TABLE I

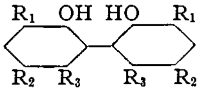
NEW 3,4,6-TRIALKYLPHENOLS AND DERIVATIVES

Compound	Yield, %	M.p. or b.p. (mm.), °C.	Empirical formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
3,4-Dimethyl-6-*tt*-octylphenol	74[a]	91.5	$C_{16}H_{24}O$	81.99	81.77[b]	11.18	11.30[b]
3,4-Dimethyl-6-(α,α-dimethylbenzyl)-phenol	38[c]	64–65[d]	$C_{17}H_{20}O$	84.96	84.86[b]	8.38	8.38
3,4-Dimethyl-6-*s*-butylphenol	35	144–150 (20)	$C_{12}H_{18}O$	80.85	80.70	10.17	10.24
2-Chloro-3-methyl-4,6-di-*t*-butylphenol	95[e]	53–54	$C_{12}H_{24}OCl$	13.91[g]	14.22[g]		
2-Bromo-3-methyl-4,6-di-*t*-butylphenol	64[f]	61.5–62	$C_{12}H_{24}OBr$	26.46[h]	26.62[h]		

[a] First crop from 366 g. (3 moles) of 3,4-dimethylphenol weighed 340 g. (m.p. 90.5°); second crop weighed 175 g. (m.p. 88–89°). [b] Average of two determinations. [c] Melting point of this product was 63–64°. [d] Crude product distilled at 178–190° at 10 mm. [e] Melting point of product was 48–49°. [f] Yield of purified product. [g] Chlorine, %. [h] Bromine, %.

TABLE II

HEXASUBSTITUTED DIHYDROXYBIPHENYLS OBTAINED BY OXIDATION OF 3,4,6-TRISUBSTITUTED PHENOLS



Compound	Yield, %	M.p., °C.	Empirical formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Mol. wt. Calcd.	Mol. wt. Found	Act. H per molecule (Zerewitinoff) Calcd.	Act. H per molecule (Zerewitinoff) Found
$R_1 = R_2 = t\text{-}C_4H_9$ $R_3 = CH_3$	76[a]	241–242	$C_{30}H_{46}O_2$	82.13	81.94	10.57	10.82	438.7	423	2	1.79[b]
$R_1 = t\text{-}C_4H_9$ $R_2 = R_3 = CH_3$	76[c]	160.5–161.5	$C_{24}H_{34}O$	81.31	81.16[b]	9.67	9.78[b]	354.5	346[b]	2	1.82[b]
R_1 = *tt*-Octyl $R_2 = R_3 = CH_3$	89[d]	122–123	$C_{32}H_{50}O_2$	82.35	81.98	10.80	11.12	466.7	430	2	1.79[b]
R_1 = (α,α-dimethylbenzyl) $R_2 = R_3 = CH_3$	50[e]	205–207	$C_{34}H_{38}O_2$	85.31	85.15	8.00	7.95	475.6	441	2	1.74[b]
$R_1 = CH_3$; R_2 = Cl R_3 = *t*-Butyl	23[f]	149–151	$C_{22}H_{28}O_2Cl_2$[g]	66.80	66.84[b]	7.09	7.14[b]	395	287[b]		

[a] At this yield, m.p. 232–235°. [b] Average of two determinations. [c] At this yield, m.p. 140–142°. [d] At this yield, m.p. 106°. [e] Essentially pure product. [f] At this yield, m.p. 137–142°. [g] Calcd.: Cl, 18.0. Found: Cl, 17.7.

TABLE III

OXIDATION OF HIGHLY SUBSTITUTED PHENOLS TO QUINONES

Phenolic cmpd. oxidized	Product, -quinone	Yield, %	M.p., °C.	Empirical formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Mol. weight Calcd.	Mol. weight Found
4-*t*-Butyl-2,5-dimethylphenol	2,5-Dimethyl-	21[a]	126–127[b]	$C_8H_8O_2$	70.57	70.66	5.92	6.18		
2-Bromo-3-methyl-4,6-di-*t*-butylphenol	2-Bromo-3-methyl-6-butyl-	24[c]	103.5–105	$C_{11}H_{13}O_2Br$[d]	51.38	51.43	5.09	5.34	257.2	257
2-Chloro-3-methyl-4,6-di-*t*-butylphenol	2-Chloro-3-methyl-6-*t*-butyl-	18	93.5–94	$C_{11}H_{13}O_2Cl$[e]	62.12	62.44	6.16	6.24	212.6	214
3-Methyl-4,6-di-*t*-butylphenol	2-Methyl-5-*t*-butyl-	22[f]	99–100[g]	$C_{11}H_{14}O_2$	74.13	74.00	7.92	8.19		

[a] At this yield, m.p. 121.5–122°. [b] R. Nietzke, *Ann.*, **215**, 168 (1882), reports 125°; L. I. Smith, J. W. Opie, S. Wawzonek and W. W. Prichard, *J. Org. Chem.*, **4**, 318 (1939), report 123.5–125°; L. I. Smith and J. W. Opie, *ibid.*, **6**, 427 (1941), report 123–125°. [c] Yield of purified product. [d] Calcd.: Br, 31.1. Found: Br, 31.7. [e] Calcd.: Cl, 16.67. Found: Cl, 16.89. [f] Based on 3-methyl-4,6-di-*t*-butylphenol not converted to dihydroxybiphenyl. [g] M. Battegay and P. Haeffely, *Bull. soc. chim.*, [4] **35**, 988 (1924), report 95°; O. A. Zeide and B. M. Dubinin, *J. Gen. Chem. U.S.S.R.*, **2**, 455 (1932); *C. A.*, **27**, 961 (1933), report 96°.

hours, orange-red crystals were obtained which were filtered and dried. The gummy solid (weight 13.2 g.) was recrystallized from petroleum ether to give 3.2 g. of yellow-orange crystals, m.p. 102–104°; recrystallized from methanol, yield 3.1 g., m.p. 103.5–105°.

Acknowledgment.—The author wishes to express his gratitude to Dr. G. E. P. Smith, Jr., for his valuable advice and encouragement during this investigation. The interest of Dr. F. W. Stavley and Dr. R. F. Dunbrook in this work and the permission of the Firestone Tire and Rubber Company to publish this material were greatly appreciated. The author wishes to thank Mr. D. M. Kimble for the Zerewitinoff determinations of active hydrogen. Acknowledgment is made to Dr. W. C. Sears for carrying out the infrared absorption studies referred to in this paper and to Dr. A. W. Scholl for the ultraviolet absorption work.

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Some New Amino Alkylphenols

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Although a considerable number of alkylaminophenols in which the alkyl group is attached to nitrogen have been reported in the literature, relatively few amino alkylphenols having the alkyl group attached to the benzene ring have been described. Aminothymol is reported in the early literature[1] and the preparation of pure samples of this compound and other amino alkylphenols is the subject of three United States patents.[2-4] Stevens and Beutel[5] describe aminothymol as well as aminocarvacrol and several *o*-aminophenols having an alkyl group in the position *para* to the hydroxyl group, and they have patented derivatives of *m*-ethyl-*p*-aminophenol.[6] The preparation of some 4-*n*-alkyl-2-aminophenols has been reported by Baranger.[7] The patent literature contains a number of other references to amino alkylphenols,[8-10] but in some cases these compounds were used as intermediates and were not characterized.

In this work an alkylphenol was used as the starting material in each case. Where possible, the corresponding nitroso compound was prepared and this was then reduced to the corresponding amino compound. Alkylphenols which would not nitrosate were nitrated in acetic acid or benzene solution and the resulting compound was reduced by zinc and acetic acid. When the nitration was carried out in acetic acid solution, the nitro compound was not isolated in some instances, but was reduced in this solution with tin and hydrochloric acid. The amino alkylphenol was then isolated as the hydrochloride, which was purified and converted to the free base.

Another convenient preparative method utilized to some extent was the coupling of the alkylphenol with diazotized sulfanilic acid, followed by reduction of the intermediate azo compound by sodium hydrosulfite to give the desired amino alkylphenol.

All compounds have been named using the convention that the phenol group is in the 1-position. There has been some confusion in the literature on alkylated phenols because of the existence of different systems of nomenclature and the failure in some publications to define the system used. For example, the methyl substituted phenols have been named by numbering from a methyl group, contrary to present accepted practice in this country, without clearly indicating this fact. Thus, a compound which is actually 6-*t*-butyl-*m*-cresol[11,12] was marketed in this country for a number of years as 4-*t*-butyl-*m*-cresol.

Certain assumptions have been made regarding the structure of some of the alkylphenol starting materials. Since under ordinary alkylation conditions the monobutylation of *m*-cresol gives 6-*t*-butyl-*m*-cresol,[11,12] it has been assumed that the corresponding monoisobornyl and mono-*tt*-octyl derivatives are similarly substituted. The 4-isomer has been assumed to predominate in the products from the monobutylation or mono-*tt*-octylation of *o*-cresol.[13-15] These assumptions are in agreement with the fact that the above mentioned alkyl-*m*-cresols readily give crystalline nitroso derivatives while the alkyl-*o*-cresols do not, since nitrosation occurs only at the 4-position in phenolic compounds of the benzene series.[16,17]

The ease of nitration of the alkylphenols employed varied considerably with the position and kind of alkyl groups. For example, an excellent yield of amino compound was obtained by nitration of 4-*tt*-octylphenol followed by reduction, a fair yield was obtained using 2-methyl-4-*tt*-octylphenol, and a poor yield was obtained from 2-*tt*-octyl-4-methylphenol. In the case of the last mentioned compound the hindrance caused by the large octyl group in the position *ortho* to the OH

TABLE I[a]

ALKYLPHENOLS NOT PREVIOUSLY REPORTED

Phenol	Yield, %	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
3,4-Dimethyl-6-*tt*-octyl-[b]	73.4	81.99	81.83	11.18	11.33[a]
3-Methyl-6-iso-[d] bornyl-[c]	43.0	83.55	83.35[d]	9.90	9.93[d]

[a] Analyses reported in all tables are averages of two values except where indicated. [b] Prepared by the reaction of 3,4-dimethylphenol and diisobutylene: m.p. 91.5°. [c] Prepared by the reaction of *m*-cresol and camphene: b.p. 195–199° (10 mm.), n^{20}_D 1.5482. [d] Average of three determinations.

TABLE II

NITROSO ALKYLPHENOLS

4-Nitroso-	Purified material, %	M.p., °C.	Empirical formula	Nitrogen, % Calcd.	Nitrogen, % Found
3,5-Dimethylphenol	43.2	173–174[a]	$C_8H_9NO_2$	9.27	9.38
2-*t*-Amylphenol	64.3	115–116[b]	$C_{11}H_{15}NO_2$	7.26	7.15
2-*t*-Butyl-5-methylphenol	81.8	184 dec.[c]	$C_{11}H_{15}NO_2$	7.26	7.15
2-*tt*-Octyl-5-methylphenol	94.0	146–147[d]	$C_{15}H_{23}NO_2$	5.62	5.36

[a] Recrystallized from methanol. [b] Recrystallized from toluene–petroleum ether. [c] Recrystallized from toluene. [d] Recrystallized from gasoline.

TABLE III

NITRO ALKYLPHENOLS

2-Nitro-	Purified material, %	M.p., °C.	Empirical formula	Nitrogen, % Calcd.	Nitrogen, % Found
4-*t*-Butyl-6-methylphenol[a]	47.2	39–40[c]	$C_{11}H_{15}NO_3$	6.70	6.49
4-Methyl-6-*t*-butylphenol[b]	23.3	93.5[d]	$C_{11}H_{15}NO_3$	6.70	6.70
3-Methyl-4,6-di-*t*-butylphenol[a]	61.8	83–84[e]	$C_{15}H_{23}NO_3$	5.28	5.19

[a] Prepared in benzene solution. [b] Prepared in acetic acid solution. [c] Recrystallized from acetic acid-water. [d] Recrystallized from methanol. [e] Recrystallized from methanol and water.

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(2) Ostromislensky and A. V. Tolstoouhov, U. S. Patent 2,035,502 (1936).

(3) S. Semenoff, U. S. Patent 2,035,510 (1936).

(4) A. V. Tolstoouhov, U. S. Patent 2,013,394 (1935).

(5) J. R. Stevens and R. H. Beutel, THIS JOURNAL, **63**, 308 (1941).

(6) J. R. Stevens and R. H. Beutel, U. S. Patent 2,362,508 (1944).

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TABLE IV

HYDROCHLORIDES OF AMINO ALKYLPHENOLS

Hydrochloride of	Yield of purified material %	M.p., °C.	Empirical formula	Nitrogen, % Calcd.	Nitrogen, % Found	Chlorine, % Calcd.	Chlorine, % Found
2-Amino-4-*tt*-octylphenol	Quant.	220–222[c]	$C_{14}H_{24}NOCl$	5.43	5.22		
4-Amino-2-*tt*-octyl-5-methylphenol[b]	71.2	240 d.[d]	$C_{15}H_{26}NOCl$	5.15	4.89	13.04	13.23
2-Amino-4-methyl-6-*tt*-octylphenol[a]	3.0[g]	211–213[d]	$C_{15}H_{26}NOCl$	5.15	4.86		
2-Amino-3,4-dimethyl-6-*tt*-octylphenol[a]	17.9	213 d.[e]	$C_{16}H_{28}NOCl$	4.90	4.63	12.40	12.53
2-Amino-4,6-di-*t*-amylphenol[a]	24.5	210–215[f]	$C_{16}H_{28}NOCl$	4.90	5.22	12.40	12.24

[a] Prepared from corresponding nitro compound. [b] Prepared from corresponding nitroso compound. [c] Recrystallized from methanol–water: J. B. Niederl, *Ind. Eng. Chem.*, **30**, 1269 (1938), reports m.p. 210°. [d] Recrystallized from acetic acid. [e] Recrystallized from water. [f] Recrystallized from methanol–concentrated hydrochloric acid. [g] Based on phenol.

TABLE V

AMINO ALKYLPHENOLS

Compound	Method of prepn.	Yield of purified material, %	M.p., °C.	Empirical formula	Nitrogen, % Calcd.	Nitrogen, % Found
6-Amino-3,4-dimethylphenol	B	20.6	170.5–171.5[a]	$C_8H_{11}NO$	10.19	10.19
4-Amino-3,5-dimethylphenol	B	80.3	183–184[b]	$C_8H_{11}NO$	10.19	10.19
6-Aminothymol[h]	A	52.3[i]	175–177[c]	$C_{10}H_{15}NO$	8.48	8.13
2-Amino-4-*t*-butylphenol	C	4.1[j]	158–159[d]	$C_{10}H_{15}NO$	8.48	8.28
4-Amino-2-*t*-amylphenol	A	58.5	82–83[e]	$C_{11}H_{12}NO$	7.82	7.60
4-Amino-2-*t*-butyl-5-methylphenol	A, B	(A) 84.3 (B) 76.0[j]	189–190[f]	$C_{11}H_{17}NO$	7.82	7.73
2-Amino-4-*t*-butyl-6-methylphenol	C	50.3	121–122[d]	$C_{11}H_{17}NO$	7.82	7.82
2-Amino-4-methyl-6-*t*-butylphenol	C	32.6	138–139[d]	$C_{11}H_{17}NO$	7.82	7.70
2-Amino-4-*tt*-octylphenol	C	60.2[j]	129–129.5[e]	$C_{14}H_{23}NO$	6.34	6.17
4-Amino-2-*tt*-octyl-5-methylphenol	A	98.5	180–181[e]	$C_{15}H_{25}NO$	5.95	5.76
2-Amino-4-*tt*-octyl-6-methylphenol	C	31.0	118–118.5[d]	$C_{15}H_{25}NO$	5.95	5.95
2-Amino-4-methyl-6-*tt*-octylphenol	D	79.8	108–109.5[f]	$C_{15}H_{25}NO$	5.95	5.88
2-Amino-3-methyl-4,6-di-*t*-butylphenol	C	43.6	165–165.5[g]	$C_{15}H_{25}NO$	5.95	5.95
2-Amino-3,4-dimethyl-6-*tt*-octylphenol	D	91.5	138–139[e]	$C_{16}H_{27}NO$	5.62	5.53
2-Amino-4,6-di-*t*-amylphenol	D	19.6	129–131[e]	$C_{16}H_{27}NO$	5.62	5.47
4-Amino-2-isobornyl-5-methylphenol	A	58	170–172[f]	$C_{17}H_{25}NO$	5.40	5.25

[a] Recrystallized from toluene–gasoline; A. W. Crossley and D. J. Bartlett, *J. Chem. Soc.*, **103**, 1299 (1913), give m.p. 173–175°. [b] Recrystallized from methanol: L. I. Smith and W. B. Irvin, THIS JOURNAL, **63**, 1036 (1941), report m.p. 179–180°. [c] Recrystallized from toluene–petroleum ether: m.p. 179° has been reported.[2] [d] Recrystallized from benzene–petroleum ether. [e] Recrystallized from toluene–petroleum ether. [f] Recrystallized from methanol–water. [g] Recrystallized from ethanol. [h] 4-Amino-2-isopropyl-5-methylphenol. [i] Based on thymol. [j] Based on phenol.

group apparently was sufficient to make the nitration difficult.

In general, nuclear substitution by alkyl groups stabilized the aminophenol against oxidation. The compounds having three alkyl groups in the nucleus were particularly easy to purify by recrystallization because, compared to an unsubstituted aminophenol, they had less tendency to oxidize in solution and on drying.

Experimental

Alkylphenols.—The alkylphenols were prepared by the reaction of 1.0 mole of phenolic compound with 1.7 moles of olefin using an amount of stannic chloride as the catalyst equal to about 10% of the weight of the phenolic material used. The catalyst was removed by washing with alkali and the product was purified by crystallization or distillation.

Nitroso Alkylphenols.—The nitrosation procedure employed was essentially the same as that described for nitrosothymol in reference 17. A solution of 0.66 mole of phenolic compound in 500 ml. of 95% ethyl alcohol was prepared and then 500 ml. of concentrated hydrochloric acid was added. This mixture was cooled to 0° and 1 mole of sodium nitrite was added in 5-g. portions during stirring. After completion of the addition, the product was transferred to a 12-liter flask containing about 8 liters of cold water. The yellow precipitate was filtered by suction. With phenolic compounds having a considerably higher molecular weight than thymol, such as 6-*tt*-octyl-*m*-cresol and 6-isobornyl-*m*-cresol, it was necessary to use additional quantities of alcohol to permit stirring of the reaction mixture throughout the addition of sodium nitrite.

Nitro Alkylphenols. 1. Nitration in Benzene Solution.—The general procedure for the nitration of the alkylphenols in benzene was the one used by Schulz[18] for the nitration of *p*-cresol. The phenolic compound, in solution in approximately twice its weight in benzene, and a trace of sodium nitrite were treated with almost twice the theoretical amount of dilute nitric acid (1 volume of concentrated acid plus 1 volume of water) at about 20°. The stirring was continued for several hours after the addition of nitric acid had been completed. The benzene layer was washed with water and then the benzene removed by evaporation to give the crude product.

2. **Nitration in Acetic Acid Solution.**—The phenolic compound was dissolved in acetic acid (90–95%) and then a trace of sodium nitrite was added. While the temperature was maintained at 5–10°, the theoretical amount of nitric acid, in solution in an equal weight of acetic acid, was added slowly during stirring. The crude product was obtained by dilution with water.

Purification of the crude product was effected by recrystallization or by conversion to the sodium salt followed by recrystallization. If neither the free nitrophenol nor the sodium salt was crystalline, the crude product was used for reduction to the amino compound.

3. **Hydrochlorides of Aminoalkylphenols.**—The procedure employed was a modification of that used by Simon[19] for the preparation of the hydrochloride of 2-amino-4-*tt*-octylphenol. One-half mole of phenolic compound was dissolved in 500 ml. of acetic acid, 50 ml. of water and a few

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[18] G. Schulz, *Ber.*, **40**, 4324 (1907).

[19] J. Simon, M.Sc. Thesis, N. Y. University, 1936.

crystals of sodium nitrite were added, and then the resulting solution was cooled to 10°. A solution of about 0.6 mole of concentrated nitric acid in an equal volume of acetic acid was added during stirring while the temperature was maintained at 5–10°. After the reaction mixture had been allowed to stand 1 hour, 300 g. of mossy tin and 1 liter of hydrochloric acid were added. The resulting reaction mixture was heated on a steam-bath for four hours. At the end of this reflux period, the reaction mixture was decanted into 2 liters of concentrated hydrochloric acid. On standing, the hydrochloride of the amino alkylphenol separated. It was filtered and washed with hydrochloric acid and then with petroleum ether.

In some cases, the nitroso alkylphenol was dissolved in acetic acid and reduced as described above to give the corresponding amine hydrochloride.

Amino Alkylphenols. 1. Reduction of Nitroso Compounds. Method A.—The procedure used for the reduction of nitroso alkylphenols is described in reference 20. The nitroso compound (1.39 moles) was dissolved in 1.5 liters of water plus 300 cc. of 5 N sodium hydroxide. The solution was filtered and 1200 cc. of 5 N sodium hydroxide was added. The reaction mixture was heated to 35° and 600 g. of sodium hydrosulfite was added in small portions during stirring. The temperature of the solution rose to 60–65° and was maintained at that temperature for 0.5 hour, stirring being carried out for about 20% of the time during this period. At the end of 15 minutes, the solution became light in color and usually some of the amino alkylphenol precipitated from solution.

The addition of a kilogram of ice cooled the reaction mixture of about 20° and 500 ml. of concentrated hydrochloric acid was added. The solution was made slightly alkaline with ammonia and a small amount of sodium hydrosulfite was added to prevent oxidation during the filtering operation. The product was filtered, washed with water containing a small amount of sodium hydrosulfite and dried.

2. Coupling with Sulfanilic Acid followed by Reduction. Method B.—This procedure is described in reference 21. Sulfanilic acid (0.5 mole), an equivalent amount (25 g.) of sodium carbonate and 500 cc. of water were heated and stirred until all the sulfanilic acid had dissolved and then the solution was cooled to 15°. A solution of 37 g. (0.54 mole) of sodium nitrite in 100 ml. of water was added and the resulting solution was poured at once onto a mixture of 106 cc. (1.25 moles) of concentrated hydrochloric acid and 600 g. of ice contained in a 2-liter beaker. The resulting solution, from which some of the diazonium sulfate separates, was allowed to stand in an ice-bath for 15 to 25 minutes.

One-half mole of alkylphenol was dissolved in the warm solution obtained by dissolving 110 g. (2.75 moles) of sodium hydroxide in 600 ml. of water in a 5-liter flask. The addition of 400 g. of ice cooled the solution to 5°. In order to obtain a homogeneous solution in the case of high molecular weight phenols, it was necessary to use some 95% ethyl alcohol and then the minimum amount of water to effect solution of sodium hydroxide. To the cooled solution of alkylphenol, the diazonium salt was added and the resulting reaction mixture was allowed to stand without external cooling for 1 hour. In all cases, the solution became red but there was no separation of a precipitate.

The solution of azo dye was then heated to 45–50° and 230 g. (1.1 moles) of sodium hydrosulfite was added portionwise. The temperature of the reaction mixture rose to about 60–65° and was heated at that temperature for about 0.5 hour. The product which separated was filtered, washed with water containing a small amount of sodium hydrosulfite, and dried.

3. Reduction by Zinc and Acetic Acid. Method C.—The nitro alkylphenol was dissolved in acetic acid and then zinc dust was added during stirring until the solution became colorless. During this reduction, the temperature usually rose to about 60°. The colorless solution was cooled, filtered to remove excess zinc and the filtrate was diluted with water and cooled by the addition of ice. Ammonia was added to make the solution slightly alkaline and a small amount of sodium hydrosulfite was added to minimize oxidation of the amino compound by air. The product was filtered, washed with water containing a small amount of sodium hydrosulfite and dried.

4. Preparation from Hydrochlorides. Method D.—The hydrochloride of the amino alkylphenol was dissolved in methanol, and an ammonia solution containing a small amount of sodium sulfite was added to make the solution slightly alkaline. Addition of water containing a small amount of sodium hydrosulfite caused precipitation of the product which was filtered and dried.

5. Purification of Amino Alkylphenols.—Aromatic–aliphatic solvent combinations, such as toluene–petroleum ether, were found to be very satisfactory for recrystallization of most of the amino alkylphenols reported in this work. Some oxidation in these solutions did occur in certain cases, but it could be minimized by avoiding moisture.

The use of methanol or ethanol in combination with water was satisfactory in most cases, but oxidation in solution was greater than in the hydrocarbon solvent combinations. It was found that the use of water containing a small amount of sodium sulfite or sodium hydrosulfite in these recrystallizations minimized the oxidation and gave very satisfactory results.

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AKRON, OHIO

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[20] C. S. Marvel, "Organic Syntheses," Vol. XI, John Wiley and Sons, Inc., New York, N. Y., page 8.

[21] L. F. Fieser, "Organic Syntheses," Vol. XVII, John Wiley and Sons, Inc., New York, N. Y., p. 9.

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sym-Tetraphenylacetone. II. Its Reactions and Derivatives

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As a continuation of our studies on tetraphenylacetone,[3] I, we have prepared several of its substituted derivatives and examined its behavior toward a variety of carbonyl reagents. Only lithium aluminum hydride reacted with the carbonyl group. Six other carbonyl reagents failed to react.[4] A Huang-Minlon modification of the Wolff–Kishner reduction[5] cleaved I to diphenylmethane.[6]

When treated with oxygen in the presence of base, I was cleaved almost quantitatively to benzophenone and diphenylacetic acid.[7] The reaction of I with oxygen in the presence of acid will be reported at a later date.

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[1] Taken in part from (a) Ph.D. Dissertation, D. O. Dean, Emory University, 1950; (b) M.S. Thesis, W.B. Dickinson, Emory University, 1947; and (c) Ph.D. Dissertation, G. B. Hoey, Emory University, 1954.

[2] Responsible co-author.

[3] D. O. Dean, W. B. Dickinson, O. R. Quayle and C. T. Lester, THIS JOURNAL, **72**, 1740 (1950).

[4] D. Vorlander and E. Rack, *Ber.*, **56B**, 1125 (1923), have reported the inertness of I toward several carbonyl reagents.

[5] Huang-Minlon, THIS JOURNAL, **68**, 2387 (1946).

[6] The other product of the cleavage should be diphenylacetic acid, which could, under the experimental conditions, decarboxylate to form additional diphenylmethane. The quantity of hydrocarbon isolated exceeded the theory for a simple cleavage and was 73% of theory for cleavage followed by decarboxylation. No diphenylacetic acid was isolated.

[7] W. von E. Doering and R. M. Haines, THIS JOURNAL, **76**, 482 (1954). An interesting by-product of this reaction was a 3% yield of α-hydroxy-*sym*-tetraphenylacetone.