between the Mulliken atomic charges in methyl ethyl sulfide and in the anions **1** and **2** (see Figure 1).

The CH_2 group at the carbanionic center bears 0.04 less negative charge when it is α to sulfur than when it is β. This is surely a consequence of the fact that the sulfur atom next to the carbanionic center in **1** bears 0.07 more negative charge than the methylene group adjacent to this center in **2**. Nevertheless the hyperconjugative stabilization of the carbanion is also apparent, for the π bond order between the p_y orbitals on the carbanionic center and sulfur increases by 0.10, while the p_y-p_y bond order between sulfur and the methylene carbon decreases by 0.03 in **1**.

The hyperconjugative mechanism appears to be even more important for stabilization of **2**, where the bond order between the p_y orbital at the carbanionic center and p_y at the adjacent carbon increases by 0.17 on carbanion formation,[10] 70% more than the corresponding π bond order in **1**. Since the C–C bond is shorter than the C–S bond, the π overlap integral for the C–C bond is greater (0.171 vs. 0.116) than that for C–S. Thus, the increase in π overlap population between carbanionic center and adjacent atom is nearly three times as large in **2** as in **1**. Nevertheless, it is clear from the relative energies computed for **1** and **2** that the apparently greater hyperconjugative stabilization of the latter anion is not sufficient to overcome the larger stabilization of the former by polarization of the C–S bond.[11] Therefore, we conclude that, while hyperconjugation accounts for the stereochemical aspects of C–H bond acidification by sulfur, the polarizability of the C–S σ bond at the carbanionic site accounts for the regiochemistry.

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(7) The pK_a value for Ph_3CH is for Me_2SO solutions with K^+ as the counterion (F. G. Bordwell, J. E. Bares, J. E. Bartmess, G. E. Drucker, J. Gerhold, G. J. McCollum, M. VanDer Puy, N. R. Vanier, and W. S. Matthews, *J. Org. Chem.*, **42**, 326 (1977)); under these conditions the pK_a of 2-phenyl-1,3-dithiane is 30.7 but 1,3-dithiane cannot be measured ($pK_a > 32.5$). Streitweiser[1] reports the following for the $Cs–C_6H_{11}NH_2$ system: Ph_3CH, $pK_a = 31.45$; 2-phenyl-1,3-dithiane, $pK_a = 29.6$; and 1,3-dithiane, $pK_a = 31.1$.
(8) The geometrical parameters were those used by Lehn and Wipff,[4] including the 97.3° bond angle at sulfur.
(9) When d orbitals were included on sulfur, the energy difference between **1** and **2** increased to 9.2 Kcal/mol. Without d orbitals the SCF energy of **1** was calculated to be −508.9250 hartrees. With the inclusion of d orbitals on sulfur it became −509.0056 hartrees. Exponents for d orbitals were taken from B. Roos and P. Siegbahn, *Theor. Chim. Acta*, **17**, 139 (1970).
(10) Since these two carbons lie on a line that makes a 12.2° angle with a line parallel to the x axis, the p_y orbitals on these carbons do not overlap in a pure π fashion. The actual change in the π bond order (0.18) between these carbons is, therefore, slightly different from the change in the bond order between the p_y orbitals (0.17).
(11) NOTE ADDED IN PROOF. Professor Lehn has pointed out (private communication) that the dominance of polarization over hyperconjugation in the stabilization of carbanions α to sulfur is implicit also in the proton affinities calculated[4] for the 1-propyl carbanion and the two conformations of the carbanion formed by deprotonation of dimethyl sulfide.

Weston Thatcher Borden,* Ernest R. Davidson
Niels H. Andersen,* Alan D. Denniston
Nicholaos D. Epiotis
Chemistry Department, University of Washington
*Seattle, Washington 98195*

Lewis Acid Catalyzed Acyl Migration with Optically Active (Z)- and (E)-1,3-Diphenyl-2-buten-1-one Oxide. Evidence of a Concerted Pathway

Sir:

It is becoming increasingly evident that carbonyl migrations have assumed an important role in biosynthesis. It is now established that conversion of methylmalonyl-SCoA to succinyl-SCoA involves the intramolecular[1] migration of the carbonyl-SCoA group.[2] A nonenzymatic model for this reaction has been reported by Dowd.[3] Similarly, Wemple[4] has unequivocally proven the intramolecular 1,2 migration of a thiol ester in a biochemically patterned synthesis of tropic acid. We recently provided the first evidence that 1,2-carbethoxy migration in the optically active epoxy ester ethyl (E)-3-methyl-3-phenylglycidate is a highly concerted process that occurs without loss of optical activity.[5] Although it has been shown that carbonyl migration[6] with epoxy ketones[7] and esters[8] is intramolecular, the more subtle features of the overall reaction mechanism remain obscure. The questions regarding the concertedness of these acyl rearrangements remain largely unresolved.[5,8,9]

It was the purpose of the present study to probe for the intermediacy of a carbenium ion in the 1,2 migration of an acyl group by the use of diastereomerically related optically active epoxy ketones which are treated under identical reaction conditions. Two diastereomers, however, can afford a common long-lived cationic intermediate if carbon–carbon bond rotation is rapid resulting in a stereospecific 1,2 shift of a migrating group.[10] If the rearrangement is concerted, different diastereomers need not necessarily give different diastereomeric products, although, if this does occur, then a freely rotating cation may be excluded.[4c] The combined efforts of Collins,[10a,11] Cram,[12] Winstein,[13] and others[14] all concur that concerted 1,2 migrations must be attended by complete stereospecificity. If a stereoselective reaction is observed, where even a minor amount of retention accompanies inversion, then a concerted pathway is not possible. We now report that Lewis acid catalyzed 1,2-benzoyl migration with both (Z)- and (E)-1,3-diphenyl-2-buten-1-one oxide (dypnone oxide) proceeds in nonpolar solvents with 100% inversion of configuration at the migration terminus excluding a long-lived freely rotating carbenium ion intermediate on the reaction pathway.

Because of the variety of methods available for the conversion of a carbonyl functional group to a ketone, we again intended to use optically pure sodium (+)-$(2S,3R,E)$-3-methyl-3-phenylglycidate (**1**)[5] as the precursor to (E)-dypnone oxide (**3**). However, all known conversions[15] failed to produce the acid- and base-sensitive epoxy ketone and we were required to develop a new reaction sequence that used a mixed carbonate functional group to activate the carbonyl group. Taking advantage of the water solubility of **1**, the sodium salt was dissolved in a buffered ($NaHCO_3$) aqueous solution and stirred at an interface with a second phase consisting of an excess of ethyl chloroformate dissolved in ethyl ether containing tri-*n*-propylamine. The resulting mixed carbonate **2** (93%) ($[\alpha]^{25}_D$ 126.2° (c 1.63, $CHCl_3$); IR (neat)[16] 1830, 1765 cm^{-1}; NMR

$(+)$-(2S, 3R)-**1** $(+)$-(2S, 3R)-**2**   (eq 1)

$(+)$-(2S, 3R)-**3**
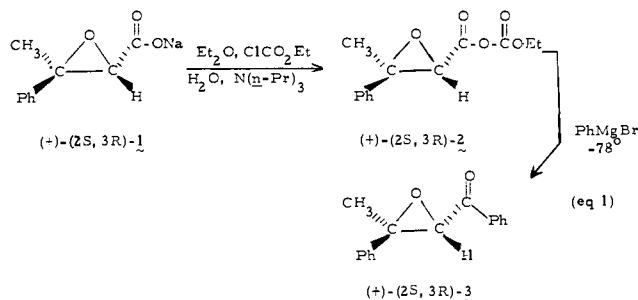
(CCl₄) δ 7.36 (s, 5 H), 4.33 (q, 2 H, J = 7 Hz), 3.43 (s, 1 H), 1.78 (s, 3 H), 1.35 (t, 3 H, J = 7 Hz)) was converted to optically pure (+)-dypnone oxide (3) by the low temperature reaction of 2 with PhMgBr in ethyl ether (50%), $[\alpha]^{25}_D$ 147.2° (c 1.3, CHCl₃) (eq 1).

(Z)-Dypnone oxide (5) was prepared by an established procedure.[17] Treatment of 3, $[\alpha]^{25}_D$ 56.9° (38.0% optically pure)[18] with cold glacial acetic acid saturated with gaseous hydrogen chloride for 2 h afforded (+)-(2S,3R)-α-chlorohydrin (4, 50%) *with complete retention of configuration*.[17,19] Dissolution of 4 in THF containing a catalytic amount of ethanol and 1.2 equiv of sodium hydride resulted in oxirane formation with complete inversion of configuration at carbon 3. Trituration in ethanol-water gave (−)-(2S,3S,Z)-dypnone oxide (5, 22%) (mp 160–163 °C (lit.[17] 161–163 °C), $[\alpha]^{25}_D$ −38.5° (c 1.1, CHCl₃)) of 38% optical purity[18] (eq 2).

(eq 2)
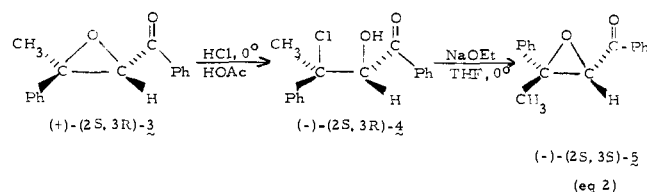
The stereospecificity of acyl migrations in α,β-epoxy ketones was tested by effecting rearrangement with a Lewis acid in nonpolar solvents. Accordingly, optically pure (+)-3 was treated with boron trifluoride etherate in refluxing ether for 30 min and gave (−)-1,2-diphenyl-2-methyl-1,3-propanedione (6, 98%), $[\alpha]^{25}D$ −411.0° (c 1.1, CHCl₃) (Scheme I). A similar experiment using 1 drop of BF₃·Et₂O in methylene chloride solvent also afforded optically pure (−)-(S)-6, $[\alpha]^{25}_D$ −415.9°, in 2 min; the 2,4-dinitrophenylhydrazone had mp 194–195 °C, $[\alpha]^{25}_D$ −163.4° (c 0.26, CH₂Cl₂).

When (−)-(Z)-dypnone oxide (5, 24% optically pure)[18] was subjected to the identical reaction conditions used for the E isomer 3, (+)-(R)-6 (98%), $[\alpha]^{25}_D$ 99.7° (c 1.0, CHCl₃), was obtained (24% optically pure based upon a maximum rotation for 6, $[\alpha]^{25}_D$ 416°). These data establish acyl migration in 5 to be stereospecific within experimental error.

The absolute configuration and optical purity of 6 was established by its conversion to the keto ether 8 and independently relating the configuration of 8 to (−)-(S)-α-methyltropic acid (9)[20] (Scheme I). Reduction of 6 with sodium cyanoborohydride in ethanol/acetic acid (10:1) produced the keto alcohol 7 (49%), $[\alpha]^{25}_D$ −223.5° (c 0.96, CHCl₃). Methylation of (−)-7 with trimethyloxonium tetrafluoroborate afforded optically pure[18] (−)-(S)-8 (60%), $[\alpha]^{25}_D$ −122.0° (c 1.1, CHCl₃). (−)-(S)-α-Methyltropic acid (9), $[\alpha]^{25}_D$ −29.9° (c 1.1, absolute EtOH) (lit.[21] $[\alpha]^{25}_D$ −28°), was converted to its methyl ester 10 (100%), $[\alpha]^{25}_D$ −60.8° (c 1.7,
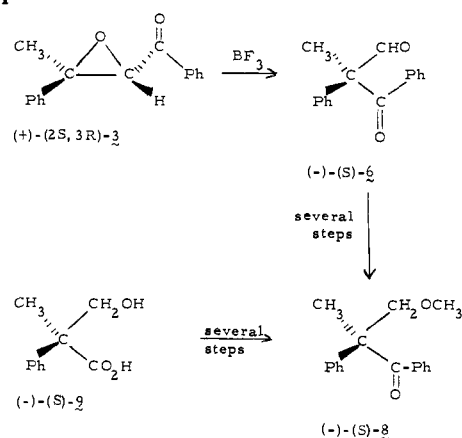
CHCl₃), by a Fischer esterification. The methyl ether functionality was introduced by reacting 10 with excess methyl iodide and silver oxide to give 11 (87%), $[\alpha]^{25}_D$ −30.8° (c 1.4, CHCl₃), which upon treatment with phenyllithium in ethyl ether at −78 °C afforded the desired optically pure phenyl ketone 8 (50%), $[\alpha]^{25}_D$ −122.0° (c 1.2, CHCl₃). The sign and magnitude of rotation of 8 prove conclusively that acyl migration in (E)-dypnone oxide also occurs with 100% stereospecificity and with complete inversion of configuration at the migration terminus. Since no racemization (i.e., partial migration with retention) was observed, our data is consistent with a concerted migration in which the carbonyl moiety migrates concurrently with oxirane ring opening. Examination of Newman projections clearly indicates that rearrangement should not occur with 100% inversion from *both* epoxides if a rapidly rotating cation were involved. Our data cannot rule out a short-lived carbenium ion where migration is faster than bond rotation.

Finally, our rearrangement studies with protic acids provide further support for the highly concerted nature of carbonyl migration in nonpolar solvents. Treatment of (E)-3 with chlorosulfonic acid for 30 min at 0 °C in methylene chloride gave exclusively stereospecific benzoyl migration affording 6. However, in a polar solvent like methanol, the highly solvated α-methylbenzyl cation was captured by methanol affording a mixture of diastereomers of 1,3-diphenyl-2-hydroxy-3-methoxy-1-butanone as the only products (82%). No trace of carbonyl migration could be detected. These data suggest that acyl migration in nonpolar media is facilitated by carbonyl participation in the rate-determining step.[22]

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Scheme I

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John M. Domagala,[23] Robert D. Bach*

Department of Chemistry, Wayne State University
Detroit, Michigan 48202
Received September 12, 1977

## The 1,3-Dimethyltriazaallyl Radical

Sir:

Although a number of neutral radicals with the unpaired electron interacting with two adjacent nitrogen atoms have been detected by ESR spectroscopy,[1-8] little is known about radicals with three adjacent nitrogen atoms. Recently Roberts and co-workers[9] detected some radical of this type by addition of silyl radicals to alkyl azides. Two alternate structures were proposed, viz.,

$$R^2-N=N-\overset{\cdot}{N}-R^1 \qquad R^1R^2-N-N=N\cdot$$
$$\textbf{1} \qquad\qquad\qquad \textbf{2}$$
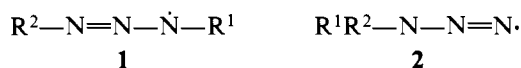
but the authors favored structure **2** since it appeared to be in better agreement with the ESR parameters. We have now obtained a radical having structure **1** which is different from those obtained by Roberts et al.[9]

Photolysis in the cavity of an ESR spectrometer of a mixture of di-*tert*-butyl peroxide (Bu^tOOBu^t) and 1,3-dimethyltriazene[10] ($CH_3NHN=NCH_3$) in a variety of solvents (cyclopropane, isooctane, methylcyclohexane) at about -100 °C yields a radical having the ESR spectrum shown in Figure 1 (the computer simulation obtained with hfs constants of Table I is also displayed). On enhancing the ESR signals, two more experimental lines are detected, as predicted by the spectral simulation. The radical disappears when the temperature is raised (cf. ref 9). The equivalence of two nitrogens and of the two methyls, plus the large couplings with the methyl hydrogens and the fact that the radical has been produced by a typical hydrogen abstraction reaction, seems to confirm that we actually detect the first triazaallyl radical.

$$CH_3-N\underset{N}{\underset{\diagdown\diagup}{\cdots}}N-CH_3$$
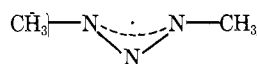
None of the above-mentioned features were observed for the radicals derived from additions to alkyl azides.[9] It is also worth mentioning that photolysis of $CH_3NHN=NCH_3$ in absence of $(Bu^tO)_2$ produces the methyl radical, whose spectrum was also detected in some samples superimposed to the radical of Figure 1.

As for the electronic configuration of the 1,3-dimethyltriazaallyl radical, there are two possibilities worth discussion. In the allyl radical the unpaired electron can only be localized on a π system; however, in its nitrogen analogue the presence of a molecular orbital (MO) formed by the nitrogen lone pairs having an energy comparable with that of the π system leads to two alternate possibilities: (i) a π radical, where only the $2p_z$ atomic orbitals of the three nitrogens are involved in building
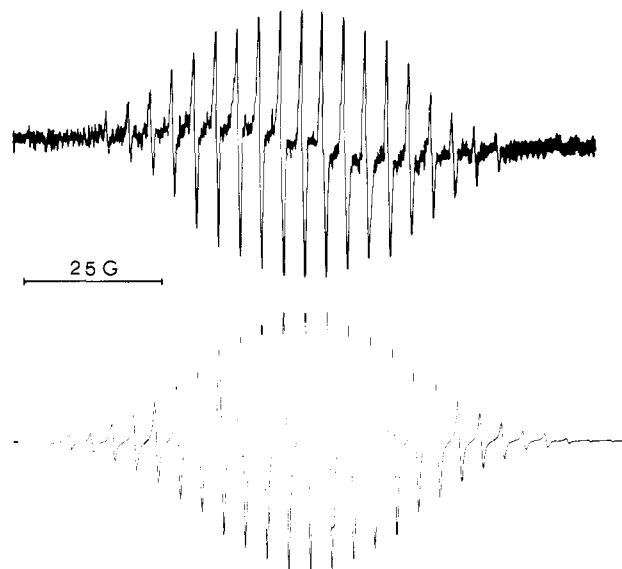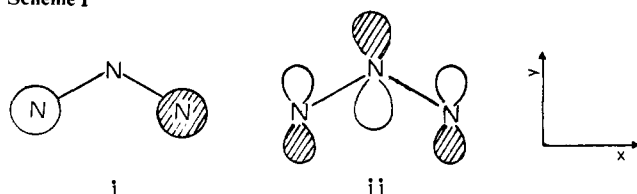
Scheme I

$$i \qquad\qquad\qquad ii$$

Figure 1. Experimental (top) and computer-simulated (line width 0.45 G) ESR spectrum of 1,3-dimethyltriazaallyl radical ($CH_3\overset{\cdot}{N}N = NCH_3$) in cyclopropane at -100 °C.

Table I. Experimental and Computed (INDO)[a,b] Hfs Constants (gauss) for the 1,3-Dimethyltriazaallyl Radical (g factor is 2.0020)

	Experimental	Computed π model	σ model
1 N	3.9 ± 0.2	-5.98	15.59
2 N	7.7 ± 0.2	9.67	1.66
2 CH_3	11.6 ± 0.2	15.58	2.36

[a] In the calculations only the NN distance was optimized (1.283 Å for the π and 1.255 Å for the σ configuration). The remaining geometrical parameters have been kept fixed at standard values. [b] Only the anti–anti geometry of the 1,3-dimethyltriazenyl radical has been considered. A similar investigation on the relative stabilities of the syn–syn, syn–anti, and anti–anti geometries of the triazaallyl radical has shown that the anti–anti geometry is significantly more stable.

up a π-nonbonding singly occupied molecular orbital (see Scheme I); (ii) a σ radical, where the singly occupied MO consists mainly of an antibonding combination of the nitrogen $2p_y$ atomic orbitals (the corresponding INDO percentage is $\sim 80\%$).

An INDO calculation on the two different electronic configurations[11] showed that model i has an energy 5 kcal mol^{-1} lower than ii. This difference is rather small for an unambiguous assignment of the electronic configuration. However a completely different distribution of the spin density should occur in the two cases, in that a much smaller value on the central nitrogen is expected in model i with respect to ii. In Table I it is quite clear than the trend of the hfs constants computed for the π radical is similar to the experimental one, which is certainly not the case for the σ radical. Attempts to fit the experimental spectrum with groups of constants following the trend of model ii were unsuccessful. In no case could the exact sequence of line intensities be reproduced.

It may therefore be concluded that a true allyl-like radical containing three nitrogens instead of carbons has been detected. The calculations also suggested that substitution of methyls with less electronegative groups (e.g., H, SiH_3) would favor the σ configuration. As a consequence, although the assignment of structure **2** to the radicals of ref 9 (R = silyl substituents) seems quite likely, our finding might suggest a structure of type **1**, with the unpaired electron located on a σ instead of a π molecular orbital.