallization from acetonitrile of a mixture of diastereomeric 2-butylsuccinic acids, obtained by hydrolysis and hydrogenation of the Stobbe condensation product from 2-butanone and succinic ester

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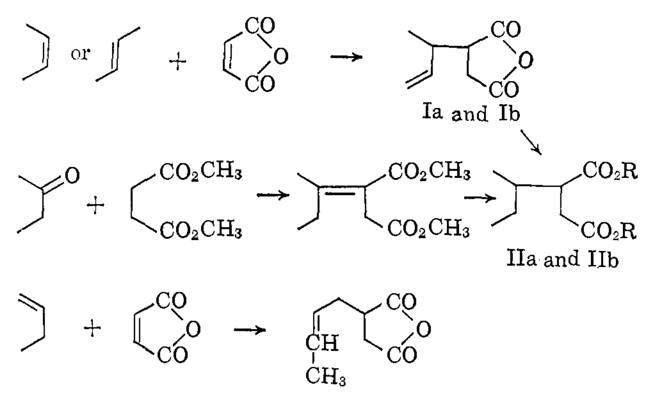
[1] This work was supported in part by grants from the Petroleum Research Fund. Grateful acknowledgment is made to the donors of this fund and also to the National Science Foundation for additional support.

[2] K. Alder and H. von Brachel, *Ann.*, **651**, 141 (1962), and references therein cited.

[3] Olefins sometimes react with azodicarboxylic ester to give direct rather than indirect allylic substitution, a result that is consistent with a free-radical chain mechanism. It now seems likely[4] that these reactions should be considered in a separate category from true ene syntheses.

[4] W. A. Thaler and B. Franzus, *J. Org. Chem.*, **29**, 2226 (1964).

[5] For references and discussion, see J. C. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961); J. A. Berson, Z. Hamlet, and W. A. Mueller, *J. Am. Chem. Soc.*, **84**, 297 (1962).

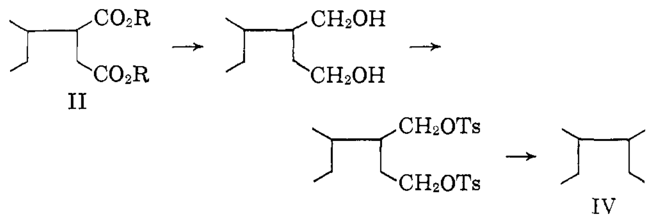


Ia and Ib

IIa and IIb

III

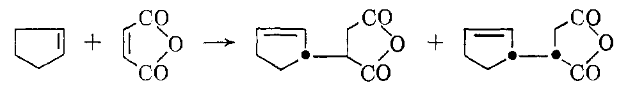
(II, R = H), gives a diastereomerically pure acid IIa (R = H), convertible with diazomethane to pure IIa (R = CH$_3$), which is identical with the ester corresponding stereochemically to the major component of the *trans*-2-butene–maleic anhydride adduct. Ester IIa (R = CH$_3$) is shown to have the *erythro* configuration by the following procedure. Partial resolution of IIa (R = H) *via* the cinchonidine salt and conversion to methyl ester give IIa (R = CH$_3$), $[\alpha]_D$ +13.3°. A portion of the optically active sample of IIa (R = CH$_3$) is made structurally symmetrical by a sequence involving lithium aluminum hydride reduction, conversion to a di-*p*-toluenesulfonate, and further lithium aluminum hydride reduction, from which is obtained *optically inactive* 3,4-dimethylhexane (IV). The optical inactivity of this hydrocarbon sample is a consequence of *meso* stereochemistry, since *optically active* 3,4-dimethylhexane (IV) is obtained by a sequence in which the remainder of the above diastereomerically pure *erythro* optically active ester IIa (R = CH$_3$) is first epimerized to an *erythro–threo* (IIa–IIb) mixture with sodium methoxide and then subjected to the same symmetrization sequence. Thus, the major product from *trans*-2-butene is *erythro* and that from *cis* is *threo*.



II

IV

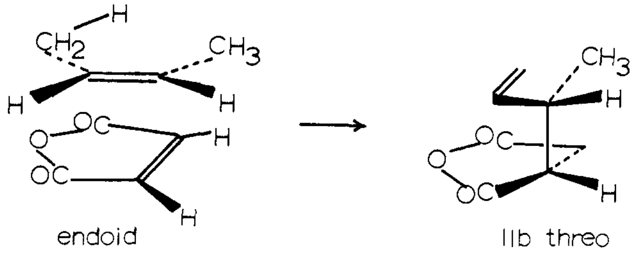
Similarly, the major isomer of the cyclopentene–maleic anhydride adduct mixture,[6] which is formed in a 3.5:1 predominance in the ene synthesis, is shown to have the *erythro* configuration Va by symmetrization of an optically active derivative to give *meso*-methyl 1,3,4,6-hexanetetracarboxylate.



Va

Vb

On the likely but unproven assumption that carbon–carbon and carbon–hydrogen bond formation in the ene synthesis is concerted,[7] the results in the three examples reported here indicate a preference for endoid addition, which is illustrated below for the case of *cis*-2-butene. This orientation is the one favored on



simple steric grounds for the assumed concerted mechanism, in accord with the proposal of steric control made by Hill and Rabinovitz.[9] However, some electronic influence of the type that favors *endo* Diels–Alder addition cannot be excluded.[10] Furthermore, because of logical circularity, neither the present nor the previous[9] stereochemical result can be interpreted as *requiring* the concerted mechanism. Perhaps the strongest evidence against a stepwise diradical mechanism (carbon–carbon bond formation followed by intramolecular hydrogen transfer) is the apparent absence of cyclo adducts in the ene syntheses or of ene adducts in those cyclo additions[11] which clearly proceed *via* diradicals.

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(6) K. Alder, F. Pascher, and A. Schmitz, *Ber.*, **76**, 27 (1943).

(7) The evidence frequently cited in support of this consists of obligatory double bond movement (only one of two allylic isomers formed)[8a] and preservation of asymmetry in the product of ene syntheses with optically active olefins of the type R$_1$R$_2$CHCH=CH$_2$.[9] These are necessary but insufficient conditions, since a stepwise mechanism in which the carbon–carbon bond is formed *first* is also compatible with them.[8b]

(8) (a) R. T. Arnold and J. F. Dowdall, *J. Am. Chem. Soc.*, **70**, 2590 (1948); (b) Arnold and Dowdall[8a] recognized the possibility of a stepwise mechanism *via* a zwitterionic intermediate. A diradical intermediate is also conceivable.

(9) R. K. Hill and M. Rabinovitz, *ibid.*, **86**, 965 (1964).

(10) The orbital symmetry relationships that rationalize the Diels–Alder case [see R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 4388 (1965)] are also applicable to the ene synthesis. By personal communication these authors inform us that endoid addition should be the more favorable process on orbital symmetry grounds but that the preference should be smaller than in Diels–Alder reactions.

(11) P. D. Bartlett, L. K. Montgomery, and B. Seidel, *ibid.*, **86**, 616 (1964), and subsequent papers.

(12) National Science Foundation Cooperative Fellow, 1963; National Institutes of Health Predoctoral Fellow, 1964–1965.

(13) National Institutes of Health Postdoctoral Fellow, 1964–1965.

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Received November 1, 1965

Participation of a Neighboring Ketonic Carbonyl Group in Phosphonate Ester Hydrolysis

Sir:

The carboxylate ion, imidazole, carboxylic acid, carboxamide, aromatic and aliphatic hydroxyl groups, and the carbonyl group can participate as intramolecular catalysts in the hydrolysis of carboxylic esters.[1] Similarly, a variety of neighboring groups can participate in the hydrolysis of phosphates.[2] These reactions may

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(1) (a) M. L. Bender, *Chem. Rev.*, **60**, 53 (1960); (b) B. Capon, *Quart. Rev.* (London), **18**, 45 (1964); (c) Y. Shalitin and S. A. Bernhard, *J. Am. Chem. Soc.*, **86**, 2291 (1964); (d) *ibid.*, **86**, 2292 (1964).

(2) J. R. Cox, Jr., and O. B. Ramsay, *Chem. Rev.*, **64**, 317 (1964).