The slow decay of the emission signals due to A and B-d_1 can be rationalized by the assumption that products are still being formed after the irradiation is stopped. This could conceivably occur in two ways: (1) *via* a one-step reaction of intermediate paramagnetic species which have relatively long lifetimes, or (2) by way of a radical-chain mechanism.

The one-step reactions which could conceivably occur are the insertion of carbomethoxycarbene into a carbon–chlorine bond or the combination of a pair of radicals, chlorocarbomethoxymethyl and trichloromethyl (or dichloromethyl-d_1), which are originated by the abstraction of a chlorine atom by carbomethoxycarbene. However, the limited selectivity of carbomethoxycarbene in reactions with hydrocarbons[13] as well as the fast combination rates reported for the trichloromethyl radical[14] are inconsistent with the relatively slow decay rate of the emission lines. We, therefore, favor the alternative, radical chain mechanism, involving a reaction sequence similar to the one proposed by Urry and Wilt.[5]

Our experimental observations cannot rule out the possibility that product formation also occurs *via* competing mechanism such as the insertion, in one or two steps, of the intermediate carbene into carbon–chlorine bonds. At the present time, studies are under way to further elucidate the mechanism of the reactions discussed and the electronic spin state of the divalent-carbon intermediate.

Acknowledgment. The authors are indebted to Dr. A. M. Trozzolo for stimulating discussions.

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[13] Photolytically generated carbomethoxycarbene was found to insert into the aromatic carbon–hydrogen bonds of benzene and toluene: H. D. Roth, manuscript in preparation.

[14] Reference 7, pp 247–272.

[15] Department of Chemistry, University of Guelph, Guelph, Ontario, Canada.

Michael Cocivera,[15] Heinz Dieter Roth
Bell Telephone Laboratories, Inc.
Murray Hill, New Jersey

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Stereoselectivity in the Boron Trifluoride Catalyzed Rearrangement of a 1,1-Disubstituted Ethylene Oxide

Sir:

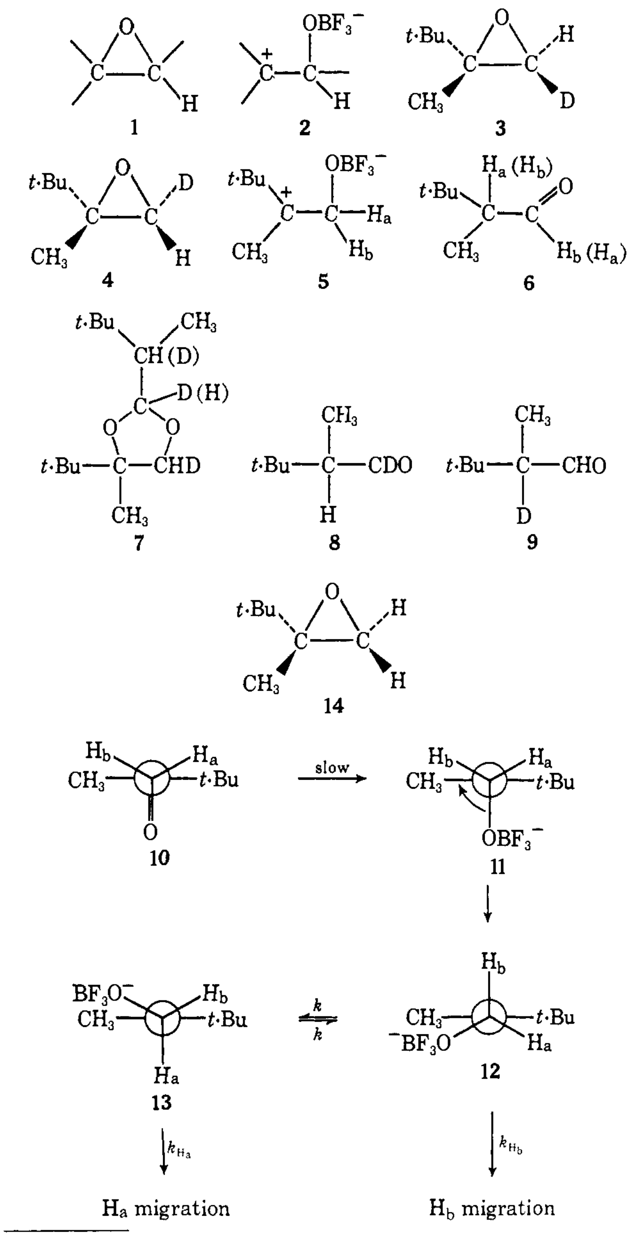
For the boron trifluoride catalyzed rearrangement of epoxides **1** stereochemical data have been obtained[1–4] which are most satisfactorily interpreted in terms of the intermediacy of the discrete carbonium ion **2**.

As part of an attempt to identify the factors which influence the rearrangement of the intermediate carbonium ion we examined the rearrangement of the monodeuterated epoxides **3** and **4**. The intent was to determine whether or not the selection of the migrating hydrogen atom in the carbonium ion **5** → aldehyde **6** reaction depends upon the stereochemical origin of the proton relative to the bulky *t*-butyl group and the smaller methyl group.

The stereochemistry of the deuterated epoxides **3** and **4** followed not only from the synthetic routes used[5] but also the nmr spectra (60 Mc): epoxide **3**,[6] 0.90 (s, 9 H, *t*-butyl), 1.21 (d, $J_{CH_3,H}$ = 0.8 cps, 3 H, methyl), 2.64 ppm (q, J_{H,CH_3} = 0.8 cps, 1 H); epoxide **4**,[7] 0.91 (s, 9 H, *t*-butyl), 1.22 (s, 3 H, methyl), 2.27 ppm (s, $W_{h/2}$ = 2.1 cps, 1 H). In particular the long-range CH$_3$–H coupling[5,8] in epoxide **3** and its absence in epoxide **4** confirm the stereochemical assignments.

Reaction of each epoxide, **3** and **4**, with boron trifluoride in carbon tetrachloride at 0° gave, in addition to dioxolanes (**7**; 50%) and an unidentified component (12%) of high boiling point, mixtures (*ca.* 33%) of

Scheme I



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[1] J. M. Coxon, M. P. Hartshorn, and B. L. S. Sutherland, *Tetrahedron Lett.*, 4029 (1969).

[2] B. N. Blackett, J. M. Coxon, M. P. Hartshorn, and K. E. Richards, *Tetrahedron*, **25**, 4999 (1969).

[3] J. M. Coxon, M. P. Hartshorn, and C. N. Muir, *ibid.*, **25**, 3925 (1969), and references cited therein.

[4] B. N. Blackett, J. M. Coxon, M. P. Hartshorn, B. L. J. Jackson, and C. N. Muir, *ibid.*, **25**, 1479 (1969).

[5] B. N. Blackett, J. M. Coxon, M. P. Hartshorn, and K. E. Richards, to be published.

[6] Deuterium content 99.5%; isomer **3** 93.4%, isomer **4** 6.6%.

[7] Deuterium content 98.2%; isomer **4** 96.3%, isomer **3** 1.8%, undeuterated epoxide **14** 1.8%.

[8] *Cf.* N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, New York, N. Y., 1964, p 115 ff.

the aldehydes **8** and **9** identified by their nmr spectra: aldehyde **8**, 1.00 (s, 9 H, *t*-butyl), 1.01 (d, $J_{CH_3,H}$ = 6.8 cps, 3 H, methyl), 2.08 ppm (q, J_{H,CH_3} = 6.8 cps, 1 H, methine); aldehyde **9**, 1.00 (s, 9 H, *t*-butyl), 1.00 (methyl), 9.68 ppm ($W_{h/2}$ = 1.1 cps, 1 H, CHO). The ratio of **8**:**9** for each epoxide was determined from the relative integral of the 2.08- and 9.68-ppm nmr signals. For epoxide **3** the ratio of deuteride: hydride migration, *i.e.*, **9**:**8**, was 1:0.89 (standard deviation 0.03), while for epoxide **4** it was 1:2.65 (standard deviation 0.08).

These results reveal a marked preference for the migration of the group (hydrogen or deuterium) *cis* to the methyl group in epoxides **3** and **4**. This stereoselectivity may be rationalized in terms of Scheme I. Slow C–O bond heterolysis in **10** gives the discrete carbonium ion **11**. The direction of rotation about the central C–C bond is controlled by the larger nonbonded interaction between the *t*-butyl and solvated OBF_3^- groups and gives conformer **12** in which H_b is favorably oriented for migration. Competing with the H_b migration process is the establishment of conformational equilibrium (K = 1) between **12** and **13**.[9] In conformer **13** H_a is now in the favored migration orientation. The origin of the stereoselectivity of the rearrangement lies in the relative magnitude of the rate constants, k and k_{H_a} (or k_{H_b}), which may if they are comparable[10] lead to a concentration bias, relative to **13**, in favor of conformer **12**. This conformer (**12**) can undergo H_b migration (rate constant k_{H_b}) or conformationally equilibrate (rate constant k).

On the basis of this mechanistic model[11] and substituting the results from the rearrangement of epoxides **3** and **4**, the relative values of the rate constants for deuteride (k_D = 1.0) and hydride (k_H = 1.71) migration and the **12** → **13** conformational change (k = 1.84) were evaluated using the expressions

$$9/8 = 1/0.89 = (k_D/k_H)[1 + (k_H/k)]$$
$$8/9 = 2.65 = k_H/k_D[1 + k_D/k]$$

The formation of dioxolane **7** by reaction[12] of the aldehydes **8** and **9** with epoxides **3** or **4** introduces a correction due to the secondary isotope effect (A) for that reaction. The magnitude of this secondary isotope effect is not known, but the relative values of k, k_H, and k_D have been evaluated (Table I) for reasonable values of A. For the epoxide **14**, the data allow the estimation of a preference for the migration of that hydrogen atom *cis* to the methyl group in the range 1.81–1.93:1.

Table I. Effect of the Magnitude of the Secondary Isotope Effect (A)

A	k_D	k_H	k	Stereo-selectivity
1.00	1.00	1.71	1.84	1.93
1.05	1.00	1.64	1.83	1.90
1.10	1.00	1.57	1.81	1.87
1.15	1.00	1.51	1.80	1.84
1.20	1.00	1.46	1.80	1.81

B. N. Blackett, J. M. Coxon, M. P. Hartshorn, K. E. Richards
Department of Chemistry, University of Canterbury
Christchurch, New Zealand
Received December 16, 1969

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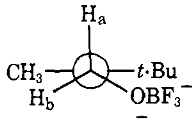
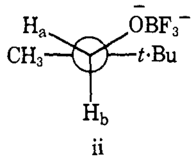
[9] While conformations i and ii could also lead to H_a and H_b migration, respectively, they may be neglected since their populations would be small as a result of the near-eclipsing of the *t*-butyl and OBF_3^- groups.



i



ii

[10] Such comparability of rates has been noted earlier in other carbonium ion studies: C. J. Collins, W. A. Bonner, and C. T. Lester, *J. Amer. Chem. Soc.*, **81**, 466 (1959); C. J. Collins and B. N. Benjamin, *ibid.*, **85**, 2519 (1963).

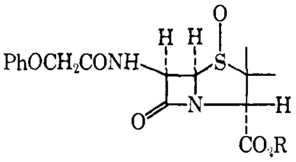
[11] The possibility of the reversible collapse of conformer **12** to epoxide **10**, *via* **11**, and the analogous collapse of conformer **13** to the epimeric epoxide does not invalidate the results derived using this simplified model.

[12] B. N. Blackett, J. M. Coxon, M. P. Hartshorn, A. J. Lewis, G. R. Little, and G. J. Wright, *Tetrahedron*, in press.

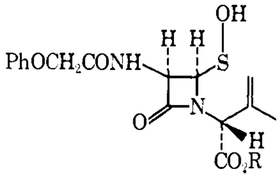
Structural Studies on Penicillin Derivatives.
IV. A Novel Rearrangement of Penicillin V Sulfoxide

Sir:

The penicillin sulfoxides, which were first prepared[1] over 20 years ago, have far greater β-lactam stability than the corresponding sulfides; indeed, Morin and coworkers[2] have shown that it is possible to achieve considerable modification of the thiazolidine ring without concomitant rupture of the β-lactam. They proposed that a sulfenic acid (**2b**) was the intermediate in their transformations of **1b** to the β-lactam containing products.



1



2

a, R = CH_2CCl_3
b, R = Me

In connection with our investigation into chemistry involving this proposed intermediate, we caused the penicillin sulfoxide ester (**1a**) to react with trimethyl phosphite in refluxing benzene and obtained, after 30 hr, a crystalline, less polar compound, **3**, mp 138°, [α]D −105° ($CHCl_3$), in high yield (>80%). High-resolution mass spectrometry and elemental analysis[3] indicated a molecular formula of $C_{18}H_{17}Cl_3N_2O_4S$, which represents a loss of the elements H_2O_2 from the starting sulfoxide. The ir spectrum had maxima at ν_{max} ($CHCl_3$) 1770 and 1745 cm^{-1}, and showed no absorption attributable to the amido side chain, *e.g.*, 3350 (NH), 1700 (amide I), and 1550 cm^{-1} (amide II).

Compound **3**, on treatment with triethylamine in methylene chloride, gave an isomer **4**, mp 70°, [α]D

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[1] (a) P. Sykes and A. R. Todd, "Committee on Penicillin Synthesis," Reports 526, 677; (b) "The Chemistry of Penicillin," H. T. Clarke, J. R. Johnson, and R. Robinson, Ed., Princeton University Press, Princeton, N. J., 1949, pp 156, 927, 946, 1008.

[2] R. B. Morin, B. G. Jackson, R. A. Mueller, E. R. Lavagnino, W. B. Scanlon, and S. L. Andrews, *J. Amer. Chem. Soc.*, **85**, 1896 (1963); **91**, 1401 (1969).

[3] Satisfactory microanalytical data were obtained for all new compounds.