the dimerization, is subject to experimental test. Should the dimerization occur in the normal cis manner, it will be necessary to abandon the assumption of identity in this case. By extension, in each future application, the assumption and its use for the estimation of $\Delta H_f°$ of thermal transition states will require explicit scrutiny.

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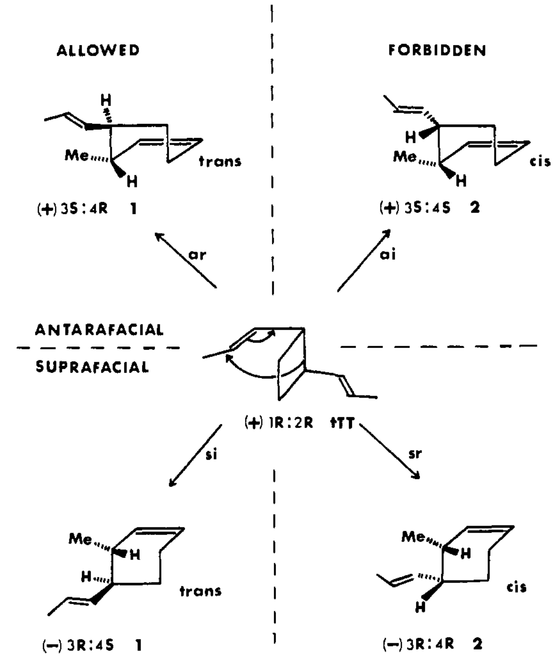
A Mechanistic Analysis of the Four Pathways in the 1,3-Sigmatropic Rearrangements of *trans*-1,2-*trans,trans*- and *trans*-1,2-*cis,trans*-Dipropenylcyclobutane[1]

Sir:

The orbital symmetry allowed and forbidden 1,3-sigmatropic rearrangements of a *trans*-2-substituted-1-*trans*-propenylcyclobutane (*e.g.*, tTT, Scheme I) would give, respectively, a trans- and a cis-3,4-disubstituted cyclohexene (*e.g.*, **1** and **2**). Thus, an evaluation of the relative importance of the two processes would be available merely from a determination of the trans/cis product ratio.[2] However, a more complete mechanistic analysis would require dissection of the allowed and forbidden reactions into two subreactions each. These can be categorized according to whether the migrating carbon retains or inverts its configuration (r or i) and whether the allylic receptor framework participates in a suprafacial or antarafacial way (s or a). The use of optically active reactants now permits this analysis.

Scheme I



The allowed pathways, ar and si, lead from one enantiomer of *trans*-1,2-*trans,trans*-dipropenylcyclobutane (tTT) to optical antipodes of *trans*-3-methyl-4-*trans*-propenylcyclohexene (**1**), whereas the forbidden ones, ai and sr, lead to antipodes of the cis compound (**2**, Scheme I). Thus, the relative rates of each of the four processes can be evaluated from the product composition combined with the relationships of the observed rotations, absolute configurations, and maximum rotations of tTT, **1**, and **2**. This information is provided by synthesis of optically active tTT, **1**, and **2** from appropriate precursors of known configuration and maximum rotation.[3]

Pyrolysis of (1*R*,2*R*)-(+)-tTT, [α]D +48.1° (*c* 10.08, CCl_4), 40.3% optically pure, in the liquid phase at 146.5°, is a clean first-order reaction which leads to 60.1% of 1,3-rearrangement products, **1** and **2**, 27.6% of *cis*-3,4-dimethyl-*cis,cis*-cyclooctadiene, 7.9% of piperylene, and 4.4% of unidentified products.

The starting material tTT suffers partial racemization during pyrolysis. To correct for this, the first-order rate constants for racemization of tTT and for formation of **1** and **2** are used to calculate values of $\bar{P}$, the effective optical purity[6] of the tTT in the 1,3 rearrangements ($\bar{P} = 0.832$ for **1** and 0.829 for **2**, during a 24.37-hr pyrolysis, about 2 half-lives for disappearance of tTT).

The trans compound **1** constitutes 56.2% of the 1,3-rearrangement product. The maximum enantiomeric purity it could have is 0.832 × 40.3% = 33.5%, so that the observed rotation, [α]D −17.5° (*c* 12.83, CCl_4), corresponding to 27.1% optical purity, means that the rearrangement of the tTT that has not suffered prior racemization is rather highly stereospecific, 80.9% of the permissible activity having been preserved. The cis compound **2**, [α]D −63.4° (*c* 10.69, CCl_4), 32.1% optically pure, is formed even more stereospecifically, with 96.1% of the permissible activity intact.

Studies with (1*R*,2*R*)-(−)-*trans*-1,2-*cis,trans*-dipropenylcyclobutane (tCT), the 1,3 rearrangement of which gives almost exclusively products of migration across the *trans*-propenyl chain (*cis*- and *trans*-3-methyl-4-*cis*-propenylcyclohexene), reveal similarly high stereospecificity. The assignments of relative rates to the four pathways in each case are summarized in Table I. The values are estimated to be reliable to ±2 units.

We now can interpret more sharply the observation[4]

Table I. Analysis of Pathways in 1,3-Sigmatropic Rearrangements of *trans*-1,2-Dipropenylcyclobutanes

	Rel rate of product formation			
	Allowed		Forbidden	
Reactant	si	ar	sr	ai
tTT	50.8	5.4	43.0	0.8
tCT	49.5	2.7	47.8	0.0

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[1] We thank the National Science Foundation (Grant No. GP-33909X) and the Hoffmann-La Roche Foundation for partial support of this work.

[2] Experiments with racemic substrates leading to the two-path dissection of the rearrangement of 2-substituted-1-alkenylcyclopropanes have been reported by (a) P. Mazzochi and H. J. Tamburin, *J. Amer. Chem. Soc.*, 92, 7220 (1970), and by (b) W. R. Roth, work cited in ref 2a.

[3] (1*S*,2*S*)-(+)-Cyclobutane-1,2-dicarboxylic acid[4] → (1*R*,2*R*)-(+)-tTT and (1*R*,2*R*)-(−)-tCT; (3*S*,4*R*)-(+)-*cis*-3-methylcyclohexene-4-carboxylic acid[5] → (3*S*,4*R*)-(+)-1 and (3*S*,4*S*)-(+)-2. Characterizations of new substances rest on spectra and elemental analyses.

[4] J. A. Berson and P. B. Dervan, *J. Amer. Chem. Soc.*, 95, 267 (1973).

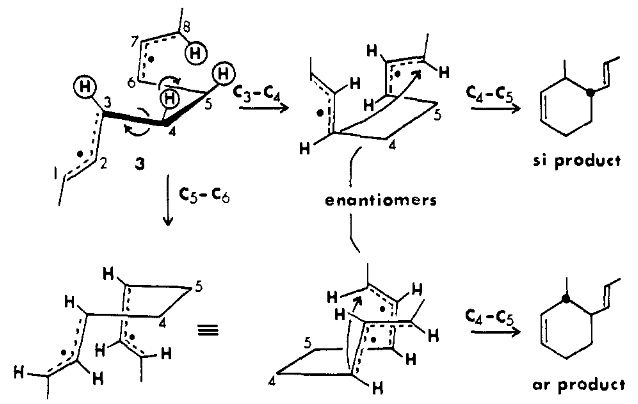
[5] Correlated with (*R*)-(+)-3-methylcyclohexanone: L. M. Jordan, Ph.D. Dissertation, Yale University, 1973; E. J. Eisenbraun and S. M. McElvain, *J. Amer. Chem. Soc.*, 77, 3383 (1955).

[6] S. Winstein and D. Trifan, *ibid.*, 74, 1154 (1952).

that *trans*-1,2-divinylcyclobutane (tDV) gives 4-vinylcyclohexene with 54% inversion (si + ai) and 46% retention (sr + ar) of configuration (8% net inversion, 92% racemization). In the case of tDV, where the four-pathway analysis cannot be achieved for lack of a stereochemical label to distinguish antarafacial from suprafacial migration, the gross inversion:retention ratio might suggest a small inversion component superimposed upon a largely stereorandom, chirality-destroying process passing through planar or rapidly rotating diradical intermediates. The present results show that for tTT and tCT (and by analogy, for tDV), this is not the case. Although the gross inversion: retention ratios (51.6:48.4 and 49.5:50.5) again might suggest near-randomization of stereochemistry, this would require the formation of substantial amounts of antarafacial products. Table I shows that not more than 12% of the tTT and 5.5% of the tCT 1,3 rearrangements can involve a rapidly rotating diradical intermediate.

In one interpretation of the present results (Scheme II), tTT gives a diradical intermediate **3**. All four pathways from **3** require bond rotation about C_4-C_5 to permit juncture of the migrating carbon (C_3) to the terminus (C_8). Pathway sr (not shown), a shearing motion of the two allylic units past each other, requires no additional rotations. Pathways si and ar each require one (or an odd number) of additional rotations, si about C_3–C_4, and ar about C_5–C_6. Pathway ai (not shown) requires an odd number of additional rotations about each of C_3–C_4 and C_5–C_6.

Scheme II



If the C_3–C_1 and C_5–C_6 rotational barriers were identical and the ring-closure rates to products **1** and **2** were not very different, the relative rates through each of the pathways would be controlled largely by probability and would rank sr > si = ar > ai. The experimental order (Table I) is si > sr ≫ ar > ai from both tTT and tCT. It seems unlikely that product stabilities make any significant contribution to the ordering, and in two cases, si ≫ ar, and sr ≫ ai, this factor is ruled out rigorously because the pairs of products are enantiomeric.

Since the magnitudes of rotational barriers in diradicals are imperfectly known, it is conceivable that, perhaps because of differences in steric interactions between the circled hydrogens, the rotational rate ratios (C_3–C_4)/(C_5–C_6) could be as large as the values (9.4 from tTT and 18.4 from tCT) needed to fit the observed si/ar ratios. On the other hand, the diradical mechanism offers no obvious explanation for the observations that in the suprafacial mode, inversion is preferred over retention, but the reverse is true in the antarafacial mode. At the least, the present results provide an experimental basis for refinement of the diradical theory.

For the present, a simpler and hence preferable interpretation would describe the major reactions si and sr as concerted processes, si allowed,[7] but only slightly preferred over sr, which is forbidden.[8] Both antarafacial reactions are slow because of the difficulty of migration through the π-nodal plane.

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(7) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, p 114.

(8) J. A. Berson and L. Salem, *J. Amer. Chem. Soc.*, 94, 8917 (1972).

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A Criticism of the Use of the Hammett Equation in Structure–Reactivity Correlations

Sir:

The theoretical interpretation of σ, σ^+, and σ^- values derived from the Hammett equation as indices of measurement of substituent-ring electronic interactions receives abundant acceptance. The significance of ρ is also assumed, in numerous publications, diagnostic of the extent of charge development in the transition state of a kinetic process. However legitimate such concepts may or may not be, it is essential that the reasoning should be consistent; *if* it is accepted that the (entirely empirical) Hammett equation as applied to the effect of a perturbation in a benzene ring on rate of reaction of a side chain or nuclear position can be "explained" in this way, *then it inevitably follows*, despite many reports implying the contrary, that it is entirely inconsistent to use ρ as indicative of the ability of other ring systems to transmit substituent effects, or to substantiate selectivity–reactivity relationships in accordance with the Hammond postulate.[1]

We illustrate the point with three examples taken from recent work on the application of Hammett equations to areas of major mechanistic interest.

Electrophilic Substitution in Heteroaromatic Systems. Consistent σ^+ values have been attached to the effect produced by replacement of CH=CH in the benzene ring system by S and O, so that the α and β reactivity of thiophene and furan toward electrophiles follows the Stock–Brown "extended selectivity relationship" very closely.[2,3] The observation that apparent ρ values evaluated from substituent effects on the reactivity of such rings are different from those of the substituted benzenoid compounds indicates only that the effects of substituent and heteroatom are not additive; it cannot indicate different transition state structures.[4-6] Thus, the ρ value for the chlorination (CH_3COOH, 25°) of the

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(1) G. S. Hammond, *J. Amer. Chem. Soc.*, 77, 334 (1955).

(2) S. Clementi, P. Linda, and G. Marino, *J. Chem. Soc. B*, 1153 (1970); G. Ciranni and S. Clementi, *Tetrahedron Lett.*, 3833 (1971).

(3) G. Marino, *Advan. Heterocycl. Chem.*, 13, 235 (1971).

(4) S. Clementi and G. Marino, *Chem. Commun.*, 1642 (1970).

(5) S. Clementi and G. Marino, *J. Chem. Soc. B*, 71 (1972).

(6) A. R. Butler and J. B. Hendry, *ibid.*, 848 (1970).