Preparation of Diacyl Peroxides with N,N'-Dicyclohexylcarbodiimide[1]

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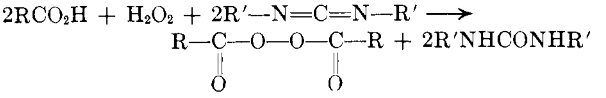
Dicyclohexylcarbodiimide effects the condensation of carboxylic acids and hydrogen peroxide to diacyl peroxides under mild conditions. Unsymmetrical diacyl peroxides may be prepared by the action of the carbodiimide on an acid–peracid mixture.

Diacyl peroxides comprise a class of compounds that continues to receive much attention.[2] Many members of this class may be readily synthesized by standard methods[2] of which the most general involves treatment of an acid chloride with aqueous alkaline hydrogen peroxide. For the preparation of peroxides under nonaqueous conditions, a method utilizing a complex of urea and hydrogen peroxide has found some use,[3] but this also employs the acid chloride. We wish to report a nonaqueous, nonbasic method for the preparation of symmetrical and unsymmetrical diacyl peroxides that appears to have some generality.

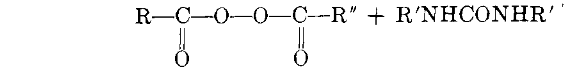
Results

Dicyclohexylcarbodiimide, a valuable condensing agent of many applications,[4] has been found to effect the condensation of acid and hydrogen peroxide in an inert medium at 0° to diacyl peroxide and N,N'-dicyclohexylurea. The stoichiometry is given in equation 1. In practice, acid and carbodiimide are employed in stoichiometric ratio with a severalfold excess of hydrogen peroxide.



$$2RCO_2H + H_2O_2 + 2R'{-}N{=}C{=}N{-}R' \longrightarrow R{-}\underset{\underset{O}{\|}}{C}{-}O{-}O{-}\underset{\underset{O}{\|}}{C}{-}R + 2R'NHCONHR' \qquad (1)$$

Reaction of an acid and carbodiimide in the presence of a peracid affords the unsymmetrical diacyl peroxide (equation 2).



$$RCO_2H + R''CO_3H + R'{-}N{=}C{=}N{-}R' \longrightarrow R{-}\underset{\underset{O}{\|}}{C}{-}O{-}O{-}\underset{\underset{O}{\|}}{C}{-}R'' + R'NHCONHR' \qquad (2)$$

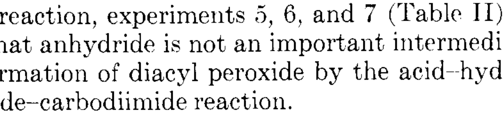
Reaction of a cyclic anhydride and hydrogen peroxide in the presence of carbodiimide represents a potential route to cyclic diacyl peroxides. In this way, phthalic anhydride was converted to monomeric phthaloyl peroxide. Attempted application to bicyclo[2.2.2]octane-1,2-dicarboxylic anhydride[5] was unsuccessful. Reaction of benzoic anhydride and hydrogen peroxide in the presence of carbodiimide proceeds slowly.

Examples of these reactions are summarized in Table I. Yields are generally good and purity of product high. (Diacyl peroxides have been reported to react with carbodiimides but only at temperatures greatly exceeding those of this study.)[6] The preparation of diacyl peroxides by this method, which obviates the need of prior conversion of acid to acid chloride, constitutes a mild route for the preparation of peroxides possessing other functional groups and peroxides in which the carboxyl group is attached at a site that under more vigorous methods of preparation might undergo epimerization.

The carbodiimide employed in this study, the N,N'-dicyclohexyl derivative, was selected because of the low solubility of the corresponding urea which facilitated purification of the diacyl peroxides. In special cases, for reason of rate of reaction or ease of isolation of products, other carbodiimides may be preferred. The success of the carbodiimide in this study and the recent disclosure of the use of N,N'-carbonyldiimidazole[7] indicate that other condensing agents, that have found use in the formation of peptides and esters, also may be of use in the preparation of diacyl peroxides.

Evidence on the Course of the Reaction.—The formation of diacyl peroxide from the combination of acid–hydrogen peroxide–carbodiimide would appear to involve the intermediate formation of peracid, a supposition supported by the good conversion of a mixture of acid and peracid to diacyl peroxide by the action of carbodiimide. In order to obtain a more detailed view of the reaction, a number of control experiments were carried out, testing the behavior of various combinations of reactants and possible intermediates. The results are summarized in Table II.

The acid–hydrogen peroxide–carbodiimide reaction is considered to proceed by the steps outlined in equations 3–5. The specific mode of attack of peracid (or hydrogen peroxide) on the complex A is left unspecified (*i.e.*, attack by peroxygen atom at carbonyl carbon of complex A with expulsion of urea, or at "imine" carbon followed by cyclic decomposition). Although anhydride formation from acid and carbodiimide (*e.g.*, equation 3 followed by attack of acid on complex A) is a facile reaction, experiments 5, 6, and 7 (Table II) indicate that anhydride is not an important intermediate in the formation of diacyl peroxide by the acid–hydrogen peroxide–carbodiimide reaction.



$$RCO_2H + R'NCNR' \longrightarrow \left[\begin{array}{c} R'NH{-}C{=}NR' \\ | \\ O \\ | \\ O{=}C{-}R \end{array}\right] \qquad (3)$$

Complex A

$$\text{Complex A} + H_2O_2 \longrightarrow RCO_3H + (R'NH)_2CO \qquad (4)$$

$$\text{Complex A} + RCO_3H \longrightarrow RCO_2{-}O_2CR + (R'NH)_2CO \qquad (5)$$

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[1] Supported in part by the research program of the Atomic Energy Commission under contract no. AT(30-1)-905. Reproduction is permitted for any purpose of the United States Government.

[2] (a) A. G. Davies, "Organic Peroxides," Butterworth and Co., Ltd., London, 1961 (and bibliography therein); (b) J. G. Wallace, "Hydrogen Peroxide in Organic Chemistry," E. I. du Pont de Nemours and Co., Inc., Wilmington, Del., 1959; (c) E. G. E. Hawkins, "Organic Peroxides," E. and F. F. Spon, Ltd., London, 1961.

[3] DeLos F. Detar and L. A. Carpino, *J. Am. Chem. Soc.*, **77**, 6370 (1955).

[4] H. G. Khorana, *Chem. Rev.*, **53**, 145 (1953).

[5] J. Kazan and F. D. Greene, *J. Org. Chem.*, in press.

[6] D. B. Denney and G. Feig, *J. Am. Chem. Soc.*, **81**, 225 (1959).

[7] H. A. Staab, *Angew. Chem. Intern. Ed. Engl.*, **1**, 359 (1962).

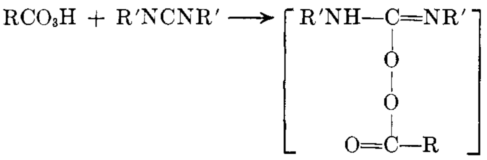
TABLE I

PREPARATION OF DIACYL PEROXIDES BY USE OF DICYCLOHEXYLCARBODIIMIDE

Peroxide	Starting material	Yield, %	M.p., °C.	Lit. m.p.[a]	Yield of urea, %
Benzoyl	Acid + H_2O_2	90[b,c]	105–106	106–107	90
Bis-*p*-nitrobenzoyl	Acid + H_2O_2	85[b,d]	154 dec.	155–156	90
Bis-*p*-bromobenzoyl	Acid + H_2O_2	90[b,d]	143 dec	143.5 dec.[e]	95
Bis-*p*-methoxybenzoyl	Acid + H_2O_2	80[b,d]	124.5–125	126	90
Palmitoyl	Acid + H_2C_2	75[f,g]	70.5–71.5	71.4–71.9[h]	85
trans-*t*-Butylcyclohexanoyl	Acid + H_2O_2	75[b,i]	89–90	89[j]	90
mono-*p*-Bromobenzoyl	*p*-Bromoperbenzoic acid + benzoic acid	85[b,d]	93.4–94.5	94–95	85
p-Methoxy-*p*'-nitrobenzoyl	*p*-Methoxybenzoic acid + *p*-nitroperbenzoic acid	70[f,d]	107–108 dec.	108 dec.	80
3,4-Dichlorophenylacetyl benzoyl[k]	Perbenzoic acid + 3,4-dichlorophenylacetic acid	65[b,d]	65–66 dec.		95
trans-*t*-Butylcyclohexanoyl benzoyl	Perbenzoic acid + *trans*-*t*-butylcyclohexanecarboxylic acid	40[b,d]	81 dec.		85
Phthaloyl	Phthalic anhydride	40[b,l]	114 dec.	124–125 dec.[m]	90
Benzoyl	Peracid	80[f,d]	105–105.5	106–107	50
Bis-*p*-nitrobenzoyl	Peracid	70[f,n]	155–156	155–156	60

[a] Unless otherwise indicated the literature melting points were taken from Davies (ref. 2a, p. 66). [b] Purity, 99%. [c] Recrystallizing solvent, CCl_4–CH_3OH. [d] Recrystallizing solvent, $CHCl_3$–CH_3OH. [e] C. C. Price, R. W. Kell, and E. Krebs, *J. Am. Chem. Soc.*, **64**, 1103 (1942); [f] Purity, 95%. [g] Recrystallizing solvent, $CHCl_3$–ether. [h] L. S. Silbert and D. Swern, *J. Am. Chem. Soc.*, **81**, 2364 (1959). [i] From pentane. [j] H. H. Lau and H. Hart, *ibid.*, **81**, 4897 (1959). [k] Prepared by Dr. C. Chu in this laboratory. [l] Recrystallized from ethyl acetate–pentane. [m] Ref. 16. [n] Recrystallized from $CHCl_3$–pentane.

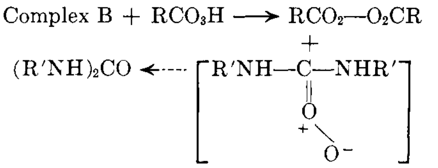
A point of some interest is the conversion of peracid to diacyl peroxide by carbodiimide (experiments 8 and 9 of Table II). This reaction is improved by the use of an excess of the carbodiimide (experiment 9 *vs.* 8); but even under these circumstances, this combination affords a poorer yield of diacyl peroxide than is obtained from acid–hydrogen peroxide–carbodiimide. Formation of diacyl peroxide from peracid and carbodiimide leaves one oxygen unaccounted for. This does not appear as hydrogen peroxide or as molecular oxygen. A possible interpretation of the peracid–carbodiimide reaction involves initial reaction of the two to afford complex B followed by reaction of B with peracid to afford diacyl peroxide and "urea oxide." A major fraction of the carbodiimide ultimately is isolated as the dicyclohexylurea, in addition to a considerable amount of residue towards the further characterization of which no success has been realized.



$$RCO_3H + R'NCNR' \longrightarrow \left[\begin{array}{c} R'NH\text{—}C\text{=}NR' \\ | \\ O \\ | \\ O \\ | \\ O\text{=}C\text{—}R \end{array}\right]$$

Complex B

(6)



$$\text{Complex B} + RCO_3H \longrightarrow RCO_2\text{—}O_2CR$$
$$+$$
$$(R'NH)_2CO \dashleftarrow \left[\begin{array}{c} R'NH\text{—}C\text{—}NHR' \\ \| \\ \overset{+}{O} \\ \diagdown \\ O^- \end{array}\right]$$

(7)

The high conversion of acid–hydrogen peroxide–carbodiimide to diacyl peroxide and urea (experiment 4 *vs.* 8 and 9), coupled with the good conversion of acid–peracid–carbodiimide to unsymmetrical diacyl peroxide, indicates that carboxylic acid is more reactive than peracid towards carbodiimide; and both of these are more reactive towards carbodiimide than is hydrogen peroxide (experiment 1, Table II). The order of reactivity indicated for reaction with complex A is peracid > hydrogen peroxide > acid. The low position of acid in this sequence is based on experiments 5–7 which indicate that anhydride is not an important intermediate. The reactivity of peracid towards A is considered to exceed that of hydrogen peroxide; if the latter were the more reactive, acid would largely be converted to peracid followed by conversion of peracid to diacyl peroxide. As discussed in the preceding paragraph, diacyl peroxide is formed from peracid–carbodiimide less efficiently than from acid–hydrogen peroxide–carbodiimide.

The apparent facility of hydrogen peroxide in this reaction is suggestive that reagents such as carbodiimides also may be of use in the preparation of peresters and perlactones.

TABLE II

CONTROL EXPERIMENTS FOR THE RCO_2H–H_2O_2–R'NCNR' REACTION[a]

Experiment number	Combination	Result	Yield of $(C_6H_5COO)_2$, %
1	R'NCNR', H_2O_2	No reaction	
2	R'NCNR', RCO_2H	$(RCO)_2O$[b]	
3	$(R'NH)_2CO$, H_2O_2	No reaction	
4	$C_6H_5CO_2H$, H_2O_2, R'NCNR'		90[c]
5	$(C_6H_5CO)_2O$, H_2O_2, R'NCNR'		15
6	$(C_6H_5CO)_2O$, H_2O_2, $C_6H_5CO_2H$[d]		30, 30[e]
7	$(C_6H_5CO)_2O$, $C_6H_5CO_3H$, $C_6H_5CO_2H$[d]		60, 60[e]
8	$C_6H_5CO_3H$, R'NCNR'		55[f]
9	$C_6H_5CO_3H$, R'NCNR'		80[g]

[a] In CH_2Cl_2–ether at 0°. [b] See ref. 4. [c] Yield of N,N'-dicyclohexylurea, 90%. [d] Trace. [e] In presence of added dicyclohexylurea. [f] From 2:1 ratio of reactants. [g] From 1:1 ratio of reactants.

Experimental

All melting points are corrected. The iodometric titrations used to establish the purity of the peroxides were performed according to the procedure of Silbert and Swern.[8] Peracids used in the reactions were prepared by the method of Silbert, Siegel, and Swern.[9]

General Procedure for the Preparation of Symmetrical Diacyl Peroxides (see Table I).—In a flask equipped with an efficient mechanical stirrer and thermometer, and cooled by means of an ice bath, is placed enough reagent-grade ether so that the final volume of this solvent, after the addition of the ethereal hydrogen peroxide solution, will be 25 ml. An amount of N,N′-dicyclohexylcarbodiimide equivalent to the number of moles of acid (plus 1% excess) is weighed into the flask as a liquid.[10] The volume of a standard ethereal hydrogen peroxide solution[11] (**caution**) necessary to deliver a 5-fold excess of the reagent is added to the stirred solution. If the acid (approx. 2 g.) is soluble in methylene chloride, it is dissolved in 25 ml. of the solvent and the resulting solution is cooled and added with stirring to the ethereal solution. If the acid is insoluble, 25 ml. of cold methylene chloride is added to the ethereal solution and the acid is subsequently added as a finely divided solid. The internal temperature should be kept below 5° during the course of the reaction. The resulting mixture is stirred at ice-bath temperatures until the infrared spectrum of the carbonyl region indicates that the reaction is complete.[12] The mixture is filtered by suction through a medium-grade sintered glass funnel and the urea remaining in the funnel is slurried three times with 20-ml. portions of cold methylene chloride which are added to the main filtrate by suction.[13] An equal volume of cold ether is added to the filtrate and it is washed with three 25-ml. portions of cold saturated ammonium sulfate solution, two 25-ml. portions of cold 10% sodium carbonate solution, and two 25-ml. portions of cold saturated sodium chloride solution. The washed solution is dried over magnesium sulfate. The solvent is completely removed under reduced pressure,[14] the residue is dissolved in a minimum amount of the crystallizing solvent (heating should be avoided), and a co-solvent is added if necessary.

Preparation of Unsymmetrical Peroxides. *p*-Methoxy-*p*′-nitrobenzoyl Peroxide.—To a cold, stirred solution of 1.3 g. (0.0063 mole) of dicyclohexylcarbodiimide in 10 ml. of ether was added, in one portion, a solution of 1.16 g. (0.0063 mole) of *p*-nitroperbenzoic acid and 0.96 g. (0.0063 mole) of *p*-methoxybenzoic acid in 45 ml. of ether and 45 ml. of methylene chloride. The resulting mixture (urea appeared after 6 min.) was stirred at 2° for 16 hr. The peroxide was isolated by the foregoing procedure. Crystallization of the solid from chloroform–methanol gave the peroxide as a yellow microcrystalline solid, 1.40 g. (70%), m.p. 107–108° dec. (lit.[15] m.p. 108°).

***trans-t*-Butylcyclohexanoyl Benzoyl Peroxide.**—To a stirred, cooled solution (2°) of 1.2 g. (0.0058 mole) of dicyclohexylcarbodiimide in 12.5 ml. of ether was added, in one portion, a solution of 1.07 g. (0.0058 mole) of *trans-t*-butylcyclohexanecarboxylic acid and 0.8 g. (0.0058 mole) of perbenzoic acid in 25 ml. of ether and 13 ml. of methylene chloride. The resulting mixture (urea appeared after 9 min.) was stirred for 24 hr. at 2°. The peroxide was isolated by the procedure previously described. Recrystallization from chloroform–methanol gave 0.84 g. (42%) of colorless needles, m.p. 80–81° (explodes at 81°); titrimetric purity, 99%.

Anal. Calcd. for $C_{18}H_{24}O_4$: C, 71.03; H, 7.95. Found: C, 71.28; H, 7.99.

The infrared spectrum of the solid (chloroform) shows a close doublet at 1765 and 1795 cm.$^{-1}$ attributable to the acyl peroxide linkage.

Reaction of Perbenzoic Acid with N,N′-Dicyclohexylcarbodiimide (1:1 Mole Ratio).—To a stirred solution of 7.5 g. (0.0362 mole) of N,N′-dicyclohexylcarbodiimide in 50 ml. of methylene chloride, cooled in an ice bath, was added, in one portion, 5 g. (0.0362 mole) of perbenzoic acid in 51 ml. of methylene chloride. Upon addition of the acid a precipitate began to appear after 1.5 min. Gas buret measurements indicated that no gas was evolved during the reaction. The reaction was allowed to proceed for 1 hr. Filtration of the resulting mixture gave 3.6 g. (49%) of N,N′-dicyclohexylurea, m.p. 225–228°.

The filtrate was washed with 50 ml. of cold saturated sodium bicarbonate solution (two portions), 25 ml. of cold saturated ammonium sulfate solution, 25 ml. of cold 10% sodium carbonate solution, and 25 ml. of cold water. The solution was dried over magnesium sulfate. Filtration and evaporation of the solvent left 7.3 g. of a yellow semisolid material. Solution of the material in chloroform and addition of methanol with cooling and concentration gave 4 crops of solid material totaling 3.8 g. Recrystallization from chloroform–methanol gave 3.5 g. (81%) of benzoyl peroxide in the form of white needles, m.p. 105–105.5°. Iodometric titration of the solid indicated that it was 97% pure; the infrared spectrum was identical with authentic material. No further crystalline material was obtained from the 3.6 g. of residual oil remaining after the removal of the peroxide.

Conduction of this reaction with a 2:1 ratio of peracid to carbodiimide afforded a 55% yield of benzoyl peroxide. An infrared spectrum of the crude reaction solution (chlofororm) indicated that peracid was present and that all of the carbodiimide was consumed.

Control Experiments. A. Benzoic Acid, Hydrogen Peroxide, and Dicyclohexylcarbodiimide.—To a cold stirred solution of 1.7 g. (0.00824 mole) of dicyclohexylcarbodiimide in 10 ml. of ether was added 3.42 ml. of an ethereal solution of hydrogen peroxide containing 205 mg./ml. (0.7 g., 0.021 mole). To the stirred solution was added, in one portion, 1 g. (0.00824 mole) of benzoic acid in 13 ml. of cold methylene chloride. The reaction was terminated after 3 hr. when the infrared analysis had indicated that the carbodiimide was consumed (2150-cm.$^{-1}$ band had disappeared). Work-up procedure was the same as described in the "general procedure." The yield of isolated benzoyl peroxide was 0.809 g. (81%), m.p. 105–105.5°. The total yield of peroxide as determined by iodometric titration of the crude reaction product was 93%. The yield of urea was 1.63 g. (88%), m.p. 232–233°. The infrared spectrum of the peroxide (chloroform) was identical with that of an authentic sample.

B. Benzoic Anhydride, Hydrogen Peroxide, and Dicyclohexylcarbodiimide.—To a cold (2°), stirred solution of 0.85 g. (0.00412 mole) of dicyclohexylcarbodiimide in 13 ml. of ether was added 3.42 ml. (0.7 g., 0.021 mole) of an ethereal solution of hydrogen peroxide[11] containing 205 mg./ml. To the stirred solution was added 0.933 g. (0.00412 mole) of benzoic anhydride in 13 ml. of methylene chloride. There was no visible appearance of urea over the 3-hr. period. There was no change in the infrared spectrum of the carbonyl region; it showed only anhydride bands. The work-up procedure was the same as that used in the previous experiment. Iodometric titration of the crude reaction product indicated that approximately 16% of the anhydride had been converted to peroxidic material.

C. Benzoic Anhydride and Hydrogen Peroxide in the Presence of Dicyclohexylurea and a Trace of Benzoic Acid.—To a cold, stirred solution of 300 mg. (0.00132 mole) of benzoic anhydride in 8.2 ml. of a 1:1 mixture of methylene chloride–ether was added 16.2 mg. (0.000132 mole) of benzoic acid, 296 mg. (0.00132 mole) of dicyclohexylurea (m.p. 233–234°), and 0.55 ml. of an ethereal solution of hydrogen peroxide[11] containing 205 mg./ml. (112 mg. 0.0033 mole). The solution was stirred at 2° for 6 hr. Filtration and washing of the precipitate with methylene chloride gave 225 mg. of recovered urea, m.p. 232–234°. An equal volume of ether was added to the combined filtrates and the

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(8) L. S. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958).

(9) L. S. Silbert, E. Siegel, and D. Swern, *J. Org. Chem.*, **27**, 1336 (1962).

(10) N,N′-Dicyclohexylcarbodiimide (Aldrich Chemical Co.) was distilled under vacuum [b.p. 95–97° (0.02 mm.)] and stored in the refrigerator under nitrogen. This material, m.p. 34–35°, is best handled as a liquid.

(11) The ethereal hydrogen peroxide was prepared by slowly adding 90% hydrogen peroxide (Food Machinery and Chemical Corp.) to ice-cold reagent-grade ether (**caution**) with subsequent removal of the water by drying over magnesium sulfate. The solution should be kept under refrigeration; standardization can be achieved by iodometric titration. The concentration of the solutions used ranged from 6 to 7 *M*. The solution should be standardized and dispensed at the same temperature since ether undergoes large volume changes with changes in temperature.

(12) The reactions were followed by the disappearance of the carbodiimide band at 2150 cm.$^{-1}$ coupled with the appearance of a close doublet between 1750 and 1850 cm.$^{-1}$ in the infrared. The disappearance of the acid carbonyl band also is indicative, but care must be taken in interpretation since this band is shifted to higher frequency in this solvent mixture.

(13) Care should be exercised at this point since some peroxides precipitate with the urea and a considerable loss in yield can occur if the peroxide is not dissolved away from the precipitate. An indication of the presence of peroxide is the melting point of the urea. Pure dicyclohexylurea melts at 233–234°.

(14) The material should not be heated above 40° during this procedure as sensitive peroxides may decompose, sometimes with explosive violence.

(15) See Table I.

resulting solution was extracted with three 10-ml. portions of cold saturated ammonium sulfate solution. The bulk of the solvent was removed under reduced pressure and the residue was dissolved in chloroform and titrated iodometrically. Titration indicated that approximately 30% of the anhydride had been converted to peroxidic materials. The reaction was followed by taking infrared spectra of the carbonyl region (5 to 6 μ) at intervals. At the end of 6 hr. there were bands at 1730, 1775, and 1800 cm.$^{-1}$ attributable to peroxide, peracid, acid, and anhydride groups.

Repetition of this reaction in the absence of the urea afforded the same result—a 30% conversion of anhydride to peroxidic products.

D. **Benzoic Anhydride and Perbenzoic Acid in the Presence of a Trace of Benzoic Acid.**—To 290 mg. (0.00128 mole) of benzoic anhydride and 15.7 mg. (0.000128 mole) of benzoic acid in a mixture of 4 ml. of methylene chloride and 2 ml. of ether, stirred and cooled to 2°, was added 3 ml. of an ethereal solution containing 58.2 mg./ml. of perbenzoic acid (177 mg., 0.00128 mole). The resulting solution was stirred for 3 hr. At the end of this period 25 ml. of cold ether was added and the solution was extracted with three 10-ml. portions of cold saturated sodium bicarbonate (acidification with concentrated hydrochloric acid, extraction with ether, drying, and evaporation of the solvent gave 130.4 mg. of benzoic acid, m.p. 121.5–122.5°), three 10-ml. portions of cold sodium carbonate solution, and two 10-ml. portions of saturated sodium chloride solution. Combination of the latter washings and treatment as indicated previously gave 55.6 mg. of benzoic acid, m.p. 119–121°. The washed ethereal solution was dried over calcium sulfate. Filtration and evaporation of the solvent gave 290 mg. of a solid, 62% benzoyl peroxide by titration. Crystallization of a portion of the crude solid from chloroform–methanol gave benzoyl peroxide, m.p. 104–104.5°, infrared spectrum superimposable with that of authentic sample.

Repetition of this experiment in the presence of dicyclohexylurea (288 mg.) afforded the same result—61% conversion of benzoic anhydride to benzoyl peroxide.

Phthaloyl Peroxide.—To a cold (2°), stirred solution of 2.64 g. (0.0128 mole) of dicyclohexylcarbodiimide in 20 ml. of ether was added 4.7 ml. of an ethereal solution of hydrogen peroxide containing 265 mg./ml. (1.25 g., 0.0366 mole). To the resulting solution was added over a 4-hr. period a solution of 1.8 g. (0.0122 mole) of phthalic anhydride (recrystallized from chloroform) in 25 ml. of methylene chloride. The total reaction time was 8 hr. The resulting mixture was filtered and the precipitate was triturated with three 20-ml. portions of cold methylene chloride (yield of urea, 2.38 g., m.p. 231–233°). The combined filtrates were washed with three 20-ml. portions of cold saturated ammonium sulfate solution and one 10-ml. portion of cold saturated sodium chloride solution. The solution was dried over calcium sulfate and the solvent was evaporated giving a residual solid. The solid was crystallized from ethyl acetate–pentane giving 1.55 g. of a yellow solid, m.p. 95–100°. The solid was redissolved in ethyl acetate and the solution was extracted with two 10-ml. portions of cold saturated sodium bicarbonate solution and 10 ml. of saturated sodium chloride solution. Treatment of the resulting material as indicated previously gave 0.81 g. of phthaloyl peroxide[16] in the form of off-white granular crystals, m.p. 112–113° (exploded at 114°), titrimetric purity 99%. The infrared spectrum of the solid (chloroform) is the same as that of an authentic sample.

Reaction of Bicyclo[2.2.2]octane-1,2-dicarboxylic Anhydride[6] with Hydrogen Peroxide and Dicyclohexylcarbodiimide.—Several reactions were attempted varying the time of addition of the anhydride and the quantity of hydrogen peroxide. In all cases the only materials isolated were colorless oils of varying peroxide content (30–60%). Attempts to crystallize or resolve the oils on cellulose pulp or Florisil (Floridin Co.) were unsuccessful.[17]

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[16] F. D. Greene, *J. Am. Chem. Soc.*, **78**, 2246 (1956).

[17] Further details may be found in the Ph.D. thesis of J. Kazan, Ph.D. thesis in chemistry, Massachusetts Institute of Technology, February, 1963.

Vinylborinic and α-Bromoalkylborinic Esters[1]

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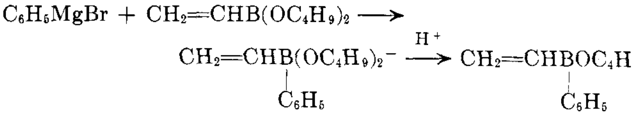
B-Aryl-*B*-vinylborinic esters have been prepared by the addition of aryl Grignard reagents to dibutyl ethyleneboronate. Light-initiated addition of bromotrichloromethane to the vinyl group yielded the corresponding *B*-aryl-*B*-(1-bromo-3,3,3-trichloro-1-propyl)borinic esters. *B*-Alkyl-*B*-(1-bromo-3,3,3-trichloro-1-propyl)borinic esters were prepared by addition of the alkyl Grignard reagent to dibutyl 1-bromo-3,3,3-trichloropropane-1-boronate.

We undertook the synthesis of some α-bromoalkylborinic esters with the expectation that their behavior toward nucleophiles would clarify the role of boron in assisting the displacement of the neighboring halogen atom[3] and the hope that they might be useful synthetic intermediates. The radical-catalyzed addition of bromotrichloromethane to dibutyl ethyleneboronate[4] suggested possible synthetic routes to compounds of this class. The extraneous trichloromethyl group introduced concurrently in the synthesis does not interfere with essential behavior of α-bromoalkylboron function.

B-Aryl-*B*-vinylborinates were prepared to serve as precursors of the corresponding *B*-aryl-*B*(1-bromo-3,3,3-trichloro-1-propyl)borinates as well as a logical extension of our studies of the properties of vinylboron compounds. Butyl *B*-phenyl-*B*-vinylborinate[5] was synthesized by the addition of phenylmagnesium bromide to dibutyl ethyleneboronate.



$$C_6H_5MgBr + CH_2{=}CHB(OC_4H_9)_2 \longrightarrow \underset{\textstyle C_6H_5}{CH_2{=}CHB(OC_4H_9)_2^-} \xrightarrow{H^+} \underset{\textstyle C_6H_5}{CH_2{=}CHBOC_4H_9}$$

The yield was almost insensitive to the temperature of addition between −70 and +40°, although at the higher temperature, 12% of the dibutyl ethyleneboronate was converted to dibutyl benzeneboronate. Since early experiments seemed to indicate that addition of vinylmagnesium bromide to dibutyl benzeneboronate gave lower yields, addition of the aryl Grignard to dibutyl ethyleneboronate was adopted as the standard method. However, subsequently observed erratic

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[2] National Science Foundation Cooperative Predoctoral Fellow, 1961–1962; abstracted in part from the Ph.D. thesis of R. W. H. M.

[3] D. S. Matteson and R. W. H. Mah, *J. Am. Chem. Soc.*, **85**, 2599 (1963).

[4] D. S. Matteson, *ibid.*, **82**, 4228 (1960).

[5] Under the customary nomenclature of borinic esters [*Chem. Abstr.*, **56**, 46N (1962)], this would be called butyl phenylvinylborinate. We have inserted *B*'s to clarify which groups are attached to boron, names such as butyl 3-methyl-1-butyl-(1-bromo-3,3,3-trichloro-1-propyl)borinate being almost incomprehensible.