was allowed to stand at room temperature overnight. After removal of the manganese dioxide, the solution was acidified with 10 cc. of concentrated hydrochloric acid. Concentration *in vacuo* to a volume of approximately 100 cc. yielded a turbid emulsion. After saturation with sodium chloride the reaction mixture was extracted with two 100-cc. portions of ethyl acetate. After drying over anhydrous sodium sulfate the ethyl acetate was removed by distillation. The solid residue was macerated with ether, and filtration yielded 15.9 g. of a white solid. Purification by crystallization from ethyl acetate yielded the γ-acetamido-γ-carbethoxy-γ-cyanobutyric acid melting at 154–154.5°.

Anal. Calcd. for $C_{10}H_{14}O_5N_2$: C, 49.99; H, 5.87; N, 11.66; neut. equiv., 240. Found: C, 49.68; H, 6.06; N, 11.55; neut. equiv., 241.7.

DL-Glutamic Acid.—The γ-acetamido-γ-carbethoxy-γ-cyanobutyric acid (5 g.) was mixed with 25 cc. of concentrated hydrochloric acid. The resulting reaction mixture was refluxed for a period of sixteen hours and then concentrated *in vacuo*. The residual solid was dissolved in 12 cc. of water. After filtration the filtrate was neutralized by addition of 10% aqueous sodium hydroxide solution to a *p*H of 3.2. When cooled, the resulting solution yielded a crystalline product (2.3 g.) which melted at 193–194° with decomposition after drying *in vacuo*. The melting point was not depressed when mixed with an authentic sample. The N-benzoyl derivative was prepared and it melted at 156–157.5°.

Summary

1. New syntheses of DL-tryptophan, DL-ornithine and DL-glutamic acid have been reported.

2. These amino acids result from the aldehydo intermediates prepared by the 1,4-addition of acylamidomalonates to acrolein.

MINNEAPOLIS, MINNESOTA RECEIVED MARCH 24, 1948

[CONTRIBUTION FROM SHELL DEVELOPMENT COMPANY, EMERYVILLE, CALIFORNIA]

Some Free Radical Reactions of Hydrogen Chloride

BY JOHN H. RALEY, FREDERICK F. RUST AND WILLIAM E. VAUGHAN

Although the chain addition of hydrogen bromide to ethylenic linkages is readily brought about by peroxides (the well known Kharasch "peroxide effect")[1] or actinic radiation,[2] it has been generally recognized that the analogous reaction with hydrogen chloride is much less likely. In fact, at the time the present study was begun, there was no report of a free radical hydrogen chloride–olefin combination.[3]

In this paper the vapor phase addition of hydrogen chloride to ethylene, as initiated by ultraviolet light or di-*t*-butyl peroxide, is described. Evidence for the corresponding, but much slower, reaction with propylene, is presented. Hydrogen chloride sensitizes the vapor phase decomposition of di-*t*-alkyl peroxides. This reaction, apparently a chain process involving chlorine atoms, is related to the photochlorination of di-*t*-butyl peroxide which is also described.

Experimental

Photochemical Experiments.—The cell was a fused quartz cylinder (22 mm. o.d. × 150 mm.) provided with plane windows. The body of the cell was wrapped with metal foil and jacketed by an aluminum pipe which was heated electrically. A thermocouple imbedded in the foil gave an approximate measure of the reaction temperature.

The light source was a hydrogen discharge tube of the Kistiakowsky type[4] (Hanovia Mfg. Co.) operated from a 2.5-kw. transformer. Since mercury vapor (from the vacuum line) could be present in the cell, radiation absorbable by this element was excluded to prevent the occurrence of mercury-sensitized reactions. The filter was a quartz cylinder dimensionally identical with the cell, containing carbon dioxide saturated with mercury vapor at room temperature. Ethylene absorbs appreciably only below the quartz region[5] but continuous absorption by hydrogen chloride begins at about 2500 Å. and increases rapidly below 2200 Å.[6]

The pressure change was measured with a quartz spiral manometer[7] sealed to the cell. After irradiation, the cell contents were transferred directly to a bulb by means of a Toepler pump, measured, and subsequently analyzed mass spectrometrically.

Experiments with Di-*t*-alkyl Peroxides.—The closed system apparatus used has been described in an earlier communication.[8] For certain experiments the 500-cc. reaction vessel was packed with 2-mm. Pyrex rods to effect an increase in the surface:volume ratio from 0.61 to 7.0 cm.$^{-1}$.

After reaction, the vessel contents were condensed with Dry Ice–acetone and the volatile products, excepting a portion of the dissolved ethyl chloride, pumped into a sample bulb for mass spectrometric analysis. The cold trap contents were dissolved in water containing a little isopropyl alcohol and aliquots taken for carbonyl[9] and chloride ion (Volhard) determinations.

Larger scale runs with a flow type apparatus provided material for product identification. This apparatus also has been described previously.[10] Because of the complexity of the effluent, particularly when the peroxide content of the feed was high, product yields could be determined only very roughly. However, isobutylene chlorohydrin was isolated (in *ca.* 10% yield) from the products of both the di-*t*-butyl peroxide–hydrogen chloride and di-*t*-butyl peroxide–hydrogen chloride–ethylene re-

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[1] For literature review, see Mayo and Walling, *Chem. Rev.*, **27**, 351 (1940).

[2] Vaughan, Rust and Evans, *J. Org. Chem.*, **7**, 477 (1942).

[3] In a recent patent (U. S. 2,418,832, April 15, 1947), Hanford and Harmon report the preparation of a homologous series of primary alkyl chlorides by a high pressure reaction between ethylene and hydrogen chloride. Catalysts employed include oxygen, peroxides, and lead tetraphenyl. This work was presented as Paper No. 57 before the Organic Division of the American Chemical Society, 113th National Meeting, Chicago, Ill., April 19–23, 1948.

[4] Kistiakowsky, *Rev. Sci. Instruments*, **2**, 549 (1931).

[5] Noyes and Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941, p. 331; also, Price, *Phys. Rev.*, **47**, 444 (1935).

[6] H. Trivedi, *Proc. Nat. Acad. Sci. India*, **6**, 18 (1936).

[7] Vaughan, *Rev. Sci. Instruments*, **18**, 192 (1947).

[8] Raley, Rust and Vaughan, THIS JOURNAL, **70**, 88 (1948).

[9] This procedure, based on reaction with hydroxylamine hydrochloride, is a modification of the method of Marasco (*Ind. Eng. Chem.*, **18**, 701 (1926)), and is described in "Methyl Ethyl Ketone, Its Uses and Data on Its Properties," Shell Chemical Co., San Francisco, Calif., 1938, p. 45.

[10] Rust, Seubold and Vaughan, THIS JOURNAL, **70**, 95 (1948).

actions (b. p. 126.6–126.7°, $n^{20}\text{D}$ 1.4375, acidimetric equivalent weight, 114; literature or theoretical values for $(CH_3)_2COHCH_2Cl$, respectively, 126.6–128.8°, 1.4388, and 108.5). The product from the di-*t*-butyl peroxide–hydrogen chloride–propylene reaction contained small amounts of both *n*- and isopropyl chlorides, as shown by infrared absorption analysis.

Materials.—The various gases used in the static apparatus were taken from commercial cylinders (stated purity more than 99% except hydrogen chloride (97.5%)), redistilled under high vacuum (collection of middle one-third), out-gassed, and stored in glass bulbs. For the flow experiments no purification was made. Di-*t*-butyl and di-*t*-amyl peroxides were purified in the manner described previously.[8]

Photochlorination of Di-*t*-butyl Peroxide.—Chlorine (2.0 moles) was bubbled through a sintered glass plate into di-*t*-butyl peroxide (3.0 moles) at a rate which maintained the temperature at 30-40°. A 500-watt projection lamp adjacent to the Pyrex reaction flask served as the source of radiation. The product was water-washed, dried, and fractionated under reduced pressure. The monochloride (b. p. 55° (20 mm.), f. p. −31°, $n^{20}\text{D}$ 1.4211, Cl, 19.7% (theory, 19.62%)) was obtained in 42.5% yield based on input chlorine. The dichloride fraction, probably consisting of three possible isomers, boiled at 55-70° at 4-5 mm.; $n^{20}\text{D}$ 1.4454, Cl, 33.3% (theory, 32.96%).

Photo-addition of Hydrogen Chloride to Ethylene.—The effect of radiation from the hydrogen lamp on hydrogen chloride–ethylene mixtures at two temperatures is illustrated in Fig. 1. It will be noted that there is no appreciable "dark" reaction. Ethyl chloride is the only significant product detected mass spectrometrically, and the composition after illumination agrees, within the analytical error, with that calculated from the pressure decrease on the assumption that only the addition reaction occurs. For example, at 26° the composition by analysis was 13 ± 1% C_2H_5Cl and 41 ± 2% C_2H_4, while that calculated was 14.5% C_2H_5Cl and 42.2% C_2H_4. The hydrogen and ethane contents were both 0.1% or less.

Since light absorption by hydrogen chloride leads to the production of chlorine and hydrogen atoms, the probable path of the reaction is

$$HCl + h\nu \longrightarrow H + Cl \quad (1)$$

$$Cl + C_2H_4 \longrightarrow CH_2Cl\underset{\cdot}{C}H_2 \quad (2)$$

$$CH_2Cl\underset{\cdot}{C}H_2 + HCl \longrightarrow CH_2ClCH_3 + Cl \quad (3)$$

Addition reactions such as

$$CH_2Cl\underset{\cdot}{C}H_2 + C_2H_4 \longrightarrow CH_2Cl(CH_2)_2\underset{\cdot}{C}H_2 \quad (4)$$

are apparently much slower than (3) under the present conditions since higher molecular weight products were not detected.

The hydrogen atoms could also initiate a chain, *viz.*

$$H + HCl \longrightarrow H_2 + Cl, \text{ or} \quad (5)$$

$$H + C_2H_4 \longrightarrow CH_3\dot{C}H_2 \quad (6)$$

$$CH_3CH_2 + HCl \longrightarrow C_2H_6 + Cl \quad (7)$$

and, from the yields of hydrogen and ethane the chain length is estimated to be at least 30 at room temperature.

In keeping with the characteristics of a chain process, the reaction is inhibited by oxygen and a number of other substances (Fig. 2). The pro-

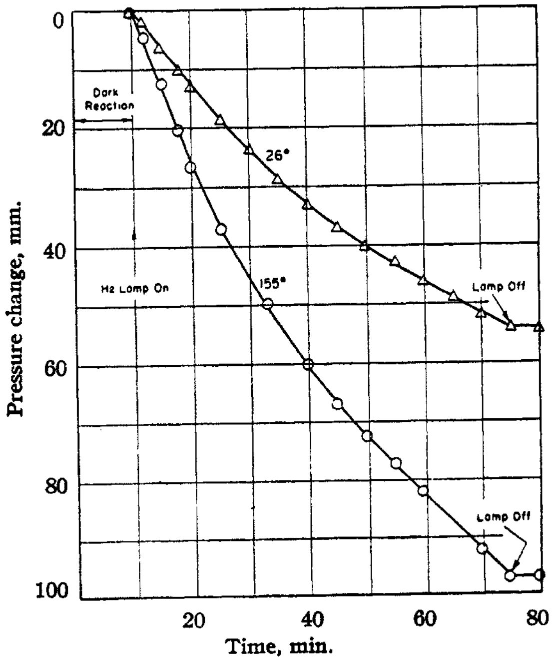


Fig. 1.—Photo-addition of hydrogen chloride to ethylene: (0.0116 mole/liter HCl, 0.0113 mole/liter C_2H_4).

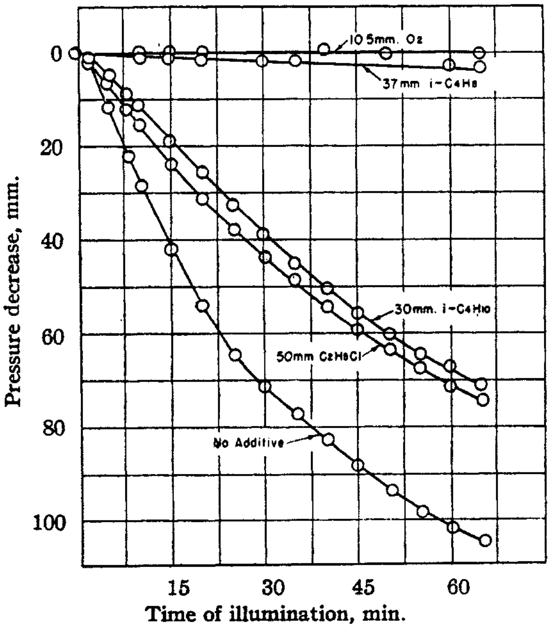
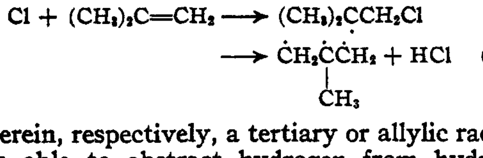


Fig. 2.—Effect of additives on the photochemical hydrogen chloride–ethylene reaction: temperature, 155°; HCl 309 mm.; C_2H_4, 300 mm.

nounced effect of small oxygen concentrations is attributed to the relatively rapid reaction

$$CH_2ClCH_2\cdot + O_2 \longrightarrow CH_2ClCH_2O_2\cdot \qquad (8)$$

the peroxy radical being incapable of continuing the chain. Retardation by isobutylene is probably due to the reactions



$$Cl + (CH_3)_2C{=}CH_2 \longrightarrow (CH_3)_2\underset{\cdot}{C}CH_2Cl \qquad (9)$$

$$\longrightarrow \dot{C}H_2\underset{\underset{\displaystyle CH_3}{|}}{\dot{C}}\dot{C}H_2 + HCl \qquad (10)$$

wherein, respectively, a tertiary or allylic radical, less able to abstract hydrogen from hydrogen chloride is produced. In the presence of isobutylene only a trace of ethyl chloride formed, the chief product being C_4 chloride(s). With isobutane as the additive, chlorine atom attack at the tertiary carbon–hydrogen bond is the most likely mode of interference. Since ethyl chloride is also a retardant, the reaction must be self-inhibiting. In this case the effect is apparently due to the formation of the $CH_3\underset{\cdot}{C}HCl$ radical which is less capable of metathetical reaction with hydrogen chloride than its isomer, $CH_2Cl\text{-}\underset{\cdot}{C}H_2$. This difference in reactivity might be expected from the results of studies on the thermal chlorination of ethyl chloride.[11]

Peroxide-catalyzed Addition of Hydrogen Chloride to Olefins.—The reaction with ethylene, as initiated by a small amount of di-*t*-butyl peroxide, is illustrated in Fig. 3. A complete product analysis has not been made but ethyl chloride was identified again as a major component. A small amount of methane was also produced. In view of the known decomposition of di-*t*-butyl peroxide to *t*-butoxy and methyl radicals,[8,12] the initiation steps are probably

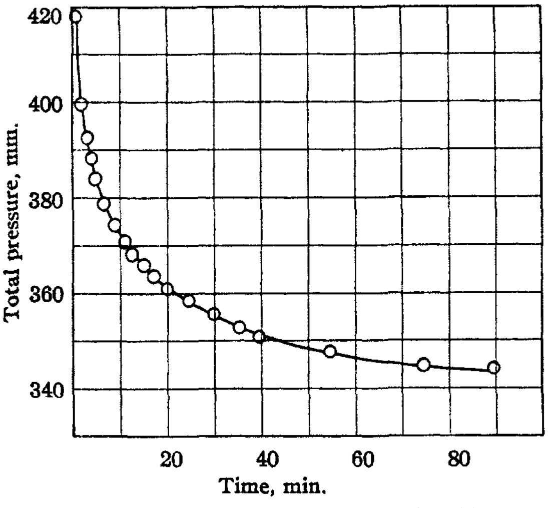


Fig. 3.—Di-*t*-butyl peroxide—catalyzed addition of hydrogen chloride to ethylene: 200.7 mm. HCl, 200.3 mm. C_2H_4, 10.5 mm. peroxide, 6.4 mm. nitrogen, temperature 154.7°.

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)_3CO\cdot \qquad (13)$$

$$(CH_3)_3CO\cdot + HCl \longrightarrow (CH_3)_3COH + Cl \qquad (14)$$

$$(CH_3)_3CO\cdot \longrightarrow (CH_3)_2CO + CH_3 \qquad (15)$$

$$CH_3 + HCl \longrightarrow CH_4 + Cl \qquad (16)$$

The reaction has been carried out at 140–185° in both types of apparatus.

The analogous reaction with propylene is much slower. For example, at 155° a mixture of 200 mm. propylene, 200 mm. hydrogen chloride, and 13 mm. di-*t*-butyl peroxide undergoes a pressure decrease of only 10 mm. in sixty minutes. The hydrogen transfer step involving a secondary radical

$$CH_3\underset{\cdot}{C}HCH_2Cl + HCl \longrightarrow CH_3CH_2CH_2Cl + Cl \qquad (17)$$

would be more endothermic than the corresponding process in the ethylene reaction, (3). Furthermore, allyl radical formation could occur by

$$Cl + CH_3CH{=}CH_2 \longrightarrow HCl + \dot{C}H_2\dot{C}H\dot{C}H_2, \text{ or} \qquad (18)$$

$$CH_3\underset{\cdot}{C}HCH_2Cl + CH_3CH{=}CH_2 \longrightarrow$$

$$CH_3CH_2CH_2Cl + \dot{C}H_2\dot{C}H\dot{C}H_2 \qquad (19)$$

Di-*t*-alkyl Peroxide–Hydrogen Chloride Reaction.—In addition to a simple dissociation into two *t*-alkoxy radicals, di-*t*-alkyl peroxides in the presence of a minor amount of hydrogen chloride undergo a sensitized decomposition (Fig. 4).

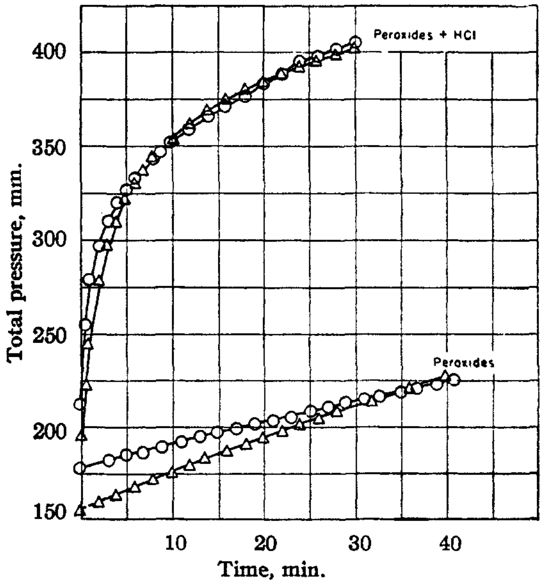


Fig. 4.—Effect of hydrogen chloride on di-*t*-alkyl peroxides: O, di-*t*-butyl peroxide (139.7(8)°) 173.4 mm. peroxide, 180 mm. peroxide + 27.6 mm. HCl; △, di-*t*-amyl peroxide (136.7(4)°) 149.2 mm. peroxide, 160 mm. peroxide + 30.8 mm. HCl.

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(11) From the data of Rust and Vaughan (*J. Org. Chem.*, 6, 479 (1941)), reaction (11) is known to be faster than (12):

$$Cl + CH_3CH_2Cl \longrightarrow HCl + CH_3\underset{\cdot}{C}HCl \qquad (11)$$

$$Cl + CH_3CH_2Cl \longrightarrow HCl + CH_2Cl\underset{\cdot}{C}H_2 \qquad (12)$$

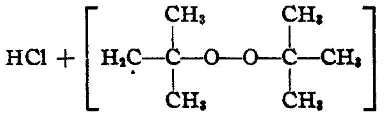
Therefore, the reverse of (11) might be expected to be slower than the reverse of (12).

(12) Milas and Surgenor, THIS JOURNAL, 68, 205 (1946).

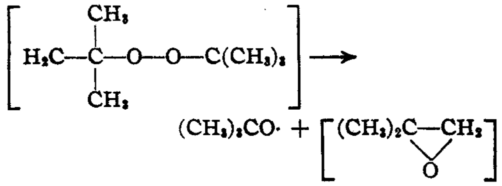
The major hydrocarbon product contains only half as many carbon atoms as that produced in the unsensitized reaction, and substantially less than two molecules of ketone are produced from each peroxide molecule decomposed. Additional products that appear in the case of di-*t*-butyl peroxide include isobutylene chlorohydrin and *t*-butyl chloride. This sensitized reaction is essentially homogeneous since the rate of pressure increase is unaffected by the presence of Pyrex rod packing. Furthermore, various compounds readily attacked by free radicals or atoms (ethylene, propylene, isobutane, etc.) have a retarding influence. These observations indicate a chain, the mechanism for which is postulated to be:

Steps (13) to (16) followed by

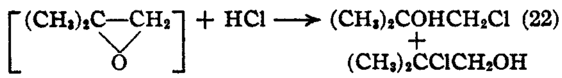
$Cl + (CH_3)_3COOC(CH_3)_3 \longrightarrow$



$$HCl + \left[H_2\dot{C}{-}C(CH_3)_2{-}O{-}O{-}C(CH_3)_2{-}CH_3 \right] \quad (20)$$



$$\left[H_2\dot{C}{-}C(CH_3)_2{-}O{-}O{-}C(CH_3)_3 \right] \longrightarrow (CH_3)_3CO\cdot + \left[(CH_3)_2C{-}CH_2 \ (\text{>O}) \right] \quad (21)$$



$$\left[(CH_3)_2C{-}CH_2 \ (\text{>O}) \right] + HCl \longrightarrow (CH_3)_2COHCH_2Cl + (CH_3)_2CClCH_2OH \quad (22)$$

Evidence for the step involving chlorine atom attack on the peroxide comes from experiments on the photochlorination of the peroxide described elsewhere in this paper. The production of monochloride, $ClCH_2(CH_3)_2COOC(CH_3)_3$, by a photo reaction must certainly involve (20). Because of the lower temperature and the presence of molecular chlorine, however, the resultant radical does not decompose but instead forms the chloride. It is interesting to note the differing reactivities of chlorine atoms and methyl radicals toward the peroxide. In the vapor phase the latter apparently do not readily abstract hydrogen atoms from the peroxide since the thermal decomposition of this compound is not a chain reaction.[8] Although isobutylene oxide has not been isolated, the chlorohydrin, (22), is a recognized derivative.

The preponderance of ethane over methane observed in the sensitized decomposition of di-*t*-amyl peroxide is in agreement with earlier observations that *t*-amyloxy radicals yield acetone and ethyl radicals.[8,13] A partial product analysis for both peroxides is given in Table I. Carbonyl and methane yields are nearly equivalent for the di-*t*-butyl compound, as are the carbonyl and (methane + ethane) yields for the amyl analog. Products characteristic of the combination of two alkyl radicals (*i. e.*, butane from ethyl radicals) are unimportant. These data illustrate the predominance of (16) and the analogous ethyl radical reaction over other processes involving alkyl radicals. This is particularly interesting inasmuch as (16) is almost energetically neutral while the ethyl-hydrogen chloride reaction is somewhat endothermic. It is clear that (15) is more important than (14) although the exact ratio of these two reactions cannot be determined without knowledge of either the amount of alcohol produced or the fraction of input peroxide decomposed.

TABLE I

HYDROGEN CHLORIDE–DI-*t*-ALKYL PEROXIDE REACTIONS

Reaction time, 31 minutes

Produced, mm.	Di-*t*-butyl peroxide 139.8°	Di-*t*-amyl peroxide 136.7°
Carbonyl	114	135
CH_4	110	6.5
Ethane	...	124
Butane	...	1
Input, mm.		
Peroxide	180	160
HCl	28	31

Under comparable conditions hydrogen bromide has little effect on the decomposition of di-*t*-butyl peroxide. Although hydrogen bromide reacts readily with methyl radicals to produce methane, the resultant bromine atoms apparently are less capable of attacking the peroxide to continue the chain. This is in agreement with the observation that photobromination of the peroxide is more difficult than photochlorination.

Summary

The vapor phase addition of hydrogen chloride to ethylene can be initiated photochemically or by di-*t*-butyl peroxide. A free radical, chain mechanism is proposed and the influence of added inhibitors is interpreted in terms of this mechanism. Propylene reacts much more slowly.

Hydrogen chloride sensitizes the vapor phase decompositions of di-*t*-butyl and di-*t*-amyl peroxides. A chain mechanism involving chlorine atom attack on the peroxide is suggested for these reactions. The latter step is demonstrated by the photochlorination of di-*t*-butyl peroxide.

EMERYVILLE 8, CALIFORNIA RECEIVED MARCH 30, 1948

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[13] Milas and Surgenor, THIS JOURNAL, 68, 643 (1946).