small portion of the aminophenol (0.7 g.) was dissolved in benzene, precipitated with ligroin, filtered, and dried. 2-Isopropyl-4-aminophenol, m.p. 126.5–128° (dec.), was unstable in the presence of air and its hydrochloride was too hygroscopic to be characterized. Acetylation[20] yielded the triacetyl derivative,[21] m.p. 99.5–100.5° (from petroleum ether).

Anal. Calcd. for $C_{15}H_{19}NO_4$: C, 64.96; H, 6.91. Found: C, 65.29; H, 6.74.

2-Isopropyl-1,4-quinone. The aminophenol was treated with stannous chloride and hydrochloric acid as described in the preparation of 1,4-aminonaphthol hydrochloride,[7] diluted with water (4000 ml.), diazotized with sodium nitrite (170 g.) and concentrated sulfuric acid (110 ml.), heated to 60° and steam-distilled.[6] Filtration and subsequent ether extraction of the steam distillate yielded 67 g. (60% based on the starting phenol) of 2-isopropyl-1,4-quinone, m.p. 34–36° (lit. m.p. 28°[16]).

2-Isopropyl-1,4-hydroquinone. To a vigorously stirred solution of 2-isopropyl-1,4-quinone (118 g., 0.78 mole) in ether (300 ml.) technical sodium hydrosulfite (191 g., about 1 mole) in water (400 ml.) was added gradually. After stirring (3 hr.) the ether phase was separated and the aqueous phase extracted with ether (2 × 100 ml.). The residue left after evaporation of the ether extracts was recrystallized from benzene, giving 98 g. (82%) 2-isopropyl-1,4-hydroquinone, m.p. 127–128°. A sample, recrystallized twice from benzene and sublimed, colorless needles, m.p. 129–131° (lit. m.p. 130–131°[16], 147–148°[17]).

2-Isopropyl-4-methoxyphenol. To 2-isopropyl-1,4-hydroquinone (97 g., 0.64 mole) stirred at 9° in sodium hydroxide (4*N*, 350 ml.), dimethylsulfate (71.5 ml., 0.76 mole) was added over a period of 2.5 hr. and stirred for another hour at 9°.[9] The mixture was extracted with six 100-ml. portions of ether (extract I), acidified with 6*N* hydrochloric acid (250 ml.) and re-extracted with four 100-ml. portions of ether (extract II). Following removal of ether, distillation of extract I (81.3 g.) yielded 26.5 g. of 2-isopropyl-1,4-dimethoxybenzene, b.p. 122–124° (11 mm.), $n_D^{23} = 1.5130$. (Lit.[22] b.p. 114–116° (15 mm.) $n_D^{17} = 1.5105$).

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.50; H, 8.87. Further distillation of extract I yielded 27.2 g. (40%) of 2-isopropyl-4-methoxyphenol, b.p. 136–141° (12 mm.), $n_D^{23} = 1.5280$, $\log \epsilon_{max} = 3.539$ (292 mμ) and $\log \epsilon_{min} = 2.050$ (252 mμ) in 95% ethanol. (Lit.[18] 118–119°/4.5 mm.).

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.03; H, 8.53. Extract II (in ether) was passed through a column of activated alumina, giving 34.2 g. of material, m.p. 110–122°, which was assumed to be impure isopropylhydroquinone.

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Synthesis of 2-Tolyl-1-ethynylcyclohexanols

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Tertiary acetylenic carbinols are often conveniently prepared by the reaction of an alkali metal acetylide with the appropriate ketone in liquid ammonia. Under these conditions sodium acetylide has been used successfully with cyclohexanone,[2,3] and with several methyl substituted cyclohexanones[3] to give the corresponding 1-ethynylcyclohexanols; lithium acetylide in liquid ammonia has been used with good results for a number of tertiary acetylenic carbinols.[4] Application of the above methods to 2-(*o*-tolyl)cyclohexanone resulted in poor yields of 2-(*o*-tolyl)-1-ethynylcyclohexanol with recovery of almost half of the unreacted starting ketone in each case. This low yield could result from the low solubility of the tolylcyclohexanone in liquid ammonia. Dropwise addition of an ether solution of 2-(*o*-tolyl)cyclohexanone to the sodium or lithium acetylide–liquid ammonia mixture resulted in precipitation of the solid ketone. Much better yields were obtained by treating 2-(*o*-tolyl)cyclohexanone with lithium aceytlide in purified, anhydrous methylal (dimethoxymethane) at room temperature. The three 2-tolyl-1-ethynylcyclohexanols were prepared by this method.

The fact that only one 3,5-dinitrobenzoate was obtained from each 2-tolyl-1-ethynylcyclohexanol is not considered a proof that only one isomer, either cis or trans, was obtained because the 3,5-dinitrobenzoates were not obtained quantitatively and there is always a possibility that one isomer could undergo dehydration under the conditions of esterification.

EXPERIMENTAL

The preparation of 2-(*o*-tolyl)-1-ethynylcyclohexanol illustrates the general procedure used for obtaining all three isomers. Anhydrous acetylene was bubbled through 300 ml. of anhydrous liquid ammonia (distilled after addition of sodium) and 1.1 g. (0.16 g. atom) of lithium metal was added in small pieces at such a rate that not much blue color was allowed to accumulate. When the lithium had all reacted 100 ml. of purified, anhydrous methylal was slowly added and the NH_3 was allowed to evaporate while bubbling acetylene slowly through the mixture. An additional 50-ml. portion of methylal was added to the resulting white, curdy mixture. A solution of 15 g. (0.08 mole) of 2-(*o*-tolyl)-cyclohexanone[5] in 60 ml. of methylal was added dropwise at room temperature with stirring and the mixture was stirred at room temperature for 16 hr. while passing a slow stream of acetylene through the mixture. The mixture was hydrolyzed by pouring into 400 ml. of ice water mixture containing 20 ml. of concentrated HCl. The mixture was extracted with ether, the ether solution washed with 5% sodium bicarbonate solution and dried over calcium sulfate. Removal of the ether gave 16.2 g. of oily substance which was treated with Girard T reagent giving 13.8 g. of nonketonic oily substance and 2 g. of unreacted ketone. Distillation of the oily sub-

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TABLE I

2-TOLYL-1-ETHYNYLCYCLOHEXANOLS AND CORRESPONDING 3,5-DINITROBENZOATE DERIVATIVES

2-Tolyl-1-ethynyl-cyclohexanols	B.P., ° C.	Mm.	C Calcd.	C Found	H Calcd.	H Found
1. 2-(*o*-Tolyl)-	131–132	~2	84.07	84.11	8.47	8.38
2. 2-(*m*-Tolyl)-	115	0.45	84.07	84.02	8.47	8.48
3. 2-(*p*-Tolyl)-	134	~2	84.07	84.19	8.47	8.11

3,5-DINITROBENZOATES OF ABOVE CYCLOHEXANOLS

Derivative of:	M.P., ° C.	C Calcd.	C Found	H Calcd.	H Found	N Calcd.	N Found
1. 2-(*o*-Tolyl)-	168–169	64.69	64.52	4.94	4.82	6.86	6.75
2. 2-(*m*-Tolyl)-	161.5–162.5	64.69	64.51	4.94	4.90	6.86	6.80
3. 2-(*p*-Tolyl)-	161–162	64.69	64.83	4.94	4.82	6.86	6.70

stance gave 12 g. of colorless viscous liquid, b.p. 131–132° at about 2 mm.

Under the same conditions 21 g. of 2-(*m*-tolyl)cyclohexanone gave 16.4 g. of 2-(*m*-tolyl)-1-ethynylcyclohexanol and 1.54 of unreacted ketone. With the para isomer less than one gram of unreacted ketone was recovered from 18 g. of starting ketone. All three products gave a precipitate when treated with alcoholic ammoniacal silver nitrate solution.

The methylal was treated with sodium for a few days then fractionated through a Todd precise fractionation assembly with a 90 cm. column packed with glass helices and subsequently stored over sodium wire.

3,5-Dinitrobenzoates. A mixture of 0.5 g. of the cyclohexanol, 0.52 g. of 3,5-dinitrobenzoyl chloride, and 5 ml. of pyridine was allowed to stand at room temperature for 24 hr. The mixture was then warmed on a water bath for 5 min., poured into 20 ml. of water and extracted with ether. The ether solution was washed with 1% HCl followed by 1% sodium carbonate and water.

Infrared absorption spectra. The I. R. spectra[6] of all three isomers, taken on pure liquid samples, have a sharp $\equiv$C—H stretching absorption band at 3270 cm.$^{-1}$ and what could be a weak C$\equiv$C stretching band at 2090 cm.$^{-1}$; Wotiz *et al.*[7] have reported a frequency of 2080 cm.$^{-1}$ for the latter in 1-heptyn-3-ol. A strong band appears at 970, 973, and 974 cm.$^{-1}$ in the spectrum of the ortho, para, and meta isomer respectively, a region which falls within the range of characteristic absorption for cyclohexane derivatives.[8] With each isomer in the pure liquid state the O—H stretching absorption band has two distinct peaks of almost equal intensity, one at 3490 and the other at 3380 cm.$^{-1}$. These are attributed to unassociated and to hydrogen bonded hydroxyl groups. This is substantiated by the fact that when measured in 0.03*M* solution in carbon tetrachloride, with a 1 mm. liquid cell, a single sharp band appears at 3560 cm.$^{-1}$.

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(6) The spectra were obtained on a Perkin-Elmer Model 21 spectrophotometer with NaCl prism.

(7) J. H. Wotiz, F. A. Miller, and R. J. Palchak, *J. Am. Chem. Soc.*, **72,** 5055 (1950).

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An Improved Synthesis of Monoperphthalic Acid

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Other experiments[1] have shown the Böhme procedure[2] for preparing monoperphthalic acid from phthalic anhydride and hydrogen peroxide to be very sensitive to slight variations in experimental conditions. A modified procedure, requiring a 24 hour reaction time, has been devised, and a 65% yield of peracid reported.[1]

We have also encountered difficulty with the Böhme preparation and have overcome it by substituting sodium carbonate for sodium hydroxide as the basic agent. In this manner reproducible yields of 76–78% of ethereal solutions of monoperphthalic acid were secured in 0.5 hour reaction times. Essentially no decomposition of hydrogen peroxide was observed; this allowed the use of only a slight excess of that material, rather than the 100% excess employed in the earlier procedures.[1,2]

EXPERIMENTAL

Monoperphthalic acid. To a 1-l., round-bottomed flask, equipped with mechanical stirrer and thermometer, and cooled by an ice-salt bath, was added a solution of 62 g. (0.50 mole) of sodium carbonate monohydrate in 250 ml. of water. This was cooled to 5° and 70 g. (0.6 mole) of 30% hydrogen peroxide was added in one portion. When the temperature of the mixture reached 0°, there was added 75 g. (0.50 mole) of phthalic anhydride which had previously been pulverized to pass a 14-mesh sieve. After vigorous stirring at −5–0° for 30 min., all but a trace of the anhydride had dissolved. The solution was poured into a 2-l. separatory funnel, covered with 350 ml. of ether and treated with an

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(2) H. Böhme, *Ber.* **70,** 379 (1937); *Org. Syntheses,* Coll. Vol. III, 619 (1955). See also G. B. Bachman and D. E. Cooper, *J. Org. Chem.*, **9,** 307 (1944).