the reaction. There was obtained 18 g. (84%) of 4-bromoacetanilide; m.p. 165°; lit.[6a] 167°.

5-Bromoisatin. A suspension of 16.2 g. (0.11 mol.) of isatin in 100 ml. of carbon tetrachloride was treated with 21.2 g. (0.11 mol.) of *N*-bromocaprolactam. The reaction mixture was heated to reflux to initiate bromination, following which it was stirred at room temperature overnight. The insoluble product was filtered, washed with carbon tetrachloride to insure the removal of residual caprolactam, and finally dried. There was obtained 19 g. (77%) of 5-bromoisatin; m.p. 254–256°; lit.[7] m.p. 255–256°.

Cyclohexanone. Into a flask equipped with a stirrer and reflux condenser were placed 5 g. (0.05 mol.) cyclohexanol, 75 ml. benzene, and 10 ml. pyridine. While agitating, 9.6 g. (0.05 mol.) of *N*-bromocaprolactam was added all at once. After a short induction period (*ca.* 15 min.), an exothermic reaction occurred, causing the benzene to reflux. The mixture was then allowed to stir without further application of heat for 18 hr. The solid pyridine hydrobromide was filtered. The filtrate was washed with a dilute aqueous solution of sodium hydrosulfite to decompose any unreacted *N*-bromocaprolactam, following which the organic layer was washed successively with two 50-ml. portions of $2N$ sulfuric acid, two 50-ml. portions of distilled water, and finally dried over anhydrous sodium sulfate. After removing the benzene by distillation, there was obtained 4 g. (82%) of cyclohexanone. The ketone was identified by converting it to its 2,4-dinitrophenylhydrazone; m.p. 159°; lit.[6b] 162°.

Benzophenone. To a solution of 9.2 g. (0.05 mol.) of benzhydrol in 75 ml. of benzene was added 10 ml. of pyridine, following which 9.6 g. (0.05 mol.) of *N*-bromocaprolactam was added all at once. The solution was refluxed for 1 hr. to initiate the reaction, following which the mixture was stirred at room temperature for 18 hr.

The product was isolated as in the previous experiment. There was obtained 8 g. (88%) of benzophenone; 2,4-dinitrophenylhydrazone; m.p. 239–240°; lit.[6c] 239°.

Acknowledgment. The authors are indebted to Mr. M. D. Edelman for his helpful suggestions during the course of this investigation.

ALLIED CHEMICAL CORPORATION
NATIONAL ANILINE DIVISION
BUFFALO 5, N. Y.

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(6) R. L. Shriner and R. C. Fuson, *The Systematic Identification of Organic Compounds*, J. Wiley and Sons, Inc., New York, 1948, (a) p. 232, (b) p. 262, (c) p. 264.

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Oxidation of Hindered Phenols. Preparation of Bis(1,3,5-tri-*t*-butyl-2,5-cyclohexadiene-4-one) Peroxide

HARRY S. BLANCHARD

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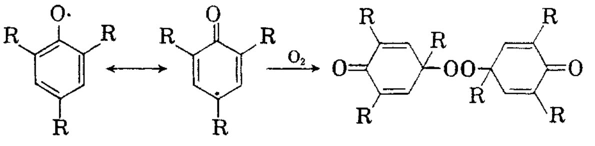
Cook and Woodworth[1] have reported the quantitative preparation of the stable 2,4,6-tri-butylphenoxy radical (I) by oxidation of 2,4,6-tri-*t*-butylphenol (II) with alkaline ferricyanide. Moreover, they found that I could be converted to bis-(1,3,5-tri-*t*-butyl-2,5-cyclohexadiene-4-one) peroxide (III) if the oxidation of II were carried out in the presence of air or oxygen. In this manner they were able to prepare III in a crude yield of 81% utilizing a reaction time of a few hours. We have found that III can be prepared quickly in a state of high purity and in essentially quantitative yield by oxidizing II with silver oxide in the presence of oxygen. Interestingly enough, although the yield of III is nearly quantitative, the solutions never absorb the theoretical amount of oxygen. Thus, in a typical experiment, when 0.01 mol. of II was oxidized in 100 ml. of benzene with 0.022 mole of silver oxide, 0.0035 mol. of oxygen was absorbed. This corresponds to only 70% of the theoretical quantity of oxygen, although 0.0049 mol. (98%) of III was isolated. This finding suggests that some of the oxygen which ultimately ends up in the peroxide must come directly from the silver oxide.



I R = *t*-butyl III

Silver oxide is known to undergo a rather facile thermal decomposition to silver metal and oxygen although the reaction is very slow below 160°.[2] However, as the decomposition is catalyzed by light as well as by silver metal itself, it is perhaps not unreasonable that some of the oxygen does come from the oxide. Moreover, as silver metal is a catalyst for the decomposition, it may not be unreasonable to suggest that I can also function as a catalyst for this decomposition. In this connection, Witsiepe[3] has recently investigated the use of silver oxide in preparing stable phenoxy radicals, including I. He found that II could be converted quantitatively to I only when freshly prepared silver oxide was employed under rather special conditions. Most of the present work was carried out utilizing a sample of commercial silver oxide. However, the same results were also obtained when we employed a sample of silver oxide freshly prepared according to Witsiepe's directions. In view of these results we would suggest that silver oxide is a poor choice as a reagent when the object is to prepare I itself. Along these same lines Müller and co-workers[4] found that when II was oxidized with lead dioxide, the yield of I was not quantitative, apparently because of reaction of I with the lead dioxide. In view of the present results it would seem likely that here too there is a direct reaction

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(1) C. D. Cook and R. C. Woodworth, *J. Am. Chem. Soc.*, **75**, 6242 (1953).

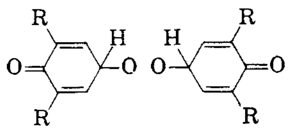
(2) H. Remy, "Treatise on Inorganic Chemistry," Elsevier Publishing Co., New York, 1956, p. 398.

(3) W. K. Witsiepe, *The Effect of t-Butyl Groups and Phenyl Groups on the Dissociation of Phenoxy Radicals*, University Microfilms, Publication No. 20,540, Ann Arbor, Michigan, 1956, pp. 61–65.

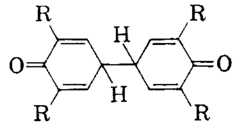
(4) E. Müller, K. Ley, and W. Keidaisch, *Ber.*, **87**, 1605 (1954).

between I and lead dioxide probably resulting in III.

As we were also interested in obtaining bis(1-hydro-3,5-di-*t*-butyl-2,5-cyclohexadiene-4-one) peroxide (IV), we briefly examined the oxidation of 2,6-di-*t*-butylphenol (V) with silver oxide and also with alkaline potassium ferricyanide. Recently Kharasch and Joshi[5] oxidized V with alkaline ferricyanide in the absence of air and isolated 3,5,3′,5′-tetra-*t*-butyl-1,1′-dihydro-2,5,2′,5′-biscyclohexadiene-4,4′-dione (VI), along with the known of 2,6,-2′,6′-tetra-*t*-butyldiphenoquinone. This interesting keto tautomer was reported by Kharasch and Joshi to be stable in non-polar solvents, but to tautomerize immediately to the bisphenol in hydroxylic solvents such as alcohols.



IV R = *tert*-butyl



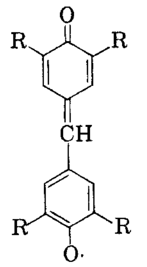
VI R = *t*-butyl

We found that V is oxidized by silver oxide to essentially the same mixture as reported by Kharasch and Joshi. Moreover, this same mixture results even when the oxidation is run in the presence of oxygen. We could find no evidence for a reaction between the phenoxy radical intermediates and oxygen. Further, we were somewhat surprised by the fact that VI itself did not react directly with oxygen yielding the corresponding diphenoquinone, particularly in the presence of the silver oxide.

As VI rearranges to the corresponding bisphenol in polar solvents, it seemed of interest to examine the oxidation in methanol and ethanol. Here we found, as expected, that a good yield of the tetra-*t*-butyldiphenoquinone resulted, apparently via the rearrangement of VI to the bisphenol and further oxidation of this to the diphenoquinone.

Because we were unable to prepare IV via the silver oxide route, it seemed of interest to oxidize V under Kharasch's and Joshi's conditions, except in the presence of oxygen. To this end we oxidized V with alkaline potassium ferricyanide in the presence of oxygen. However, as in the silver oxide oxidations oxygen had no effect on this reaction, and the same mixture of VI and the tetra-*t*-butyldiphenoquinone was obtained in the presence as well as in the absence of oxygen.

Recently, Müller and co-workers[6] presented convincing evidence that the oxidative coupling of V proceeds via the corresponding phenoxy radical. In view of this it seems somewhat surprising that oxygen is such an inefficient scavenger for these radicals. By way of comparison, carbon radicals are scavenged very effectively by oxygen even in the presence of efficient phenolic type inhibitors.[7] It should be pointed out that certain phenoxy radicals such as VII have been shown to be unreactive toward oxygen.[8] However, such phenoxy radicals as VII possess unique resonance stabilization, a characteristic difficult to ascribe to the phenoxy radical resulting from oxidation of V. Rather, one must conclude either that the intermediate 2,6-di-*t*-butylphenoxy radicals prefer to undergo a coupling reaction or that V itself is a very efficient scavenger for the corresponding 2,6-di-*t*-butylphenoxy radical, resulting in the observed products.



VII R = *t*-butyl

EXPERIMENTAL

Materials. 2,4,6-Tri-*t*-butylphenol (II) was prepared by the procedure of Stillson, Sawyer, and Hunt.[9] It was purified by recrystallization from ethanol, m.p. 131–132° (lit.[6] m.p. 130–131°. 2,6-Di-*t*-butylphenol (V) (Eastman Kodak) was purified by several recrystallizations from *n*-hexene, m.p. 36–37°. Silver oxide (Eastman Kodak) was used without further purification. The freshly prepared silver oxide was made according to the directions of Witsiepe.[3]

Bis(1,3,5-tri-t-butyl-2,5-cyclohexadiene-4-one) peroxide (II). In a typical experiment 2.62 g. (0.01 mol.) of 2,4,6-tri-*t*-butylphenol in 100 ml. of benzene containing 5 g. (0.022 mol.) of commercial silver oxide was agitated at room temperature with oxygen. Adequate mixing was obtained by the use of a Fisher "Vibro-Mixer." After 0.5–1 hr., the solids were removed by filtration and the benzene evaporated at room temperature. In this manner 2.7 g. (98%) of a very pale green solid was isolated, m.p. 148–149° (lit.[1] m.p. 148–149°). Recrystallization from ethanol had no effect on the melting point. Several experiments were run in which the oxygen absorption was followed by means of a gas burette. In every instance including the use of freshly prepared silver oxide, only 60–70% of the theoretical quantity of oxygen was absorbed while the yield of III varied between 90–100%.

3,5,3′,5′-Tetra-t-butyl-1,1′-dihydro-2,5,2′,5′-bis-cyclohexadiene-4-one (VI). a. *Silver oxide in benzene.* In a typical experiment 4.12 g. (0.02 mol.) of 2,6-di-*t*-butylphenol in 300

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[5] M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1439 (1957).

[6] K. Ley, E. Müller, R. Mayer, and K. Scheffler, *Ber.*, **91**, 2670 (1958).

[7] C. E. Boozer, G. S. Hammond, C. E. Hamilton, and J. N. Sen, *J. Am. Chem. Soc.*, **77**, 3233 (1955).

[8] M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1435, 1957; G. M. Coppinger, *J. Am. Chem. Soc.*, **79**, 501 (1957).

[9] G. H. Stillson, D. W. Sawyer, and C. K. Hunt, *J. Am. Chem. Soc.*, **67**, 303 (1945).

ml. benzene was stirred for 2 hr. with 9.3 g. (0.04 mol.) of commercial silver oxide. The solids were removed by filtration and the red colored filtrate evaporated in a rotary film evaporator at 15–20 mm. The dark residue was transferred with the aid of petroleum ether to a filter funnel and the solids washed with petroleum ether leaving very light lemon colored crystals, 2.8 g., m.p. 151–152° (lit.[5] m.p. 151–152°) mixed m.p. 151–152°. The filtrate was evaporated leaving 1 g. of a dark brown solid, m.p. 243°, which was identified by infrared comparison as 2,6,2′,6′-tetra-*t*-butyldiphenoquinone. This same mixture resulted when the reaction was carried out in the presence of oxygen.

b. *Alkaline ferricyanide in benzene.* The experiment reported by Kharasch and Joshi[5] was repeated in both a nitrogen atmosphere as well as in an oxygen atmosphere. In the case of the experiments with oxygen, mixing was accomplished with a Fisher "Vibro-Mixer." The reactions were worked up as described by Kharasch and Joshi and in each instance the same mixture of VI and the tetra-*t*-butyldiphenoquinone was obtained regardless of the presence or absence of oxygen. Thus oxygen appears to have no effect on this reaction.

2,6,2′,6′-Tetra-t-butyldiphenoquinone. In a typical experiment 2.06 g. (0.01 mol.) of 2,6-di-*t*-butylphenol in 200 ml. of methanol or ethanol was stirred with 4.7 g. (0.02 mol.) of silver oxide for 1 hr. The solids were removed by filtration and washed with hot benzene, the benzene being combined with the filtrate. The filtrate was then concentrated to approximately one quarter of its original volume and the red solids (2.0 g., 97%) which had separated were collected by filtration, m.p. 246° (lit.[5] for the diphenoquinone, 245°). The material was further identified by infrared comparison with an authentic sample.

General Electric Research Laboratory
Schenectady, New York

Improved Synthesis of Salts and Esters of Nitroacetic Acid

Virgil E. Matthews and Donald G. Kubler[1]

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The esters of nitroacetic acid are usually prepared from nitromethane by means of a two-step synthesis. The dipotassium salt of nitroacetic acid is made *via* the self-condensation of two molecules of nitromethane in the presence of strong, aqueous alkali[2] and the salt is then esterified directly by acidification in the presence of the appropriate alcohol.[3] The best yields reported by previous investigators were about 57% of relatively pure salt for the first step and 60% for the esterification, or an over-all yield of nitroacetate ester of 34%, based on nitromethane.[3]

In an effort to improve these yields, a study of both the salt formation and the esterification procedures was undertaken in this laboratory. The first step contains an inherent disadvantage in that the salts of nitroacetic acid are unstable in aqueous base solution, decomposing to give the alkali metal salt of nitromethane and the corresponding alkali carbonate.[4,5] Consequently, there

$$KO_2N{=}CHCOOK + KOH \longrightarrow K^+CH_2NO_2^- + K_2CO_3$$

is an upper limit to the yield of dipotassium nitroacetate which can be obtained by the self-condensation of nitromethane in aqueous potassium hydroxide. It appeared that if the amount of water in the reaction system could be minimized, the decomposition of the nitroacetate salt could be lessened and higher yields obtained.

The ultraviolet absorption spectra of nitroacetate ion and its precursors, nitromethane and methazonate ion, have been determined under a variety of conditions[5] and the effect of *p*H on the position and intensity of the methazonate absorption band has been investigated.[6] An analytical method based on the ultraviolet absorption spectra of the various entities was developed for the determination of nitroacetate in mixtures. This method is described further in the Experimental section.

Application of the optical analytical method to the study of the reaction of nitromethane with potassium hydroxide in various alcohols showed that when the condensation is carried out in *n*-butanol, yields of dipotassium nitroacetate of from 80–90% can be obtained. Results found using various solvents are listed in Table I.

TABLE I

Effect of Solvent on the Reaction of Nitromethane with Potassium Hydroxide

Mole Ratio of KOH/CH_3NO_2, 4/1

Solvent	Max. Reaction Temp.	Reflux Time, Hr.	Yield, % Nitroacetate (±2%)	Yield, % Methazonate
50% aq. KOH	118	25 min.	51	0
CH_3OH	73	38.3	0	17[a]
C_2H_5OH	95	23.25	0	81
C_4H_9OH[b]	118	20	84	3
n-Hexanol	142	20	83	0

[a] Recovered some material which had a λ_{max} of 288 mμ in 1*N* KOH. [b] When potassium butoxide was substituted for potassium hydroxide, no dipotassium nitroacetate was formed, but high yields (90–100%) of potassium methazonate were recovered.

Further studies of the reaction in butanolic potassium hydroxide gave the results shown in Table II.

The crude solids obtained from the reaction mixtures are always contaminated with varying amounts of alkali, alcohol, and unconverted potassium methazonate. However, they may be recrystal-

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(1) Present address: Hampden-Sydney College, Hampden-Sydney, Va.

(2) W. Steinkopf, *Ber.*, **42**, 3925 (1909).

(3) H. Feuer, H. B. Hass, and K. S. Warren, *J. Am. Chem. Soc.*, **71**, 3078 (1949).

(4) W. Steinkopf, *Ber.*, **42**, 2026 (1909).

(5) A. Hantzsch and K. Voigt, *Ber.*, **45**, 85 (1912).

(6) C. M. Drew, J. R. McNesby, and A. S. Gordon, *J. Am. Chem. Soc.*, **77**, 2622 (1955).