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REACTIONS OF t-BUTYL PERESTERS—VII*

PHOTOCHEMICAL REACTIONS OF PERESTERS IN THE PRESENCE OF COPPER IONS†‡

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Abstract—t-Butyl peracetate and t-butyl perbenzoate readily react with a variety of substances below 35° upon exposure to UV light in the presence of Cu ions. This photochemical reaction extends the scope of the peroxyester reaction. It provides a simple method for the reaction of low boiling substrates and permits the isolation of heat sensitive acyloxy derivatives. The reaction was studied with the following substrates: ethyl ether, tetrahydrofuran, tetrahydrothiophene, 1,4-dioxane, N,N-dimethylformamide, cyclohexene, cumene and benzaldehyde. The reaction catalyzed by light only, or by copper ions only, proceeds at a much slower rate than the reaction catalyzed by both light and Cu ions.

IN A previous communication[1] it was indicated that a variety of substances readily react with t-butyl peracetate and t-butyl perbenzoate below 35° upon exposure to UV radiation in the presence of a trace of copper ions. The present paper contains the experimental details which amplify the original observations.

Since the discovery of the copper ion catalyzed peroxyester reaction[2,3] investigators in this field have employed essentially the same experimental procedure as that originally developed.[2,3] Namely, the perester is gradually added to a mixture of the substrate and the catalyst, maintaining the temperature of the reaction mixture at 65–115°. The narrow temperature range has been imposed mainly by the properties of the commercially readily available peresters. Thus, t-butyl peracetate and t-butyl perbenzoate are both fairly stable compounds around room temperature, and undergo homolytic cleavage readily only at somewhat elevated temperatures. The half-life of t-butyl peracetate and t-butyl perbenzoate is 133 hr at 80° and 130 hr at 85°, respectively. This temperature requirement imposes certain experimental limitations. Thus, with low boiling substrates the peroxyester reaction must be carried out under pressure in an autoclave, and heat sensitive acyloxy derivatives can undergo further transformation before they are isolated. These disadvantages of the peroxyester reaction can be avoided if the mixture of the reactants is irradiated with ultraviolet light in the presence of copper ions.

In the present photochemical work a Hanau Quartz Lamp S81 was used. Because

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† This paper is dedicated to my former teacher at the University of Innsbruck, Professor Dr. Erika Cremer, on the occasion of her 65th birthbay on May 20, 1965.

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[1] G. Sosnovsky, *J. Org. Chem.* **28**, 2934 (1963).

[2] G. Sosnovsky and S. -O. Lawesson, *Angew. Chem.* **76**, 218 (1964).

[3] G. Sosnovsky and S. -O. Lawesson, *Angew. Chem.* (Internat. edition) **3**, 269 (1964).

of the radiation of intense heat this lamp could not be immersed into the reaction mixture and had to be placed at a distance of 6–6½ inches from the reaction flask. The flask was made of a special Vycor glass which had a high transmittance to UV radiation. The reaction mixture was either composed of neat reactants or it contained a small quantity of benzene. The presence of benzene had no decisive effect upon the reaction. Benzene absorbs weakly at 200 mμ and 260 mμ, whereas t-butyl peracetate and t-butyl perbenzoate absorb at 205 mμ and 220 mμ, respectively. The more significant results of the photochemical investigation are listed in Table 1.

The reaction of t-butyl peracetate and t-butyl perbenzoate with low boiling ethers, such as ethyl ether, proceeds at a slow rate at the boiling point temperature of the ether. The reaction can be carried out at a faster rate at an elevated temperature in an autoclave. However, under these conditions the reaction is sometimes difficult to control and also some decomposition of the heat sensitive acyloxy derivatives can take place. The benzoyloxy derivative of ethyl ether, 1-ethoxyethyl benzoate, was first prepared by Cass[4] who used benzoyl peroxide as the benzoyloxylating agent. However, the peroxyester reaction is a more convenient method for the preparation of this compound. The copper ion catalyzed photochemical reaction proceeds below 35° at a faster rate than the thermal reaction. It has the advantage that no decomposition of the benzoyloxy derivative takes place. The reaction of t-butyl peracetate with ethyl ether produces similar results (Table 1). In the presence of copper ions only, this reaction proceeds at a slower rate than the copper ion catalyzed photochemical reaction, and after 408 hr about 90% of perester is still unreacted.

The preparation of the acyloxy derivatives of aliphatic and cyclic ethers is of interest because these compounds can be readily pyrolyzed at rather low temperatures (100–160°) to give vinyl ethers. Thus, l-ethoxyethyl benzoate when heated to 100° decomposes to give ethyl vinyl ether and benzoic acid. Similarly, 2-benzoyloxytetrahydrofuran can be thermally decomposed to give 2,3-dihydrofuran. This product was briefly described in an earlier paper.[5] Additional data are here presented. Since benzoyloxytetrahydrofuran can not be distilled without decomposition, the crude product is directly used for the preparation of 2,3-dihydrofuran. However, care must be exercised to remove, prior to pyrolysis, all volatile byproducts, in particular the t-butyl alcohol, which reacts readily at elevated temperatures with benzoyloxytetrahydrofuran to give 2-t-butoxytetrahydrofuran.[2,3] The yields of 2,3-dihydrofuran vary considerably since the compound is very reactive and polymerizes readily even in the presence of weak acid.[6] The b.p., IR spectrum and gas chromatographic analysis of our sample were identical with those of a sample prepared by the method of Dimroth and Pasedach,[6] and they were at difference with those of 3,4-dihydrofuran prepared by DePuy and Goeders by pyrolysis of 3-acetoxytetrahydrofuran.[7]

In contrast to the copper ion catalyzed reaction of ethers, the reaction of t-butyl peracetate with tetrahydrothiophene proceeded at a slow rate and the catalyst was rapidly inactivated. After 312 hr only a 13% yield of the desired product, 2-acetoxytetrahydrothiophene,[8] was obtained, and 50% of the peracetate was still unreacted.

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[4] W. E. Cass, *J. Amer. Chem. Soc.* **69**, 500 (1947).

[5] G. Sosnovsky, *Tetrahedron* **13**, 241 (1961).

[6] P. Dimroth and H. Pasedach, *Angew. Chem.* **72**, 865 (1960).

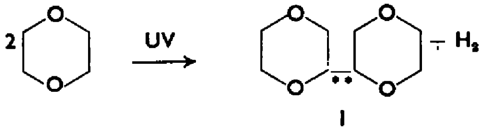
[7] C. H. DePuy and C. N. Goeders, *J. Org. Chem.* **28**, 1147 (1963).

[8] G. Sosnovsky, *Tetrahedron* **18**, 15 (1962).

TABLE 1. PHOTOCHEMICAL REACTIONS OF PERESTERS

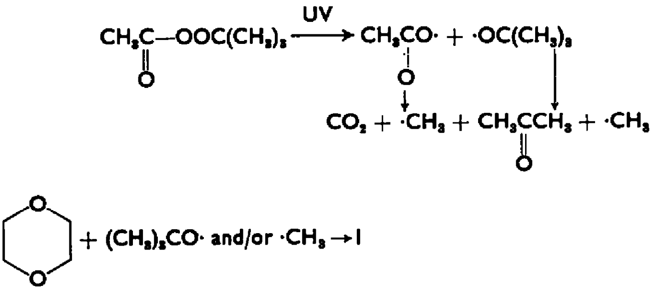
Substrate (mole)	t-Butyl perester (mole)	Reaction conditions					Product	Yield (%)
		Solvent (benzene)	Copper ions	UV light	Temp °C	hr		
Ethyl ether (1·00)	Peracetate (0·2)	+	+	+	30–32	91½	1-Ethoxyethyl acetate	73
Ethyl ether (1·00)	Peracetate (0·2)	+	−	+	30–32	240	Peracetate + 1-Ethoxyethyl acetate 3:1	—
Ethyl ether (1·45)	Perbenzoate (0·1)	+	+	+	30–32	96	1-Ethoxyethyl benzoate	77
Ethyl ether (1·45)	Perbenzoate (0·1)	−	+	−	28–32	408	Perbenzoate	89
Tetrahydrofuran (3·67)	Peracetate (0·92)	−	+	+	30–34	120	2-Acetoxytetrahydrofuran	75
Tetrahydrofuran (1·88)	Peracetate (0·32)	−	−	+	32–35	480	2-Acetoxytetrahydrofuran	25
Tetrahydrofuran (2·45)	Perbenzoate (0·2)	−	+	+	33–35	64½	2-Benzoyloxytetrahydrofuran	51·5
Tetrahydrothiophene (1·0)	Peracetate (0·3)	+	+	+	32–34	312	2-Acetoxytetrahydrothiophene + peracetate	13 50
1·4-Dioxane (1·13)	Peracetate (0·3)	−	+	+	33–35	144	Dioxanyl acetate	45
1·4-Dioxane (1·13)	Peracetate (0·3)	+	+	+	25–30	168	Dioxanyl acetate	92
1·4-Dioxane (1·13)	Peracetate (0·3)	+	+	−	25–30	168	Peracetate	83·5
1·4-Dioxane (1·13)	Peracetate (0·26)	−	−	+	32	312	Peracetate + Dioxanyl dioxane	56 20
Dimethylformamide (0·65)	Peracetate (0·3)	+	+	+	25–30	168	N-acetoxymethyl-N-methylformamide	42
Dimethylformamide (0·65)	Peracetate (0·3)	+	−	+	30–34	312	Peracetate	88
Cyclohexene (0·43)	Perbenzoate (0·1)	+	+	+	30–34	408	Cyclohex-1-en-3-yl benzoate	76
Cyclohexene (0·43)	Perbenzoate (0·2)	−	−	+	32–35	504	Perbenzoate + Cyclohex-1-en-3-yl benzoate	45·5 3·7

The copper ion catalyzed thermal reaction of t-butyl peracetate with dioxane proceeds smoothly at 85–90° to give dioxanyl dioxane, a water soluble product. This compound is also produced in high yield by the copper ion catalyzed photochemical reaction below 35°. However, when the reactants are stirred at 35° in the presence of copper ions but in the absence of UV light, 84% of peracetate remains unreacted (Table 1). A different result was obtained from the photochemical reaction at 35° in the absence of copper ions. No dioxanyl acetate was formed. Instead, large quantities of a gas, presumably a mixture of carbon dioxide and methane, unreacted peracetate, and a white crystalline solid were obtained. The white solid was first purified by sublimation. Subsequent fractional recrystallization yielded two products, melting at 132° and 157°. The combustion analyses, mol. wt determinations, and IR analyses leave no doubt that the two products are dimers of dioxane (I). The two dioxanyld ioxanes have two asymmetric carbon atoms and thus are the meso- and the D,L-isomers. No attempt was made either to resolve the enantiomers or to assign the configurations to these compounds. These compounds were obtained earlier by Pfordte[9] who irradiated dioxane with UV light in the absence of a peroxide. Pfordte proposed the following reaction scheme



I

Under the present reaction conditions the following reaction sequence seems to be more probable



The thermal decomposition of t-butyl peracetate also yields the dimers; however, the products are less pure than those obtained from the light catalyzed reaction.

In recent years it has been shown that amides undergo free radical reactions in the presence of peroxides or UV light.[10–14] Thus, Elad has achieved the photosensitized amidation of aromatic hydrocarbons with formamide.[14] Rieche *et al.*[10] Elad,[12,13] and Friedman and Shechter[11] have condensed various olefinic substrates with amides to give 1:1 adducts (II). Friedman and Shechter[11] reported that N,N-dimethylformamide reacts with n-octene-1 at 130° in the presence of di-t-butyl peroxide

[9] K. Pfordte, *Liebigs Ann.* **625**, 30 (1959).

[10] A. Rieche, E. Schmitz and E. Gründemann, *Angew. Chem.* **73**, 621 (1961).

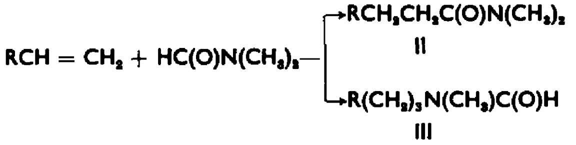
[11] L. Friedman and H. Shechter, *Tetrahedron Letters* No. 7, 238 (1961).

[12] D. Elad, *Proc. Chem. Soc.* 225 (1962).

[13] D. Elad, *Chem. Ind.* 362 (1962).

[14] D. Elad, *Tetrahedron Letters* No. 2, 77 (1963).

to give a mixture consisting of II and III



$$RCH = CH_2 + HC(O)N(CH_3)_2 \longrightarrow \begin{cases} RCH_2CH_2C(O)N(CH_3)_2 & \text{II} \\ R(CH_2)_3N(CH_3)C(O)H & \text{III} \end{cases}$$

In the absence of the olefine the decomposition of di-t-butyl peroxide in dimethylformamide yielded 72% of N,N'-diformyl-N,N'-dimethylethylene diamine, indicating a predominance of the $HCON(CH_3)CH_2\cdot$radical.[11]

Bamford and White[15] found that the decomposition of benzoylperoxide in dimethylformamide at 40–70° results in a 60% yield of N-benzoyloxymethyl-N-methylformide (IVa). This result shows again the predominance of the $HCON(CH_3)CH_2\cdot$ radical[15]

$$HC(O)N(CH_3)CH_2\text{–}OC(O)R$$

$$\text{IVa } R = C_6H_5$$

$$\text{IVb } R = CH_3$$

The structure of product IVa was established by an unequivocal synthesis and by hydrolysis of IVa which yielded benzoic acid, formaldehyde and methylamine.[15] Berglund and Lawesson[16] showed that IVa can be more conveniently prepared by the peroxyester reaction. Now it was found that the copper ion catalyzed photochemical reaction of t-butyl peracetate with N,N-dimethylformamide yields a product which is identical with that obtained by the thermal peroxyester reaction. By analogy with N-benzoyloxy-N-methyl derivative the structure of N-acetoxymethyl-N-methylformamide (IVb) wax assigned to this product.[1,2] This compound was recently obtained in a small yield by Ross *et al.*[17] by electrolysis of potassium acetate in N,N-dimethylformide. It was synthesized in a 90% yield by acetylating N-hydroxymethyl-N-methylformamide.[17] The physical data of this product are in agreement with those of our sample.

The photochemical reaction in the absence of copper ions proceeded at a much slower rate and most of the perester was unreacted even after 312 hr of illumination (Table 1).

The copper catalyzed photochemical reaction of t-butyl perbenzoate with cyclohexene proceeded at a slow rate (Table 1) to give the expected cyclohexenyl benzoate[18] in high yield. The catalyst was deactivated during the reaction. The cause of this deactivation is not known at the present time. The uncatalyzed reaction proceeded at a much slower rate and only traces of cyclohexenyl benzoate were detected.

A deviation from the general pattern of the copper ion catalyzed photochemical reactions of peresters was observed with cumene and with benzaldehyde.

Cumene reacts with t-butyl peracetate at 95–105° in the absence of a copper salt catalyst to give mainly a large volume of gas and 2,3-dimethyl-2,3-diphenylbutane (dicumyl). In the presence of a trace of cuprous bromide, the reaction yields 36%

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[15] C. H. Bamford and E. F. T. White, *J. Chem. Soc.* 1860 (1959).

[16] C. Berglund and S. -O. Lawesson, *Arkiv Kemi* **20**, 225 (1963).

[17] S. D. Ross, M. Finkelstein and R. C. Petersen, *J. Amer. Chem. Soc.* **86**, 2745 (1964).

[18] M. S. Kharasch, G. Sosnovsky and N. C. Yang, *J. Amer. Chem. Soc.* **81**, 5819 (1959).

α-cumyl acetate[2,3,19] with only small amounts of gas and dicumyl. The photochemical reaction in the presence of copper ions gave a small quantity of oily products which could not be identified. No α-cumyl acetate and no dicumyl were found.

Inconclusive results were also obtained with benzaldehyde. It was shown by Sosnovsky and Yang[20] that the reaction of benzaldehyde with t-butyl perbenzoate in the presence of copper ions yields benzoic anhydride, while the uncatalyzed reaction results in the formation of diphenylglycol dibenzoate. The photochemical reaction of benzaldehyde with t-butyl perbenzoate yielded a brown rosinlike material, but no benzoic anhydride.

EXPERIMENTAL

t-Butyl perbenzoate (neat liquid) and t-butyl peracetate (75% benzene solution) were obtained from Lucidol Division, Wallace and Tiernan, Inc. The CuBr used was an anhydrous, reagent-grade product, and the cupric 2-ethylhexoate a 1% benzene solution. Progress of the reactions was either followed by periodic IR analyses or by iodometric titrations.[21] All experiments were carried out in a N_2 atm. The reaction vessel was equipped with a stirrer and a reflux condenser and was connected to a gas meter. The photochemical reactions were carried out in a Vycor flask 7910. The UV source was an Original Hanau Quartz Lamp S81 provided with an aluminum reflector. For better control of heat the UV source was measured externally at that side of the flask which was exposed to the radiation. An immersion thermometer was provided for measuring the temp of the reaction mixture. All experiments were carried out below 35°. The b.ps and m.ps are uncorrected. The mol. ws of the liquids were determined cryoscopically in benzene, the mol. ws of solids were determined by Micro-Rast method using camphor as solvent.

1-*Ethoxyethyl acetate*. A mixture of ethyl ether (100 ml, 1·0 mole), t-butyl peracetate (57 ml of a 75% benzene solution, 0·3 mole) and cupric 2-ethylhexoate (24 ml of a 1% benzene solution) was boiled at reflux for 284 hr. No gas was evolved during this period. After removal of excess ether on a steam bath, the remaining oil was washed 3 times with 10 ml water, dried and distilled at red. press. The product obtained was: 1-ethoxy-ethyl acetate (25·2 g, 64%), b.p. 64–68°/68 mm, n_D^{25} = 1·3936 ν_{max} 1735 cm^{-1} (C=O). (Found: C, 54·60; H, 9·23; mol. wt. 129. $C_6H_{12}O_3$ requires: C, 54·53 H, 9·14%; mol. wt. 132).

1-*Ethoxyethyl benzoate* (a). A mixture of ethyl ether (250 ml), t-butyl perbenzoate (80 ml, 0·4 mole) and CuBr (0·1 g 0·35 mmole) was placed in a glass lined stainless steel autoclave. The temp of the mixture was raised in 3 hr to 70° (34 psi), and then in 4 hr to 90° (55 psi). The reaction mixture was kept at 85–90° for 2 hr. The cooled reaction mixture was extracted with 2N Na_2CO_3 to remove benzoic acid (6·3 g, 12·8%). The etheral solution was washed with water, dried (Na_2SO_4) and concentrated on a steam bath. The remaining oil was distilled at red. press. The product obtained was: 1-ethoxyethyl benzoate (48 g, 62%), b.p. 63–64°/0·2 mm, n_D^{25} 1·4869 (lit.[4] b.p. 63°/0·3 mm, n_D^{25} 1·4868), ν_{max} 1725 cm^{-1} (C=O). (Found: C, 68·33; H, 7·05 mol. wt. 189. Calc. for $C_{11}H_{14}O_3$: C, 68·02; H, 7·27%; mol. wt. 194).

1-*Ethoxyethyl benzoate* (b). A mixture of ethyl ether (200 ml, 1·9 moles), t-butyl perbenzoate (20 ml, 0·1 mole), and CuBr (0·1 g, 0·35 mmole) was kept boiling for 190 hr. After cooling the reaction mixture was worked up by the procedure of the preceding experiment. The product, 1-ethoxyethyl benzoate, (16·1 g, 82%) b.p. 77·5°/0·6 mm, n_D^{25} 1·4869 contained about 5% of t-butyl perbenzoate (by titration).

Pyrolysis of 1-ethoxyethyl benzoate

Vinyl ethyl ether. 1-Ethoxyethyl benzoate (48 g, 0·25 mole) was pyrolyzed at 155–171°. The volatile product was condensed in a trap cooled by a mixture of dry ice and isopropanol. The condensate was purified by distillation. The product obtained was: vinyl ethyl ether (14·2 g, 81%) b.p. 31–37°/735 mm, n_D^{25} 1·3738. The IR spectrum and the gas chromatogram was identical with that of a sample of an authentic product (Union Carbide Chem. Co.).

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[19] C. Walling and A. A. Zavitsas, *J. Amer. Chem. Soc.* **85**, 2084 (1963).

[20] G. Sosnovsky and N. C. Yang, *J. Org. Chem.* **25**, 899 (1960).

[21] L. S. Silbert and D. Swern, *Analyt. Chem.* **30**, 385 (1958).

Pyrolysis of 2-benzoyloxytetrahydrofuran

2,3-*Dihydrofuran.* 2-Benzoyloxytetrahydrofuran (28·0 g, 0·146 mole) was pyrolyzed at 130°/15 mm Hg. The volatile product was condensed in a trap cooled by a mixture of dry ice and isopropanol. The product obtained after repeated distillation was: 2,3-dihydrofuran (2·9 g, 29%), b.p. 54–55°/745 mm, n_D^{25} 1·4198. The pyrolysis residue in the flask was extracted with 2N Na_2CO_3 to give benzoic acid (17 g, 96%) plus an oil (2·8 g) which was not further investigated. (Found: C, 68·42; H, 8·58; mol. wt. 71. Calc. for C_4H_6O: C, 68·54; H, 8·63%; mol. wt. 70). The IR and gas chromatographic analysis of this sample was identical with that of a sample obtained from BASF, Germany (b.p. 54–55°/745 mm; n_D^{25} 1·4187), prepared by a different method.[6]

N-*Acetoxymethyl*-N-*methylformamide.* t-Butyl peracetate (57 ml of a 75% benzene solution, 0·3 mole) was added over a period of 4 hr to a mixture of N,N-dimethylformamide (50 ml, 0·64 mole) and CuBr (0·1 g, 0·35 mmole) maintained at 90°. After 36 hr of heating (no gases were evolved) the reaction mixture was distilled at red. press. The products obtained were: dimethylformamide (25 g, 0·43 mole), b.p. 40–41°/9 mm, and N-acetoxymethyl-N-methylformamide (10 g, 25%), b.p. 66°/0·1 mm, n_D^{25} 1·4412, ν_{max} 1725 cm^{-1} (C=O). (Found: C, 46·13; H, 7·27; N. 10·79; mol. wt. 135. $C_5H_9O_3N$ requires: C, 45·79; H, 6·92%; N, 10·68; mol. wt. 131).

Dioxanyl acetate. t-Butyl peracetate (57 ml of a 75% benzene solution, 0·3 mole) was added over a period of 5 hr to a mixture of 1,4-dioxane (100 ml, 1·13 mole) and CuBr (0·1 g, 0·35 mmole) maintained at 85–90°. The reaction mixture was distilled at red. press. After removal of excess dioxane at 15 mm Hg, the product, dioxanyl acetate (31·2 g, 73%) was obtained as water soluble oil: b.p. 55–58°/0·1 mm, n_D^{25} = 1·4390, ν_{max} 1735 cm^{-1} (C=O). (Found: C, 49·73; H, 6·98; mol. wt. 147. $C_6H_{10}O_4$ requires: C, 49·35; H, 6·90%; mol. wt. 146).

Thermal decomposition of t-butyl peracetate in dioxane

Dioxanyl dioxane. A mixture of 1,4-dioxane (100 ml, 1·13 mole) and t-butyl peracetate (19 ml of a 75% benzene solution, 0·1 mole) was heated at 90–95° for 77 hr. The reaction mixture was concentrated at red. press., b.p. 35°/63 mm-98°/0·7 mm. A liquid (88 ml) was collected, which according to its boiling behaviour, refractive index (n_D^{25} = 4200) and the IR spectrum (ν_{max} 1785, 1735, 1720 cm^{-1} (C=O), ν_{max} 3450 cm^{-1} (–OH), ν_{max} 1375, 1355 cm^{-1} (–C(CH$_3$)$_3$) consists of a mixture of t-butyl alcohol, acetic acid, dioxane, benzene, and dioxanyl acetate. The residue in the flask gave a white sublimable solid (1·8 g) which could be separated by fractional crystallization into two dioxanyl dioxane dimers, m.p. 157° and m.p. 133°, and a rosin like light yellow brittle solid (3 g) which did not sublime. It was not further investigated. The IR spectra of the dioxanyl dioxane dimers were identical with those obtained by the photochemical method.

α-Cumyl acetate. t-Butyl peracetate (57 ml of a 75% benzene solution, 0·3 mole) was added to a mixture of cumene (60 g, 0·5 mole) and CuBr bromide (0·1 g, 0·35 mmole) at 90–105°. The peracetate was consumed in 24 hr. During this time 2 l. gas was evolved. The cooled reaction mixture was washed with 2N Na_2CO_3 and water, dried (Na_2SO_4) and distilled. The products obtained were: unreacted cumene (29 g), b.p. 50°/22 mm, n_D^{25} 1·4912, and α-cumyl acetate[8,9,10] (19 g, 36%), b.p. 93°/10 mm, n_D^{25} 1·4950, 1725 cm^{-1} (C=O). Gas chromatographic analysis showed only one large peak. (Found: C, 74·30; H, 8·05: mol. wt., 178. Calc. for $C_{11}H_{14}O_2$: C, 74·13; H, 7·92%; mol. wt., 178). The residue gave 4 g of dicumyl, m.p. 119°, plus 14 g of an oil which was not further investigated.

Reaction of t-butyl peracetate with cumene in the absence of cuprous bromide

Dicumyl. t-Butyl peracetate (57 ml of a 75% benzene solution, 0·3 mole) was added over 4 hr to cumene (60 g, 0·5 mole) at 95–105°. After 74 hr of heating, the reaction mixture contained only traces of the perester (1·2 g). During the reaction 11 l. gas was evolved. From the reaction mixture dicumyl (31 g, 66% based on recovered cumene, m.p. 119°) was isolated as the only identifiable product.

Photochemical reactions of peresters in the presence of copper ions

t-Butyl perbenzoate with ethyl ether. A mixture of ethyl ether (150 ml, 1·45 moles), t-butyl perbenzoate (20 ml, 0·1 mole) and cupric 2-ethylhexoate (24 ml of a 1% benzene solution) was irradiated with UV light for 96 hr maintaining the temp at 30–32°. The reaction mixture was extracted with 2N Na_2CO_3 to remove benzoic acid (0·9 g). The solution was washed with water, dried (Na_2SO_4)

and concentrated at 15 mm Hg. The remaining oil was distilled at red. press. The product obtained was: 1-ethoxyethyl benzoate (15·1 g, 77%), b.p. 50–54, 0·02 mm, n_D^{25} 1·4862, ν_{max} 1725 cm^{-1} (C=O), identical with an authentic sample obtained in a preceding experiment.

t-Butyl peracetate with ethyl ether. A mixture of ethyl ether (100 ml, 1·0 mole), t-butyl peracetate (38 ml of a 75% benzene solution, 0·2 mole) and cupric 2-ethyl hexoate (24 ml of a 1% benzene solution) was irradiated with UV light for 91½ hr maintaining the temp at 30–32°. No gas was evolved during this period. The reaction mixture was distilled on a steam bath to remove benzene, t-butyl alcohol, and ethyl ether. The remaining oil was washed with a 2N Na_2CO_3 and water, dried and distilled at red. press. The product obtained was: 1-ethoxyethyl acetate (19 g, 73%) b.p. 58°/63 mm, n_D^{25} = 1·3928, ν_{max} 1735 cm^{-1} (C=O). (Found: mol. wt. 134. Calc. for $C_6H_{12}O_3$: mol. wt. 132). Residue 1·6 g.

t-Butyl peracetate with N,N-*dimethylformamide.* A mixture of N,N-dimethylformamide (50 ml, 0·64 mole), t-butyl peracetate (57 ml of a 75% benzene solution, 0·3 mole) and cupric 2-ethylhexoate (24 ml of a 1% benzene solution was irradiated with UV-light for 168 hr, maintaining the temp at 25–30°. No gas was evolved during this period. The reaction mixture was distilled on a steam bath. After removal of a mixture of benzene and t-butyl alcohol, the remaining oil was distilled under red. press. The products obtained were: dimethylformamide (31 g, 54%) b.p. 39°/10 mm, n_D^{25} 1·4260. N-acetoxymethyl-N-methylformamide[17] (15·3 g, 42%), b.p. 55–57°/0·08 mm, n_D^{25} 1·4416, ν_{max} 1730 cm^{-1} (C=O). The IR spectrum was identical with that of an authentic sample. The residue (6·3 g) was not further investigated.

t-Butyl peracetate with tetrahydrofuran. A mixture of tetrahydrofuran (300 ml, 3·67 mole), t-butyl peracetate (121 ml, neat liquid, 0·92 mole) and CuBr (0·1 g, 0·7 mmole) was irradiated with UV light for 120 hr at 30–34°. No gas was evolved during this period. The reaction mixture was distilled on a steam bath to remove the excess of tetrahydrofuran. The remaining oil was distilled at red. press. The products obtained were: a light fraction (8·6 g) b.p. 40–65°/18 mm. The IR spectrum indicated that this liquid was probably a mixture of t-butyl alcohol, acetic acid and acetoxytetrahydrofuran. It was not further investigated. The remaining oil was 2-acetoxytetrahydrofuran (90·5 g, 75%) b.p. 83°/22 mm, n_D^{25} 1·4290 ν_{max} 1730 cm^{-1} (C=O). (Found: C, 55·41; H, 7·88. $C_6H_{10}O_3$ requires: C, 55·37; H, 7·74%).

t-Butyl perbenzoate with tetrahydrofuran. A mixture of tetrahydrofuran (200 ml, 2·45 moles), t-butyl perbenzoate (40 ml, 0·2 mole) and CuBr (0·2 g, 0·7 mmole) was irradiated with UV light for 64·5 hr at 33–35°. No gas was evolved during this period. The reaction mixture was washed with 2N Na_2CO_3 to extract benzoic acid (6·2 g, 25·5%). The remaining solution was washed with water, dried (Na_2SO_4) and concentrated at red. press. (15 mm Hg). The remaining oil was 2-benzoyloxytetrahydrofuran (19·5 g, 51·5%) ν_{max} 1720 cm^{-1} (C=O). The IR spectrum was identical with that of a sample prepared by the thermal method. The product could not be distilled without decomposition. It was used in the preparation of 2,3-dihydrofuran.

t-Butyl peracetate with 1,4-*dioxane* (*in the absence of benzene*). A mixture of dioxane (100 ml 1·13 moles), t-butyl peracetate (39·6 g, neat liquid, 0·3 mole) and cupric 2-ethyl hexoate (0·2 g, 0·56 mmole) was irradiated with UV light for 144 hr at 33–35°. No gas was evolved during this period. The product, dioxanyl acetate (19·6 g, 45%) was obtained by distillation of the reaction mixture at red. press. b.p. 52°/0·05 mm, n_D^{25} = 1·4390, ν_{max} 1735 cm^{-1} (C=O). The IR spectrum was identical with that of a sample prepared by the thermal method. The residue (12·8 g), a viscous oil, was not further investigated.

t-Butyl peracetate with 1,4-*dioxane* (*in the presence of benzene*). A mixture of dioxane (100 ml, 1·13 moles) t-butyl peracetate (57 ml of a 75% benzene solution, 0·3 mole) and cupric 2-ethylhexoate (0·2 g) was irradiated with UV light maintaining the temp at 25–30°. The reaction mixture was stirred for 168 hr. No gas was evolved during this period. The reaction mixture was distilled at red. press. to give an oil, (48 g) b.p. 100–105°/15 mm, plus a higher boiling residue (4 g). The oil was redistilled several times. The obtained product was: dioxanyl acetate (40 g, 92%) b.p. 51–53°/ 0·1 mm; n_D^{25} 1·4390; ν_{max} 1725 cm^{-1} (C=O). The IR spectrum was identical with that of an authentic sample.

t-Butyl perbenzoate with cyclohexene. A mixture of cyclohexene (44 ml, 0·43 mole), t-butyl perbenzoate (20 ml, 0·1 mole) and cupric 2-ethyl hexoate (24 ml of a 1% benzene solution) was irradiated with UV light for 408 hr at 30–34°. After 360 hr it was necessary to add a portion of fresh catalyst (CuBr 0·1 g, 0·35 mmole) since the old catalyst became ineffective and the reaction slowed down substantially. During the reaction no gas was evolved. The reaction mixture was washed with 2N Na_2CO_3 to remove benzoic acid (trace). The solution was then washed with water, dried and distilled at 75 mm Hg to remove a mixture of cyclohexene and benzene. The remaining oil was distilled at red. press. The product obtained was: cyclohex-1-en-3-yl benzoate (15·5 g, 76%) b.p. 94°/0·15 mm, ν_{max} 1720 cm^{-1} (C═O), (lit.[19] b.p. 100–5°/0·25 mm). (Found: mol. wt. 190. Calc. for $C_{13}H_{14}O_2$: mol. wt. 202). The IR spectrum was identical with that of an authentic sample.

t-Butyl peracetate with cumene. A mixture of cumene (100 ml, 1·0 mole), t-butyl peracetate (35 ml of a 75% benzene solution, 0·183 mole) and CuBr (0·2 g, 0·7 mmole) was irradiated with UV light for 240 hr at 30–34°. The IR analysis showed no cumyl acetate. The irradiation was continued after addition of cupric 2-ethylhexoate (24 ml of a 1% benzene solution). After 312 hr of total irradiation time the reaction mixture was washed with Na_2CO_3aq and water, dried (Na_2SO_4 and distilled. The products obtained were: a mixture of cumene and t-butyl peracetate, b.p. 41–44°/14–17 mm. Titration showed 20·4 g (85%) of unreacted peracetate. Distillation of the remaining liquid produced a residue (4·4 g) and a product (5·8 g), b.p. 87–89°/10–12 mm, n_D^{25} 1·5170 ν_{max} 1680″ (C═O), ν_{max} 3450 (OH) which could not be identified. No α-cumyl acetate and no dicumyl were found.

t-Butyl perbenzoate with benzaldehyde. A mixture of benzaldehyde (106 ml, 1·0 mole), t-butyl perbenzoate (20 ml, 0·1 mole) and CuBr (0·2 g, 0·7 mmole) was irradiated with UV light for 46 hr at 34°. No gas was evolved during the reaction. The reaction mixture was washed with Na_2CO_3aq to extract benzoic acid (trace). The mixture was further washed with water, dried (Na_2SO_4) and distilled at red. press. The products obtained were: benzaldehyde (65 ml), b.p. 45–50°/0·1–0·2 mm, n_D^{25} 1·4528, and a brown liquid (29·4 g) which could not be distilled at 170°/0·2 mm. This liquid solidified to a rosin-like solid, ν_{max} 1775 cm^{-1}, 1725 cm^{-1} (C═O). This product was not further investigated. The reaction produced no benzoic acid anhydride, b.p. 140°/0·2 mm.[20]

t-Butyl peracetate with tetrahydrothiophene. A mixture of *tetrahydrothiophene* (90 ml, 1·0 mole), t-butyl peracetate (57 ml of a 75% benzene solution, 0·3 mole) and cupric 2-ethylhexoate (24 ml of a 1% benzene solution) was irradiated with UV light for 312 hr at 32–34°. At the start the reaction proceeded smoothly; however, it soon began to slow down and for the last 168 hr no progress was observed. No gas was evolved during this period. The reaction mixture was washed with Na_2CO_3aq and water, and dried (Na_2SO_4). The IR analysis indicated the presence of about 50% of unreacted perester. The reaction mixture was concentrated at red. press. (38–40 mm) to remove a mixture of starting materials. From the remaining oil the product obtained was: 2-acetoxytetrahydrothiophene (5·8 g, 13%, calc. on the starting material; 56% calc. on the reacted tetrahydrothiophene), b.p. 56–8°/0·1 mm, n_D^{25} = 1·4882. The IR spectrum was identical with that of an authentic sample. Residue (5 g) was not further investigated.

Photochemical reactions of peresters in the absence of copper ions

t-Butyl peracetate with ethyl ether. A mixture of ethyl ether (100 ml, 1·0 mole) and t-butyl peracetate (38 ml of a 75% benzene solution, 0·2 mole) was irradiated with UV light for 240 hr at 30–32°. During this period no gas was evolved. The reaction mixture was washed with water, dried and distilled at 75 mm Hg to remove a mixture of ether and benzene. The remaining oil was distilled at red. press. to give an unseparable mixture of t-butyl peracetate and 1-ethoxyethyl acetate (18·2 g) b.p. 22–32°/8 mm n_D^{25} 1·4028, ν_{max} 1775 cm^{-1}, 1735 cm^{-1} (C═O). The ratio of the perester to the ester was about 3:1 (IR analysis).

t-Butyl peracetate with N,N-*dimethylformamide.* A mixture of dimethyl formamide (50 ml, 0·64 mole) and t-butyl peracetate (57 ml of a 75% benzene solution, 0·3 mole) was irradiated with UV light for 168 hr at 30–34°. No gas was evolved during this period. The IR spectrum indicated the presence of large amounts of unreacted t-butyl peracetate (34·9 g, 88%). The reaction mixture was washed with water, dried and distilled. The product obtained was: t-butyl peracetate (19 g 48%) b.p. 59°/22 mm, n_D^{25} 1·4036. The IR spectrum identical with that of an authentic sample.

t-Butyl peracetate with 1,4-*dioxane* (*dioxanyl dioxane*). A mixture of 1,4-dioxane (100 ml 1·13 moles) and t-butyl peracetate (38 g, neat liquid, 0·26 mole) was irradiated with UV light for 312 hr at 32°. During this period gas was evolved (3500 ml) which was not further investigated. The reaction mixture contained a large amount of unreacted t-butyl peracetate (21·4 g, 56%). The reaction mixture was concentrated at red. press. (b.p. 36°/65 mm–48°/14 mm). The distillate (n_D^{25} 1·4132) consisted of a mixture of t-butyl alcohol, acetic acid, t-butyl peracetate and dioxane. The contents of the flask solidified. The white solid could be sublimed in vacuum at 90–110°/0·1 mm. The sublimate was soluble in water, acetone and ether. It was little soluble in pet. ether. Fractional recrystallization using a mixture of acetone and pet. ether yielded two products: A(3 g), m.p. 157° (lit.[9] 157°). (Found: C, 55·21; H, 8·40; mol. wt., by Micro-Rast, 176. Calc. for $C_8H_{14}O_4$: C, 55·15; H, 8·10%; mol. wt. 174). B(1·5 g), m.p. 131–132° (lit.[9] 131°). (Found: C, 55·06; H, 8·28; mol. wt., by Micro-Rast, 178. Calc. for $C_8H_{14}O_4$; C, 55·15; H, 8·10%; mol. wt. 174). The yield of the combined dioxanyl dioxane dimers A and B was 20%, calculated on the consumed perester. One product is the meso and the other is the D,L isomer. No attempt was made either to resolve the enantiomers or to assign the configurations to these products.

t-Butyl peracetate with tetrahydrofuran. A mixture of tetrahydrofuran (150 ml, 1·88 mole) and t-butyl peracetate (42 g, neat liquid, 0·32 mole) was irradiated with UV light for 480 hr at 32–35°. No gas was evolved during this period. The reaction mixture was distilled on a steam bath to remove tetrahydrofuran. The remaining liquid was distilled at red. press. The products obtained were: a liquid (10 ml) b.p. 35–55°/22 mm. This liquid was washed with water, dried and redistilled (3·7 g) b.p. 57°/22 mm, n_D^{25} 1·4150. The IR spectrum indicated that this liquid is a mixture of t-butyl peracetate (1·7 g by titration) ν_{max} 1775 cm^{-1} (C=O), and 2-t-butoxytetrahydrofuran ν_{max} 1385, 1365 cm^{-1} (C=O). The remaining oil was 2-acetoxytetrahydrofuran (10·5 g, 25%) b.p. 80°/22 mm ν_{max} 1735 cm^{-1} (C=O). (Found: mol. wt. 131. Calc. for $C_6H_{10}O_3$: mol. wt. 130). The IR spectrum identical with that of an authentic product. Residue 1·7 g.

t-Butylperbenzoate with cyclohexene. A mixture of cyclohexane (44 ml, 0·43 mole) and t-butylperbenzoate (40 ml, 0·2 mole) was irradiated with UV light for 504 hr at 32–35°. During this period 400 ml of gas evolved, which was not further investigated. The IR spectrum showed strong peresters carbonyl absorption: ν_{max} 1770 cm^{-1} (C=O), 45·5% of perester was found by titration. The reaction mixture was washed with Na_2CO_3aq to extract benzoic acid (0·2 g). The solution was washed with water, dried and distilled at 757 mm Hg to remove cyclohexene (25 ml) b.p. 80°/757 mm; n_D^{25} 1·4440. The remaining oil was distilled at red. press. The products obtained were: t-butyl perbenzoate (12 g, 0·6 mole), b.p. 62–69°/0·07–0·1 mm, ν_{max} 1770 cm^{-1} (C=O). The IR spectrum identical with that of an authentic sample. Heating of the remaining oil to 200° produced: cyclohex-1-en-3-yl benzoate (1·5 g, 3·7%), ν_{max} 1720 cm^{-1} (C=O), contaminated with a small amount of t-butyl perester, ν_{max} 1770 cm^{-1} (C=O). The IR spectrum identical with that of an authentic sample. Residue 2·1 g.

Reactions of peresters in the presence of copper ions but in the absence of UV radiation

t-Butyl perbenzoate with ethyl ether. A mixture of ethyl ether (150 ml, 1·45 mole), t-butyl perbenzoate (20 ml, 0·1 mole) and cupric 2-ethyl hexoate (24 ml of a 1% benzene solution) was stirred for 408 hr at 30–32°. No gas was evolved during this period. The reaction mixture was washed with a 2N Na_2CO_3 and water, dried (Na_2SO_4) and concentrated at red. press. The remaining oil consisted mainly of unreacted perbenzoate (17·5 g, 89% recovery) and small amounts of 1-ethoxyethylbenzoate, ν_{max} 1720 cm^{-1} (C=O). The IR spectra identical with those of authentic samples.

t-Butyl peracetate with 1,4*-dioxane.* A mixture of dioxane (100 ml, 1·13 moles), t-butyl peracetate (57 ml of a 75% benzene solution, 0·3 mole) and cupric 2-ethylhexoate was stirred for 168 hr maintaining the temp at 25–30°. No gas was evolved during this period. The reaction mixture was distilled under red. press. Only the starting materials were obtained: dioxane (67 g) b.p. 40°/65 mm, and t-butyl peracetate (32·8 g, 83·5%), b.p. 32°/8 mm. The IR spectrum was identical with that of an authentic sample.

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