The Preparation and Properties, Including Carbon-13 Nuclear Magnetic Resonance Spectrum, of Per-*tert*-butylcarbonic *p*-Nitrobenzoic Anhydride[1]

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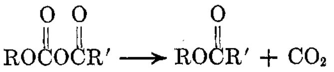
A stable percarbonic anhydride was prepared by the reaction of CO_2 with sodium *tert*-butyl hydroperoxide and subsequent reaction with *p*-nitrobenzoyl chloride. Spectra, including ^{13}C nmr, were taken. The compound was found to catalyze free-radical polymerization. In its decomposition at atmospheric pressure *p*-nitrobenzoic acid, methyl *p*-nitrobenzoate, and *p*-nitrobenzoic anhydride were found while in the sealed tube methyl *p*-nitrobenzoate and the acid predominated. Acetone and *tert*-butyl alcohol were found in both while 2,2-dimethoxypropane was found in the former and chlorotoluene in the latter. Reasons for this, including free-radical and Criegee decompositions, are discussed.

The synthesis and study of a variety of carbonic carboxylic anhydrides (1), of di- and tricarbonates, and

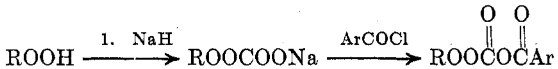


$$\text{RO}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{O}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{R}' \longrightarrow \text{RO}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{R}' + CO_2$$

1

of carbonic anhydrides containing phosphorus and silicon moieties, have been reported.[3] The mode of decomposition of these materials is ionic, as inferred from a variety of criteria.[3d]

We have therefore prepared[4] a peroxy compound (2) as shown below, which could decompose by ionic or



$$\text{ROOH} \xrightarrow[\text{2. } CO_2]{\text{1. NaH}} \text{ROOCOONa} \xrightarrow{\text{ArCOCl}} \text{ROO}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{O}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{Ar} \quad (1)$$

2, R = *t*-Bu
Ar = $p\text{-}O_2NC_6H_4$

free radical modes, including the Criegee reaction of the peroxide group.

Per-*tert*-butylcarbonic *p*-nitrobenzoic anhydride (PCA) was prepared as indicated and was obtained as a pure crystalline solid, mp 69–71°. An attempt was also made to prepare it from the chlorocarbonate of *tert*-butyl hydroperoxide, but the triethylamine used for the removal of HCl catalyzed the elimination of carbon dioxide to give the per ester.

In an attempt to confirm the position of the peroxide moiety, the carbon-13 nmr spectra of PCA and some related compounds were taken. The shifts are given in Table I. The assignments for the aromatic carbons were made on the basis of the size of the coupling to the aromatic hydrogens and the expected shift effects of the aromatic substituents.[5] An examination of the data shows that the peroxide group causes only minor changes in the spectra as compared to that of the carbonic anhydride and that these changes are in different directions from those observed in the two esters. Therefore, it is not possible to assign conclusively the position of the peroxide group from the carbon-13 spectra.

A test of PCA's ability to initiate the copolymerization of styrene and methyl methacrylate showed that it was much less effective than benzoyl peroxide; however, the 50:50 mixture of monomers in the polymer shows that it was a radical-induced polymerization.[6,7]

Decompositions.—The products of decomposition varied dramatically depending upon the mode of decomposition. The CO_2 given off was measured for decompositions in both the solid state and chlorobenzene solution. In the solid-state decomposition 1.03 mol of CO_2 was given off per mole of PCA, while in the chlorobenzene case 0.78 mol of CO_2 was obtained.

In the solid-state decomposition the only solid product isolated was *p*-nitrobenzoic acid. In the decompositions of PCA in chlorobenzene, either open to the atmosphere or under nitrogen, both *p*-nitrobenzoic acid and *p*-nitrobenzoic anhydride were observed as well as a small amount of methyl *p*-nitrobenzoate. Finally, the PCA was decomposed in chlorobenzene after the samples had been degassed and sealed under vacuum. In this case the solids isolated were *p*-nitrobenzoic acid and methyl *p*-nitrobenzoate, but no evidence could be found for the existence of any anhydride. After isolation of the two compounds, 47.9 mol % of the ester and 51.2 mol % of the acid were obtained.

The products derived from the *tert*-butyl end of the molecule were also investigated. In the solid-state decomposition, these products were lost owing to the rapid decomposition of the PCA. In the undegassed chlorobenzene samples, acetone, *tert*-butyl alcohol, and the dimethyl ketal of acetone were identified by gc–mass spectroscopy, but no percentages could be obtained.

In the decomposition in degassed chlorobenzene *tert*-butyl alcohol and chlorotoluene were identified by gc–mass spectroscopy, and there was also some evidence for a small amount of isobutylene in the fraction captured in liquid nitrogen. By observing the nmr of the liquid fractions from the sealed tubes, it was possible to make an estimate of the amounts of the various compounds produced. Based on the amount of PCA decomposed, there was 16.6 mol % of chlorotoluene, 32.8 mol % of acetone, and 29.8 mol % of *tert*-butyl alcohol. The calculations were made assuming that the peak for

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[1] This work was aided by Grant GP-15795 from the National Science Foundation.

[2] National Science Foundation Undergraduate Research Participant, summer, 1971.

[3] Most recent papers: (a) Y. Yamamoto and D. S. Tarbell, *J. Org. Chem.*, **36**, 2954 (1971); (b) C. S. Dean and D. S. Tarbell, *ibid.*, **36**, 1180 (1971); (c) D. S. Tarbell, Y. Yamamoto, and B. M. Pope, *Proc. Nat. Acad. Sci. U. S.*, **69**, 730 (1972); for review (d) D. S. Tarbell, *Accounts Chem. Res.*, **2**, 296 (1969).

[4] *Cf.* preparation of the nonperoxy analog ROC(=O)OC(=O)Ar (R = *tert*-butyl, Ar = $p\text{-}O_2NC_6H_4$): C. J. Michejda and D. S. Tarbell, *J. Org. Chem.*, **29**, 1168 (1964).

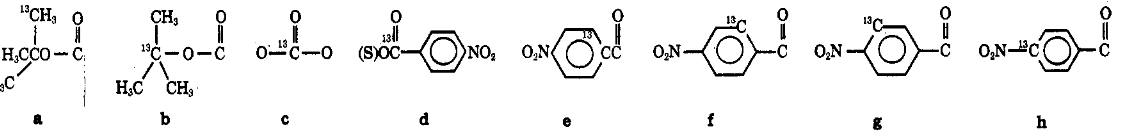
[5] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, Oxford, 1966, p 1004.

[6] F. M. Lewis, F. R. Mayo, and W. F. Halse, *J. Amer. Chem. Soc.*, **67**, 1701 (1945).

[7] C. Walling, E. R. Briggs, W. Cummings, and F. R. Mayo, *J. Amer. Chem. Soc.*, **72**, 48 (1950).

TABLE I

CHEMICAL SHIFTS[a]



Compd	Structure a	b	c	d	e	f	g	h
$CH_3\overset{CH_3}{\underset{CH_3}{C}}OO\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}\text{-}p\text{-}C_6H_4NO_2$	167.7	107.2	45.3	32.3	61.2	61.4	69.3	41.8
$CH_3\overset{CH_3}{\underset{CH_3}{C}}\text{—}O\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}\text{-}p\text{-}C_6H_4NO_2$	165.5	106.7	46.4	32.7	60.0	61.9	69.4	41.1
$CH_3\overset{CH_3}{\underset{CH_3}{C}}\text{—}OO\overset{O}{\overset{\|}{C}}\text{-}p\text{-}C_6H_4NO_2$	166.7	108.8		30.8	59.9	62.7	69.1	42.4
$CH_3\overset{CH_3}{\underset{CH_3}{C}}\text{—}O\overset{O}{\overset{\|}{C}}\text{-}p\text{-}C_6H_4NO_2$	164.9	111.0		29.5	55.7	62.6	69.7	42.6
$CH_3\overset{CH_3}{\underset{CH_3}{C}}\text{—}S\overset{O}{\overset{\|}{C}}\text{-}p\text{-}C_6H_4NO_2$	162.6	143.5		2.8	49.4	65.0	69.3	42.6

[a] In parts per million from CS_2, assuming $\delta(C_6D_6) - \delta(CS_2) = 65.0$ (ref 5, p 1003).

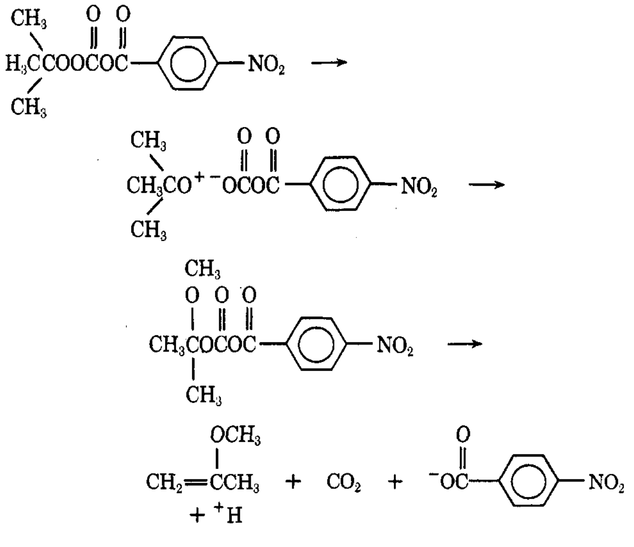
methyl *p*-nitrobenzoate represented 0.835 mmol. There was also a fairly strong unidentified peak at δ 1.11. There was a moderate amount of variation in these values in different samples, particularly in the peak at δ 1.11, which was very small in some cases. It must be remembered that a molecule of methyl *p*-nitrobenzoate or chlorotoluene and a molecule of acetone can both come from the same molecule of PCA.

Discussion

Of the products isolated from the various decompositions, chlorotoluene and *tert*-butyl alcohol must arise from a radical decomposition, while 2,2-dimethoxyethane, *p*-nitrobenzoic anhydride, and isobutylene (if it is truly present) are probably products from ionic decompositions. For the other products, carbon dioxide, *p*-nitrobenzoic acid, methyl *p*-nitrobenzoate, and acetone, it is possible to visualize both ionic and radical mechanisms for their production.

The only conceivable mechanism for the formation of the chlorotoluene would be the addition of a methyl radical to chlorobenzene,[8] since the possibility of having a methyl cation in this system is very remote. The most likely mode of formation of the *tert*-butyl alcohol is hydrogen abstraction by a *tert*-butoxy radical, probably from another *tert*-butyl group.

The formation of the 2,2-dimethoxypropane is most certainly due to the heterolytic cleavage of the peroxide bond to give the Criegee rearrangement.[9] The vinyl ether can be hydrolyzed to methanol and acetone and subsequently the methanol can form 2,2-dimethoxypropane upon reaction with the vinyl ether. The benzoic acid anion could react with the hydrogen ion to give the acid or attack another mole of the percarbonic anhydride to give di-*p*-nitrobenzoic anhydride.



Walling suggests that both the radical decomposition

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[8] C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, p 483.

[9] E. Hedaya, *et al.*, *J. Amer. Chem. Soc.*, **89**, 4875 (1967); R. Criegee and R. Kaspar, *Justus Liebigs Ann. Chem.*, **560**, 127 (1948); P. D. Bartlett and J. L. Kice, *J. Amer. Chem. Soc.*, **75**, 5591 (1953).

and the Criegee rearrangement may arise from a common radical pair–ion pair transition state.[10]

The formation of acetone, already explained in the Criegee rearrangement, could be explained in the radical decomposition by loss of a methyl radical from the *tert*-butoxy radical.

The loss of one molecule of CO_2 per mole of PCA would be expected in the ionic decomposition, while as many as 2 mol of CO_2 could be lost in the radical decomposition. In the solid-state decomposition, which is suspected to be a radical chain reaction owing to the very rapid decomposition, there is only 1 mol of CO_2 given off, while in the case of the chlorobenzene decomposition under nitrogen, where both ionic and radical mechanisms are probably involved, about 1 mol of CO_2 is evolved. Finally, in the sealed tube decomposition the most CO_2 that could be given off is 1 mol, since almost all (99%) of the *p*-nitrobenzoate group was recovered as *p*-nitrobenzoic acid or methyl *p*-nitrobenzoate.

The production of benzoic acid in the Criegee rearrangement has already been explained, while in the radical reaction it would have to arise from the hydrogen abstraction by the *p*-nitrobenzoyloxy radical.

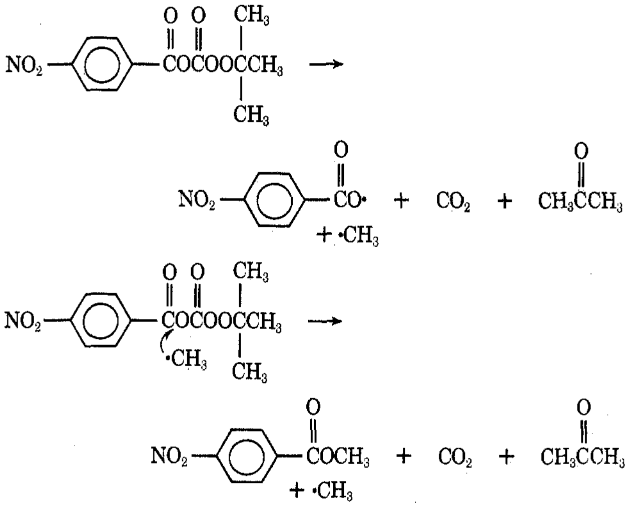
The most problematical of the compounds isolated is the methyl *p*-nitrobenzoate. One possible reaction leading to it would be the formation of methanol from the Criegee rearrangement and the attack of the methanol on PCA to give the ester. *tert*-Butyl hydroperoxide and CO_2 would probably be the other products. The hydroperoxide would go to *tert*-butyl alcohol and oxygen.[11]

The main argument against this mechanism is that no 2,2-dimethoxypropane was observed in the nmr of the products of the sealed-tube decomposition, which would be expected in the Criegee decomposition.

The second possible mechanism is a radical cage reaction where there is a homolytic scission of the O–O bond followed by loss of CO_2 and acetone and finally recombination of the methyl and *p*-nitrobenzoyloxy radical. One referee suggested that this would be unlikely, since he felt that the energy for β scission (13 kcal/mol)[12] would be substantially greater than that of the decarboxylation of the *p*-nitrobenzoyloxy radical. If the *p*-nitrobenzoyloxy radical does exist in the decomposition it certainly does not decarboxylate under these conditions, since 99% of it was recovered as *p*-nitrobenzoic acid or methyl *p*-nitrobenzoate. The formation of a moderate amount of chlorotoluene would certainly suggest that there is a strong likelihood of the presence of *p*-nitrobenzoyloxy radicals.

Cook estimates the energy of decarboxylation of the benzoyloxy radical at 18–23 kcal/mol, but this was based on only two points done over a 10° range.[13] Walling, however, is not willing to say which β scission, *tert*-butoxide or benzoyloxy, has the greater activation energy.[14] Similar data could not be found for the *p*-nitrobenzoyloxy radical; however, Ol'dekop observed that *p*-chlorobenzoyloxy radical adds to metals and salts in the cold or on heating, abstracts hydrogen from solvent, and loses CO_2 while the *p*-nitrobenzoyloxy radical adds to metals and abstracts hydrogen from solvent.[15] It was also observed that the *p*-nitrobenzoyloxy radical abstracts hydrogen from toluene at 100° to give *p*-nitrobenzoic acid.[16]

Another possible mechanism would be the radical-chain reaction in the following series of reactions.[17]



This mechanism is favored by the fact that chlorotoluene is formed, since this would suggest a proliferation of methyl radicals.

Another radical chain mechanism (2) might involve a cyclic transition state. This mechanism is less likely, though, because one would expect some attack of radical **3** on the peroxide bond to give other products, which were not observed.

The best way to distinguish between these mechanisms would be to follow the kinetics of the reaction. The rates of reaction for the ionic mechanism should vary with the polarity of the solvent while the others should not. The cage mechanism should be first order while the chain mechanism and the ionic mechanism should not.

The reason for the variation in the decomposition products in the sealed and open decompositions is not evident. One possible reason is the fact that the open decompositions were not degassed and the dissolved gases might have affected the decomposition. If the formation of the methyl *p*-nitrobenzoate is from a radical-chain reaction it might be quenched, allowing the Criegee reaction to take precedence. However, this explanation is somewhat in doubt owing to the fact that decompositions in sealed undegassed tubes gave essentially the same results as the degassed tubes.

It is not a matter of decomposition temperature or concentrations either, since variation of these factors in the open decompositions all gave at least a moderate amount of anhydride.

If Walling's proposal is correct then it might be profitable to seek a condition that would affect the separation of the radical pair–ion pair.

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[10] C. Walling, H. P. Waits, J. Milovanoic, and C. G. Pappiaonnou, *J. Amer. Chem. Soc.*, **92**, 4927 (1970).

[11] W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, p 115.

[12] J. A. Howard in "Advances in Free-Radical Chemistry," Vol. IV, G. H. Williams, Ed., Academic Press, New York, N. Y., 1972, p 61.

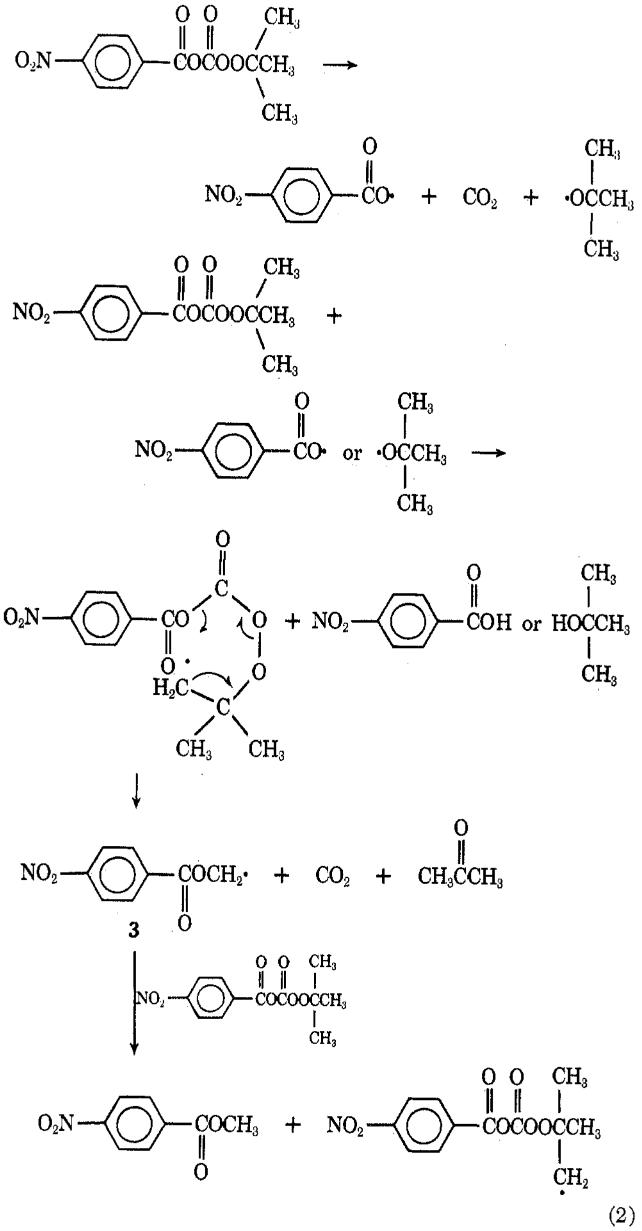
[13] C. D. Cook and C. B. Depatic, *J. Org. Chem.*, **24**, 1144 (1959).

[14] C. Walling and J. C. Azar, *J. Org. Chem.*, **33**, 3885 (1968).

[15] Yu. A. Ol'dekop, *Sb. Nauch. Rab., Akad. Nauk Beloruss., SSR, Inst. Khim.*, 243 (1958); *Chem. Abstr.* **53**, 9999c (1959).

[16] R. I. Milyutinskaya, Kh. S. Bagdasaryan, and Yu. Kopytocskii, *Zh. Fiz. Khim.*, **32**, 428 (1958); *Chem. Abstr.*, **52**, 20022*d* (1958).

[17] We would like to thank Dr. D. L. Tuleen for this suggestion.



(2)

Experimental Section

Carbon-13 Nmr.—Spectra were taken on a Varian Model XL-100 nmr spectrometer. The samples were dissolved in perdeuteriobenzene and run in 12-mm tubes with heteronoise decoupling. A single scan was taken at 2500-Hz sweep width.

Preparation of PCA (I).—*tert*-Butyl hydroperoxide was purified by vacuum reflux and distillation by the procedure of Bartlett, *et al.*[18]

Sodium hydride (1.2 g of 50% in mineral oil, 0.026 mol) was washed twice with tetrahydrofuran (THF), which had been dried over $CaCl_2$ and distilled from lithium aluminum hydride. Dry THF (50 ml) was added to the sodium hydride in a 100-ml three-neck flask and *tert*-butyl hydroperoxide (2.2 g, 0.03 mol) was added dropwise to the sodium hydride suspension at room temperature. Following the evolution of H_2, carbon dioxide, bubbled through concentrated H_2SO_4, was bubbled through the suspension at −78° for 2.5 hr. A solution of 3.5 g (0.02 mol) of *p*-nitrobenzoyl chloride in 15 ml of $CHCl_3$ was added dropwise. After the temperature was increased to −10 to 0° the solution was stirred for 20 hr. The CO_2 addition was stopped 2 hr after the addition of the acid chloride.

The suspension was vacuum filtered through a fritted glass into a cooled flask and the solvents were removed from the filtrate under vacuum. The remaining solid was dissolved in a 1:1 mixture of $CHCl_3$–petroleum ether (bp 30–60°) and the solution was filtered. A large amount of petroleum ether was added and the solution was filtered again. After crystallization at −78° the precipitate was collected. After a second recrystallization 1.48 g (28%) was obtained: mp 69–71° dec; nmr δ 7.94 (narrow m, 4 H), 1.00 (s, 9 H); ir carbonyl bands at 1840 and 1763 cm^{-1}.

Anal. Calcd for $C_{12}H_{13}NO_7$: C, 50.88; H, 4.63; N, 4.95. Found: C, 50.60; H, 4.66; N, 4.68.

Titration of the Peroxide Group.—A determination of the peroxide content was done by the transesterification method of Hedaya and Winstein.[19] After correction for a blank run two titrations yielded values of 104 and 97.5% peroxide assuming 1 mol of peroxide per 283 g (1 mol) of percarbonic anhydride.

Polymerization.—Methyl methacrylate was fractionally distilled at 100° (760 mm) and styrene was fractionally distilled at 60° (40 mm). Five grams of each were mixed for each experiment and placed in a 25-ml flask. Benzoyl peroxide (0.0024 g) or 0.0028 g of PCA were added to one of the three flasks. The third was left blank. The solutions were heated at 79.5° for 4 hr. After cooling, the contents of each flask were added to 100 ml of absolute methanol with vigorous stirring. The white precipitate was filtered and washed with 15 ml of methanol. The samples were dried for 26 hr at 0.5 mm, and weighed. The yields of the polymer follow: blank, 0.0005 g; benzoyl peroxide, 1.5225 g; PCA, 0.3576 g. This is the method of Walling, *et al.*[6]

The polymers were reprecipitated from a mixture of methanol–benzene, dried under vacuum, and analyzed. The results are given in Table II.

TABLE II

Initiator	C, %	Mol % styrene[a]
Benzoyl peroxide	76.71	50.9
PCA	76.93	51.5

[a] Assuming that polystyrene requires 92.26 C and polymethyl methacrylate requires 59.98 C.

Solid-State Decomposition.—PCA (497.7 mg, 1.767 mmol) was placed in a two-neck flask. A stream of nitrogen was passed through the flask into an ice–salt bath and then through an Ascarite tube. The solid was heated in an oil bath until it melted, at which time it began to decompose. At 82° the PCA decomposed very quickly. After 3 hr, 80.1 mg (1.82 mmol) of carbon dioxide was collected in the Ascarite tube. The solid material left was recrystallized from ethanol, and *p*-nitrobenzoic acid (34.6 mg, 0.212 mmol), identified by ir, was isolated.

Decomposition in Undegassed Chlorobenzene.—PCA (1.048 g, 3.81 mmol) was dissolved in 30 ml of chlorobenzene (distilled). A stream of nitrogen was passed over the chlorobenzene through a reflux condenser in a Dean–Stark trap and then through a Dry Ice trap. After decomposition at 90° for 3 hr, the volatile materials were separated and identified by gc–mass spectroscopy. The products were separated on a 6-ft SE-30 column. No products were isolated from the Dry Ice trap. *tert*-Butyl alcohol and the dimethyl ketal of acetone were found in the Dean–Stark trap, while acetone was found in the residual chlorobenzene.

The spectrum of the acetal was identified by comparison with a known spectrum.[20]

Measurement of CO_2 in Chlorobenzene Decomposition.—PCA (0.9274 g, 3.28 mmol) was dissolved in 30 ml of chlorobenzene. A stream of nitrogen was passed over the solvent, through a condenser, an ice–salt trap, and finally an Ascarite tube. After decomposition at 90°, 0.1161 g (2.54 mmol) of CO_2 was obtained.

Decomposition in Degassed Chlorobenzene.—The sample of PCA (100 mg in 9 ml of chlorobenzene) was degassed by alternate freezing and thawing under vacuum in an apparatus similar to that described.[18] The sample was decomposed at 103° for 18 hr. It was cooled to liquid nitrogen temperature, opened under vacuum, and allowed to warm to room temperature. The material that boiled off was collected in the liquid N_2 trap. The trap was warmed and a mass spectrum was taken of the gas released. In addition to a strong CO_2 peak there were peaks suggesting the presence of isobutylene. The solvent and other volatile materials were distilled off under vacuum and were collected in a Dry Ice trap. A gc–mass spectrum showed the

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(18) P. D. Bartlett and H. Minato, *J. Amer. Chem. Soc.*, **85**, 1858 (1963).

(19) E. Hedaya and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 1661 (1967).

(20) E. Stenhagen, S. Abrahamsson, and J. W. McLafferty, Ed., "Atlas of Mass Spectral Data," Vol. 1, Interscience, New York, N. Y., 1969, p 307.

presence of *tert*-butyl alcohol and chlorotoluene. From the solids remaining *p*-nitrobenzoic acid and methyl *p*-nitrobenzoate were identified.

PCA (503 mg) was dissolved in 5 ml of chlorobenzene. The sample was degassed by alternated freezing and melting and was then sealed. The sample was heated at 107° for 24 hr. It was then cooled and opened, and an nmr was taken of the filtered solution. The peaks at δ 1.2 (*tert*-butyl alcohol), 1.83 (acetone), 2.09 (chlorotoluene), and 3.71 (methyl *p*-nitrobenzoate) and an unidentified peak at 1.11 were integrated. The peak at δ 1.11 was shown not to be *tert*-butyl *p*-nitrobenzoate, *tert*-butyl *p*-nitroperbenzoate, or the dimethyl ketal of acetone. This is the procedure of Hideya, *et al.*[9]

The solvents were removed and the residue was dissolved in ether and extracted with 2% NaOH solution. The ether was dried and removed under vacuum. Fairly pure (ir, mp 78–89°) methyl *p*-nitrobenzoate (148 mg) remained. The NaOH was neutralized with concentrated HCl, and the precipitate was collected. After drying the *p*-nitrobenzoic acid weighed 149.4 mg.

Decomposition in Undegassed Sealed Tubes.—Two 100-mg. samples of PCA were dissolved in 1-ml portions of chlorobenzene. The solutions were sealed in unevacuated tubes without degassing, and the samples were heated for 24 hr at 107°. (One sample turned dark while the other remained light.) The samples were opened and nmr spectra were taken as in the previous case. The spectra were similar to those of the degassed samples except that the dark sample had less *tert*-butyl alcohol and more of the material with the peak δ 1.11. The solid that crystallized out was examined and found to be *p*-nitrobenzoic acid. No evidence was obtained for the presence of *p*-nitrobenzoic anhydride.

Registry No.—**2,** 38401-55-7; *tert*-butyl hydroperoxide, 75-91-2; *p*-nitrobenzoyl chloride, 122-04-3; methyl *p*-nitrobenzoate, 619-50-1.

Correlation between Nuclear Magnetic Resonance and Infrared Studies of Conformational Preferences in Chloro Sulfides

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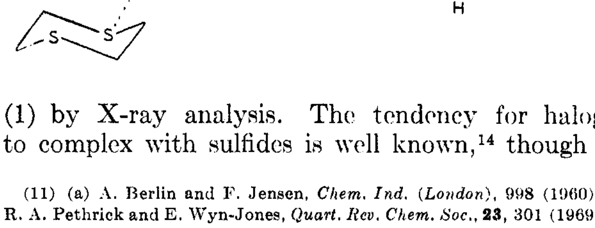
Nmr and ir methods of determining conformational preferences in alkyl substituted 1-chloro-2-ethyl 2,4-dinitrophenyl sulfides are in fair agreement. For *erythro*-2-chloro-3-butyl 2,4-dinitrophenyl sulfide, a preference for gauche chlorine–sulfur groups is evident. However, the study of model compounds shows that the chlorine–sulfur interaction is probably slightly repulsive. A very unusual preference for a conformer having gauche hydrogens is noted in both isomers of the above compound.

Conformational reasoning has been deeply affected by the early work on butane and on cyclohexane systems.[1,2] This work led to the idea that alkyl groups, and presumably other large groups, prefer a trans orientation in order to minimize repulsive nonbonded interactions.[3] In recent years, there has been a growing realization that many groups, some sizable, have attractive rather than repulsive interactions. In substituted propanes, $XCH_2CH_2CH_3$, the conformer having X gauche to methyl is slightly more stable or of equivalent stability to the trans conformer where X is F, Cl, Br, CN, NC, C=CH, and OH.[4] A slight dipolar attraction is presumed to overcome steric repulsions. Notable among other interections that are considered attractive in nature are the interactions of oxygen-containing groups,[5,6] cyano–cyano groups,[7] mercury–amine,[8] sulfoxide–hydrogen,[9] and chlorine–hydrogen.[10] Halogen–halogen interactions are complex, and these may vary from compound to compound depending upon bond angle and internuclear distance.[11] However, it is noteworthy that, in a large variety of dihaloethylenes, the cis isomer is the more stable.[11c] In acyclic compounds capable of internal rotation, the gauche X–X conformer is stabilized in solvents of high dielectric constant, since the solvent effect counteracts the repulsive effects of the halogen dipoles.[6a,7,12] The list of attractive interactions is diverse enough so as to suggest that the phenomenon is widespread, though many times rather weak.

The present work is an inquiry into the possibility of an attractive interaction between sulfur and halogen. Precedent for considering this interaction as attractive exists in the work of Bjorvatten and Hassel,[13] who observed the alignment of molecules shown in



(1)

(1) by X-ray analysis. The tendency for halogens to complex with sulfides is well known,[14] though this

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(1) D. H. R. Barton, *Experientia*, **23**, 316 (1950).

(2) S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, New York, N. Y., 1954.

(3) E. L. Eliel, N. Allinger, J. Angyal, and G. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965, pp 5–22.

(4) E. B. Wilson, *Chem. Soc. Rev.*, **1**, 293 (1972).

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