with three 150-ml. quantities of carbon tetrachloride. The carbon tetrachloride was evaporated and the residue was extracted with 75 ml. of hot water. After decanting and cooling, white crystals resulted. Upon filtering and drying, 60 mg. of material melting at 110–117° was isolated. The total crude benzoic acid isolated corresponded to a 5% yield. Vacuum sublimation gave material with m.p. 119.5–121.0°.

The solid material which was insoluble in carbon tetrachloride was heated and stirred for 2 hr. in ethanol. After filtering and cooling, 0.2 g. of white crystals was isolated. An additional 0.11 g. was obtained as second and third crops. This crude yield (19%) of terephthalic acid was further purified by vacuum sublimation.

Oxidation of 4-Nitro-4'-methylbibenzyl.—To a solution of 75 ml. of saturated potassium permanganate containing 0.5 g. of potassium hydroxide was added 140 mg. (0.58 mmole) of 4-nitro-4'-methylbibenzyl-C[14]. This mixture was stirred at reflux for 120 hr. The basic solution was acidified with 20% hydrochloric acid, filtered, and the manganese dioxide was extracted with two 50-ml. quantities of 10% sodium hydroxide. Acidification of the solution gave 15 mg. of white powder. The acidified filtrates were combined and extracted with two 200-ml. quantities of ether. The ether was evaporated to 50 ml. and extracted with 50 ml. of 10% sodium hydroxide. This yielded 30 mg. of solid material upon acidification and filtration. All of the solid material was combined and extracted with three 50-ml. portions of ether. When the ether was evaporated to dryness, approximately 2–3 mg. of oily material remained. The solid which remained after ether extraction was extracted with two 30-ml. quantities of hot ethanol. Evaporation of the ethanol extracts and cooling resulted in a first crop of white crystals (approximately 10 mg.); further concentration gave 4 mg., and evaporation to dryness yielded an additional 3 mg. of material. The first crop of crystals would not sublime, but the second two crops yielded 4 mg. of terephthalic acid after sublimation. p-Nitrobenzoic acid was not isolated.

Alkylation of Naphthalene.—A solution of 12.8 g. (0.1 mole) of naphthalene in 150 ml. of benzene was stirred at 0° while 13.2 g. (0.1 mole) of aluminum chloride and 14.0 g. (0.1 mole) of 2-phenylethyl-1-C[14] chloride in 15 ml. of benzene were added. The addition required 6 min. and the mixture was stirred for a total time of 30 min. at 0–5°, then poured onto ice. The benzene layer was washed thoroughly, dried with calcium chloride, and distilled. After removal of benzene and naphthalene at reduced pressure, 1.5 g. (19%) of the product, b.p. 140–144° (2.5 mm.), was obtained. Recrystallization from alcohol and from petroleum ether to constant specific activity gave material of 132 × 10³ c.p.m./mmole.

Chromic Acid Oxidation.—To a mixture of 10 ml. of water, 5.5 ml. of concentrated sulfuric acid, and 4.5 g. (15 mmoles) of potassium dichromate there was added 0.16 g. (0.7 mmole) of reaction product. Nitrogen was used to flush the lines which led to a Dry Ice-cooled water trap and a liquid nitrogen trap; after addition the mixture was heated to reflux for 3 hr. The carbon dioxide in the nitrogen trap was purified by transfers on a vacuum line then counted by proportional counting in the gas phase.[39] The activity was 61.3 × 10² c.p.m./mmole, compared with an activity of 132 × 10³ ÷ 11, or 120 × 10² c.p.m./mmole, to be expected if all of the carbon-14 were in the β-position. After dilution, the oxidation mixture was extracted with ether and the ether solution was extracted with 10% sodium hydroxide. The benzoic acid obtained by acidification was in turn extracted with ether; after drying and removal of the solvent, two vacuum sublimations gave material of 64.2 × 10³ c.p.m./mmole, compared with 132 × 10³ c.p.m./mmole to be expected if all of the carbon-14 were in the α-position.

Alkylation of Phenol.—In preliminary investigations of the reaction of 2-phenylethyl chloride (0.1 mole) with phenol (0.12 mole) and aluminum chloride (0.24 mole), no reaction was noted at 25° in nitroethane, nitrobenzene, or n-heptane solution. Slow evolution of hydrogen chloride was noted at 180° when excess phenol was used as the solvent. A mixture of 56.5 g. (0.6 mole) of phenol, 18 g. (0.127 mole) of 2-phenylethyl-1-C[14] chloride (282 × 10³ c.p.m./mmole), and 0.3 g. of aluminum chloride was heated at 180–190° for 78 hr. After cooling, the mixture was dissolved in ether and washed with dilute hydrochloric acid. After distillation of the ether, phenol was separated by distillation from a Claisen flask (b.p. 95° at 35 mm.). The cooled solid residue was dissolved in dilute sodium hydroxide solution, washed with ether, treated with decolorizing carbon, and filtered. Addition of hydrochloric acid at 0° gave 16.8 g. (66%), m.p. 70–75°, 240 × 10³ c.p.m./mmole. Both the melting point and infrared spectra indicated that this product was a mixture, including ortho, para, and probably some meta isomers. Oxidation with chromic acid gave carbon dioxide with activity 15.4 × 10³ c.p.m./mmole, compared with an activity of 240 × 10³ ÷ 7 or 34.3 × 10³ c.p.m./mmole to be expected if all the carbon-14 were in the β-position. The acid fraction, obtained as previously described, except that sodium bicarbonate rather than sodium hydroxide was used, gave benzoic acid which, after sublimation, had m.p. 120° and an activity of 118 × 10³ c.p.m./mmole.

(39) See footnote a in Table I.

Anchimerically Accelerated Bond Homolysis. IV.[1] Participation of a Neighboring Olefinic Double Bond in the Decomposition of a t-Butyl Perester

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First-order rate constants for the decompositions of a series of o-vinyl-substituted benzoyl peroxides and t-butyl perbenzoates have been determined. All compounds studied decompose faster than unsubstituted benzoyl peroxide or, in the case of the peresters, t-butyl perbenzoate. The accelerations are ascribed to neighboring group participation by the olefinic groups in the homolytic cleavage of the O–O bond. Solvent and substituent effects support the postulated charge separation in the transition state. Products isolated from one of the peresters and one of the peroxides are compatible with the proposed bonding interaction in the transition state leading to free-radical fragments.

Previous studies[3,4] have shown that the first-order rate constants observed in the thermal decomposition of o-methylthio-, o-iodo-, and o-phenylthio-substituted t-butyl perbenzoates are unusually large. This acceleration has been attributed to a stabilization of the transition state leading to radical intermediates by means of a bonding interaction between the perester group and the neighboring group. The postulation of charge separation in the transition state for the decomposition of the o-phenylthio perester has been well supported by studies of the variation in the first-order

(1) For paper III, see D. L. Tuleen, W. G. Bentrude, and J. C. Martin, *J. Am. Chem. Soc.*, **85**, 1938 (1963).

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rate constants with substituents,[5] solvent ionizing power,[5,6] and ionic strength of the decomposition medium.[5]

During the course of this work Lamb and co-workers[7] reported kinetic evidence for an acceleration of the first-order decomposition of *trans*-γ-benzylidenebutyryl peroxide, presumably involving an interaction with the olefinic double bond. The rate of decomposition of this diacyl peroxide is also dependent on solvent composition, varying in a manner qualitatively correlated with solvent ionizing power. The decompositions of the *t*-butyl perester[8] and the diacyl peroxide[9] of *endo*-norbornene-5-carboxylic acid give lactone products which may be a result of some assisted cleavage of the O–O bonds.

This paper reports the synthesis and complete results of kinetic studies on the decompositions of peresters I and II, peroxides III–VIII, and the products of the decompositions of I and VI in chlorobenzene solution. The results of these studies support the previously
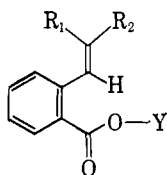
    I, $R_1 = R_2 = C_6H_5$; $Y = OC(CH_3)_3$
    II, R_1R_2C = fluorenylidene; $Y = OC(CH_3)_3$
    III, $R_1 = R_2 = p\text{-}NO_2C_6H_4$; $Y = C_6H_5CO_2$
    IV, $R_1 = H$; $R_2 = C_6H_5$; $Y = C_6H_5CO_2$
    V, $R_1 = H$; $R_2 = m\text{-}NO_2C_6H_4$; $Y = C_6H_5CO_2$
    VI, $R_1 = H$; $R_2 = p\text{-}NO_2C_6H_4$; $Y = C_6H_5CO_2$
    VII, $R_1 = H$; $R_2 = p\text{-}NOC_6H_4$; $Y = p\text{-}NO_2C_6H_4CO_2$
    VIII, $R_1 = H$; $R_2 = p\text{-}NO_2C_6H_4$; $Y = p\text{-}CH_3OC_6H_4CO_2$

mentioned[6] conclusion (for compound I) that neighboring olefinic groups can participate in the acceleration of the O–O bond cleavage in a manner formally identical with that postulated[3] for the neighboring sulfur in the decomposition of *t*-butyl o-(phenylthio)perbenzoate.

Experimental[10]

Materials.—The purification of chlorobenzene, pentane, pyridine, and *t*-butyl hydroperoxide and the preparation of galvinoxyl have been described.[3]

o-(2,2-Diphenylvinyl)benzoic Acid.—A Grignard sequence similar to that described by DeTar[11] was used to prepare o-(2,2-diphenylvinyl)bromobenzene, m.p. 75–76° (63%).

Anal. Calcd. for $C_{20}H_{15}Br$: C, 71.66; H, 4.50. Found: C, 71.92; H, 4.66.

A solution of tetrahydrofuran (150 ml.) containing o-(2,2-diphenylvinyl)bromobenzene (80 g., 0.23 mole) was added to a flask containing tetrahydrofuran (30 ml.) and magnesium turnings (5.3 g., 0.23 g.-atom). Addition of the bromide was complete in 30 min. after the reaction was initiated and the mixture was boiled for an additional 2.5 hr. and poured into a Dry Ice–ether slurry. The acid was recrystallized from dilute acetic acid to yield 40 g., 0.14 mole, 56%, m.p. 166–168°, lit. m.p. 169°.[12]

The infrared and n.m.r. spectra were identical with those of the same acid prepared in 5% yield by the method of Loewenthal and Pappo.[12] The acid chloride was prepared by refluxing the acid in excess thionyl chloride for 2 hr. (70%, m.p. 115–116.5°).

Anal. Calcd. for $C_{21}H_{51}ClO$: C, 79.14; H, 4.71. Found: C, 78.87; H, 4.96.

t-Butyl **o-(2,2-Diphenylvinyl)perbenzoate (I).**—This perester was prepared by the published procedure[3] using ether solvent. Recrystallization from pentane gave a 42% yield of perester, a white solid, m.p. 74–75°.

Anal. Calcd. for $C_{25}H_{24}O_3$: C, 80.63; H, 6.54. Found: C, 80.84; H, 6.48.

o-Carboxybenzalfluorene.—The ψ-methyl ester of o-phthaladehydic acid (45 g., 0.27 mole) was boiled for 12 hr. in a methanol solution of fluorene (45 g., 0.30 mole) and sodium methoxide (from 6.9 g., 0.30 g.-atom, of sodium) under nitrogen.[13] The solvent was evaporated and the residue was dissolved in water and extracted with chloroform and ether. Acidification of the aqueous phase and recrystallization of the precipitated solid from ethanol gave 55 g. (0.16 mole, 60%) of the pure acid, m.p. 187–189°.

Anal. Calcd. for $C_{21}H_{14}O_2$: C, 84.59; H, 4.79. Found: C, 84.61; H, 4.83.

The acid was converted in 73% yield to the acid chloride by boiling with thionyl chloride for 1 hr.

t-**Butylperoxy o-Carboxybenzalfluorene (II).**—Treatment of the acid chloride by the same' procedure gave a 16% yield of the pure perester, m.p. 76–78°.

Anal. Calcd. for $C_{25}H_{22}O_3$: C, 81.05; H, 5.99. Found: C, 80.94; H, 6.11.

trans-**Stilbene-2-carboxylic Acid.**—This acid was prepared by the literature method[10] in 48% yield, m.p. 162.5–163° (lit.[10] m.p. 158–160°).

Wittig Reaction.—o-(Carbomethoxy)benzyltriphenylphosphonium bromide was prepared by the addition o-(carbomethoxy)-benzyl bromide to a benzene solution of triphenylphosphine. The solid phosphonium salt was added to a stirred solution of the reaction product of sodium hydride in dimethyl sulfoxide.[14] To the resulting bright orange solution was added the appropriate carbonyl compound (p-nitrobenzaldehyde, m-nitrobenzaldehyde, or p,p'-dinitrobenzophenone) in solid form. The exothermic reaction resulted in a color change from orange to green. The solution was stirred under nitrogen for 2 hr., the mixture was poured onto ice–hydrobromic acid, and the precipitated mass was recrystallized. The crude yield of the methyl esters obtained in this way varied from 53–87%. These esters were converted to the acids by basic hydrolysis. The melting points and analytical data for these compounds are given in Table I. The assignment of geometry to the products isolated from these reactions, when aldehydes were used, was made on the basis of the n.m.r. spectra (*cis* isomers, doublet at τ 3.4; *trans* isomers, doublet at τ 3.1). The two isomers were found to be formed in roughly equal amounts.

Diacyl Peroxides.—The diacyl peroxides listed in Table I were prepared by addition of an acetone solution of the appropriate acid chloride to a cold aqueous solution of the appropriately substituted sodium perbenzoate. The peroxides precipitated after 15–45 min. and were filtered, washed with cold 5% aqueous bicarbonate and methanol, and recrystallized from benzene–pentane. The only exception to this procedure was that of the synthesis of o-(*trans*-2-phenylvinyl)benzoyl peroxide. In this case, the acid chloride was added in cyclohexane solution and stirred for 3 hr. The peroxide crystallized from the cyclohexane solution on cooling overnight.

3-Benzhydrylidenephthalide.—Phthalic anhydride (10.5 g., 0.071 mole) and diphenylacetic acid (15.0 g., 0.071 mole) were heated together with freshly fused sodium acetate (0.4 g., 0.006 mole) to 280° in a sand bath according to the general method of Weiss.[15] This temperature was maintained until water ceased to distil from the reaction vessel. The resulting brown mixture was dissolved in chloroform and extracted with 10% aqueous sodium hydroxide. The solid residue from evaporation of the chloroform was recrystallized from absolute ethanol. Chromatographic purification of this material on silica gel afforded a colorless crystalline solid, m.p. 151.5–152°, 9 g., 0.032 mole, 45%.
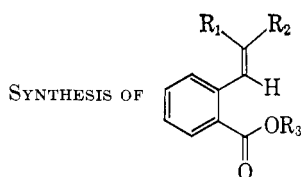
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(10) We thank Mr. Joseph Nemeth for the microanalysis and molecular weight determinations and Mr. Richard Johnson for n.m.r. and infrared spectra. Spectra are reproduced in full in the Ph.D. thesis of T. W. Koenig, available from University Microfilms, Inc., Ann Arbor, Mich.

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TABLE I

SYNTHESIS OF

Compound	R_1	R_2	R_3	M.p., °C.	Calcd. C	Calcd. H	Found C	Found H
	p-$NO_2C_6H_4$	p-$NO_2C_6H_4$—	H—	198–199	64.61	3.61	64.55	3.77
	H	p-$NO_2C_6H_4$—	H—	207–208	66.91	4.12	66.66	4.22
	H	m-$NO_2C_6H_4$—	H—	212–214	66.91	4.12	66.54	4.19
III	p-$NO_2C_6H_5$	p-$NO_2C_6H_4$—	$C_6H_5CO_2$—	114 dec.	65.88	3.55	66.15	3.81
IV	H	C_6H_5—	$C_6H_5CO_2$—	58–59	76.73	4.68	77.01	4.84
V	H	m-$NO_2C_6H_4$—	$C_6H_5CO_2$—	114 dec.	67.86	3.88	67.67	4.14
	H	C_6H_5—	p-$NO_2C_6H_4CO_2$—	95 dec.	67.86	3.88	68.38[a]	4.25[a]
VI	H	p-$NO_2C_6H_4$—	$C_6H_5CO_2$—	114 dec.	67.86	3.88	67.95	3.86
VII	H	p-$NO_2C_6H_4$—	p-$NO_2C_6H_5CO_2$—	114 dec.	60.83	3.25	61.00	3.42
VIII	H	p-$NO_2C_6H_4$—	p-$CH_3OC_6H_8CO_2$—	110–112	65.86	4.09	66.07	4.17

[a] This compound is extremely unstable. We were, therefore, unable to obtain a sample with the desired degree of purity.

Anal. Calcd. for $C_{21}H_{14}O_2$: C, 84.55; H, 4.73. Found: C, 84.83; H, 4.69.

The ultraviolet spectrum of this material in chloroform [λ_{max} 343 mμ (log ϵ 4.26), 310 (4.13), and 298 (4.12)] was nearly identical with that of 3-benzylidenephthalide.[16]

3-Benzhydrylphthalide.—Crude 3-benzhydrylidenephthalide (5.0 g., 0.017 mole) was boiled for 3 hr. in a mixture of 15% aqueous potassium hydroxide (20 ml.) and 2 g.-atoms of zinc dust. After cooling and filtration, the solution was extracted with chloroform and the acidified with 20% aqueous hydrochloric acid. Recrystallization from ether–pentane gave 3 g. (0.010 mole, 59%) of the pure lactone, m.p. 149–149.5°.

Anal. Calcd. for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found: C, 84.20; H, 5.47.

The n.m.r. spectrum of this material showed doublets at τ 5.78 and 3.78 (relative area 1) and an aromatic multiplet (relative area 14). The ultraviolet spectrum was typical of a phthalide structure [λ_{max} 282 and 275 mμ (log ϵ 3.20)].

3-(Diphenyl-t-butoxymethyl)phthalide.—Recrystallization of a sample of the perester which had stood for several weeks at room temperature gave a material which was insoluble in pentane. Recrystallization of this material from ether–pentane gave a white solid, m.p. 184°.

Anal. Calcd. for $C_{25}H_{24}O_3$: C, 80.63; H, 6.54. Found: C, 80.21; H, 6.45.

The structure of this material was assigned on the basis of its microanalysis and comparison of its infrared, ultraviolet, and n.m.r. spectra with those of 3-benzhydrylphthalide.

p-**Nitrobenzylphthalide.**—A solution of o-[*trans*-2-(p-nitrophenyl)-vinyl]benzoic acid (1 g.) in 100 ml. of 10% hydrobromic acid in acetic acid was refluxed for 16 hr. Evaporation of solvent and recrystallization of the residue from ethanol gave 200 mg., 20% yield, of the pure lactone, m.p. 165–166° (lit.[17] m.p. 162–163°).

Anal. Calcd for $C_{15}H_{11}NO_4$: C, 66.90; H, 4.12. Found: C, 66.73; H, 4.17.

p-**Nitrobenzylidenephthalide.**—The substituted benzalphthalide was prepared by the known[18] method in 22% yield, m.p. 226–227° (lit.[18] m.p. 223–223.5°).

Product Studies.—The procedures and apparatus used in the determination of products from the decomposition of this perester were similar to those described earlier.[3]

Products of the Decomposition of t-Butyl o-(2,2-Diphenylvinyl)-perbenzoate. A. Gaseous Products.—The gaseous products from decomposition of 1.02 g. (2.74 mmoles) of the perester in chlorobenzene at 90° were methane (480 ml. at 30° and 12 mm., 0.31 mmole, 11%) and carbon dioxide (less than 3%) detected by absorption on Ascarite. The methane was identified by comparison of its infrared spectrum with published A.P.I. spectrum.[19]

B. Volatile Products.—The amounts of acetone and t-butyl alcohol could be measured by decomposition of the perester in a sealed n.m.r. tube and determining the ratio of the area of acetone or t-butyl alcohol n.m.r. peaks to the total area of nonaromatic protons. The amount of acetone found in this manner from the decomposition of 0.269 mmole of perester in 0.5 ml. of chlorobenzene was 0.156 mmole or 58%. The amount of t-butyl alcohol was 0.073 mmole or 27%. These values were in agreement with amounts of acetone and t-butyl alcohol determined by n.m.r. analysis of the distillate collected by a bulb-to-bulb distillation at high vacuum.

The n.m.r. of this distillate also showed peaks attributable to toluenes. An authentic mixture of toluene and o-chlorotoluene in chlorobenzene gives only one peak (τ 7.78) as does a solution of m-chlorotoluene and p-chlorotoluene in chlorobenzene (τ 7.93). The total area of these two peaks either in the distillate or the crude reaction mixture corresponds to a 24% yield.

C. Nonvolatile Products.—The nonvolatile residue from the decomposition of the perester (1.09 g., 2.93 mmoles) amounted to 0.860 g. The infrared spectrum of this solid mixture in chloroform solution was very similar to that of a mixture of 3-benzhydryl- and 3-benzhydrylidenephthalides. There was very little absorption in the carbonyl region below 1750 cm.$^{-1}$. The n.m.r. spectrum of this crude product mixture shows doublets characteristic of benzhydrylphthalide (τ 3.78 and 5.68). In addition there is a sharp singlet at τ 8.86 characteristic of 3-(diphenyl-t-butoxymethyl)phthalide. These peaks in the n.m.r. spectrum were used to estimate the amounts of the compounds corresponding to them by using an accurately weighed internal standard (3-benzhydrylphthalide, 35%; 3-(diphenyl-t-butoxymethyl)phthalide, 10%). The ultraviolet absorption of the product mixture at 343 mμ was used to estimate the amount of 3-benzhydrylidenephthalide (16%, a maximum value).

Chromatographic separation of the product mixture (285 mg.) using silica gel and eluting with chloroform gave 42 mg. or 15% of pure 3-benzhydrylidenephthalide in the first fraction. This compound was identified by comparison of infrared and ultraviolet spectra and mixture melting point with an authentic sample. The succeeding fractions from the chromatographic separation had infrared and ultraviolet spectra which were very similar to those of the 3-benzhydrylphthalide, but single compounds could not be obtained from them.

3-Benzhydrylidenephthalide and 3-benzhydrylphthalide could be separated by g.l.p.c. using an Aerograph Hi Fi gas chromatograph with flame ionization detection. The column used was packed with 5% SE-30 on Chromosorb-W. This method was used to estimate the amounts of the two phthalides using an internal standard technique. The product mixture contained 15%

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TABLE II

KINETICS OF THE DECOMPOSITION OF PERESTER I IN CHLOROBENZENE

Run	Wave length	Scavenger concn., M	Perester concn., M	Temp., °C.	$k \times 10^4$ sec.$^{-1}$	$n/2^a$
1	8.40 μ	None	0.06	89.8	1.16 ± 0.01	
2	8.40 μ	None	0.6	90.0	1.32 ± 0.00	
3	316 mμ	None	$1 \times 10^{6\,4}$	90.0	1.29	
4	8.40 μ	0.2, S^b	0.06	90.0	0.86 ± 0.00	
5	8.40 μ	None	0.06	100.0	3.27 ± 0.05	
6	8.40 μ	None	0.06	115.0	13.7 ± 0.3	
7	575 mμ	1.4×10^{-3}, G^c	1×10^{-2}	90.3	0.745 ± 0.00^d	0.76
8	575 mμ	1.0×10^{-3}, G^c	0.4×10^{-3}	90.4	0.985 ± 0.02	0.76
9	575 mμ	1.3×10^{-3}, G^c	0.7×10^{-3}	105.5	4.64 ± 0.05	0.86
10	575 mμ	1.4×10^{-3}, G^c	0.5×10^{-3}	119.3	15.4 ± 0.02	0.91
11^e	575 mμ	1.0×10^{-3}, G^c	0.7×10^{-3}	90.4	23	0.7
12^e	316 mμ	None	1.5×10^{-4}	90.4	21.6	
13^f	316 mμ	None	1.5×10^{-4}	90.0	0.35	
14^g	316 mμ	None	1.5×10^{-4}	90.0	3.75	
15^{e,g}	316 mμ	None	1.5×10^{-4}	90.0	24.7	

^{a} Trapping efficiency. ^{b} S means styrene. ^{c} G means galvinoxyl. ^{d} $(n/2)k_d$. ^{e} In methanol. ^{f} In cyclohexane. ^{g} Fluorenyl perester (II).

benzhydrylidenephthalide and 33% benzhydrylphthalide as analyzed by this method.

The average molecular weight of the nondistillable residue as determined by osmometry in benzene and in chloroform was 360. This value is compatible with a mixture of 65% monomer (mol. wt., 300) and 35% dimer (mol. wt., 600). Sublimation of the product mixture (1.03 g.) gave 0.658 g. of sublimate (64%) and 0.378 g. of nonvolatile residue (36%). G.l.p.c. analysis of the sublimate showed it to contain a total of 70% 3-benzhydrylphthalide and 3-benzhydrylidenephthalide. The average molecular weight of this sublimate was 307. The average molecular weight of the residue was 700. The n.m.r. spectrum of the residue had no characteristic absorption other than the aromatic multiplet. Its infrared spectrum showed carbonyl absorption at 1760 and phthalide lactone absorption at 1290 cm.$^{-1}$. The material was not further purified.

Products of the Decomposition of Benzoyl o-[$trans$-2-(p-Nitrophenyl)vinyl]benzoyl Peroxide. A. Gaseous Products.—Decomposition of this diacyl peroxide (90 mg., 0.231 mmole) in chlorobenzene (1.8 ml.) gave 131 ml. of carbon dioxide at 27° and 8.5 mm. (0.06 mmole or 0.26 mole/mole of peroxide). Decomposition of the peroxide in a solution of 10% 1,4-cyclohexadiene in chlorobenzene gave no detectable gaseous products.

B. Nonvolatile Residue.—The peroxide (3.142 g., 8.11 mmoles) was heated at 70° for 12 hr. in a mixture of chlorobenzene (27 ml.) and 1,4-cyclohexadiene (3 ml.). Extraction of the chlorobenzene solution with aqueous sodium carbonate gave, upon acidification of the extract, o-[$trans$-2-(p-nitrophenyl)vinyl]-benzoic acid, 300 mg. (14%), m.p. 198–204 (m.m.p. 200–204°). The n.m.r. spectrum of this material showed no detectable amount of cis isomer.

Chloroform extractions of acidified sodium carbonate extract gave 602 mg. (62%) of benzoic acid.

Chromatography, on Fluorisil, of the product mixture from decomposition of 5.60 mmoles of peroxide gave 345 mg. (23%) of a material, m.p. 239–240°, which was assigned the structure 3-(p-nitrophenyl)isocoumarin on the basis of its nonidentity with the isomeric 3-(p-nitrobenzylidene)phthalide (m.m.p. 180–190°) and its infrared and n.m.r. spectra.

Anal. Calcd. for C$_{15}$H$_9$NO$_4$: C, 67.04; H, 3.39; N, 5.24. Found: C, 67.18; H, 3.30; N, 5.43.

A second chromatographic fraction contained a mixture of two substances which were obtained pure by fractional recrystallization from ether-pentane. One of these was shown to be 3-(p-nitrobenzyl)phthalide, m.p. 164–165° (m.m.p. 164–165°). The second, m.p. 149–150°, is considered to be 2-(p-nitrophenylbenzoyloxymethyl)phthalide.

Anal. Calcd. for C$_{22}$H$_{15}$NO$_6$: C, 67.98; H, 3.96. Found: C, 67.98; H, 3.96.

The n.m.r. spectra of these two pure components were used in the interpretation of the spectrum of the mixture in a determination of the relative amounts of the two present in the unresolved chromatographic fraction.

Methanol elution provided a further fraction with an average molecular weight (osmometric) of 558. No pure constituents of the mixture were isolated.

Kinetics.—The procedure for the kinetic runs analyzed by infrared spectroscopy was the same as that given in ref. 3 except that the frequency used was 1190 cm.$^{-1}$. The procedure for the measurement of the rate of disappearance of galvinoxyl involved degassing the solution carefully. The flask used in this procedure was fitted with a manifold which was used to distribute the solution to sample tubes which were sealed under vacuum giving twelve aliquots of the same solution, identically degassed. Blank solutions degassed as outlined previously changed in optical density by less than 3% under the conditions of the kinetic runs. Optical densities were measured at 575 and 313 mμ on a Bausch and Lomb Spectronic 505 spectrophotometer.

Results

Kinetic Studies.—The rates of decomposition of compound I were measured by the published[3] method using infrared spectroscopy, except that the wave length used was 8.40 (1190) instead of 5.68 μ (1760 cm.$^{-1}$). The rates obtained by this method follow first-order rate laws for more than three half-lives. Styrene (0.2 M) causes a decrease of 34% in the rate constant observed for the decomposition of this perester. This probably reflects the inhibition by styrene of a small amount of radical chain-induced decomposition.

The rates of decomposition of all of these o-vinyl-substituted peroxides were measured by ultraviolet spectroscopy using the adsorption at ∼320 mμ. The rate of decomposition of compound I at 90°, measured by the latter method, agrees very well with that found by the infrared method, though there was a more than 1000-fold variation in initial perester concentration (Table II). This agreement indicates that any induced decomposition is probably first order in peroxide.

Rate constants for the decompositions of these compounds also were determined by following the decolorization (575 mμ) of the colored scavenger "galvinoxyl" which has been shown to be an efficient trap for t-butoxy and 2-cyano-2-propyl radicals.[20] At scavenger concentrations in excess of the minimum required to trap all of the free radicals produced by complete destruction of the peroxide, the rate law for disappearance
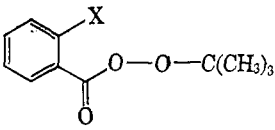
(20) P. D. Bartlett and Toshio Funahashi, *J. Am. Chem. Soc.*, **84**, 2596 (1962).

of the scavenger is pseudo first order, using a measured value for the infinity absorption, and gives a measure of R_d (the rate constant for thermal decomposition). A rate constant so obtained is free from error resulting from contributions of radical chain-induced decomposition[21] processes. Under these conditions of initial peroxide and scavenger concentrations, the total change in scavenger concentration from zero to infinite reaction times can be used to estimate the fraction of the reaction which gives scavengeable radicals $(n/2)$.[7] The product $(n/2)k_d$ can be determined by following the pseudo-zero-order disappearance of the scavenger in the presence of a large excess of radical source.[3,21]

The results of the kinetic studies of compounds I and II by one or more of these methods are summarized in Table II. The galvinoxyl run in methanol (run 11 in Table II) can only be regarded as semiquantitative since the scavenger reacts slowly with solvent at 90°. This reaction could not be eliminated by more elaborate degassing, but it was slow enough that the very fast disappearance of the scavenger in the presence of the perester was approximately first order for the first three half-lives.

Activation parameters and relative rates of these and related peresters are given in Table III.

TABLE III

DECOMPOSITION OF

IN CHLOROBENZENE

ortho substituent X	Rel. rate[a] at 60°	H^*, kcal./mole	S^*, e.u.
—S—C$_6$H$_5$	2.05×10^b	23.0^4	-3.4^b
—S—CH$_3$	1.41×10^b	22.6^4	-5.5^b
—CH:C(C$_6$H$_5$)$_2$	67.0	$26.3^{c,d}$	$-5.0^{c,e}$
—CH:C[o,o'-(C$_6$H$_4$)$_2$]	200		
—I	43.4	28.0^b	-0.8^b
—C(CH$_3$)$_3$	3.0	34.2^b	12.5^b
—H[f]	1	34.1^g	10.0^g

[a] Calculated using values for H^* and S^* given in this table. [b] Determined in the absence of scavenger. [c] Determined in excess galvinoxyl. [d] ± 0.7. [e] ± 1.6 e.u. [f] Values from ref. 1. [g] Determined in the presence of 0.2 M sytrene.

The results of kinetic studies of the diacyl peroxides (compounds III–VIII) are summarized in Table IV.

Product Studies.—The products of decomposition of *t*-butyl *o*-(2,2-diphenylvinyl)perbenzoate (I) in chlorobenzene at 90° are summarized in Table V. A similar product study for one of the diacyl peroxide decompositions is described in Table VI.

Discussion

Peresters.—The first-order rate constants observed for the decomposition of *t*-butyl *o*-(2,2-diphenylvinyl)-perbenzoate show a definite acceleration in comparison with the unsubstituted perester (a factor of $\sim 10^3$ in methanol). The entropy of activation is similar in magnitude to other *ortho*-substituted *t*-butyl perbenzoates, already investigated,[3] which undergo anchimerically accelerated decomposition. The relatively large solvent effect observed for the decomposition of this

(21) C. E. H. Bawn and D. Verdin, *Trans. Faraday Soc.*, **56**, 815 (1960).

CHART I
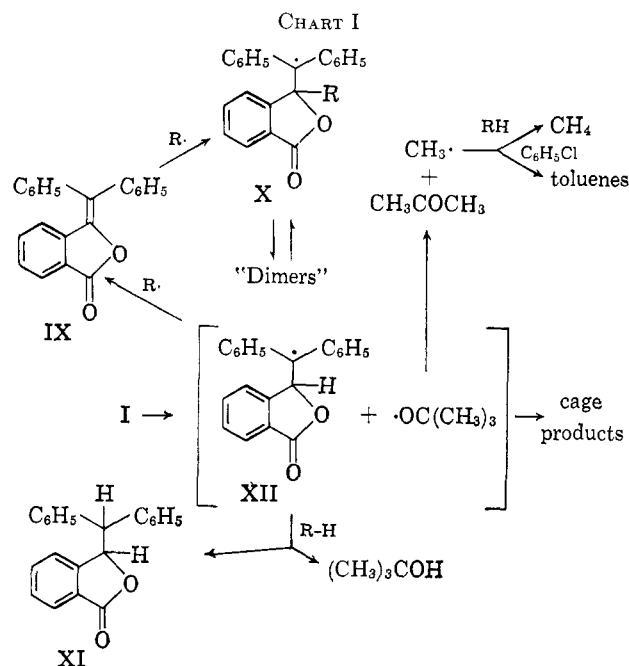
perester (faster in methanol than in cyclohexane by a factor of 62 at 90°) also is expected by analogy with these earlier studies.

The radical nature of the intermediates is supported both by the decolorization of galvinoxyl solutions and by the products observed in the decomposition of this perester. All of the products can be explained by postulating the formation of the *t*-butoxy and benzhydrylphthalidyl radicals as intermediates in the reaction.
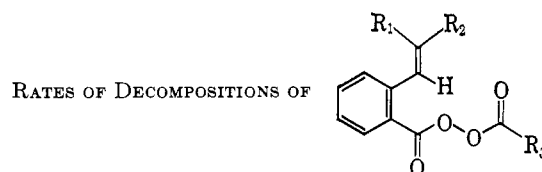
The presence of methane, *t*-butyl alcohol, and 3-benzhydrylphthalide can be explained as the result of the reactions of intermediate radicals which function as hydrogen abstractors. The total yield of these products is 0.75 mole/mole of perester. The toluenes and 3-benzhydrylidenephthalide can be explained as the result of the reactions of intermediate radicals which functioned as hydrogen donors. The 3-benzhydrylidenephthalide could very well function as a radical scavenger[22] giving rise to radical species which could dimerize. This "dimeric material" would then represent the final product of reactions of a compound which has functioned as a hydrogen donor. These hydrogen donor products also amount to approximately 0.75 mole/mole of perester.

It is interesting to note that an electron spin resonance (e.s.r.) signal is detected on heating to 100° a sample of compound I in chlorobenzene solution. The intensity of this signal is temperature dependent disappearing with cooling to room temperature and reappearing as the temperature is again raised to 100–140°. At temperatures greater than 140°, the signal rapidly and permanently disappears. The lack of hyperfine structure attributable to the aliphatic proton in XII suggests that the primary source of this radical is the addition of reactive radicals to IX to give X (Chart I).

The best explanation for all these observations appears to be a bonding interaction between the perester group and the neighboring olefin in a transition state

(22) 3-Benzylidenephthalide can be copolymerized with styrene using radical initiators: D. T. Mowry (to Monsanto Chemical Co.), U. S. Patent 2,475,150 (July 5, 1949); *Chem. Abstr.*, **43**, 7753 (1949).

Table IV

Rates of Decompositions of

Run no.	Compound	R_1	R_2	R_3	Temp., °C.	Solvent	$k \times 10^4$ sec.$^{-1}$	k (rel.)[a]	$n/2$
16	IV	H	C_6H_5—	C_6H_5—	35.0	CH_3OH	9.77[c]	2.57×10^b	...
17		H	C_6H_5—	p-$NO_2C_6H_4$—	35.0	C_6H_5Cl	8.09[c]	2.13×10^b	0.02[d]
18	IV	H	C_6H_5—	C_6H_5—	35.0[b]	C_6H_5Cl	0.942[c]	2.48×10^g	0.13[d]
	Benzoyl peroxide				35.0	C_6H_6	0.00038[e]	1	...
19	IV	H	C_6H_5—	C_6H_5—	70.0[b]	C_6H_5Cl	30.21[f]	387	0.11[g]
20	V	H	m-$NO_2C_6H_4$—	C_6H_5—	70.0	C_6H_5Cl	1.87[f]	24	0.15[g]
21	VI	H	p-$NO_2C_6H_4$—	C_6H_5—	70.0	C_6H_5Cl	1.18 ± 04[f]	150	0.39[g]
22	VII	H	p-$NO_2C_6H_4$—	p-$NO_3C_6H_4$—	70.0	C_6H_5Cl	3.81 ± 12[f]	49	0.34[g]
23	VIII	H	p-$NO_2C_6H_4$—	p-$CH_3OC_6H_4$—	70.0	C_6H_5Cl	0.606 ± 0.008[f]	7.8	0.41[g]
24	III	p-$NO_2C_6H_4$	p-$NO_2C_6H_4$—	C_6H_5—	70.0	C_6H_5Cl	15.4	198	0.13[d]
25	VI	H	p-$NO_2C_6H_4$—	C_6H_5—	70.0	Tetrahydrofuran	0.62[h]	8.0	...
	Benzoyl peroxide				70.0	C_6H_6	0.078[e]	1	...

[a] Relative to benzoyl peroxide at the same temperature. [b] Rates at 35 and 70° allow the determination of $\Delta H^* = 20.2$ kcal./mole and $\Delta S^* = -8.7$ e.u. [c] Measured without scavenger by ultraviolet spectroscopy, 320 mμ. [d] Estimate from measurement of the change in absorbance at 575 mμ of a solution of excess galvinoxyl and peroxide after complete decomposition of peroxide (one point). [e] Extrapolated from the data of P. D. Bartlett and K. Nozaki, *J. Am. Chem. Soc.*, **68**, 1686 (1946). [f] Measured with excess galvinoxyl, *i.e.*, pseudo-first-order disappearance of scavenger at 575 mμ. [g] From the amount of galvinoxyl decolorized during the kinetic run. [h] Measured with excess peroxide, $(n/2)k_d$.

Table V

Products of the Decomposition of t-Butyl o-(2,2-Diphenyl-vinyl)perbenzoate at 90° in Chlorobenzene (5×10^{-3} M)

Product	Mole/mole of perester
CO_2	0.02
CH_4	0.11
t-Butyl alcohol	0.29
Toluenes	0.24
Acetone	0.58
3-Benzhydrylphthalide	0.35 (0.59)[a]
3-Benzhydrylidenephthalide	0.16 (0.16)[a]
3-(Diphenyl-t-butoxymethyl)phthalide	(0.10)[b]
Dimeric material	35% by weight of the solid residue

[a] Determined by g.l.p.c. from decomposition of the perester in 10% 1,4-cyclohexadiene in chlorobenzene at 70°. [b] Inferred from the n.m.r. spectrum of the product mixture.

Table VI

Decomposition Products from Benzoyl o-[$trans$-2-(p-Nitrophenyl)vinyl]benzoyl Peroxide in 10% 1,4-Cyclohexadiene in Chlorobenzene at 70°

Product	Mole/mole of peroxide
CO_2[a]	0.26
CO_2	0.02
Benzoic acid	0.62
o-[$trans$-2-(p-Nitrophenyl)vinyl]benzoic acid	0.14
3-p-Nitrophenylisocoumarin	0.23
3-p-Nitrobenzylphthalide	0.08
3-(p-Nitrophenylbenzoyloxymethyl)phthalide	0.13
Higher mol. wt. residue	25% by weight of the residue

[a] Without 1,4-cyclohexadiene.

formally identical with the one already proposed for the o-phenylthio, o-methylthio, and o-iodo peresters. The transition state for the decomposition of o-(2,2-diphenylvinyl)perbenzoate is postulated to be a dipolar singlet represented by canonical structures such as XIII, XIV, and XV (Chart II).

Chart II
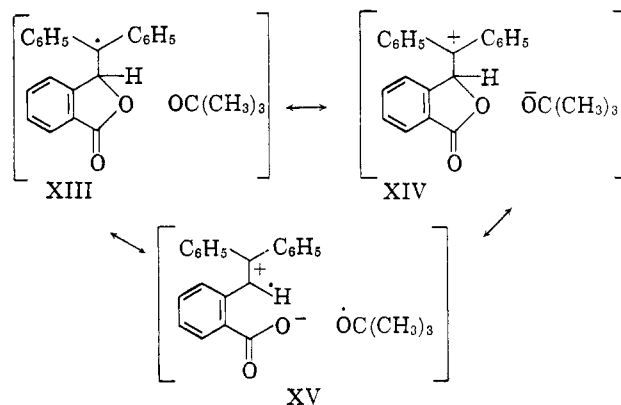
Decomposition of the fluorenylidene perester (II) is somewhat faster at 90° in chlorobenzene than that of I, but the rates are quite similar in methanol. This apparent lesser sensitivity of perester II to solvent may be interpreted as indicating that the contribution from a canonical form such as XIV is less important in the transition state for decomposition of II, reflecting its resemblance to a fluorenyl cation.

Diacyl Peroxides.—All of the peroxides of Table IV decompose faster than unsubstituted benzoyl peroxide. The fraction of the reaction which gives scavengable free radicals is rather low for compounds III, IV, and V. As mentioned in a previous publication,[3] there are several possible explanations for inefficient radical production in peroxide decompositions, all of which could apply here. The fractions of radicals trapped for compounds VI, VII, and VIII are nearer to those observed in other cases,[3,7] though they do not approach the values observed in the decomposition of the o-vinyl-substituted perester (I). In spite of low free-radical efficiencies observed here, the conclusion that o-vinyl substituents do participate in the radical decompositions of these diacyl peroxides seems valid.

The variation of solvents used as media for the decompositions of the diacyl peroxides was limited by the insolubility of many of the compounds. Compound IV shows an acceleration in its rate of decomposition of approximately ten (at 35°) on going from chlorobenzene to methanol solvent. The rates of radical production in the decomposition of VI in tetrahydrofuran and in chlorobenzene are almost identical at 70°. These solvent effects are smaller than those observed for the *o*-vinyl-substituted peresters and much less pronounced than the effect observed for the decomposition of *t*-butyl *o*-(phenylthio)perbenzoate.[5,6]

The products of the decomposition of benzoyl *o*-[*trans*-2-(*p*-nitrophenyl)vinyl]benzoyl peroxide are compatible with the proposed mechanism. The formation of carbon dioxide in the absence of cyclohexadiene and its elimination from the products in the presence of hydrogen donor are consistent with a radical decomposition. The formation of benzoic acid would be expected to result from hydrogen abstraction by benzoyloxy radical and a lower concentration of hydrogen donor would increase the importance of decarboxylation of this intermediate. The benzoic acid could, of course, also arise by an ionic path or by some secondary decomposition of initially formed products.

The *o*-substituted benzoic acid in the product mixture could have its genesis in an unassisted O–O bond cleavage to give unbridged carboxy radicals which might either abstract hydrogen or undergo ring closure to the bridged radical. The relatively small acceleration (a factor of fifteen, run 21) attributed to bridging in this reaction would make it possible to account for a part of the acid by this route. A small amount of radical chain-induced decomposition involving cyclohexadiene also might give this acid *via* decomposition of the initially formed unstable cyclohexadienyl ester.

The 3-(*p*-nitrobenzyl)phthalide is expected by analogy with the products of the perester decomposition. It is surprising that the corresponding 3-(*p*-nitrobenzylidene)phthalide was not isolated. There was meager evidence that it was present in small amount from the ultraviolet spectra of some chromatography fractions. An isomeric compound was isolated in relatively high yield. This material was shown not to be the same as the *trans*-3-(*p*-nitrobenzylidene)phthalide obtained by the literature preparation. The compound was not changed by boiling overnight in chloroform with a trace of trifluoroacetic acid, an indication that it is probably not *cis*-3-(*p*-nitrobenzylidene)phthalide. On the basis of infrared and ultraviolet spectra, the structure proposed is XVI.

XVI   XVII
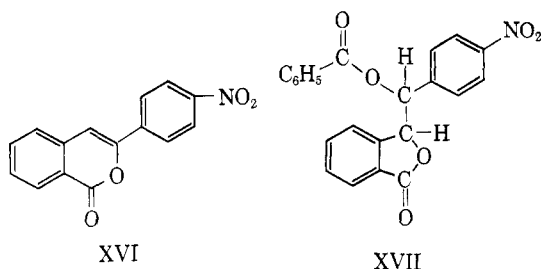
Another sharp melting compound was obtained from the product mixture after chromatography and fractional crystallization. From the twin carbonyl peaks at 1760 and 1720 cm.$^{-1}$ in the infrared spectrum, the

microanalysis, and the n.m.r. spectrum, the structure proposed for this material is XVII.

The latter two products could be formed by a number of mechanisms both radical and ionic. Without more extensive studies on the formation of these products under varying conditions, any statement as to their origin is rather speculative.

Substituent Effects.—The relative rates of decomposition of peroxides IV, V, and VI in chlorobenzene at 70° correlate with σ⁺-constants with a ρ of −1.8. The rates of radical production ($n/2 \cdot k_d$) for the same compounds gives a poorer correlation (ρ −1.2). The rates of decomposition of compounds VI, VII, and VIII correlate with σ-constants with a ρ of +0.7. The rates of radical production, $(n/2)k_d$, by the latter three compounds also correlate with the same substituent constants with a ρ of +0.6. Although the small value of ρ indicates a small sensitivity to substituent polarity it is significant that the sign of this reaction constant is opposite that observed for the decompositions of *meta*- and *para*-substituted benzoyl peroxides (ρ −0.4[23]) and *t*-butyl perbenzoates (ρ −0.6[24]). The positive sign is an expected result if stabilization of a negative charge on the leaving group contributes to the stability of the transition state (*i.e.*, structure XIX).

XVIII   XIX   XX
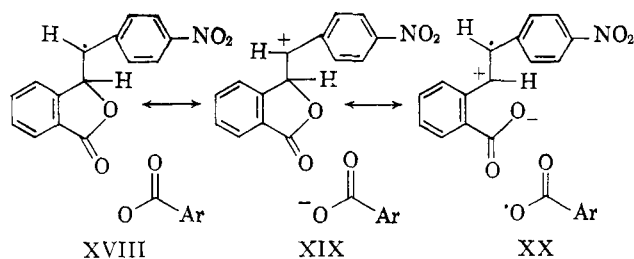
Greene and co-workers[25] have reported similar substituent effects in the bimolecular reactions of stilbenes and benzoyl peroxides. The reaction constant for the substituted *trans*-stilbene–benzoyl peroxide reactions is −1.0 and that for *trans*-stilbene–substituted benzoyl peroxide reactions is +0.8. These authors found that the rate of scavengable free-radical production with olefin present was greater than that from the peroxide alone under identical conditions. The explanation given to these observations was the formation of an olefin–peroxide complex which could give rise to radical intermediates.

The explanation given by Lamb[7] for the acceleration in the rate of decomposition of *trans*-γ-benzylidene-butyryl peroxide and its sensitivity to solvent polarity, compared to the saturated analog, involved the postulation of a structure analogous to XX for the transition state leading to free-radical formation. The substituent effects observed in the *o*-vinyl-substituted benzoyl peroxides of this work indicate that this structure cannot be the sole contributor to the transition state. At least part of the negative charge is shared by the leaving group (*i.e.*, structure XIX is also important). There is no real evidence for or against a contribution from XX.

Conclusion.—We may summarize our results by saying that *o*-vinyl substituents can participate in the

(23) C. G. Swain, W. H. Stockmayer, and J. T. Clarke, *J. Am. Chem. Soc.*, **72**, 5426 (1950).
(24) A. T. Blomquist and A. F. Ferris, *ibid.*, **73**, 3408 (1951).
(25) F. D. Greene, W. Adam, and J. E. Cantrill, *ibid.*, **83**, 3461 (1961).

homolysis of the O–O bond in t-butyl perbenzoates and benzoyl peroxides in a manner formally identical with that already postulated for neighboring sulfur and iodine. The 2,2-diphenylvinyl group is a better neighboring group than iodide (see Table III) but not so effective as the phenylthio group in anchimeric acceleration of perester O–O bond homolysis. Substituent effects are compatible with the postulated dipolar transition state involving a five-membered ring with a concentration of positive charge on the neighboring group involved in the displacement on oxygen and a negative charge on the oxygen leaving group (see structures XIV or XIX).

Chlorination and Bromination of Alkyl s-Triazines

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Liquid-phase chlorination or bromination of alkyl s-triazines produced exclusively α-substitution by an acid-catalyzed process regardless of the halogenation reagent used. Nuclear halogenation of mono- and dialkyl s-triazines does not compete. Special emphasis has been given to the development of synthetic procedures using elementary chlorine and bromine for the preparation of mono- and polyhalogenation products from trimethyl- and triethyl-s-triazine. The chemistry of the wide variety of products has been explored to provide an insight into their potentialities as reactive intermediates.

Perhaps the most promising opportunities for exploitation of the newly available alkyl s-triazines[1-3] lie in the study of their halogenation products. The work reported here was undertaken to explore the range of compounds which could be obtained in preparatively useful processes. Principal attention has been given to the particularly practical use of 2,4,6-trimethyl-s-triazine (I) and 2,4,6-triethyl-s-triazine (II) as substrates for chlorination or bromination, and a surprising number of different types of products has been obtained in good yield. Somewhat less work has been done with 2-alkyl s-triazines where unsubstituted nuclear positions are available and might have been competitive sites for halogenation. An exploratory study of the chemistry of the halogenation products was also carried out.

A substantial amount of work on the synthesis of chloro- and bromoalkyl s-triazines has been reported, but the bulk of this deals with compounds prepared by synthesis of the s-triazine system from reagents containing the halogenated alkyl group.

Only a very small number of references report the direct halogenation of an alkyl s-triazine group.[4] The work of Reinhardt and Schiefer, who prepared mono- and dibrominated and -chlorinated derivatives from 2-ethyl-4,6-diphenyl-s-triazine by direct halogenation is particularly pertinent to the present study.[5] Also significant is the reaction of 2,4-dichloro-6-methyl-s-triazine with elemental chlorine under rather strenuous conditions to give 2-trichloromethyl-4,6-dichloro-s-triazine.[6]

The halogenation of alkyl groups attached to electron-withdrawing substituents has received a great deal of attention in recent years.[7,8] The experimental work in this field provides an excellent basis for the selection of reaction procedures. The literature did not permit prediction of the reactivity of alkyl s-triazines, but combined with the present findings gives a satisfactory basis for interpretation of the results.

Monochlorination and Bromination.—N-Chloro- and N-bromosuccinimide (NBS) were used as halogenating agents in the initial experiments because of their wide applicability for the monosubstitution of methyl aromatics.[7,9,10] Reactions under conventional conditions were sluggish, but 2-chloromethyl-4,6-dimethyl-s-triazine (III), 2-(1-chloroethyl)-4,6-diethyl-s-triazine (IV), and 2-(1-bromoethyl)-4,6-diethyl-s-triazine (V) were obtained in moderate yield. Bromination of I with NBS was impractically slow. Small amounts of

III, X = Cl; R = H
IV, X = Cl; R = CH₃
V, X = Br; R = CH₃

I, R = H
II, R = CH₃
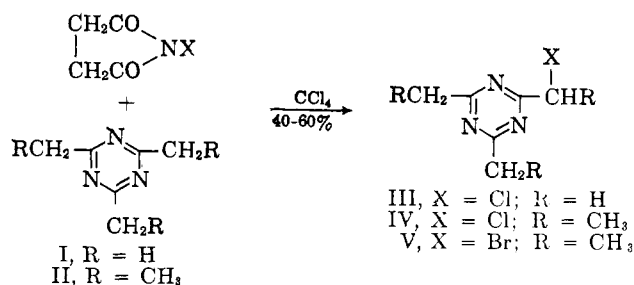
dihalogenation products were also obtained in these reactions, but it is clear that loss of the desired compounds through side reactions was the major obstacle to higher yields. It was found that III itself is surprisingly stable to N-chlorosuccinimide (NCS).

(1) F. C. Schaefer and G. A. Peters, *J. Org. Chem.*, **26**, 2778 (1961).

(2) F. C. Schaefer, *ibid.*, **27**, 3362 (1962).

(3) F. C. Schaefer, *ibid.*, **27**, 3608 (1962).

(4) Reaction of N-bromosuccinimide with 2-methyl-4,6-bisphenylamino-s-triazine is reported to give the bromomethyl derivative [H. K. Reimschuessel and N. T. McDevitt, *J. Am. Chem. Soc.*, **82**, 3756 (1960)]. However, it is clear from the published infrared spectrum that the product is in fact 2-(p-bromophenylamino)-4-methyl-6-phenylamino-s-triazine. See related work by C. G. Overberger and S. L. Shapiro, *ibid.*, **76**, 93, 1061 (1954).

(5) H. Reinhardt and E. Schiefer, *Chem. Ber.*, **90**, 2643 (1957).

(6) E. Kober and C. Grundmann, *J. Am. Chem. Soc.*, **81**, 3769 (1959).

(7) See C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, Chapter 8.

(8) (a) B. R. Brown, D. L. Hammick, and B. H. Thewlis, *J. Chem. Soc.*, 1145 (1951); (b) B. R. Brown, D. L. Hammick, B. H. Thewlis, and D. J. Walbridge, *ibid.*, 1369 (1953); (c) G. M. Bennett and G. H. Willis, *ibid.*, 1960 (1928).

(9) (a) C. Djerassi, *Chem. Rev.*, **43**, 271 (1948); (b) B. H. Walker, *J. Org. Chem.*, **25**, 1047 (1960); (c) H. Gershon, K. Dittmer, and R. Braun, *ibid.*, **26**, 1874 (1961).

(10) (a) N. P. Buu-Hoi, *Ann.*, **556**, 1 (1944); (b) A. Hirschberg and P. E. Spoerri, *J. Org. Chem.*, **26**, 2356 (1961).