Table I. Organocobalt Cluster Derivatives Prepared from the Carbonium Ion Hexafluorophosphates

R in $(OC)_9Co_3$-CC^+HR	Reactant	Product (% yield)	Mp, °C
H	MeOH	$(OC)_9Co_3CCH_2OMe$ (85)	128–129
H	EtOH	$(OC)_9Co_3CCH_2OEt$ (76)	54–56
H	$PhNH_2$	$(OC)_9Co_3CCH_2NHPh$ (67)	69–71
H	$C_6H_5NMe_2$	$(OC)_9Co_3CCH_2C_6H_4NMe_2$-*p* (49)	Unstable
Me	MeOH	$(OC)_9Co_3CCH(Me)OMe$ (85)	176–177
Me	EtOH	$(OC)_9Co_3CCH(Me)OEt$ (82)	61–63d
Me	PhSH	$(OC)_9Co_3CCH(Me)SPh$ (42)	73–75
Me	$PhNH_2$	$(OC)_9Co_3CCH(Me)NHPh$ (73)	117–119
Me	$C_6H_5NMe_2$	$(OC)_9Co_3CCH{=}CH_2$ (68)	144–146
Ph	MeOH	$(OC)_9Co_3CCH(Ph)OMe$ (59)	70–72
Ph	EtOH	$(OC)_9Co_3CCH(Ph)OEt$ (75)	77–79
Ph	PhSH	$(OC)_9Co_3CCH(Ph)SPh$ (38)	93–95
Ph	$PhNH_2$	$(OC)_9Co_3CCH(Ph)NHPh$ (59)	126–127
Ph	$C_6H_5NMe_2$	$(OC)_9Co_3CCH(Ph)C_6H_4NMe_2$-*p* (54)	101–103

Treatment of 1.5 mmol of $(OC)_9Co_3CCH(OH)CH_3$ in propionic anhydride solution with 2 mmol of 65% aqueous HPF_6 under nitrogen resulted in precipitation of a black solid. The latter was washed with dichloromethane and dried *in vacuo* (Schlenk apparatus). The resulting black, microcrystalline solid gave the correct analytical values for II. *Anal.* Calcd for $C_{12}H_4O_9F_6PCo_3$: C, 23.48; H, 0.66; F, 18.57; Co, 28.80. Found: C, 23.45; H, 0.74; F, 18.79; Co, 29.39.

Analytically pure samples of I and III were prepared in a similar manner. These salts were quite stable in the absence of air and moisture. Initial results of our study of their reactions (with alcohols, a thiol, aniline, and *N*,*N*-dimethylaniline) are presented in Table I. Reactions were carried out under nitrogen either by adding the reactant to the solid PF_6^- salt or to its suspension in well-dried benzene. The products were purified by column chromatography and/or sublimation *in vacuo*. All were characterized by their ir and nmr spectra and by combustion analysis.

In agreement with the postulated reaction course in Scheme I, the reaction of $(OC)_9Co_3CCH(OH)CH_3$ with equimolar quantities of triethylsilane and trifluoroacetic acid, in THF at reflux, resulted in reduction to $(OC)_9Co_3CCH_2CH_3$ in 72% yield.

From these results it would appear that carbonium ions I, II, and III are readily formed and quite stable. Especially noteworthy is the ready accessibility of the primary carbonium ion, I. We suggest that the structure of these carbonium ions presents an especially favorable opportunity for σ–π stabilization. It has been recognized that organometallic substituents in the β position greatly stabilize carbonium ion centers *via* σ–π conjugation (IV).[6] In the cobalt cluster carbonium ions, I, II, and II, such σ–π stabilization should make substantial contribution to their stability. Rotation about the exocluster C–C bond presents three opportunities for such lateral σ–π overlap. In this connection, the easy accessibility of the acylium ion, $(OC)_9Co_3CC^+O$,[4b,c] is to be noted. Here also a contribution from such σ–π conjugation may be discussed.

We are continuing this investigation with further preparative studies and with more quantitative studies which we hope will provide information concerning the stability of these carbonium ions relative to other stabilized carbonium ion species.

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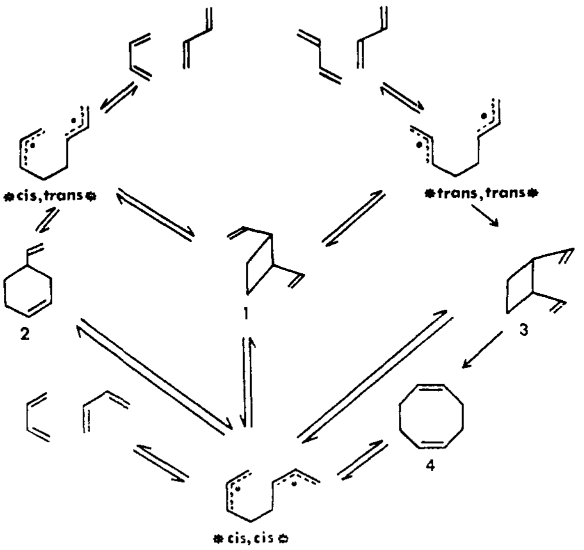
[6] T. G. Traylor, H. J. Berwin, J. Jerkunica, and M. L. Hall, *Pure Appl. Chem.*, 30, 599 (1972).

Rearrangement of *trans*-1,2-Divinylcyclobutane and the Energy Surface of the Dimers of Butadiene[1]

Sir:

In many thermal reactions, the experimentally determined heat of formation ($\Delta H_f°$) of the transition state is that predicted by bond additivity data to be appropriate for a species with one broken bond, a "diradical."[2,3] From the logical converse of this correspondence, a procedure has developed for estimation of $\Delta H_f°$ of a hypothetical diradical intermediate in a given reaction by measurement of the activation energy of a different reaction assumed to pass through the "same" intermediate. A recent important application has concerned the energy surface common to the dimers of butadiene, in which values of $\Delta H_f°$ for the hypothetical octa-1,7-diene-3,6-diyl diradicals *trans,trans*, *cis,-trans*, and *cis,cis* were estimated from various pyrolysis reactions (Scheme I) of *trans*-1,2-divinylcyclobutane (1), 4-vinylcyclohexene (2), and cycloocta-1,5-diene (4).[4,5]

Scheme I



Although there is some disagreement on the values

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[1] (a) We are grateful for partial support of this work by grants from the National Science Foundation (GP-11017X and GP-33909X) and the Hoffmann-La Roche Foundation. (b) Presented in part at the American Chemical Society 22nd National Organic Chemistry Symposium, Ann Arbor, Mich., June 1971, Abstracts, p 28.

[2] (a) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, 72, 1866 (1968); (b) *J. Chem. Eng. Data*, 15, 266 (1970); (c) *Int. J. Kinet.*, 2, 423 (1970); (d) S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas-Phase Unimolecular Reactions," National Standard Data Reference Series NBS 21, U. S. Government Printing Office, Washington, D. C., 1970.

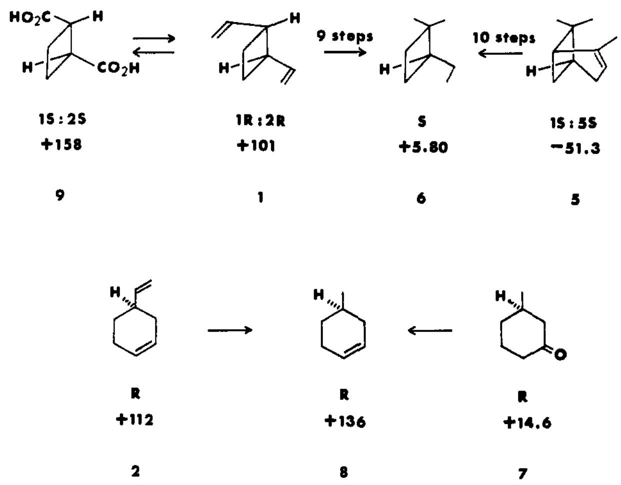
[3] H. M. Frey and R. Walsh, *Chem. Rev.*, 69, 103 (1969).

of the thermodynamic quantities,[4,5] we are concerned here not with refinement of these, but rather with the nature of the intermediates themselves. In particular, we wish to use criteria of chemical and especially of stereochemical behavior to examine the validity of the assumption that intermediates of similar energy and superficially similar structure generated in wholly different parts of the energy surface are identical.

The diradical mechanism for the formation of 4-vinylcyclohexene (**2**) from butadiene involves either or both of the species *cis,trans* and *cis,cis*, which also can arise in the pyrolysis of *trans*-1,2-divinylcyclobutane (**1**).[6] The stereochemistry of the **1** → **2** rearrangement has been studied previously[7] with optically active **1**, but since the enantiomeric configurations and purities of the starting material **1** and product **2** were unknown, the observed[7] optical activity of **2** permitted only limited conclusions.

The absolute configurations and maximum rotations ([α]D in degrees) of **1** and **2** established in the present work and shown in Scheme II follow from transformations of both **1** and α-pinene (**5**)[8] to 1,1-dimethyl-2-ethylcyclobutane (**6**) and of both **2** and 3-methylcyclohexanone (**7**)[9] to 4-methylcyclohexene (**8**). Physical and chemical evidence in the literature confirm these correlations.[5b,10–12]

Scheme II

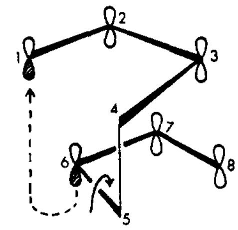


trans-Cyclobutane-1,2-dicarboxylic acid (**9**), which is readily resolved,[12b] can be converted to optically active **1** by successive treatment with diazomethane, NaAlH$_2$(OCH$_2$CH$_2$OCH$_3$)$_2$ (−70°), and CH$_2$=PPh$_3$.

Pyrolysis of (1*R*,2*R*)-*trans*-1,2-divinylcyclobutane (**1**), $[\alpha]^{23}$D +37.8° (*c* 18.16, CCl$_4$), 37.4% optically pure, at 146.5°, liquid-phase conditions, for 24.5 hr (57.7% total conversion) gives (*R*)-4-vinylcyclohexene (**2**), $[\alpha]^{19.4}$D +3.16° (*c* 18.82, CCl$_4$), 2.8% optically pure. The sign of rotation of **2** indicates that rearrangement occurs with predominant *inversion* of configuration of the migrating group.

Determination of the rotation of **1**, reisolated from this pyrolysis, shows that racemization of the starting material (**1**) is about one-fourth as fast as formation of **2**. The rate constants for racemization of **1** and formation of **2**, k_α and k_p, are used to calculate $\bar{P}$,[13] the effective optical purity of **1** during any given experimental time period. For the experiment reported here, $\bar{P} = 0.927$, so that the maximum optical purity that could be expected in the product **2** is 0.927 × 37.4% = 34.7%. The observed value corresponds to 8.0% of this. Consequently, the rearrangement of the portion of **1** that has not undergone prior racemization gives 54% of (*R*)-(+)-**2** and 46% of (*S*)-(−)-**2**, the products respectively of rearrangement with inversion and retention of configuration.[14]

In order to serve in the function ascribed to them, namely that of common immediate precursors of 4-vinylcyclohexene (**2**) in both the **1** → **2** rearrangement and the dimerization of butadiene,[15] the hypothetical diradicals *cis,cis* and *cis,trans* must adopt a conformation like that shown here (for *cis,cis*, **10**).



10, *cis,cis*

Product formation consists of making a bond between C$_1$ and C$_6$ of the diradical. The present experiments show that from **10** (and/or its *cis,trans* counterpart), it would be necessary to form this bond predominantly by juncture of the *back lobe* of C$_6$ to the front lobe of C$_1$. This implies the curious corollary that whereas the standard, concerted Diels–Alder reaction always occurs cis on the dienophile, the Diels–Alder dimerization of butadiene must occur preferentially trans.[16] It is evident that this prediction, derived from the assumption of identical intermediates in the **1** → **2** rearrangement and

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(4) S. W. Benson, *J. Chem. Phys.*, **46**, 4920 (1967).

(5) (a) W. von E. Doering, 23rd Congress of Pure and Applied Chemistry, Vol. I, Butterworths, London, 1971, p 237; (b) W. von E. Doering, M. Franck-Neumann, D. Hasselmann, and R. L. Kaye, *J. Amer. Chem. Soc.*, **94**, 3833 (1972).

(6) Note that a difference in distribution of the products **2** and **4** from butadiene and **1** does not suffice to rule out *cis,trans* and *cis,cis* as common intermediates in the dimerization and rearrangement.

(7) G. S. Hammond and C. D. DeBoer, *J. Amer. Chem. Soc.*, **86**, 899 (1964).

(8) Absolute configuration: (a) J. H. Brewster, *ibid.*, **81**, 5491 (1959), and references cited there; (b) J. A. Berson, J. S. Walia, A. Remanick, S. Suzuki, P. Reynolds-Warnhoff, and D. Willner, *ibid.*, **83**, 3986 (1961), footnote 12; (c) F. H. Allen and D. Rogers, *J. Chem. Soc. B*, 632 (1971). Maximum rotation: (d) F. H. Thurber and R. C. Thielke, *J. Amer. Chem. Soc.*, **53**, 1030 (1931); (e) R. N. McDonald and R. N. Steppel, *ibid.*, **91**, 783 (1969).

(9) Absolute configuration: (a) J. A. Mills and W. Klyne, *Progr. Stereochem.*, **1**, 177 (1954); (b) A. J. Birch, *Annu. Rep. Progr. Chem.*, **47**, 191 (1950). Maximum rotation: (c) O. Wallach, *Justus Liebigs Ann. Chem.*, **289**, 340 (1896); (d) E. J. Eisenbraun and S. M. McElvain, *J. Amer. Chem. Soc.*, **77**, 3383 (1955).

(10) (a) A. I. Scott and A. D. Wrixon, *Tetrahedron*, **27**, 2339 (1971); (b) S. I. Goldberg and F. L. Lam, *J. Org. Chem.*, **31**, 240 (1966).

(11) L. M. Jordan, Ph.D. Dissertation, Yale University, 1973.

(12) (a) F. B. Kipping and J. J. Wren, *J. Chem. Soc.*, 3246 (1957); (b) L. J. Goldsworthy, *ibid.*, 2012 (1924); (c) Y. Inouye, S. Sawada, M. Ohno, and H. M. Walborsky, *Tetrahedron*, **23**, 3237 (1967).

(13) S. Winstein and D. Trifan, *J. Amer. Chem. Soc.*, **74**, 1154 (1952).

(14) (a) We present elsewhere[14b] evidence that the stereochemistry of the **1** → **2** rearrangement results from two competing stereospecific processes rather than from a small stereospecific component superimposed on a mechanism dominated by a stereorandom intermediate. (b) J. A. Berson and P. B. Dervan, *J. Amer. Chem. Soc.*, **95**, 269 (1973).

(15) Doering, *et al.*,[5b] have explicitly considered the possibility that the two reactions may not involve the same intermediate.

(16) The possibility that the dimerization might pass through other diradical intermediates, *e.g.*, one with an extended conformation, before **10**, does not qualitatively change the argument. The magnitude of the stereospecificity of formation of **2** by this path might be lower than that from **1**, but the direction would be unchanged.

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.

[17] National Institute of General Medical Sciences Predoctoral Fellow (No. 5-F01-GM-40662), 1968–1971.

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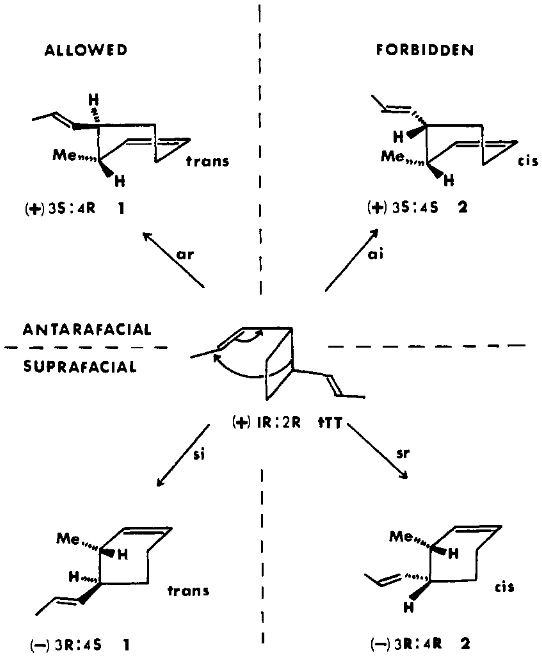
A Mechanistic Analysis of the Four Pathways in the 1,3-Sigmatropic Rearrangements of *trans*-1,2-*trans,trans*- and *trans*-1,2-*cis,trans*-Dipropenylcyclobutane[1]

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, $[\alpha]_D$ +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, $[\alpha]_D$ −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**, $[\alpha]_D$ −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).