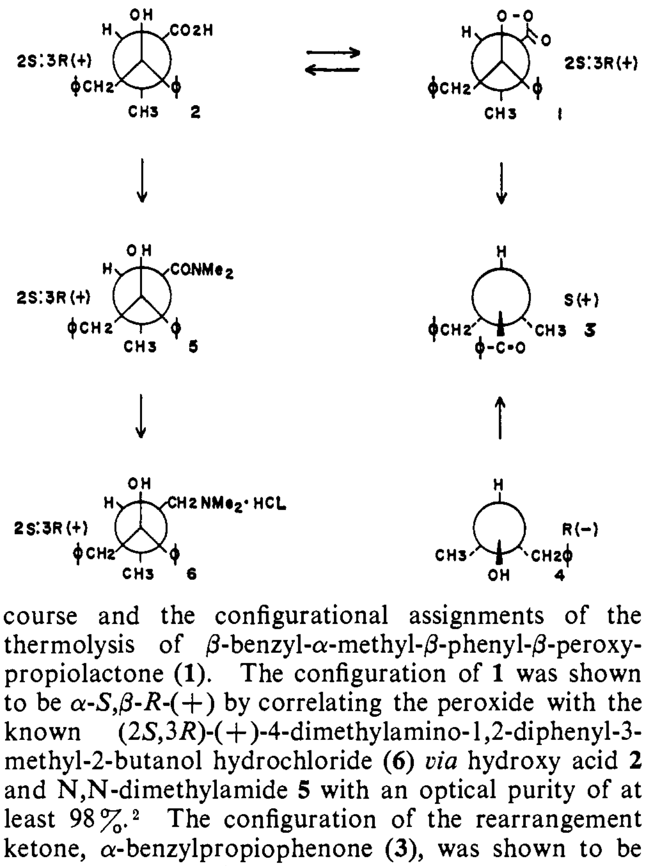
Cyclic Peroxyesters. IV.[1] Stereochemistry of the Rearrangement of Thermally Generated Oxygen Diradicals

Sir:

The preceding communication presented kinetic and product data which suggested that the thermal decomposition of β-alkyl-β-phenyl-β-peroxypropiolactones leads to an oxygen diradical which subsequently undergoes a free-radical-triggered "push-pull" transposition of the β substituent.[1] In this paper we describe a series of stereochemical studies which show that the β substituent migrates with inversion of configuration at the α carbon, the rearrangement terminus. Furthermore, the migration of an asymmetric β-alkyl substituent proceeds essentially with no loss of optical activity.

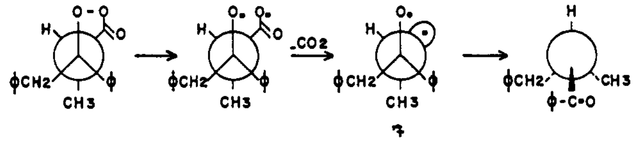
In Scheme I are summarized the stereochemical course and the configurational assignments of the thermolysis of β-benzyl-α-methyl-β-phenyl-β-peroxypropiolactone (1). The configuration of 1 was shown to be α-*S*,β-*R*-(+) by correlating the peroxide with the known (2*S*,3*R*)-(+)-4-dimethylamino-1,2-diphenyl-3-methyl-2-butanol hydrochloride (6) *via* hydroxy acid 2 and N,N-dimethylamide 5 with an optical purity of at least 98%.[2] The configuration of the rearrangement ketone, α-benzylpropiophenone (3), was shown to be *S*-(−) by correlating it with the known (*R*)-(−)-1-phenyl-2-propanol (4).[3] Ketone 3 was formed in 92% yield with an optical rotation of +88.0° (lit.[4] [α]D +87.5°). As Scheme I shows, the β-benzyl group migrates with quantitative inversion at the rearrangement terminus.

Scheme I. Configurational Assignment and Stereochemical Course of the Thermal Decomposition of β-Benzyl-β-phenyl-α-methyl-β-peroxypropiolactone



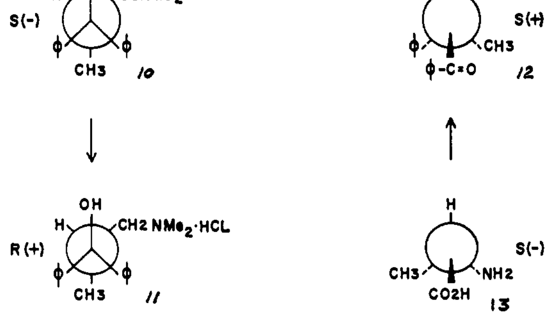
One shortcoming of the β-benzyl-α-methyl-β-phenyl-β-peroxypropiolactone (1) is the possibility of asymmetric induction due to the asymmetric center at the β carbon. It is possible, although improbable, that decarboxylation at the α center has led to the carbon radical 7 before β scission at the alkoxy radical site has commenced to a significant degree (Scheme II). Ordinarily such a carbon radical would be completely racemized;[5] however, asymmetric induction by the β center could conserve the configuration of the α carbon radical 7 during the β-alkyl group migration.

Scheme II. Asymmetric Induction by the β Center in the Rearrangement of Thermally Generated Oxygen Diradicals



To dispense with this alternative, the stereochemistry of the thermal decomposition of β,β-diphenyl-α-methyl-β-peroxypropiolactone (8) was investigated. In Scheme III are summarized the stereochemical course and the configurational assignments for this system. The configuration of 8 was shown to be *S*-(−) by correlating the peroxide with the known (*R*)-(+)-1,1-diphenyl-2-methyl-3-dimethylamino-1-propanol hydrochloride (11) *via* hydroxy acid 9 and N,N-dimethylamide 10 with an optical purity of at least 98%.[6] The configuration of the rearrangement ketone, α-methyldeoxybenzoin (12), was shown to be *S*-(+) by correlating it with (*S*)-(+)-alanine (13).[7] Ketone 12 was formed in 42% yield with an optical rotation of +210° (lit.[7] [α]D +207°). As Scheme III shows, the β-phenyl group migrates with quantitative inversion at the rearrangement terminus. Since asymmetric induction is not possible in peroxylactone 8, these results imply that expulsion of the carbon dioxide and attachment of the β substituent at the α carbon must proceed synchronously.

Scheme III. Configurational Assignment and Stereochemical Course of the Thermal Decomposition of β,β-Diphenyl-α-methyl-β-peroxypropiolactone



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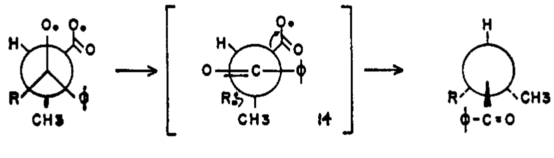
An alternative interpretation of the stereochemical data may involve complete β scission at the alkoxy radical site in the oxygen diradical forming first a solvent-caged radical pair (**14**) (Scheme IV). Before the radical pair diffuses from the solvent cage, the alkyl or phenyl radical displaces carbon dioxide by back-side attack at the asymmetric α carbon *via* a S_DR reaction.[8] Therefore, it was pertinent to examine the thermolysis of a peroxylactone in which the migrating group itself is asymmetric. Should β scission be effectively complete before decarboxylation has commenced, it would be expected that the asymmetric radical pair **14** would be extensively racemized, but not necessarily completely.[9]

Scheme IV. The S_DR Mechanism of the Rearrangement of Thermally Generated Oxygen Diradicals



The system chosen for this study was the peroxylactone derived from the optically active 3,5-diphenyl-3-hydroxy-4-methylvaleric acid (mp 160–160.5°; $\alpha^{24}\text{D}$ +3.72° (ethanol)). The thermal decomposition of the optically active peroxylactone gave a 90% yield of the rearrangement ketone 1,4-diphenyl-3-methyl-1-butanone with an optical rotation of −12.6° in benzene. The configuration of the ketone was assigned as *R*-(−) by correlating it with benzylmethylacetic acid.[10] Since the synthetic ketone had an optical rotation of $\alpha^{29}\text{D}$ −14.7° (benzene), the thermolysis ketone has a minimum optical purity of 93%. The configurational assignment and thus the assessment of the optical purity of this peroxylactone are still in progress. It is, therefore, possible that the optical purity of the rearrangement ketone is actually greater than 93%. Furthermore, the configurational assignment of this peroxylactone is important to assess whether the migration of the β-alkyl substituent proceeds stereospecifically *via* inversion or retention in view of the Woodward–Hoffmann theory of sigmatropic rearrangements.[11]

The stereochemical evidence compounded in this study along with the kinetic and product studies of the preceding communication[1] suggest that the β substituent in the oxygen diradical migrates *via* a nonclassical alkyl or phenyl bridge. The driving force for this novel process derives from the collaborated "push-pull" action between the alkoxy and carboxylate radical sites. To the best of our knowledge this is the first demonstration of a concerted rearrangement in radical reactions.

Acknowledgment. The financial assistance by the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corporation is gratefully acknowledged. We thank the Puerto Rico Nuclear Center for allowing us to use their polarimetric equipment.

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Received December 19, 1968

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Friedel-Crafts Chemistry. III.[1]

Methyl Fluoride–Antimony Pentafluoride, a Powerful New Methylating Agent. Methylation Reactions and the Polycondensation of Methyl Fluoride

Sir:

Ever since Friedel and Crafts published their initial papers[2] on the reactions of alkyl halides and aluminum chloride, organic chemists have searched to clarify the exact nature of the complexes formed in the interaction of alkyl halides and Lewis acid halides.[3] In recent years, we found that alkyl halides in antimony pentafluoride solution generally form stable carbonium ion complexes. Methyl halides, however, failed to yield the methyl cation. Infrared spectroscopic studies of methyl chlorides in $SnCl_4$ and $SbCl_5$ solution[4] and studies of methyl fluoride in BF_3 solution[5] indicated that these exist as slightly polarized donor–acceptor complexes. We now wish to present our findings on the properties and nature of solutions of methyl fluoride in SbF_5 or SbF_5–SO_2 as observed by nmr and laser Raman spectroscopy and the rather unique chemical behavior of these systems.

When methyl fluoride is dissolved in SbF_5–SO_2 solution at −78° a clear, colorless liquid solution is obtained. The pmr spectrum shows the complex formed at −60° as a sharp singlet at δ 5.56 (external TMS capillary). If excess methyl fluoride is present it appears as a doublet (J_{HF} = 45.7 Hz) at δ 4.50. Raising the temperature of the solution (to −20°) brings about the disappearance of the methyl fluoride doublet with no change in the deshielded singlet. (The pmr spectrum of methyl fluoride in SO_2 solution is a doublet at δ 4.00, J_{HF} = 45.8 Hz.)

The ^{13}C nmr shift[6] of the CH_3F–SbF_5–SO_2 system occurs at δ 117.8 (from CS_2) with $J_{^{13}C-H}$ = 166 Hz. The ^{13}C nmr parameters of CH_3F (in SO_2 solution) are δ 118.9 (from CS_2), $J_{^{13}C-H}$ = 149 Hz. Since the $J_{^{13}C-H}$ is proportional to the per cent s character[7], clearly the antimony pentafluoride strongly polarizes the C–F bond of methyl fluoride. At the same time the relatively small deshielding effect observed in the ^1H and ^{13}C chemical shifts indicates that no methyl cation is formed. The absence of hydrogen–fluorine coupling

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