Table I

activator	E_s,[a] kcal/mol	E_{ox},[b] V vs. SCE	ϕ_{fl}[c]	k_{cat},[d] $M^{-1}\ s^{-1}$
DMAC	58	0.14	0.04	9.73×10^{-2}
DMP	72	0.14	0.18	3.42×10^{-1} [e]
DMBI	68	0.46	0.88	7.07×10^{-3}
rubrene	54	0.82	0.56	1.40×10^{-4} [f]
DPAP	68	0.90	1.00	2.35×10^{-4}
perylene	65	1.00	0.84	1.19×10^{-4}
DPEA	62	1.16	0.96	3.58×10^{-5}
DPA	72	1.22	1.00	2.22×10^{-5}

[a] Assigned from the 0–0 band of the fluorescence spectrum. [b] Determined by cyclic voltammetry in CH_3CN solution with tetrabutylammonium perchlorate supporting electrolyte. [c] At 90 °C in argon saturated benzene solution. [d] Calculated by comparing relative total intensity with that of DMAC. [e] Measured by determining the apparent first-order rate constant for reaction of deuterated **1** at varying DMP concentration. [f] Unavoidable self-absorption by rubrene apparently leads to the observed low calculated value for k_{cat}.

light the energy released by the ion annihilation reaction must be at least as great as the lowest singlet-state energy of the emitter. This requirement is apparently fulfilled by all of the activators of Figure 3 *except* DMP. In this case, the ion annihilation is calculated[16] to release $\sim$59 kcal/mol and the singlet energy of DMP is 72 kcal/mol. Thus, DMP is still a powerful catalyst for the reaction of perester **1** (Table I), but it generates less than 1% of the expected chemiluminescence because of the energy deficit in the excitation step. This observation provides convincing evidence for the radical-ion intermediates proposed in the CIEEL mechanism.

This is the fourth well-documented case of an electron-transfer initiated reaction of a peroxide that leads to electronically excited-state product.[2] As in the previously described examples, the major evidence is the correlation of rate constant and oxidation potential, i.e., Figure 3. Comparison among the various peroxides reveal that the catalytic rate constant is strongly dependent upon structure. The diacyl peroxides, for example, react much more rapidly than do the more difficulty reduced peresters.[17] However, the magnitude of the slope of the line resulting from the semilog plot of rate constant against activator oxidation potential is essentially constant and equal to ca. $-0.3/RT$ for the systems investigated to date. This result is consistent with rate-limiting irreversible electron transfer from activator to peroxide occurring with a transfer coefficient of $\sim$0.3.[15,18]

In summary, we have observed two distinct reaction paths for thermolysis of secondary perester **1**. The unimolecular reaction appears to proceed by a stepwise route, the bimolecular reaction with electron donors by an electron-transfer mechanism. The electron-transfer mechanism in particular may serve as a model for the excitation step in the bacterioluminescence reaction.[19] We are continuing our investigation of this and other aspects of the chemistry of these peresters.

Acknowledgment. We thank Professor Faulkner of this department for many helpful discussions. The authors gratefully acknowledge financial support for this work by the Office of Naval Research, The National Science Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We also thank Mr. Steven P. Schmidt for preparing and purifying the DMAC, DPAP, DMP, and DMBI.

References and Notes

(1) The products were identified by comparison with authentic material. The yield of acetic acid was determined by gas chromatography on a Poropak Q column at 245 °C, the yield of acetophenone by gas chromatography on a 3% SE-30 on Chromasorb Q column at 100 °C.

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(3) Peroxy ester **1** was characterized as follows: IR (CCl_4) 3000, 1785, 1500, 1285 cm^{-1}; ^1H NMR (CCl_4 internal Me_4Si) δ 1.50 (d, 3 H, $J = 7$ Hz), 1.9 (s, 3 H), 5.17 (q, 1 H, $J = 7$ Hz), 7.3 (s, 5 H) Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.64; H, 6.73. Found: C, 66.98; H, 6.66. In addition perester **1** was reduced with triethyl phosphite to 1-phenylethyl acetate which was characterized by comparison with authentic material.

(4) We propose the following definitions. (i) Direct chemiluminescence: the emission of light is from the excited state formed as a direct result of a unimolecular thermal chemical reaction. (ii) Indirect chemiluminescence: the emission of light is from an excited state formed as a result of energy transfer from the initially generated excited state. (iii) Activated chemiluminescence: the emission of light is from an excited state directly formed from a bimolecular reaction between substrate and catalyst.

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(15) The details of the kinetic analysis will be presented in a forthcoming publication.

(16) The amount of energy released is calculated by taking the difference between the oxidation potential of the activator and the reduction potential of acetophenone after correction for the change in these values that result from change of solvent and the absence of electrolyte.

(17) For the series diphenoyl peroxide, dimethyldioxetanone, and perester **1,** we estimate that k_{cat} for DMAC is $\sim 7 \times 10^3$, 180, and 0.1 $M^{-1}\ s^{-1}$, respectively.

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Brian G. Dixon, Gary B. Schuster*[20]
Department of Chemistry, Roger Adams Laboratory
University of Illinois, Urbana, Illinois 61801

Received January 18, 1979

Silver-Catalyzed 1,2-Acyl Migration in an Optically Active Chlorohydrin. Evidence for Neighboring-Group Participation by Carbonyl Carbon

Sir:

Molecular rearrangements where the migrating substituent stabilizes the transition state by becoming bonded to an adjacent reaction center in the rate-limiting step is by definition a concerted process. A classic example of such neighboring-group participation (NGP)[1] is the phenonium ion which was introduced by Cram in his studies on stereospecific tosylate solvolyses.[2] The substrates used in these experiments usually required assistance by the migrating phenyl group to effect ionization of the leaving group and the results were best explained by a bridged-ion intermediate.

In contrast, stereochemical studies by Collins[3] on deamination reactions of amino alcohols have elegantly demonstrated that 1,2-phenyl shifts may also be nonconcerted, involve discrete carbenium-ion intermediates, and proceed with both inversion and retention at the migration terminus.[4] In fact, if steric interactions are involved in the transition state for 1,2 migration, retention may predominate.[5] Similarily, the pinacol rearrangement[6] has been shown to involve a carbenium-ion intermediate. However, if water leaves from a primary or secondary carbon, then a more concerted pathway is antici-

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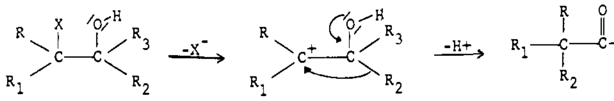
pated.[7] The formation of a carbonyl group, serving as a driving force for rearrangement, is a feature which these reactions have in common (eq 1).

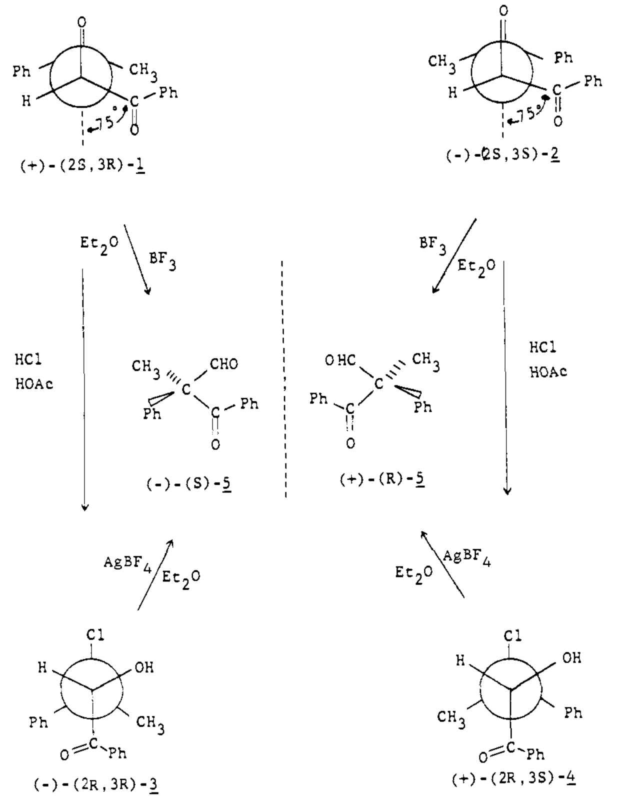


(1)

We are currently studying the mechanism of 1,2-acyl migration in a similar pinacolic type rearrangement in an effort to establish the concertedness of these 1,2 shifts and thereby provide evidence for NGP, at carbon, in the rate-limiting step. In our first report[8a] we established that 1,2-carbethoxy migration in ethyl (*E*)-3-methyl-3-phenylglycidate occurred without loss of optical purity. Our second experiment was designed to exclude a long-lived freely rotating carbenium ion in the Lewis acid induced 1,2-benzoyl migration in dypnone oxides **2** and **2** (Scheme I). Both diastereomers afforded optically active **5** and 100% inversion of configuration at the migration terminus.[8b]

The above study, however, could not rule out a short-lived cation where migration was faster than C-2–C-3 bond rotation. For a 1,2-carbonyl shift to occur, the C–Z bond (Z = migrating group) at the migration origin must lie in, or almost in, the plane described by the developing (vacant) p orbital on the adjacent carbon. Because the epoxy ketones **1** and **2** are geometrically constrained in their ground state, this requires a bond rotation of ~75°. It can be readily seen that the benzoyl group in either diasteromer can rotate downward and conceivably migrate with inversion to a fully developed carbenium ion faster than C-2–C-3 bond rotation. A carbenium-ion center adjacent to an asymmetric center has two diastereotopic faces which in principle can never be equal even if carbon–carbon bond rotation does obtain. Such ions can afford products with either retention or inversion depending upon the degree of steric perturbation by the asymmetric carbon. *If any product is observed that resulted from migration with retention, then a concerted pathway can be excluded.*

Scheme I



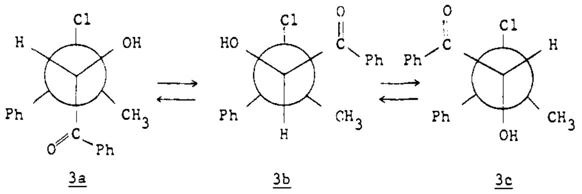
The goal of the present facet of our work is to distinguish between a pathway where carbonyl migration occurs after carbenium-ion formation or one that is concerted. Completely concerted migration, with freely rotating diastereomerically related acyclic compounds, with inversion at the migration terminus (i.e., no racemization at C-3) would serve to provide a definitive distinction in favor of the latter eventuality. This objective has been realized and we now report compelling evidence that the migrating carbonyl group is bonded to the migration terminus in the transition state.

We elected to use chlorohydrins **3** and **4** since the transition state for acyl migration should closely resemble that in the related glycidic ester[8a] and dypnone oxide[8b] rearrangements. Optically pure *trans*-dypnone oxide (**1**) was prepared as previously reported.[8b] Treatment of **1** with glacial acetic acid saturated with gaseous hydrogen chloride at 10 °C for 1.5 h afforded (−)-(2*R*,3*R*)-3-chloro-1,3-diphenyl-2-hydroxy-1-butanone (**3**, 43%), $[\alpha]^{25}{}_{\mathrm{D}}$ −7.99° (*c* 1.1, $HCCl_3$), mp 98–99 °C (lit.[9] mp 98–99 °C). Benzoyl migration was induced by the action of $AgBF_4$ in dry Et_2O. After 15 min the rearrangement product was isolated (81%) and preparative gas chromatography gave (−)-(*S*)-1,2-diphenyl-2-methyl-1,3-propanedione (**5**), $[\alpha]^{25}{}_{\mathrm{D}}$ −417° (*c* 0.78, $HCCl_3$), of 100% optical purity.[8b] These data establish that ring opening of the epoxide, which occurs with retention,[9] and 1,2-benzoyl migration, which gives inversion at C-3, *both proceed with complete stereospecificity.*[10]

The tedious resolution[8a] and stereochemical interconversions[8b] involved in the preparation of (−)-*cis*-dypnone oxide (**2**) prompted us to seek an alternate synthesis. An asymmetric epoxidation[12] was achieved in sufficient optical yield to suit our purpose. (*E*)-1,3-Diphenyl-2-buten-1-one (dypnone) in CH_2Cl_2 containing a catalytic amount of the quarternary salt of quinine and benzyl bromide was stirred at the interface of a second phase with 30% H_2O_2 (pH 11) and gave epoxides **1** and **2** in a 69:31 ratio. Recrystallization from EtOH–H_2O gave (−)-*cis*-dypnone oxide (**2**, 29%), mp 158–159 °C, $[\alpha]^{25}{}_{\mathrm{D}}$ −38.5° (*c* 1.8, $HCCl_3$), whose spectral properties were identical with those of an authentic sample.[9] The optical yield was established by ^1H NMR as 22% by integration of the enantiomeric methine singlets (300 and 308 Hz) in the presence of a chiral chemical shift reagent (Eu-OPT).

The stereospecificity of benzoyl migration in the (+)-chlorohydrin **4** was tested as described above. (−)-*cis*-Dypnone oxide (**2**, 21% optically pure) was stereospecifically converted to **4** and rearranged, without isolation, to dione **5** (97%), $[\alpha]^{25}{}_{\mathrm{D}}$ 92.7° (*c* 1.0, $HCCl_3$), which has a calculated[8b] optical purity of 22.3%. A mechanistic analysis of these data is only consistent with a concerted carbonyl migration that occurs simultaneously with departure of the chloride (AgCl) leaving group. The observation of these consequences is generally considered prima facie evidence for NGP, in a 1,2 migration.

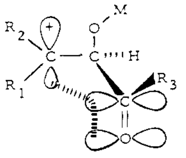
To further elaborate this mechanism we examined the Newman projections of chlorohydrin **3** (and **4**). If we assume



3a 3b 3c

that the steric bulk of Ph > CH_3 > Cl, as experimental data indicates,[13] then conformations **3b** and **3c** should be the most highly populated.[14] If rearrangement to a carbenium ion in poorly solvating media is faster than C-2–C-3 bond rotation, then the products should reflect the ground-state conformational populations.[3b] Benzoyl migration in either **3b** or **3c**, in the absence of C-2–C-3 rotation, should give retention at C-3.

However, our stereochemical studies show that migration in both **3** and **4** occurs exclusively from the *least stable conformer* where departure of the leaving group can be assisted by the *carbonyl* carbon as depicted in **6**. The resulting NGP is quite analogous to the 1,3 interaction in a homoallylic cation **7** which results in a cyclopropylcarbinyl cation. In the present reaction, however, we do not suggest that a cyclopropyloxenium ion[8c] is at an energy minimum, but, rather, a transition state. Entropic considerations favor the 1,3-carbon interaction over the more generally observed carbonyl participation at oxygen which would produce a strained four-membered oxetane that *does not lead to carbonyl migration.*[15] The overall stereochemistry of **1** → **3** → **5** also excludes an epoxide intermediate where one inversion (**3** → **2**) would be required.



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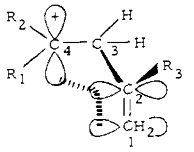

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Additional lines of evidence that support a concerted acyl migration are (a) thermal rearrangement of optically pure (+)-**1** on a gas chromatography column (20% SE-30 on Chromosorb P) afforded optically pure (−)-**5** (91%) with 100% stereospecificity at 200°; (b) quantitative rearrangement of **1** in nonpolar solvents is complete in <2 s;[8b] (c) carbonyl migration is impeded when excess (2.5 equiv) $MgClO_4$ is used as the Lewis acid catalyst and the carbonyl group is complexed (the major product from **2** is 1,3-diphenyl-1,2-butanedione as the result of a 1,2-hydride shift); and (d) in a polar solvent like CH_3OH, where the α-methylbenzyl cation at C-3 can be stabilized, and NGP is not necessary, no trace of carbonyl migration could be detected.[8b]

In conclusion, the surprising facility with which a carbonyl group migrates suggests that a unique type of stabilization is involved in the transition state. Our experimental and theoretical studies[8c,15] have provided the first evidence for NGP at carbonyl carbon.

Acknowledgment. The authors acknowledge support from the National Science Foundation (CHE 76 21992). R.D.B. also thanks Professor Roald Hoffmann for his generous hospitality during his sabbatical leave at Cornell University where this manuscript was written.

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(10) The absolute configuration of (−)-**3** and the stereospecificity attending its formation was independently established. (−)-Chlorohydrin **3** (53% optically pure) was oxidized under mild conditions with periodic acid to (−)-2-chloro-2-phenylpropanal, $[\alpha]^{25}_D$ −10.1° (*c* 3.6, C_6H_6). The aldehyde was further oxidized with CrO_3 to (−)-(*R*)-2-chloro-2-phenylpropionic acid, $[\alpha]^{25}_D$ −13.4° (*c* 4.1, C_6H_6), of known absolute configuration in 51% optical purity (based upon a reported rotation).[11] These data corroborate our earlier assignment of the absolute configuration of **1** and **2**.

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(15) Ab initio calculations on the comparable rearrangement of a protonated α,β-epoxyaldehyde clearly show that participation by carbon has a much lower E_a even though formation of the oxetane is thermodynamically favored, and an extensive search of the potential energy surface for this rearrangement is in complete accord with a concerted migration with the proposed cyclopropyloxenium ion[8c] on the reaction pathway (unpublished results).

(16) John M. Domagala was the recipient of a National Science Foundation Predoctoral Fellowship.

John M. Domagala,[16] Robert D. Bach*
Department of Chemistry, Wayne State University
Detroit, Michigan 48202

Received December 4, 1978

Applications of Homonuclear Two-Dimensional *J* Spectroscopy: an Alternative to Broad Band Heteronuclear and Homonuclear Decoupling

Sir:

The purpose of this communication is to show that high resolution homonuclear (proton) two-dimensional *J* (2-D *J*) spectroscopy[1-3] provides a convenient method for distinguishing between homonuclear and heteronuclear scalar spin couplings in complex molecules. This potential is illustrated for the $^1H-^{19}F/^1H-^1H$ couplings of 3,4,6-tri-*O*-acetyl-2-deoxy-2-fluoro-β-D-glucopyranosyl fluoride (**1**) and for the $^1H-^{31}P/^1H-^1H$ couplings of 4,4-dideuterio-2-oxo-2-phenoxy-5-phenyl-1,3,2-dioxaphosphorinane (**2**).

It is not appropriate to explain here the details of a proton 2-D *J* experiment.[1-3] Basically it involves the measurement of a series of time-domain free induction decay signals, as a function of two time variables, t_1 and t_2, which are then double Fourier transformed to give a 2-D *J* spectrum represented as a function of two frequency variables, f_1 and f_2, which are set orthogonal to each other. Distinction between homonuclear and heteronuclear couplings may be made by displaying projections[4] of the 2-D *J* spectrum onto different axes.

Homonuclear ($^1H-^1H$) couplings of a *weakly coupled* system are conveniently measured from the *partial J spectra*[5] which are obtained by projecting sections[6] of the 2-D *J* spectrum onto the f_1 axis. The lines in a *J* spectrum are symmetrically disposed about zero frequency and are separated by the $^1H-^1H$ couplings;[7] they are due to *J* modulation[5,8] of components of a resonance in the t_1 dimension, as a result of the inversion of proton spin states by the 180° refocussing pulse in the spin-echo pulse sequence.[9] Since the spin states of heteronuclei are not directly affected by this 180° pulse, the components due to heternuclear coupling are refocussed at the end of the evolution period (t_1) and hence the heteronuclear couplings are suppressed from the *J* spectrum. In this sense signals separated by heteronuclear scalar coupling behave similarly to *weakly coupled* proton chemical-shift components.

Heteronuclear scalar spin couplings, together with the proton chemical shifts, are conveniently obtained from a skew projection[2,10] of the 2-D *J* spectrum. Now, all of the $^1H-^1H$ couplings are suppressed and each proton resonance of a weakly coupled spin system gives a single line at its chemical shift, imparting to the skew projection the appearance of a proton-decoupled proton spectrum, with splittings from the

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