our results lead to a value of ρ for dimethylanilinium ion dissociation which is considerably larger than that for anilinium ion dissociation, a fact which is reflected in the specific case of relative basicities quoted above.

Now it is often found that (in water) tertiary amines are weaker bases than the corresponding primary amines, *e.g.*, methylamine and trimethylamine. Two explanations have been offered. Brown[34] suggests that on proton addition, there is a contraction in bond angles resulting in a steric strain which destabilizes the conjugate acid. An alternative view[35] is that, in the tertiary amine case, relief of electrostatic energy by solvation is sterically hindered. Our present findings appear to be explicable in terms of the second of these suggestions. When comparing dimethylanilines with anilines, the presence of the methyl groups should lead to a constant base-strengthening electronic effect and also to a base-weakening steric hindrance to solvation, the extent of which should depend upon the electronic charge on the amine nitrogen; this charge would in turn depend upon the nature of any substituent present in the aromatic ring. For dimethylaniline itself the electronic effect outweighs the steric effect but in a series in which this amine possesses a progressively more electron-withdrawing substituent in the ring, the net positive charge on the amine nitrogen is similarly increased. There should therefore be a concomitant increase in the "desire" for solvation; in other words, the "steric inhibition of solvation" term becomes larger and it is suggested that for the *p*-NO_2 substituent, this term is so large that, when one compares *p*-nitroaniline and *p*-nitrodimethylaniline, this term outweighs the electronic base-strengthening effect of the methyl groups. Thus *p*-nitrodimethylaniline is a weaker base than *p*-nitroaniline.

CHRISTCHURCH, NEW ZEALAND

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[34] H. C. Brown, H. Bartholomay, Jr., and M. D. Taylor, THIS JOURNAL, **66**, 435 (1944).

[35] (a) D. H. Everett and W. F. K. Wynne-Jones, *Proc. Roy. Soc.* (*London*), **A177**, 499 (1941); (b) R. G. Pearson, THIS JOURNAL, **70**, 204 (1948); (c) A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1293 (1949).

[CONTRIBUTION FROM THE INSTITUTE OF ORGANIC CHEMISTRY AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO]

Reactions of Grignard Reagents with Peroxy Compounds[1,2]

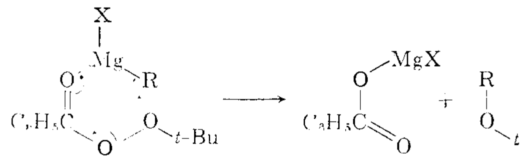
BY SVEN-OLOV LAWESSON[3] AND N. C. YANG

RECEIVED JANUARY 22, 1959

In contrast to the reactions with esters, Grignard reagents react with *t*-butyl perbenzoate at 0° to give *t*-butyl ethers and benzoic acid. The reaction may be used as a convenient laboratory method for the preparation of *t*-butyl ethers. Aryl and alkyl Grignard reagents react with *t*-butyl hydroperoxide to give in excellent yields the corresponding phenols and alcohols. The reaction constitutes a two-step displacement of a halogen atom by a hydroxyl group. This observation supports Ivanoff's mechanism for oxidation of mixed Grignard reagents by molecular oxygen. Benzoyl peroxide reacts with Grignard reagent to give an abnormally high yield of benzoic acid together with lesser amounts of the ester and the halide. The possible mechanism of this reaction is discussed. Di-*t*-butyl peroxide fails to react with phenylmagnesium bromide even at elevated temperatures.

The reaction of Grignard reagents with diacyl peroxides and dialkyl peroxides had been reported in the literature, but the extent of these investigations is primarily exploratory. Gilman and Adams[4] found that Grignard reagents reacted with benzoyl peroxide to form benzoates or tertiary carbinols and phenylmagnesium bromide reacted with diethyl peroxide to give phenetole and biphenyl. Campbell and co-workers[5] later observed that alkyl Grignard reagents reacted with di-*t*-butyl peroxide to give a mixture of products containing some *t*-butyl ether, while phenylmagnesium bromide failed to react under identical conditions. In connection with our current interest in the chemistry of peroxy compounds, the reactions of organometallic compounds with various peroxy compounds were investigated.

(a) The Reaction of *t*-Butyl Perbenzoates with Grignard Reagents.—*t*-Butyl perbenzoate (I) reacts with sodium methoxide in methanol to give methyl benzoate and the sodium salt of *t*-butyl hydroperoxide[6]; the reaction of *t*-butyl perbenzoate with different types of nucleophilic reagents, otherwise, receives little attention. Contrary to the reaction of esters with Grignard reagents, *t*-butyl perbenzoate was found to react with a variety of Grignard reagents to give good yields of *t*-butyl ethers and benzoic acid. The Grignard reagents employed were phenyl, α-naphthyl-, *p*-tolyl-, *p*-anisyl-, ethyl-, 1-octyl-, cyclohexyl- and 2-propylmagnesium halides, and the reaction may be formulated as



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[1] This investigation was supported by a grant from the Office of Naval Research, Contract No. N6ori-02040.

[2] Presented in part at the 134th Meeting of the American Chemical Society in Chicago, Ill., September, 1958.

[3] Institute of Chemistry, University of Uppsala, Uppsala, Sweden.

[4] H. Gilman and C. E. Adams, THIS JOURNAL, **47**, 2816 (1925).

[5] T. W. Campbell, W. Burney and T. L. Jacobs, *ibid.*, **72**, 2735 (1950).

[6] N. A. Milas and D. M. Surgenor, *ibid.*, **68**, 642 (1946).

The reaction of I and *t*-butylmagnesium chloride was comparatively sluggish, probably on account of the steric interference about the bulky *t*-butyl groups. The preparation of di-*t*-butyl ether by the present method usually produces a crude reaction mixture which becomes moderately explosive at high temperature. If precaution is taken to remove most of the reactive peroxide by treatment with ferrous sulfate prior to the distillation, di-*t*-butyl ether can be prepared successfully in fair yield.

Since derivatives of *t*-butyl alcohol readily undergo elimination reactions, *t*-butyl ethers cannot be prepared by the conventional Williamson synthesis; they usually are prepared by the acid-catalyzed condensation of *t*-butyl alcohol or isobutylene with the corresponding alcohols.[7,8] In the preparation of aryl *t*-butyl ethers, the acid-catalyzed condensation of isobutylene and phenols presents another major difficulty, namely, the alkylation of the phenol nucleus, and the reaction must be conducted under a condition such that phenolic alkylation is suppressed to a minimum.[8] The reaction of Grignard reagents with *t*-butyl perbenzoate, a stable and readily available material, therefore, offers a convenient laboratory approach to the synthesis of various *t*-butyl ethers.

Alternatively, phenyllithium reacts with *t*-butyl perbenzoate at −60°, comparable to Grignard reagents at 0°, to give phenyl *t*-butyl ether.

(b) The Reaction of *t*-Butyl Hydroperoxide with Grignard Reagent.—The oxidation of Grignard reagents to alcohols by molecular oxygen may be formulated to proceed in two discrete steps: the initial formation of a hydroperoxide and the subsequent reduction of the hydroperoxide by another molecule of the Grignard reagent.[9]

$$\mathrm{RMgX} + \mathrm{O_2} \longrightarrow \mathrm{ROOMgX}$$

$$\mathrm{ROOMgX} + \mathrm{RMgX} \longrightarrow 2\mathrm{ROMgX}$$

Direct experimental evidence in support of the first step had been provided by Walling and Buckler[10] that excellent yields of hydroperoxides could be isolated when alkyl Grignard reagents were treated with oxygen at low temperature. The observation implies the possibility of using a hydroperoxide in the oxidation of Grignard reagents to the corresponding alcohols, which may be significant from the standpoint of organic synthesis as well as reaction mechanism.[11]

The reaction of *t*-butyl hydroperoxide with aryl or alkyl Grignard reagents produces excellent yields of phenols or alcohols according to the stoichiometry

$$t\text{-BuOOH} + 2\mathrm{RMgX} \longrightarrow t\text{-BuOMgX} + \mathrm{ROMgX} + \mathrm{RH}$$

Since *t*-butyl hydroperoxide contains an active hydrogen, it effectively decomposes one equivalent of the Grignard reagent. In order to achieve maximum utilization of the Grignard reagents, the magnesium salt of *t*-butyl hydroperoxide, prepared from equimolar quantities of ethylmagnesium bromide and *t*-butyl hydroperoxide, had been employed as an oxidant and was found to be equally effective. Bromobenzene was converted to phenol by this modification in 80% yield. The reaction of Grignard reagents with *t*-butyl hydroperoxide provides an alternate route for the transformation of a halide to the corresponding hydroxy derivative. It is particularly useful where direct hydrolysis of the halide is difficult or is complicated by side reactions such as elimination and rearrangement. The scope of this reaction is subsequently demonstrated by the successful conversion of a number of aryl halides and neopentyl bromide to phenols and neopentyl alcohol.

The reaction of alkyl Grignard reagents with oxygen generally gives fair yields of alcohols, where reaction of aryl Grignard reagents with oxygen gives very poor yields of the phenols.[12] The yields of phenols were improved if the oxidation of the aryl Grignard reagent by molecular oxygen was carried out in the presence of an alkyl Grignard reagent. The function of the additional alkyl Grignard reagent is not clear, and two speculations had been postulated. Ivanoff[13] believed that the alkyl Grignard reagent in the "mixed" reaction was peroxidized first to an alkyl hydroperoxide which was reduced subsequently by the aryl Grignard reagent. Alternatively, Wuyts[14] suggested that the aryl Grignard reagent was peroxidized first to an aryl hydroperoxide which was reduced later by "the more reductive" alkyl Grignard reagent. Although phenyl hydroperoxide had been postulated as an intermediate in the oxidation of phenylmagnesium bromide, various attempts to isolate the aryl hydroperoxide were unsuccessful. Apparently the aryl hydroperoxide undergoes rapid decomposition at −70° to give a complex mixture of decomposition products.[10] It now has been demonstrated that an alkyl hydroperoxide or its magnesium salt can be reduced readily by an aryl or an alkyl Grignard reagent. Our observation suggests that the "reducing properties" of the Grignard reagents do not necessarily depict the course of the oxidation in these "mixed" Grignard reactions and the course of the oxidation is likely determined by a rate process. Thus the explanation of Ivanoff is favored.

(c) The Reaction of Benzoyl Peroxide and Grignard Reagents.—Benzoyl peroxide reacts with an equimolar quantity of phenylmagnesium bromide to give low yield (28%) of phenyl benzoate and an abnormally high yield of benzoic acid (140%, 1.4 moles of benzoic acid per mole of benzoyl peroxide), and partial hydrolysis of the unreacted benzoyl peroxide was suggested to account for the formation of the excess benzoic acid.[4] The reaction was reinvestigated using purified benzoyl peroxide and phenylmagnesium bromide prepared from sublimed magnesium, and it was found that benzoyl peroxide was completely consumed at the end of the reaction. Thus, the abnormally

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[7] J. F. Norris and G. W. Rigby, THIS JOURNAL, **54**, 2088 (1932).

[8] D. R. Stevens, *J. Org. Chem.*, **20**, 1232 (1955).

[9] C. W. Porter and C. Steele, THIS JOURNAL, **42**, 2650 (1920).

[10] C. Walling and S. A. Buckler, *ibid.*, **77**, 6032 (1955).

[11] Isolated cases of the reaction of hydroperoxide and organometallic compounds are known in the literature: (a) E. Müller and T. Töpel, *Ber.*, **72**, 273 (1939); (b) C. D. Hurd and H. J. Anderson, THIS JOURNAL, **75**, 5124 (1953); and (c) C. Walling and S. A. Buckler, *ibid.*, **77**, 6038 (1955).

[12] For a review on the reactions of Grignard reagents with oxygen, see M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, p. 1264.

[13] M. D. Ivanoff, *Bull. soc. chim.*, [4] **39**, 47 (1926).

[14] H. Wuyts, *Bull. soc. chim. Belg.*, **36**, 222 (1927).

high yield of benzoic acid cannot be derived from the unreacted peroxide. In addition to phenyl benzoate (35%) and benzoic acid (127%) which were obtained in substantially the same yields as reported previously, a new product, bromobenzene (21%), was isolated. Since the Grignard reagent used was shown to be free of bromobenzene, bromobenzene must be a subsidiary product during the reaction. Although the reaction of ethylmagnesium bromide with benzoyl peroxide yielded no gaseous product but ethyl benzoate (35%) and benzoic acid (145%), it is possible that ethyl bromide was produced likewise, and owing to its similar volatility with respect to ether, it had escaped isolation. The possibility was substantiated as the ether recovered was shown to give a positive Beilstein test for halogen. Recent work of Dessy and his co-workers[15] demonstrated that Grignard reagents are complex mixtures containing two types of magnesium, that of magnesium halide and that of dialkyl- or diarylmagnesium. Since two types of magnesium do not exchange readily, Grignard reagent is better represented constitutionally as $R_2Mg{\cdot}MgX_2$ rather than RMgX and the conventional Schlenk equilibrium. In view of their finding, a mechanism is postulated to account for the formation of these products which is in fair agreement with the observed stoichiometry.

$$2RMgX = R_2Mg{\cdot}MgX_2{}^{15}$$

$$MgX_2 + (C_6H_5CO_2)_2 \longrightarrow (C_6H_5CO_2)_2Mg + X_2$$

$$^1/_2R_2Mg + (C_6H_5CO_2)_2 \longrightarrow C_6H_5CO_2R + {}^1/_2(C_2H_5CO_2)_2Mg$$

$$^1/_2R_2Mg + X_2 \longrightarrow RX + {}^1/_2MgX_2$$

The foregoing mechanism is supported by the observations that (1) magnesium bromide reacts with benzoyl peroxide in the presence of cyclohexene to give good yield (83%) of *trans*-1,2-dibromocyclohexane; and (2) diethylmagnesium reacts with benzoyl peroxide to give ethyl benzoate.

The substitution of phenylmagnesium bromide by phenyllithium in the reaction with benzoyl peroxide yields, however, triphenylcarbinol.

(d) **The Reaction of Di-*t*-butyl Peroxide with Grignard Reagent.**—Di-*t*-butyl peroxide is very resistant toward aryl Grignard reagents. Campbell and co-workers[5] reported that phenylmagnesium bromide failed to react with di-*t*-butyl peroxide in refluxing ether. When the reaction was carried out at a higher temperature (80°), di-*t*-butyl peroxide again was recovered unchanged.

Acknowledgment.—The authors wish to thank Mr. William Saschek for the microanalyses, Dr. George Sosnovsky for many valuable and helpful suggestions, and Dow Chemical Co. of Midland, Mich., for a sample of pure magnesium. A fellowship to S. O. L. from the Swedish Natural Research Council is gratefully acknowledged.

Experimental[16]

The Grignard reagents were prepared under nitrogen by the reaction of freshly distilled halides with a 10% excess of magnesium pellets in dry ether. The magnesium pellets, supplied by Dow Chemical Co. of Midland, Mich., were shown spectroscopically to be free of transition metal impurities. The Grignard reagents were filtered, and their respective concentrations were determined by the addition of a 2-ml. aliquot to an excess of standard hydrochloric acid and back-titration with standard sodium hydroxide. Aliquots of the reagents were used for the various reactions unless otherwise stated. When samples of the proper Grignard reagents were hydrolyzed, no unreacted organic halides were detected. Diethylmagnesium was prepared by dilution of an ethereal solution of ethylmagnesium bromide with an equal volume of absolute dioxane and decantation of the supernatant solution from the precipitated magnesium bromide after a sedimentation period of 94 hours. Ethereal magnesium bromide was prepared by the reaction of ethylene bromide and magnesium.[17] Phenyllithium was prepared by the usual procedure. *t*-Butyl hydroperoxide was purified by distillation, b.p. 38–39° (22 mm.), n^{20}_D 1.4008, and assayed 95–98%. Benzoyl peroxide was purified by recrystallization from chloroform–ethanol at low temperature, m.p. 108° dec., and assayed 98+%. Commercial *t*-butyl perbenzoate and di-*t*-butyl peroxide were used without purification.

The Reaction of Grignard Reagents with *t*-Butyl Perbenzoate: Preparation of *t*-Butyl Ethers.—*t*-Butyl perbenzoate (0.2 mole) in 100 ml. of ether was added dropwise over a 30-min. interval to a stirred solution of the Grignard reagent (0.21 mole in 200 ml. of ether) which was maintained at 0–5°. Stirring was continued at the same temperature for two hours after which the mixture was poured into an ice–water mixture containing dilute hydrochloric acid. The aqueous layer was extracted several times with ether, and the combined ethereal solution was washed thoroughly with a 2 *N* solution of sodium hydroxide. There was obtained from the alkaline washings 19.0–21.5 g. (80–90%) of benzoic acid and from the ethereal solution, the corresponding *t*-butyl ether as listed below:

Phenyl *t*-butyl ether: yield 65%, b.p. 70–71° (11 mm.), n^{20}_D 1.4880 (literature[18] values b.p. 80° at 20 mm., n^{20}_D 1.4869).

***p*-Tolyl *t*-butyl ether**: yield 81%, b.p. 79–81° (9 mm.), n^{20}_D 1.4882 (literature[19] values b.p. 82.5 at 10 mm., n^{20}_D 1.4879).

***p*-Anisyl *t*-butyl ether**: yield 64%, b.p. 108–109° (9 mm.), n^{20}_D 1.4985. *Anal.* Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.35; H, 8.83.

1-Naphthyl *t*-butyl ether: yield 69%, b.p. 87–88° (0.4 mm.), n^{20}_D 1.5772. *Anal.* Calcd. for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.69; H, 8.28.

Ethyl *t*-butyl ether: yield 77%, b.p. 73–74° at atmospheric pressure, n^{20}_D 1.3758 (literature values[20] b.p. 72.7°, n^{20}_D 1.3755).

1-Octyl *t*-butyl ether: yield 74%, b.p. 83–85° (9 mm.), n^{20}_D 1.4190. *Anal.* Calcd. for $C_{12}H_{26}O$: C, 77.35; H, 14.07. Found: C, 77.17; H, 14.37.

Cyclohexyl *t*-butyl ether: yield 57%, b.p. 55–57° (10 mm.), n^{20}_D 1.4368. *Anal.* Calcd. for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.71; H, 12.60.

2-Propyl *t*-butyl ether: yield 55%, b.p. 87–88° at atmospheric pressure, n^{20}_D 1.3799 (literature[19] values b.p. 87.6°, n^{20}_D 1.3798).

The reaction of phenyllithium with *t*-butyl perbenzoate was carried out at −60° under the same conditions as described in the previous experiment. The yield of phenyl *t*-butyl ether was 59%.

The Preparation of Di-*t*-butyl Ether.—*t*-Butyl perbenzoate (0.05 mole) in ether (50 ml.) was added dropwise to a solution of *t*-butylmagnesium chloride (100 ml. of a 1.5 *N* ethereal solution) maintained at 0–5°. The mixture was stirred at this temperature for two hours. After hydrolysis with dilute acid, the ethereal layer was washed 5 times with a 5% solution of aqueous ferrous sulfate, but a positive test for peroxide persisted. The mixture was flash-distilled at reduced pressure (20 mm.) and a temperature below 35°, and the volatile fraction was collected by means of a Dry Ice trap. Fractional distillation of the volatile fraction at atmospheric pressure yielded 3.2 g. (44%) of colorless di-*t*-butyl ether, b.p. 104–106° and n^{20}_D 1.3955 (literature[21] values b.p. 106.5–107°, n^{20}_D 1.3949).

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(15) R. E. Dessy and G. S. Handler, THIS JOURNAL, **80**, 5824 (1958), and earlier papers.

(16) The boiling points and melting points are uncorrected.

(17) Tissier and Grignard, *Compt. rend.*, **132**, 835 (1901).

(18) R. S. Bowman, D. R. Stevens and W. E. J. Baldwin, THIS JOURNAL, **79**, 87 (1957).

(19) J. B. McKinley, *ibid.*, **69**, 1624 (1947).

(20) W. T. Olson, H. F. Hipsher, C. M. Buess, I. A. Goodman, I. Hart, J. H. Lamneck, Jr., and L. C. Gibbons, *ibid.*, **69**, 2451 (1947).

(21) J. L. E. Erickson and W. H. Ashton, *ibid.*, **63**, 1769 (1941).

The Reaction of Grignard Reagents with *t*-Butyl Hydroperoxide.—a. *t*-Butyl hydroperoxide (0.05 mole) in 50 ml. of ether was added slowly into a solution of the Grignard reagent (0.11 mole) in 50 ml. of ether maintained at 0–5°. Stirring was continued at this temperature for 2–3 hours and at room temperature for 10–16 hours. The reaction mixture was worked up by the regular procedure and the product was identified by its physical constants in comparison with an authentic sample. The yields given in parentheses were based on the amount of hydroperoxide consumed.

Thus, bromobenzene gave phenol (98%), m.p. 39–41°; 2-bromonaphthalene gave 2-naphthol (94%), m.p. 121–123°; *p*-bromotoluene gave *p*-cresol (90%), b.p. 92–94° (12 mm.), $n^{20}\text{D}$ 1.5397; benzyl chloride gave benzyl alcohol (90%), b.p. 100–101° (14 mm.), $n^{20}\text{D}$ 1.5395; 1-bromoöctane gave 1-octanol (92%), b.p. 97–98° (18 mm.), $n^{20}\text{D}$ 1.4290; bromocyclohexane gave cyclohexanol (96%), b.p. 69–71° (16 mm.), $n^{20}\text{D}$ 1.4658; and neopentyl bromide gave neopentyl alcohol (99%), b.p. 113–115°, m.p. 44°.

b. *t*-Butyl hydroperoxide (0.12 mole) in 50 ml. of ether was added during a one-hour period to an ethereal solution of ethylmagnesium bromide (70 ml. of a 2 *N* solution) which was stirred vigorously and cooled by means of a Dry Ice–acetone-bath (−70°). A solution of phenylmagnesium bromide, prepared from 0.1 mole of bromobenzene, then was added during the next 30 minutes into this cold suspension of magnesium *t*-butyl hydroperoxide. The mixture was stirred at −60° for an additional 30 minutes. At the end of this period, it was allowed to warm to 0°, and was maintained at this temperature for two hours. Vigorous stirring was required throughout the reaction in order to avoid caking. Following the usual procedure, there were obtained 7.5 g. (80%) of phenol and 0.7 g. (9%) of biphenyl.

The Reaction of Phenylmagnesium Bromide and Benzoyl Peroxide.—A solution of phenylmagnesium bromide (0.08 mole) in 110 ml. of ether was added over a period of 2.5 hours into a solution of benzoyl peroxide (19.4 g., 0.08 mole) in 175 ml. of benzene maintained at 0–5°. After 16 hours of stirring at room temperature, the resulting mixture gave a negative test for peroxide. Following the regular procedure, there was obtained benzoic acid (12.4 g., 0.102 mole), bromobenzene (2.6 g., 21%) and phenyl benzoate (5.6 g., 35%). The products were identified by comparison of physical constants and infrared spectra with the respective authentic samples.

In a parallel experiment, a portion of this Grignard reagent was hydrolyzed accordingly. With the exception of a small amount of biphenyl, no bromobenzene was detected.

The Reaction of Ethylmagnesium Bromide with Benzoyl Peroxide.—A solution of ethylmagnesium bromide (0.16 mole in 125 ml. of ether) was treated with a benzene solution of benzoyl peroxide (39.6 g., 0.16 mole in 200 ml. of benzene) at 0° by the regular procedure. There were obtained 28.8 g. (145%) of benzoic acid and 8.4 g. (35%) of ethyl benzoate. The recovered ether gave a positive Beilstein test for halogen indicating the possible presence of ethyl bromide.

The Reaction of Magnesium Bromide with Benzoyl Peroxide.—A filtered solution of magnesium bromide prepared from 5 g. (0.21 mole) of magnesium and 37.5 g. (0.20 mole) of ethylene bromide in 200 ml. of ether was added dropwise to a solution of benzoyl peroxide (24.2 g., 0.1 mole) in 20 ml. of cyclohexene and 200 ml. of benzene maintained at 0–5°. The mixture was allowed to warm to room temperature and was stirred at this temperature for two additional hours. Following the usual work-up, there was obtained benzoic acid (21 g., 86%) and *trans*-1,2-dibromocyclohexane (20.3 g., 83%), b.p. 37–39° (0.15 mm.), $n^{20}\text{D}$ 1.5529, identical in all respects with an authentic sample.

The Reaction of Diethylmagnesium with Benzoyl Peroxide.—A solution of diethylmagnesium (0.025 mole) in 125 ml. of ether–dioxane (1:1) was added dropwise to a solution of benzoyl peroxide (12.1 g., 0.05 mole) in 100 ml. of benzene. The mixture was refluxed for 11 hours after the addition, at the end of which period the supernatant solution gave a negative test for Grignard reagent but a positive test for peroxide. There was recovered from the alkaline extracts 4.0 g. of benzoic acid. The organic layer was washed thoroughly with an aqueous solution of sodium iodide in acetic acid until the washing remained colorless. Ethyl benzoate (2.5 g.), b.p. 97–99° (18 mm.), $n^{20}\text{D}$ 1.5065, was isolated from the organic layer by distillation.

The Reaction of Phenyllithium with Benzoyl Peroxide.—A solution of phenyllithium (0.143 mole) in 110 ml. of ether was added over a 40-minute period to a solution of benzoyl peroxide (34.2 g., 0.141 mole) in 250 ml. of benzene maintained at 0–5°. The mixture was stirred at 25° for 2 hours following the addition. The mixture then was hydrolyzed with water and extracted with alkaline. There was obtained from the alkaline extract 17.0 g. of benzoic acid. The organic layer was washed, dried and concentrated under reduced pressure to a semi-solid residue which was crystallized from benzene yielding 7.9 g. (61%) of triphenylcarbinol, m.p. 161–162°.

Reaction of Di-*t*-butyl Peroxide with Phenylmagnesium Bromide.—Di-*t*-butyl peroxide (0.2 mole) in 100 ml. of ether was added with stirring to an ethereal solution of phenylmagnesium bromide (0.21 mole in 200 ml.). Benzene (200 ml.) was added to the mixture and ether was removed by distillation until the boiling point of the mixture reached 80°. The mixture was then refluxed for 8 hours. After the usual work-up, di-*t*-butyl peroxide was recovered unchanged.

CHICAGO 37, ILL.

[CONTRIBUTION FROM THE WYETH INSTITUTE FOR MEDICAL RESEARCH]

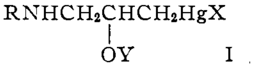
Mercurial Diuretics. I. Addition of Mercuric Chloride and Secondary Amines to Allylamides[1]

BY GERHARD WENDT, B. VITHAL SHETTY AND WILLIAM F. BRUCE

RECEIVED JANUARY 29, 1959

A series of new mercurial diuretics have been prepared by treating a N-allylamide with a secondary amine and mercuric chloride.

Since the introduction of Salyrgan as an effective diuretic in 1924, all the mercurial diuretics have been made by alkoxymercuration of substituted allylamines, resulting in compounds of the basic structure[2]



$$\underset{\text{OY}}{\text{RNHCH}_2\text{CHCH}_2\text{HgX}}$$

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Many variations of groups R and X have been reported. However, little information has been published on the alteration of group Y[3] and these few investigations dealt with changes of the alkyl group in alcohols.[3,4] The use of hydroxylic sol-

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[1] Presented before the Division of Medicinal Chemistry at the 134th Meeting of the American Chemical Society, Chicago, Ill., Sept. 7-12, 1958.

[2] In Salyrgan (Mersalyl) R = *o*-carbamylphenoxyacetic acid, Y = CH_3, X = OH.

[3] The various structures of groups R, Y and X and their effects on diuretic potency have been recently presented in a review by H. L. Friedman, *Ann. N. Y. Acad. Sci.*, **65**, 461 (1957).

[4] E. B. Robbins and K. K. Chen, *J. Am. Pharm. Assoc.*, **40**, 249 (1951); M. M. Best, W. F. Hurt, J. E. Shaw and J. D. Wathen, *Am. J. Med. Sci.*, **225**, 132 (1953); S. L. Shapiro, V. A. Parrino and L. Freedman, *J. Am. Pharm. Assoc.*, **46**, 689 (1957); C. W. Whitehead, THIS JOURNAL, **80**, 2178 (1958); C. W. Whitehead and J. J. Traverso, *ibid.*, **80**, 2182 (1958).