vinyl ester. The nmr spectrum (10% in CCl_4, standard TMS) showed signals at τ 2.34–3.00 (multiplet, C_6H_5), 8.00 (quartet, CH_2), and 9.16 (triplet, CH_3), their intensity ratio being 10:2:3. These data indicate that the compound is *trans*-α-iodo-α'-propionyloxystilbene (*trans*-IPS).

Anal. Calcd for $C_{17}H_{15}IO_2$: C, 53.98; H, 4.01; I, 33.55. Found: C, 53.7; H, 3.99; I, 33.7.

Rate Measurement for the Transfer of Active Oxygen from Peracetic Acid to Hexahydrobenzoic Acid.—Hexahydrobenzoic acid (9 ml) and 2 *M* peracetic acid in acetic acid (1 ml) were separately allowed to stand at 50° to reach temperature equilibrium, and then they were mixed quickly to start the reaction. Aliquots (each 1 ml) were pipetted out at known intervals of time and poured into a separatory funnel containing water (20 ml) and CCl_4 (5 ml). The funnel was shaken rapidly to extract hexahydrobenzoic and hexahydroperbenzoic acids. The extract was again washed with water (20 ml) and separated. The content of hexahydroperbenzoic acid in CCl_4 and that of peracetic acid in the combined aqueous layer were measured by iodometric titration with 0.02 *N* $Na_2S_2O_3$.

Registry No.—*trans*-IAS, 29478-23-7; *trans*-DAS, 35855-69-7; *trans*-DIS, 20432-11-5; *trans*-IPS, 36872-18-1; peracetic acid, 79-21-0; benzil, 134-81-6; sulfuric acid, 7664-93-9; sodium acetate, 127-09-3; iodine, 7553-56-2; anisole, 100-66-3; hexahydrobenzoic acid, 98-89-5.

CIDNP from Diffusive Encounters of Free Radicals. The Reaction of Trichloromethyl with Tetramethylethylene

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Received April 11, 1972

The trichloromethyl radical, formed by thermal decomposition of trichloroacetyl peroxide, reacts with tetramethylethylene predominantly by addition rather than by abstraction of an allylic hydrogen atom. The reaction between the adduct radical and another trichloromethyl radical proceeds primarily by donation of a hydrogen atom to form chloroform and 4,4,4-trichloro-2,3,3-trimethyl-1-butene. CIDNP emission signals with enhancement factors greater than 200 are observed for both products. At high tetramethylethylene concentration, radical pair substitution occurs.

The first observations[3] of chemically induced dynamic nuclear polarization (CIDNP) were tentatively explained[4,5] by an adaptation of the Overhauser effect. Free radicals were assumed to form with electron spin states equally populated and subsequent electron-nuclear cross relaxation was supposed to give rise to a nuclear polarization which could be retained in rapidly formed radical products. With this model it was difficult to explain polarization resulting from the diffusive encounter of free radicals, although a "reverse" Overhauser effect was suggested for this purpose.[6] It was at this point in the evolution of CIDNP that we began a study of the enhanced spectra taken during the thermolysis of trichloroacetyl peroxide, a system in which any proton polarization must necessarily result from the reactions of secondary radicals.[7] During the time that this study was underway, it was pointed out[6,8] that very large nuclear polarizations may be generated in the radicals reacting in and escaping from both geminate and diffusive encounter radical *pairs*. The results of our studies of the trichloroacetyl peroxide system are entirely in accord with the radical pair model, and, in addition, offer confirmation that proton polarization is not destroyed during hydrogen atom transfer from one radical to another. In the course of these studies, the reaction of tetramethylethylene (TME) with the trichloromethyl radical ($\cdot CCl_3$) has been examined in detail.

Results and Discussion

Reactions of $\cdot CCl_3$ with TME. Products.—TME was selected as a radical trap for $\cdot CCl_3$ because only one primary abstraction and one addition reaction are possible, and only a narrow region of the nmr spectrum (δ 1.5–1.7) is obscured by the allylic methyl absorption. The TME–$\cdot CCl_3$ reaction does not appear to have been investigated previously, and the ratio of addition to abstraction (*X*) is not known. Huyser[9] has, however, measured this ratio for *cis*- and *trans*-2-butene, for which it is found that $X = 34$ and 26, respectively, at 99° in the liquid phase. The additional methyl groups in TME should favor abstraction by a statistical factor of two, and also possibly enhance the polar character of the abstraction process, which has been suggested to involve a transition state with some electron transfer from the olefin to $\cdot CCl_3$.[10] Addition should also be accelerated by both the increased nucleophilicity of the double bond and the greater stability of the tertiary adduct radical, but decreased by steric crowding in the radical. The balancing of these effects is difficult to predict since one can find grounds on which to expect *X* to be both greater than and less than that for 2-butene.

Analyses of the products of the thermolysis of trichloroacetyl peroxide (0.08 *M*) in carbon tetrachloride were made as a function of TME concentration (Table I). Since the purpose of the product determinations was to support the CIDNP studies, reactions were run under the conditions used for recording CIDNP spectra; *e.g.*, an nmr tube containing the reagents at $<-10°$ was dropped into an nmr probe held at 60°. Under these conditions the reaction was complete in

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[1] National Center for Air Pollution Control, Special Fellow (Predoctoral), 1967–1970.

[2] Alfred P. Sloan Foundation Research Fellow.

[3] J. Bargon, H. Fischer, and U. Johnsen, *Z. Naturforsch.*, **22a**, 1551 (1967); H. R. Ward, *J. Amer. Chem. Soc.*, **89**, 5517 (1967); H. R. Ward and R. G. Lawler, *ibid.*, **89**, 5518 (1967).

[4] R. G. Lawler, *ibid.*, **89**, 5519 (1967).

[5] J. Bargon and H. Fischer, *Z. Naturforsch.*, **22a**, 1556 (1967).

[6] G. L. Closs, *J. Amer. Chem. Soc.*, **91**, 4552 (1969).

[7] For another system where polarization must take place in a random encounter, see S. R. Fahrenholtz and A. M. Trozzolo, *ibid.*, **94**, 283 (1972).

[8] R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Lett.*, **4**, 195 (1969).

[9] E. S. Huyser, *J. Org. Chem.*, **26**, 3261 (1961).

[10] E. S. Huyser, *J. Amer. Chem. Soc.*, **82**, 394 (1960).

TABLE I[a]

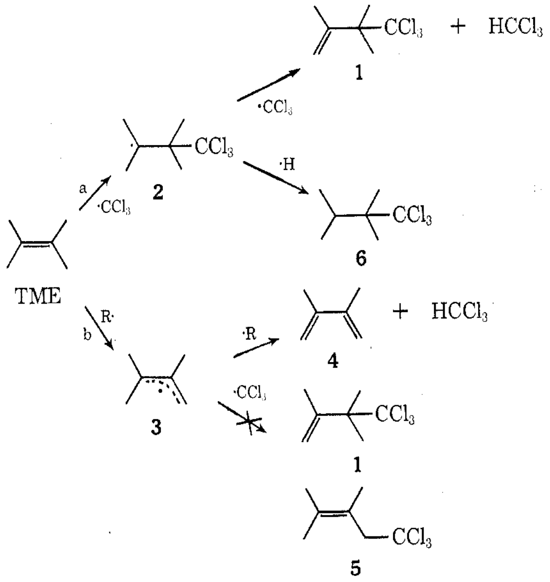
YIELDS OF THE PRODUCTS OF THE REACTION OF TME AND $\cdot CCl_3$ AS A FUNCTION OF TME CONCENTRATION

	Yield, %				
Initial [TME]	C_2Cl_6	$HCCl_3$	**1**	**4**	**6**
0.0	100				
0.078	75	13	11	0.001	
0.16	47	20	19	3	
0.26	35	25	23	9	
0.39	22	25	25	9	
0.65	22	21	46	20	7
3.25	9	18	17	31	5

[a] The initial concentration of peroxide was always 0.08 *M*. Product yields are given as per cent of initial peroxide concentration. For most points several determinations were made with a precision of approximately 2.5%. TME concentrations are in moles/liter.

ca. 5 sec after the onset of reaction.[11] At TME concentrations of less than 0.6 *M*, the major products derived from the olefin were chloroform and 4,4,4-trichloro-2,3,3-trimethyl-1-butene (**1**). Scheme I shows the addition–disproportionation (a) and the abstraction–combination (b) reactions which are reasonable candidates for the route to these products.

SCHEME I



There are two pieces of chemical evidence which seem to favor path a.

(1) There is an optimum TME concentration (~0.3 *M*) for chloroform formation, apparently the point where the product of [$\cdot CCl_3$] and [**2**] is maximized. In path b, chloroform formation should continue to increase with increasing TME concentrations. Furthermore, nearly equal amounts of $HCCl_3$ and **1** are formed at all concentrations up to 0.4 *M* even though reaction of **3** with $\cdot CCl_3$ to product 2,3-dimethylbutadiene (**4**) at high TME concentrations would have simultaneously produced an additional molecule of $HCCl_3$. The maximization of **1** at 0.65 *M* TME without a corresponding maximum in $HCCl_3$ is probably due to a peak in the concentration of the radical **2** near this concentration. Disproportionation of two **2** radicals would give **1** and **6**. The dimeric radical resulting from the addition of **2** to TME may also react with **2** to give more **1** without producing either $HCCl_3$ or **6**.

(2) Decomposition of trichloroacetyl peroxide in 3.25 *M* TME at temperatures obtained by immersing the nmr tube in a beaker of ice water and letting the system react as it warms to room temperature gives no detectable amount (<2%) of chloroform, although the same reaction mixture at 60° gives 20% chloroform. Most probably, the difference results from a much lower steady-state concentration of $\cdot CCl_3$, which decreases the probability of the encounter of **2** and $\cdot CCl_3$. The half-life of trichloroacetyl peroxide in carbon tetrachloride solution at 0° is about 10 min,[12] while at least 90% of the decomposition takes place in 3 sec in the heated reaction,[11] giving a difference in the rate of $\cdot CCl_3$ formation of at least 10^3 under the two conditions.

At higher TME concentrations the radicals **2**, formed by addition of $\cdot CCl_3$ to TME, are less likely to encounter a $\cdot CCl_3$. Consequently, self-disproportionation reactions (giving **1** and **6**) and hydrogen abstraction from TME by **2** (leading to **3** and eventually to **4**) become more probable. The measured amount of **4** is probably low since it should efficiently trap $\cdot CCl_3$ and other radicals. Indeed, in a reaction run with a mixture of TME (0.39 *M*) and **4** (0.13 *M*), chloroform and **1** were decreased by 80% (compared to the reaction in TME alone), and a new unidentified monoadduct of trichloromethyl was formed in trace amounts. The main product of the reaction in the presence of **4**, however, appeared to be a highly chlorinated polymer.[13] Even when **4** was not added, substantial polymerization occurred. The presence of chlorine in this polymer helps to account for the low material balance of CCl_3 groups in the volatile products. There is no evidence of atom transfers involving radicals resulting from TME (*i.e.*, 2,3-dimethylbutane and 2,3-dimethyl-2-chlorobutane could not be detected by gas chromatography).

CIDNP Spectra.—The radical-pair theory first proposed by Kaptein and Oosterhoff[8] and by Closs[7] and modified by Adrian[14] offers the most satisfying explanation of the CIDNP phenomena. The sign of enhancement of lines in a CIDNP spectrum can be consistently predicted from a knowledge of only the signs of hyperfine splitting, the relative magnitudes of the *g* factors of the two radical fragments, and the initial electron spin multiplicity of the radical pair. Several reviews of the theory are available,[15] as well as simplified

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[11] The onset of reaction was about 5 sec after insertion into the probe owing to a lag in heating. If the tube was heated in a block designed to simulate a heated probe [H. R. Ward, R. G. Lawler, H. Y. Loken, and R. A. Cooper, *ibid.*, **91**, 4929 (1969)] for 10 sec and then rapidly transferred to the probe, no polarization was observed, indicating a completed reaction. The block was similarly used to monitor reaction progress, since reaction taking place after transfer from block to probe would result in polarization. This method of running an exothermic reaction leads to kinetics that are almost impossible to quantify. However, an advantage is that the sudden rise in temperature, which can be monitored by inserting a miniature thermocouple into the nmr tube, counteracts the drop in rate that would otherwise take place as the reactants drop in concentration. At peroxide concentrations below about 0.1 *M*, the heat capacity of the solvent moderates the temperature increase enough to prevent the sample from boiling.

[12] J. E. Leffler and H. H. Gibson, Jr., *J. Amer. Chem. Soc.*, **90**, 4117 (1968).

[13] Analysis of a sample of the polymeric material yielded C, 18.9; H, 2.1; Cl, 78.8. This corresponds to a Cl content even higher than the empirical formula $(CCl_3)_4C_6H_{10}$ (C, 21.6; H, 1.9; Cl, 76.5) expected for addition of four CCl_3 groups to the two double bonds in **4**. This apparent excess of Cl was not investigated further.

[14] F. J. Adrian, *J. Chem. Phys.*, **53**, 3374 (1970).

[15] (a) R. G. Lawler, *Accounts Chem. Res.*, **5**, 25 (1972); (b) G. L. Closs, *Spec. Lect. XXIIIrd Int. Congr. Pure Appl. Chem.*, **4**, 19 (1971); (c) H. Fischer, *Top. Curr. Chem.*, **24**, 1 (1971); (d) R. Kaptein, Doctoral Dissertation, University of Leiden, 1971.

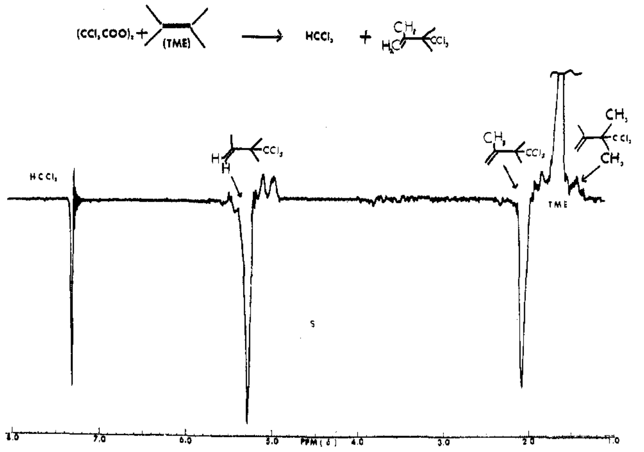

Figure 1.—CIDNP spectrum taken during the thermolysis of trichloroacetyl peroxide in carbon tetrachloride solutions of TME. The spectrum is a composite of three scans.

approaches to the predictions of the spectral characteristics.[15a,16,17] The spectrum observed in the system at hand can be predicted by these methods, and is an example of pure net polarization, resulting from the substantial difference in precessional frequencies for the two electrons in radical pairs composed of $\cdot CCl_3$ and **2**. This precessional frequency difference is reflected in the g factors ($\cdot CCl_3$, 2.0091;[18] **2**, 2.0025[19]). The only protons in the intermediate radical pair that will affect electron precessional rates (*i.e.*, are coupled to an electron) are the β-methyl protons in **2**, for which the hyperfine coupling has a positive sign. Consequently, **1** and $HCCl_3$ which are combination products arising from a diffusively formed radical pair, should both give emission lines.[16,17]

During the decomposition of trichloroacetyl peroxide in carbon tetrachloride with added TME (0.3 *M*), strong nmr emission signals are observed at δ 7.3 (chloroform) and 5.25 and 2.15 (vinyl and allyl protons of **1**) and weak enhanced absorption at δ 5.04 and 4.93 (vinyl protons of **4**) (Figure 1).[20] At the completion of the reaction, these peaks become weak absorption signals. The singlet at δ 1.54 is from the 3-methyls of **1**, and shows no polarization during the reaction. Since the protons exhibiting emission are all equivalent in the intermediate free radical, it would be expected that all three of the observed lines should have the same enhancement factor. When the reaction was run and the spectrum was obtained in times comparable to the shortest T_1 (T_1 for chloroform $\cong$ 40 sec; T_1 for the allyl and vinyl protons in **1** $\cong$ 8 sec), this expectation is realized (Figure 2). The intensities for chloroform, vinyl, and allyl protons appear in approximately the statistical ratios 1:2:3. Nuclear relaxation times were estimated directly from the rapidly reacted sample by following the decay of the polarization of the various lines as a function of time after the reaction was complete.

Figure 2.—Repeated scans of the CIDNP spectrum, taken at 19.3 MHz, during the thermolysis of trichloroacetyl peroxide in carbon tetrachloride solution of TME. The strong absorption peak is TME. Sweeps were from low to high field with flyback from 1 to 8 ppm.

The enhancement factor calculated for the chloroform proton was −220 ± 20 at 60 MHz and −300 ± 50 at 19.3 MHz. These measurements were made by a cancellation method. Enough chloroform was added to exactly cancel out the emission signal resulting from the reaction that was over in a time less than the relaxation time. The reaction was then repeated adding inert solvent (CCl_4) in an amount equal to the amount of chloroform needed to cancel the emission peak, and the amount of chloroform formed was measured. The observed enhancement factor is then simply the ratio of the amount of $HCCl_3$ needed to cancel the CIDNP emission to the amount formed in the reaction. Chloroform was not consumed under the reaction conditions.

The weak positive enhancement of the signal assigned to the vinyl protons of **4** is probably a result of the partial cancellation of the polarization developed in encounters of **3** with $\cdot CCl_3$. Two of the protons in **3** which appear in the vinyl position of **4** have a negative hyperfine coupling, while the methyl group protons which also become vinyl protons in **4** have a positive coupling. Further, using methallyl radical as a model, the magnitude of the coupling for the two positions should be nearly equal.[21] Since enhanced absorption is observed, apparently the *gem*-methyl hyperfine coupling in **3** dominates.

At very high TME concentrations (about 5 *M*) the sign of the chloroform polarization reverses (and, as expected, very little chloroform is formed). This change of polarization is probably due to the interception of one partner of the radical pair. (After leveling off at intermediate TME concentrations, the hexachloroethane yield drops again at the highest TME concentration. This constitutes independent confirmation of this interception.) Since the $\cdot CCl_3$ geminate pair is in a singlet state, this process of pair substitution[22] leads to a $\cdot CCl_3$–**2** pair which is predominantly *singlet* in character. This change in the starting multiplicity of the pair necessarily results in a change in the sign of polarization.[16]

Reactions of $\cdot CCl_3$ with Isobutylene.—CIDNP spectra taken of decomposing trichloracetyl peroxide

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[16] H. R. Ward, *Accounts Chem. Res.*, **5**, 18 (1972).

[17] R. Kaptein, *Chem. Commun.*, 732 (1971).

[18] A. Hudson and H. A. Hussain, *Mol. Phys.*, **16**, 199 (1969).

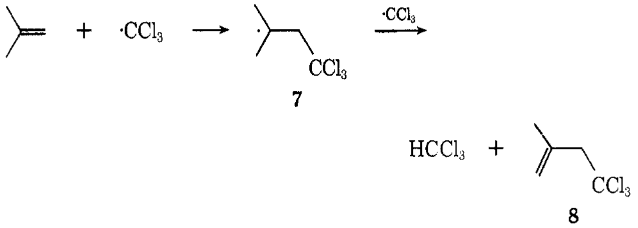
[19] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

[20] Some other unexplained enhanced nmr lines, apparently from otherwise undetectable minor products, were observed at high gain for short periods in fast reactions with high TME concentrations. The weak lines were mostly enhanced absorption, which is expected for radicals that are captured after escaping a cage where reaction leads to emission. The enhanced absorption for the vinyl protons of **4** was more intense than predicted if all $\cdot CCl_3$ that did not dimerize was assumed to react as in Scheme I to form **4**.

[21] J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **90**, 7157 (1968).

[22] For a more complete discussion of pair substitution see R. A. Cooper, R. G. Lawler, and H. R. Ward, *ibid.*, **94**, 552 (1972); and R. Kaptein, F. W. Verheus and L. J. Oosterhoff, *Chem. Commun.*, 877 (1971).

in carbon tetrachloride solutions of isobutylene can in most important respects be explained by analogy to reactions with TME. Addition of $\cdot CCl_3$ at the terminal position of isobutylene forms **7**, which, on encountering



another $\cdot CCl_3$, leads to a spin selective interaction giving emission in the proton of chloroform and all of the protons of **8** (vinyl protons at δ 5.1 and the allylic protons just downfield of those in isobutylene).

At higher concentrations of isobutylene (equal volume with carbon tetrachloride), pair substitution occurs and the chloroform proton shows enhanced absorption.

The only substantial difference in the TME and the isobutylene reactions is the appearance in the latter case of a strong emission line for pentachloroethane at δ 6.1. The same emission is observed for reactions with a variety of acetylene and diacetylenic compounds with enhancement factors of up to 10^3. Although the source of this emission, identified through its cancellation by added pentachloroethane, is uncertain, two possible sources were eliminated.

(1) A trace of dichloroacetyl chloride in the trichloroacetyl chloride used in the triacetyl peroxide preparation would provide a route to a $\cdot CCl_3$–$\cdot CHCl_2$ pair, which, on combination would show emission for pentachloroethane. Since this is a reaction occurring in a geminate pair, however, the polarization should also be observable in TME reactions, and so does not provide a suitable explanation.

(2) The formation of $\cdot C_2Cl_5$ by a chlorine abstraction from C_2Cl_6 and its subsequent encounters with **7** also would lead to a negative sign of enhancement. The addition of C_2Cl_6 to the reaction mixture, however, had no effect on the emission intensity. Further, in reactions of trichloroacetyl peroxide with 2-butyne, pentachloroethane exhibits strong emission while chloroform is unenhanced.

Owing to the strong signal enhancement caused by CIDNP, minor products formed by radical–radical mechanisms can often appear to be very important, while other products, which are not so spectacularly polarized, may tend to be ignored. The pentachloroethane emission, where it occurred, was very prominent in the spectrum during the reaction but there was no detectable absorption from the unenhanced product in the final scans. The pentachloroethane peak is therefore a striking example that a polarized peak need not come from a major reaction product.

Experimental Section

Nuclear magnetic resonance spectra were taken on a Varian A-60A and an HA60 spectrometer operating in the HR mode at 19.3 MHz.

Trichloroacetyl Peroxide Solution.—Trichloroacetyl peroxide was prepared by a modification of the method of Leffler and Gibson.[12]

A mixture of 12 g of sodium chloride, 50 g of chipped ice, 20 ml of water, and 2.8 g of sodium peroxide was cooled by a −21° bath and stirred vigorously. Trichloroacetyl chloride (9.0 g) was added by syringe. The addition was stopped for about 45 sec whenever the reaction temperature reached −15°. About 30 sec after the addition was completed, 15–30 ml of carbon tetrachloride (cooled to about −10°) was added and 20 sec later the stirrer was stopped and the carbon tetrachloride layer was removed with a syringe. The solution was stored at Dry Ice temperature.

Volumetric Determination of Trichloroacetyl Peroxide Concentration.—The following operation was carried out in its entirety in a 6° cold room. Acetic acid (20 ml, cooled almost to its freezing point) was added to a 125-ml glass-stoppered erlenmeyer flask. Sodium bicarbonate (1.5 g) was added and the contents were stirred magnetically. Potassium iodide in water (40%, 5 ml) was added, followed by 0.5 g of the carbon tetrachloride solution of the peroxide. The contents of the flask were titrated to a starch end point with standardized sodium thiosulfate. A typical peroxide concentration measurement was 0.23 *M* with a precision of better than 3% (average deviation). Satisfactory results were obtained for a benzoyl peroxide standard. With the benzoyl peroxide it was necessary to wait for about 40 min at room temperature for the peroxide to react completely. With the trichloroacetyl peroxide, 5 min at the cold room temperature was more than adequate.

Reaction of TME with $\cdot CCl_3$.—Frozen trichloroacetyl peroxide solution was warmed just to the melting point and 0.3- to 0.5-ml quantities were transferred to clean, dry nmr tubes fitted with serum stoppers and precooled with Dry Ice. To run a reaction, a tube was taken from the cooling bath, filled with the correct amount of TME and inert solvent (carbon tetrachloride or chloroform), and repeatedly inverted until the last crystal disappeared. At this point, the tube (with the spinner turbine taped in place) was placed in a variable-temperature probe.

Product concentrations at the end of the reaction were measured by gas chromatography. Nmr was not suitable because of low product concentration. A 15-ft 15% SF-96 column was used at 65° for the low-boiling products and at 180° for the higher boiling hexachloroethane and 4,4,4-trichloro-2,3,3-trimethylbut-1-ene. The high temperature did not cause decomposition of these products, since duplicate analysis on a 5-ft 5% SE-30 column at 65° gave the same yields. However, there were products that decomposed at 180°, with production of chloroform, since the apparent amount of chloroform could be increased simply by raising the injector temperature.

Registry No.—Trichloromethyl, 3170-80-7; tetramethylethylene, 563-79-1; isobutylene, 115-11-7; trichloroacetyl peroxide, 2629-78-9.

Acknowledgments.—This research was supported by the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society.