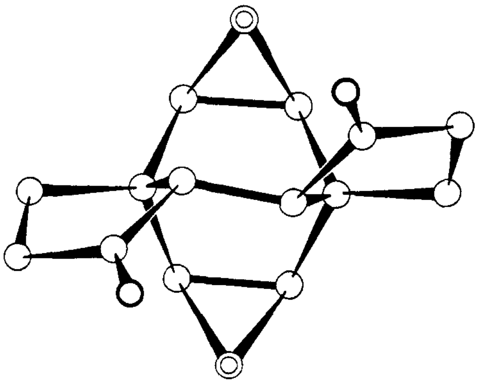


Figure 1. View of the crystallographic "molecule" along the twofold rotation axis. Carbon atoms are represented by single circles, carbonyl oxygen atoms by heavy circles, and the disordered ether oxygen "half-atoms" by double circles.

cule has an odd number of oxygen atoms, at least one of these must be either (1) located on a symmetry axis or point, or (2) orientationally disordered.

Table I

	Experimental	Theoretical Centro-symmetric	 Noncentro-symmetric
$\langle\lvert E\rvert\rangle$	0.797	0.798	0.886
$\langle\lvert E^2 - 1\rvert\rangle$	0.962	0.968	0.736
$\langle\lvert E\rvert^2\rangle$	0.975	1.000	1.000

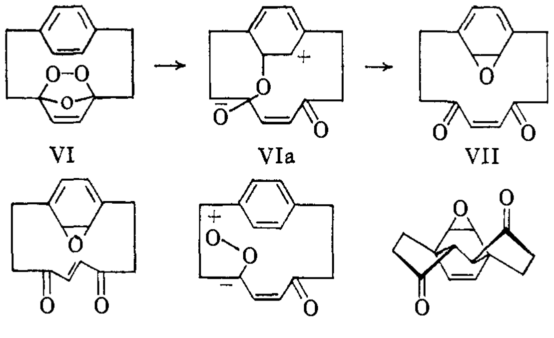
Table II

	Experimental, %	Theoretical, % Centro-symmetric	 Noncentro-symmetric
$\lvert E\rvert > 3$	0.5	0.3	0.01
$\lvert E\rvert > 2$	3.8	5.0	1.8
$\lvert E\rvert > 1$	28.6	32.0	37.0

By use of the technique of symbolic addition,[6] it was possible to deduce, in terms of three symbolic letter phases, the signs of 76 reflections with large $|E|$ values. The map computed as the sum of a Fourier series with one of these letter combinations clearly showed a skeleton corresponding to IV centered on a crystallographic twofold rotation axis. An electron density map obtained by assigning the phases corresponding to this skeleton to the observed structure amplitudes showed a peak in the proper location for the ether oxygen of V. The structure has been refined, assuming a twofold disordered structure, to an R value of 0.195 using the block diagonal approximation to the least-squares method.

Figure 1 shows a view of this crystallographic "molecule" parallel to the twofold rotation axis. The ether oxygen is presumably in either one or the other of the two indicated positions in any individual chemical molecule; it appears as 0.5 oxygen in the electron density map, which can give only the position average of a large number of molecules. Because of this disorder, the standard deviations in the coordinates of the ether oxygen are considerably higher than those for the other atoms, but the present stage of the refinement[7] establishes the structure and stereochemistry of compound C as V.

We have suggested a mechanism for the formation of V from I: (i) the intermediate *endo*-peroxide (VI) breaks down to the transient benzene epoxide VII by an intramolecular transfer of oxygen through VIa (or possibly by electrophilic substitution involving a species such as VIb); (ii) isomerization of VII to VIIa[8] followed



VI VIa VII

VIIa VIb VIII

by intramolecular Diels–Alder reaction leads to VIII, which is hydrogenated to V.

Acknowledgment. This work was supported in part by U. S. Public Health Service Grant GM 13854-01.

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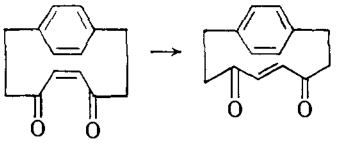
[6] I. L. Karle and J. Karle, *Acta. Cryst.*, **16**, 969 (1963). The computer program SORTE, written by A. Bednowitz, was used to facilitate application of the method.

[7] Attempts were made to refine an ordered structure in the lower symmetry space group Cc, but these also indicated the presence of only 0.5 oxygen at each of the possible ether oxygen positions. In addition, molecular dimensions were considerably less satisfactory, probably due to the more unfavorable observation:parameter ratio. Further refinement of the structure is in progress, as well as attempts to grow more satisfactory crystals, so that the nature of the disorder can be investigated further.

[8] We have observed that isomerization of the related *cis*-enedione (IX) to the *trans* form (IXa) takes place under the reaction conditions employed in the present work.



IX IXa

[9] National Institutes of Health Predoctoral Fellow, 1962–1966.

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Received August 8, 1966

Decomposition of N-Nitrosohydroxylamine Derivatives

Sir:

Studies of the decompositions of organic acyl peroxides have contributed much to our present understanding of the chemistry of organic radical species.[1] We presently wish to report the preliminary results of

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[1] (a) W. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966; (b) J. O. Edwards, "Peroxide Reaction Mechanisms," John Wiley and Sons, Inc., New York, N. Y., 1962; (c) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957.

Table I

Solvent	Products (mmole) from the decomposition of **1** at 32°						
	N_2	CO_2	$C_6H_5CO_2H$	CH_3COCH_3	C_4H_9OH	Perester	Others
Hexane	0.44	0.30	0.13	None	0.37	0.044	*a*
Carbon tetrachloride	0.67	0.62[b]	*c*	0.38[d]	*e*	0.094	*f*
Hexane–carbon tetrachloride (4:1)	0.49	0.40[g]	0.094	None	0.44	0.045	*h*

[a] Benzene (0.29 mmole). [b] After correction for a large amount of methyl chloride. [c] Chlorobenzene (0.44 mmole). [d] An overestimate due to some decomposition of *t*-butyl hypochlorite during analysis. [e] *t*-Butyl hypochlorite (0.05 mmole). [f] Phenyl *t*-butyl ether (0.07 mmole), hexachloroethane. [g] An overestimate due to contamination of gases with hexane vapors. A subsequent determination gave 64% carbon dioxide based on quantitative nitrogen evolution. [h] Benzene (0.21 mmole), chlorobenzene, hexachloroethane, chloroform.

Our studies of the decomposition of N-nitroso-N-benzoyl-O-*t*-butylhydroxylamine (**1**) which ultimately gives the same radical pair intermediates as *t*-butyl perbenzoate but at much lower temperatures than are required for decomposition of the perester.

Compound **1** is readily formed from N-benzoyl-O-*t*-butylhydroxylamine and nitrosyl chloride in the presence of pyridine at −20°. It is reasonably stable at −20° in dilute solution but a concentrated solution *exploded* on warming to room temperature. Consequently the compound was handled only in solution.

The infrared spectrum of a freshly prepared carbon tetrachloride solution of **1** showed carbonyl absorption at 1735 cm^{-1} and nitroso group absorption at 1545 cm^{-1}, in accord with other compounds[2] of this general type. The visible spectrum also exhibited the expected[2] weak absorption maxima at 407 and 426 $m\mu$.

Rearrangement of **1** is rapid at room temperature as evidenced by the disappearance of the infrared peak at 1545 cm^{-1} and the visible absorption at 426 $m\mu$. The half-life for this first-order process is *ca.* 158 sec in carbon tetrachloride at room temperature. The carbonyl absorption of the rearranged product is shifted to 1767 cm^{-1}. The *t*-butyl singlet in the nuclear magnetic resonance spectrum of the rearrangement product in carbon tetrachloride solution is shifted to $\delta = 1.45$ ppm from $\delta = 1.29$ ppm in **1** (relative to tetramethylsilane). No gas is evolved during the facile rearrangement but the rearrangement product does decompose more slowly (half-life *ca.* 100 min at 32°), evolving nitrogen and carbon dioxide. We believe these observations indicate the metastable species to be azo compound **2**.

The infrared and mass spectral analyses of the gas mixtures from the decomposition of **1** in nonhydroxylic solvents indicate the presence of nitrogen and carbon dioxide but no trace of nitrous oxide. The liquid products, analyzed by glpc and identified by spectral comparisons, are summarized in Table I. The material balances based on quantitative nitrogen evolution are satisfactory. All of the volatile products observed can be attributed to the formation of benzoyloxy and *t*-butoxy radical intermediates.

The residues from decomposition of **1** were found to oxidize iodide ion, and *t*-butyl perbenzoate was isolated from the decomposition residue in carbon tetrachloride. The occurrence of free-radical products suggests this peroxide may be a result of cage recombination of the *t*-butoxy and benzoyloxy radical intermediates. This conclusion is substantiated by the variation in products formed in the decomposition of **1** in carbon tetrachloride–hexane mixtures containing varying amounts of added paraffin oil. These results are summarized in Table II.

Table II

Vol. %[b] paraffin oil	$\eta \times 10^2$, poise	Products[a] from decompn of **1** in viscous media at 32°		
		CO_2	$C_6H_5CO_2H$	Perester
0	0.331	0.64	0.19	0.11
33.3	0.934	0.59	0.13	0.19
58.4	3.375	0.48	0.21	0.27
83.4	16.99	0.30	0.20	0.44

[a] Moles/mole of nitrogen evolved. [b] Solvents contain 16.7 vol. % carbon tetrachloride and the listed amount of paraffin oil; the remainder was made up by hexane.

The qualitative expectation of an increase in perester yield and decreased carbon dioxide yield with increasing viscosity was observed so that a cage reaction does appear to be operative. A simple treatment of the competition between viscosity-sensitive (k_3) and viscosity-insensitive (k_4) kinetic steps predicts a linear variation of the reciprocal of perester yield with the reciprocal of viscosity. A plot of the reciprocal of the yield of cage products with reciprocal of viscosity is not linear and bears a resemblance to similar data from the photodecomposition of azomethane in ethanol.[3] A similar plot with the reciprocal square root of viscosity does appear to be linear. Such a square-root dependence is predicted by the treatment of Eirich.[4] However, the fact that mixed solvents were used in this study makes any quantitative conclusions using these data premature.

The present results suggest that some recombination of *t*-butoxy and benzoyloxy radicals should occur at the higher temperatures necessary for the decomposition of *t*-butyl perbenzoate. This type of process has recently been implicated in the decomposition of acetyl peroxide[5] and may be more general than was previously thought.[1a] The formation of *t*-butyl peroxide in the decomposition of di-*t*-butylperoxy oxalate furnishes another recently observed example of an oxy radical recombination.[6]

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(2) J. H. Cooley, P. T. Jacobs, M. A. Khan, L. Heasley, and W. D. Goodman, *J. Org. Chem.*, **30**, 3062 (1965).

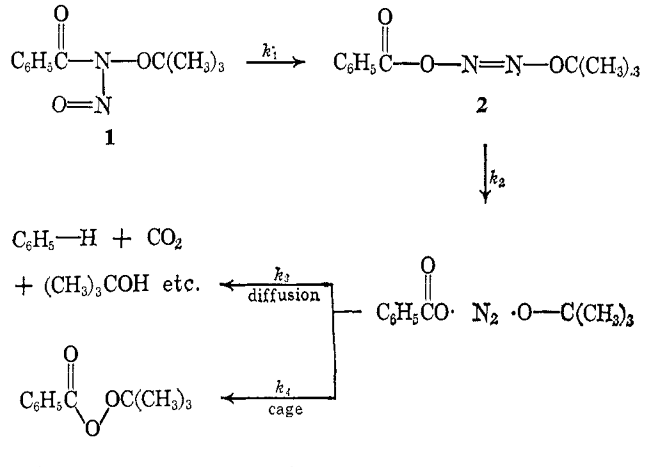
(3) S. Kodama, *Bull. Chem. Soc. Japan*, **35**, 827 (1962).

(4) W. Braun, L. Rajbenbach, and F. Eirich, *J. Phys. Chem.*, **66**, 1591 (1962).

(5) J. W. Taylor and J. C. Martin, *J. Am. Chem. Soc.*, **88**, 3650 (1966). We are grateful to Professor Martin for kindly communicating his results to us prior to their publication.

(6) R. Hiatt and T. G. Traylor, *ibid.*, **87**, 3766 (1965).

We are presently testing the above conclusions using oxygen-18 labeling techniques and hope to establish a scale of acyloxy radical stabilities with compounds analogous to **1**. We also are comparing reactivities of the acyloxy radical intermediates generated in this way with those generated from perester decompositions.



Acknowledgment. This work was supported by a grant from the National Science Foundation. We are pleased to acknowledge the assistance of Professor D. F. Swinehart in making the mass spectral measurements and to Professor R. M. Noyes for helpful discussions.

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Received July 11, 1966

Complete Stereochemical Rearrangement in a Cobalt(III) Reaction in Acidic Solution

Sir:

During investigations of intermediate-field cobalt(III) isomers, we have noted a surprisingly stereospecific reaction which appears to be the first example of complete stereochemical change for a cobalt(III) substitution reaction in acidic media. Recent stereochemical results on triethylenetetramine complexes of cobalt(III) also show unexpected results when compared with the corresponding ethylenediamine complexes,[1] but the triethylenetetramine rearrangement involves base hydrolysis, which often results in considerable configurational change.[2]

Both the blue *cis* and the violet *trans* isomers of the $[\mathrm{Co^{III}(CO_3)_2(NH_3)_2}]^-$ anion[3] yield only the *cis*-$[\mathrm{Co(acac)_2(NH_3)_2}]^+$ isomer when two acetylacetonato (acac) ligands replace two carbonato groups. Reaction conditions were such that *trans* → *cis* isomerization of the product would be negligible.

In each case, the dicarbonato complex (1 mole) was dissolved in water immediately after its preparation by a slight modification of the original synthetic method,[3] and treated with 2,4-pentanedione (2 moles) and then 6 *M* acetic acid, which was added dropwise to a pH of about 6 or until completion of carbon dioxide evolution. (Dilute HCl has also been substituted in the preceding step satisfactorily.) Rapid fractional crystallization *in vacuo* at room temperature using rotary evaporation gave no indication of any *trans*-$[\mathrm{Co(acac)_2(NH_3)_2}]^+$. Small amounts of $[\mathrm{Co(acac)_3}]$, necessarily of a *cis*-type orientation, were also formed and extracted with chloroform. These identical results were obtained for numerous runs with each isomer and were substantiated by microscopic examination, proton magnetic resonance, and infrared and visible spectroscopy. All of the properties of the products are identical with those reported for the *cis* isomer.[4]

Proof that the single isomer is not due to isomerization is based on the previous preparation of the pure *cis* and *trans* isomers of $[\mathrm{Co(acac)_2(NH_3)_2}]^+$ by a tedious fractional crystallization procedure which involved similar environmental conditions.[4] That is, the *cis* and *trans* isomers did not isomerize during the recrystallizations which involved up to several days in aqueous solution and pH and temperature conditions similar to those of the present investigation.

These results substantiate the contention of Basolo and co-workers[5] that complex ion electronic effects have been overemphasized and that more attention should be paid to steric factors. Furthermore, Chan and Tobe[6] have suggested that the aquation results of bis(ethylenediamine)-type cobalt(III) complexes can best be correlated by considering the activation process as involving a movement of the five retained coordinated species toward a trigonal bipyramidal structure, even in substitution reactions which give complete retention of configuration. If this were true, protonation of bis(carbonato) species would lead to an intermediate similar to that shown as intermediate I. The alternate intermediate in which both ends of the carbonate group are in the trigonal plane requires enlarging the O–Co–O angle of the four-membered ring beyond 90°, which is unlikely since the normally tetrahedral Co–O–C bond angles are already somewhat strained in the parent complex. The opposite effect is expected in the subsequent step since the six-membered acetylacetonato chelate ring is expected to be less strained at an angle of >90° than at the 90° angle of the octahedral complex. Hence, the intermediate II is favored for the second replacement. Aquo intermediates may be involved. Even so, it would appear that loss of the first carbonato species would be the most likely step for the stereospecific reaction.

These results also explain the predominant retention of configuration observed in the reaction of tricarbonatocobaltate(III) with 2 moles of ammonia[3] since the expected intermediate would be similar to structure III. On the other hand, the blue *cis*-dicarbonato salt has also been reported to produce *trans*-$[\mathrm{Co^{III}(NO_2)_4(NH_3)_2}]^-$ in about 75% yield,[7] with evidence for the *trans* structure based on the similarity of the ultraviolet spectrum with that of the *trans*-$[\mathrm{Co(NO_2)_4(NH_3)_2}]^-$ ion

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[1] E. Kyuno, L. J. Boucher, and J. C. Bailar, *J. Am. Chem. Soc.*, **87**, 4458 (1965); E. Kyuno and J. C. Bailar, Jr., *ibid.*, **88**, 1120, 1125 (1966).

[2] For a recent review see C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1966, Chapter 3.

[3] M. Mori, M. Shibata, E. Kyuno, and T. Adachi, *Bull. Chem. Soc. Japan*, **29**, 883 (1956).

[4] R. D. Archer and B. P. Cotsoradis, *Inorg. Chem.*, **4**, 1584 (1965).

[5] W. H. Baddley and F. Basolo, *J. Am. Chem. Soc.*, **88**, 2944 (1966); C. F. Weick and F. Basolo, *Inorg. Chem.*, **5**, 576 (1966); W. H. Baddley and F. Basolo, *J. Am. Chem. Soc.*, **86**, 2075 (1964).

[6] S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 5700 (1963).

[7] M. Shibata, M. Mori, and E. Kyuno, *Inorg. Chem.*, **3**, 1573 (1964).