column. The fraction which boiled from 103–118° (4 mm.) was examined by infrared absorption for the differences at the 2.75 μ and 10.7 μ wave lengths for the ether and its corresponding phenol, respectively. Figure 4 shows the absorption curves for the two pure compounds and the mixture. By suitable calculations from Beer's law, the composition was estimated as 123 meq. of phenol and 340 meq. of the ether.

Experiments with Dialkyl Ethers.—Di-*n*-butyl ether was distilled over sodium wire and stored over sodium until used. One-half mole of the ether was added at 15° to a heptane suspension of amylsodium which had been prepared in the usual way from 1 g. atom of sodium and 0.5 mole of amyl chloride at −10°. The mixture was allowed to react for 45 minutes and then carbonated. In addition to 83% yield of caproic acid, 11 meq. of a dicarboxylic acid and 5 meq. (1%) of unsaturated acid were found. The recovered butyl ether amounted to 87%. The decane yield was 15%.

In the second experiment, 0.5 mole of amyl chloride was added at 35° to 1 g. atom of sodium sand in heptane which contained 0.5 mole of di-*n*-butyl ether.

For the comparison of preparations of amylsodium in three different ethers and in heptane, the experimental conditions, −10° etc., were the same as regularly employed in this Laboratory.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Condensations by Sodium. XXXVI. The Alkylation of Anisole and of *o*-Cresol Methyl Ether and the Composition of a Reacting Aggregate[1,2]

BY AVERY A. MORTON AND ARMAND E. BRACHMAN

RECEIVED NOVEMBER 27, 1953

Alkylation on the aromatic ring by reaction of sodium with amyl chloride in the presence of anisole occurs readily if certain alkoxides are present, whereas earlier work in this Laboratory had been relatively unsuccessful. The necessary sodium intermediate, *o*-sodioanisole, is associated with sodium chloride in the more active portion of the ionic aggregate and reacts faster when additional sodium chloride is added. It also reacts faster with chlorobenzene than with amyl chloride. Phenylation is better than alkylation. The heterogeneous character of these reactions must be considered in interpreting these processes.

Introduction.—The alkylation of toluene[3-6] or of the xylenes[7] by reaction of an alkyl chloride with sodium metal in the presence of the hydrocarbon has been shown[3,4] to be a simple and direct procedure for preparing certain alkylbenzenes, and the sodium atom on a side methyl group has been especially recommended[3,8] for use in Wurtz type couplings. The same reaction applied to the alkylation of benzene has been reported[5] unsuccessful. The present work with anisole shows that alkylation on the aromatic nucleus can, after all, be relatively successful if done in the presence of certain alkoxides, but the alkylation of a cresyl ether at the side methyl group is still easier. Phenylation of anisole also can be carried out, probably with even greater ease than alkylation. Finally some observations on the composition and reactivity of a reacting aggregate are described wherein: (a) sodium chloride is found to accelerate the last step of a Wurtz coupling and (b) the reaction of *o*-sodioanisole with amyl chloride (alkylation) is shown to be slower than the corresponding reaction with chlorobenzene (phenylation), although the reverse order of reactivity would have been expected. The study is an outgrowth of the one immediately preceding on the metalation and cleavage of anisole.[9]

Alkylation of Anisole and its *o*-Methyl Homolog.—Alkylation proceeds in three steps: first, the formation of amylsodium as in equation 1, then the transition from amyl to anisyl (2) and, finally, the Wurtz coupling of *o*-sodioanisyl with amyl chloride as in (3). These steps follow each other in a rapid cascade when amyl chloride is added to

$$C_5H_{11}Cl + 2Na \longrightarrow C_5H_{11}Na + NaCl \quad (1)$$

$$C_5H_{11}Na + C_6H_5OCH_3 \longrightarrow NaC_6H_4OCH_3 + C_5H_{12} \quad (2)$$

$$o\text{-}NaC_6H_4OCH_3 + C_5H_{11}Cl \longrightarrow o\text{-}C_5H_{11}C_6H_4OCH_3 + NaCl \quad (3)$$

sodium and anisole in heptane. At 75° the addition of one-half mole of amyl chloride to one atom of sodium suspended in heptane that contained one-half mole of anisole gave around 4% of *o*-amylanisole, in line with the previous experience,[8] but in the presence of sodium 2-pentoxide, sodium isopropoxide, potassium isopropoxide and potassium *t*-pentoxide the yields were 4, 10, 19 and 23%, respectively. At 85° the yields were 3% and 38%, respectively, in the absence and presence of potassium isopropoxide, all yields being referred to the amyl chloride added. Clearly certain alkoxide salts improve the reaction, even as they have had pronounced effects in the alkylation of toluene,[6] in Alfin catalysis[10] in pyrolysis[11] of amylsodium and in metalations by sodium reagents.[12] These results are very good in view of the fact that anisole was not used as a solvent but was present only in equivalent amount, because in previous experiments[6] on

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[1] This work was performed as a part of the research project sponsored by The Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

[2] This paper was presented in part at the American Chemical Society Meeting, Chicago, Ill., 1953.

[3] A. A. Morton and F. Fallwell, Jr., THIS JOURNAL, **60**, 1429 (1938).

[4] A. A. Morton, G. M. Richardson and A. T. Hallowell, *ibid.*, **63**, 327 (1941).

[5] A. A. Morton, J. B. Davidson and R. J. Best, *ibid.*, **64**, 2239 (1942).

[6] A. A. Morton and A. E. Brachman, *ibid.*, **73**, 4363 (1951).

[7] A. A. Morton, E. L. Little, Jr., and W. O. Strong, Jr., *ibid.*, **65**, 1339 (1943).

[8] A. A. Morton, J. T. Massengale and T. R. P. Gibb, Jr., *ibid.* **63**, 324 (1941).

[9] A. A. Morton and A. E. Brachman, *ibid.*, **76**, 2973 (1954).

[10] A. A. Morton, F. H. Bolton, F. W. Collins and E. F. Cluff, *Ind. Eng. Chem.*, **44**, 2876 (1952).

[11] A. A. Morton and E. F. Cluff, THIS JOURNAL, **74**, 4056 (1952).

[12] A. A. Morton and M. E. T. Holden, *ibid.*, **69**, 1675 (1947).

the alkylation of toluene, the yield of *n*-hexylbenzene was cut nearly in half when one-half of the toluene as solvent was replaced by cumene.

According to equations 1, 2 and 3, the alkylation of anisole occurs in three steps, and the yield of *o*-sodioanisole in the first step has been shown[9] to be near 80%. However, the subsequent reaction with amyl chloride at this temperature was very slow and the yield of *o*-amylanisole reached only 32%. The acceleration of the reaction by heat and the presence of potassium isopropoxide led to more consumption of the sodium compound but chiefly in a disproportionation process.

The superiority[3,8] of the side methyl group over the nucleus as a point for alkylation was again demonstrated by a comparison with the *o*-cresyl homolog. The yields were 18 and 42% of *o*-amylanisole and *o*-hexylanisole, respectively.

Phenylation of Anisole.—A few tests were made also with phenylation by reaction of *o*-sodioanisole with chloro- or bromobenzene. The reactions were at 75°; nearly all of the sodium reagents were consumed, and the yield from the combined products of reaction was 46% of *o*-methoxybiphenyl, possibly more from bromobenzene than from chlorobenzene. In addition, small amounts of biphenyl, triphenylene, 2,2′-dimethoxybiphenyl and some residue—probably most of them products from disproportionation—were isolated. The intramolecular cleavage mentioned in the previous paper[9] was again low, being 0.4 and 1.0%, respectively.

These yields of Wurtz product show that alkylation on the ring is possible and indicate that a systematic study of the effect of alkoxides and other salts, such as was carried out for the alkylation of toluene,[6] would materially improve the yield. Phenylation on the aromatic ring is more successful, other conditions being equal, than alkylation.

Composition and Reactivity of the Aggregate.—Organosodium reactions of this type are heterogeneous, that is, the soluble organic halide must react with the insoluble sodium compound; and some effort has been made in this work to examine the solid aggregate while in the process of reacting. The assumption is that the halogen atom of the organic halide becomes attached by adsorption on a cation center of the ionic aggregate which is composed of organosodium reagent and sodium chloride, as per equations 2 and 3, or is made up of three salts if an alkoxide is present. The different sized ions form a highly irregular surface and some porosity is possible because the structure is not dense as is a homogeneous crystal of the sodium chloride type. No specific composition, as for a complex containing organic chloride, is implied although certain areas on an aggregate probably attain some specificity.

Sections on this aggregate, where much adsorption occurs, are assumed to have a different density or porosity than other parts, particularly the interior, and such sections should therefore break off as finely divided or flocculent pieces—hereafter called "fines"—which settle more slowly than the coarse particles and continue to adsorb organic chloride and to react. Such fines are undoubtedly the more reactive fraction from the ionic aggregate. Adsorption and reaction should take place also on the coarser particles but would cause largely the formation of more fines. Some organic halides are adsorbed more readily or cause fine fragments to be broken off more easily than other halides, and such physical factors probably affect the total amount of reaction quite as much as the comparative labilities of the individual carbon–halogen bonds of the organic halides in question.

To throw some light upon the composition of these fines, *o*-sodioanisole which contained sodium chloride as the necessary companion from its preparation was stirred for varying times at room temperature with *n*-amyl chloride or with chlorobenzene. The suspension was then centrifuged to throw down all the solids into two readily distinguishable strata, after which the liquid phase was replaced by dry pentane and the container was swirled gently by hand in order to suspend only the lightweight flocculent material, that is, the fines. During all this time, but mostly while being stirred, a reaction was taking place. For example, with *n*-amyl chloride the total *o*-sodioanisole decreased from 381 to 286 meq. over 75 minutes, as given in Table I, experiments 1 to 4. Also the different appearance of the fines with alkyl chloride present, and the extremely small quantity of finely divided solid particles in the control experiment (no. 1 in Table I) where no organic chloride had been added as compared with the larger amounts in succeeding experiments (the data in the table do not show this feature well because only a portion of the fines was suspended by swirling) were in accord with the idea that these fines were indeed the more reactive fraction of the aggregate. Analyses of the fines for the halide salt, the organic halide, and the organosodium reagent and also of the coarse particles for the sodium reagent were made by the usual methods of carbonation and conventional titrations. The liquid phase, heptane, showed no dissolved sodium compound that could be titrated as base.

One of the very interesting facts revealed by this study was that the fines from the first eight experiments (Table I) not only contained sodium chloride but actually had around two or more moles of the halide salt to one of *o*-sodioanisole, whereas the over-all ratio at the beginning of the reaction was only 1.32. This indication that sodium chloride really aided the reaction was confirmed by the addition of one-quarter mole of finely divided Wurtz sodium chloride (marked "W" in column 1 of Table I) to the reaction mixture. Without exception, the over-all reaction increased over the comparison experiment (for example, 3 W *vs.* 3 or 7 W *vs.* 7) and in proportion to the amount of sodium chloride added (3 W^c > 3 W). Granular sodium chloride, however, caused a decrease in reaction (3 G > 3) and this fact is not surprising in view of the difficulty in getting a suitable state of subdivision with such coarse material[10] unless ground by high-speed stirring for very long times. Actually granular sodium chloride seemed to abstract some sodium chloride because the ratio of sodium chloride to *o*-sodioanisole in the fines from 3 G was the lowest in any of the experiments.

The proportions of organic chloride adsorbed on

TABLE I

ANALYSIS OF THE SOLID FRACTIONS IN THE REACTION OF AN ORGANIC HALIDE (RX) WITH *o*-SODIOANISOLE (R'Na)

The effects of additional sodium halide (granular (G) and Wurtz (W)), of the kind of organic halide (amyl chloride (A), chlorobenzene (C) and bromobenzene (B)), of the amount of organic chloride, and of the presence of potassium isopropoxide (K).

Expt.	RCl		Stir. time, min.	R'Na[a] total, %	RR'[b], %	R'Na, total meq.	Anal. of fines			Mole ratio to R'Na of	
	Kind	Mole					R'Na, meq.	NaX, meq.	RX, meq.	NaX	RX
1			45	76	0	381	7	13		1.9	
2	A	0.5	15	74	5	372	40	79	24	2.0	0.6
3	A	.5	45	68	6	341	29	58	26	2.0	0.9
4	A	.5	75	57	14	286	20	44	21	2.2	1.1
5	A	.5	120	65		326	24	58	13	2.4	0.5
6	A	1.0	45	53	14	267	20	37	35	1.9	1.7
7	C	0.5	45	62	(8)	311	23	46	22	2.0	1.0
8	C	.5	120	51	(14)	255	18	51	12	2.8	0.7
9	C	.75	45	56	(9)	382	156	78	94	1.4	1.7
10	C	1.0	45	39	(12)	194	36	57	100	1.6	2.8
7 W	C	0.5	45	54	(9)	272	57	70	46	1.2	0.8
3 G	A	.5	45	72	11	362	14	13	6	1.0	.4
3 W	A	.5	45	66	12	330	28	45	13	1.6	.5
3 W[c]	A	.5	45	62	14	312	26	97	9	3.7	.3
7 K	C	.5	45	15	(20)	77					
11	B	.5	45	43	(20)	217	4	17	1	4.8	.3

[a] The percentage is based on the amyl chloride used for preparation of *o*-sodioanisole. [b] Values in parentheses are yields in grams instead of per cent. [c] In this preparation, 1 mole of Wurtz sodium chloride was added. In the others, marked "W," only 0.25 mole was added.

the organosodium reagent were in a large number of cases less than 1-to-1, and this fact is in line with the view that the high-speed stirrer breaks away the fines as soon as enough organic halide has become attached to loosen a fraction. Upon such fine fragments more organic halide can be adsorbed (or absorbed within the pores), an idea suggested by the larger amount shown in the last column to be progressively present with increased time in experiments 2, 3 and 4. The adsorption was greater with increased concentration of organic chloride as would be expected. Comparisons with bromobenzene are not suitable because it reacted too fast.

Another point of major interest is that chlorobenzene reacted faster than amyl chloride, whereas the reverse was expected. This fact had been noted earlier[3] for the reaction of phenylsodium with chlorobenzene, but the long recognized unreactivity of chlorobenzene toward hydrolysis had crowded out any impression from the prior work that chlorobenzene could possibly react faster than amyl chloride in this reaction. Yet every comparison showed chlorobenzene the more reactive (7 > 3, 8 > 5, 10 > 6 and 7 W > 3 W). Bromobenzene was still more reactive (11 > 7 > 3) and seemed to give higher yields of Wurtz product also. Any unusual effects in these cases can possibly be reconciled with conventional ideas by the mere insertion, as part of the process, of a physical factor whereby more fines are produced by the halobenzenes (and the evidence clearly showed more halobenzene adsorbed) than by amyl chloride. The reaction of each molecule of chlorobenzene could be slower than for amyl chloride but the greater number of molecules of the former reacting at any given time might more than compensate for the difference between individual molecules. The possibility also exists that adsorption itself causes activation of the carbon–chlorine bond, more so in chlorobenzene than in amyl chloride.

An effort to observe the effect of an alkoxide in this series proved unsuitable for specific measurement. However, the very fast reaction did demonstrate again the marked activation by these associated salts. The comparative difference is seen in 7 A > 7 W > 7.

Independent tests indicated that adsorption was primarily on *o*-sodioanisole. The alkoxide and sodium chloride showed progressively less adsorption.

The fine details by which these reactions progress are considered to be in line with opinions expressed in earlier papers[9,11] from this Laboratory.

Experiments

General Procedure.—The general methods of preparing and handling the organosodium reagents have been described in previous publications[6,13] and the preparation of *o*-sodioanisole has been published[9] recently.

Alkylation of Anisole.—One-half mole of *n*-amyl chloride was added to 1 g. atom of sodium sand in heptane which contained a half mole of anisole, just as for the preparation of *o*-sodioanisole[9] except that the temperatures were 50, 75 and 85°. Alkoxide if present was prepared separately from the metal and alcohol and was added before the addition of amyl chloride. At the end of the reaction time (45 min.) the mixture was carbonated and the carboxylic acid and phenol measured in the manner described.[9] The hydrocarbon portions were fractionated through a one-meter Vigreux column and eventually through a 1 mm. × 5 mm. cm. Podbielniak Whirling Heli-Band column rotated at 1600 r.p.m. *o*-Amylanisole boiled at 242°. All residues were combined and fractionated through the Podbielniak column in order to ensure that no product was overlooked. All yields were calculated on the amyl chloride and the results are recorded in Table II.

o-Amylanisole, after being distilled through the Podbielniak column, boiled at 860 (4 mm.) or 242° (cor.) 759.6 mm., n^{26}D 1.4990.

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.17; OCH_3, 17.41. Found: C, 80.69; H, 10.00; OCH_3, 16.20.

The methoxyl determination was low because of resistance to the usual methods of cleavage. The customary Zeisel hydriodic acid method yielded only 9% but after six trials

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(13) A. A. Morton and co-workers, THIS JOURNAL, **72**, 3785 (1950).

TABLE II

REACTION OF ONE-HALF MOLE OF AMYL CHLORIDE WITH 1 G. ATOM OF SODIUM IN HEPTANE THAT CONTAINED ONE-HALF MOLE OF ANISOLE UNLESS OTHERWISE STATED

Temp., °C.	Special conditions[a]	Anis. acid, %	Di-acid, %	Total[b] acid, %	Phenol, %	Anis. rec., %	o-Amyl anis., %	Res., g.
50	None	77	4	83	0.7	7	0	2
50	K isopro.	77	5	83	2.0	10	3	2
75	None	46	0.1	47	6.0	27	11[c]	2
75	4 H. stir.	61	0	61	8.0	19	4	3
75	Et_3N[d]			50	6.0	29	4	4
75	Na 2-pentox.	35	0.9	37	15.0	29	4	3
75	Na isopro.	34	0.5	35	17.0	30	10	8
75	K isopro.	25	2.0	33	18.0	37	19	13
75	K *t*-pentox.			7	7.0	55	23	13
75	$CoCl_2$			0.1	6.0	35		10[e]
75	1 mole anis.			52	5.0			
75	0.25 mole anis.	25	27.0	61	3.0	6		3
85	None	44	0.4	45	6.0	28	3	4
85	K isopro.			2	12.0	51	38	18

[a] Whenever an alkoxide was added, the quantity was 0.5 mole. [b] The total acidity is a measure of the percentage of carboxyl groups per amyl chloride. Usually this quantity is the sum of the first two columns of percentages except for a small amount of an unknown acid that was present. [c] This value is obviously out of line and cannot be higher than the 4% yield in the following experiment. When the yields are very low, the product must be differentiated from traces of decane that are obtained at the same distillation range. [d] One and one-half moles (3 equivalents) of the amine was used. [e] *o,o'*-Dimethoxybiphenyl (4%) was isolated from this residue.

with more strenuous treatment the value reached 16.20%. A pyridinium hydrochloride fusion and a treatment with 47% hydrobromic acid in a sealed tube for 24 hours at 140° were ineffective. Nitration with concentrated sulfuric acid and nitric acid for five minutes at 50° gave 2,4-dinitro-6-amylanisole which melted at 41–42.5°.

Anal. Calcd. for $C_{12}H_{16}O_5N_2$: C, 53.72; H, 6.01; N, 10.45. Found: C, 53.54; H, 5.83; N, 10.35.

An authentic sample of *o*-amylanisole was prepared by addition of *o*-anisoyl chloride to dibutylcadmium prepared from *n*-butylmagnesium bromide and anhydrous cadmium chloride, followed by reduction of the *o*-methoxyvalerophenone (80% yield) with zinc and concentrated hydrochloric acid to *o*-*n*-amylanisole (38% yield). The product was purified by fractionation and was identical in all respects—boiling point, refractive index, analysis and dinitro derivative (m.p. 42–42.8°)—with that from alkylation. Its infrared absorption curve was also identical with that of the other product.

The fractionation of the residues from a total of twenty-five experiments (some from the previous paper[9] are included) yielded more *o*-*n*-amylanisole (55 g.) and about 12 g. of material which boiled at 275° (calculated to 760° mm.) and had a composition expected for diamylanisole.

Anal. Calcd. for $C_{16}H_{26}O_2$: C, 82.19; H, 11.36. Found: C, 82.44; H, 10.49.

The 45 g. of residue obtained from this fractionation in a Podbielniak column was fractionated through the Holtzmann column. Some *o,o'*-dimethoxybiphenyl crystallized from the distillate and was recrystallized from acetone.

The Phenylation of Anisole.—The general procedure was the addition of chloro- or bromobenzene to sodium in heptane–anisole at 75° for 45 minutes exactly as described for alkylation. The yields of *o*-anisic acid were 3 and 6%, respectively. The phenylation products contained considerable tar and were therefore combined and fractionated. From the distillate 2-methoxybiphenyl crystallized. After being recrystallized from acetone, it melted at 28.5° (lit.[14] 29°). Nitration yielded 5-nitro-2-methoxybiphenyl which melted at 93.5–95° (lit.[15] 95–96°).

High-boiling Aromatic Products from the Phenylation of *o*-Amylanisole and from Other Reactions.—A description of the separation and identification of disproportionation and other high-boiling products obtained from the phenylation experiments, from the experiments on composition of the aggregate, and from the experiment with cobaltous chloride (Table II) are given in this section. From the residues of the phenylation experiments, by a combination of fractionation in the Podbielniak column at 21 mm. and crystallization, there were recovered 14 g. of anisole, 6 g. of *n*-decane, 2.5 g. of biphenyl, 30 mg. of 2,2'-dimethoxybiphenyl, 4 g. of triphenylene and 40 g. of residue which did not distil at 170° (21 mm.). This last material was fractionated through a Holtzmann column at 4 mm.

Biphenyl distilled between 130 and 145° (21 mm.). It was purified by crystallization from pentane and then from ethanol and melted at 67.5–68° (lit.[16] 70°) and showed no depression when mixed with an authentic sample.

2,2'-Dimethoxybiphenyl was obtained from the fraction which boiled 150–160° (4 mm.) and in another case from 128–133° (2 mm.) but the bulk was obtained as a solid which crystallized from some chlorobenzene residues after a month standing. Colorless crystals were obtained from ethanol and melted at 155–156.5° (lit.[17] 155°).

Triphenylene distilled with other material at 200–230° (4 mm.) and was recovered by dissolving in benzene, adding pentane and cooling in a bath with solid carbon dioxide. After being recrystallized from benzene, it melted at 198–199° (lit.[18] 198–198.5°). The picrate from acetone melted at 224–225.5° (lit.[18] 223°).

Reaction of Amyl Chloride with *o*-Sodioanisole and *o*-Methoxybenzylsodium.—*o*-Sodioanisole was prepared from amyl chloride and sodium in the presence of an equivalent amount of anisole at 35°, as described previously. The corresponding cresyl compound was prepared similarly from *o*-cresyl methyl ether. The results are given in Table III.

TABLE III

REACTION OF *o*-SODIOANISOLE AND *o*-METHOXYBENZYLSODIUM WITH AMYL CHLORIDE

Sodio cpd.[a] from	Added salt[b]	Temp., °C.	Time, min.	Alkylation, %	Carbox. acid, %
A	None	35	330	14	47
A	NaCl	35	1500	32	16
A	KOR	50	90	18[c]	1
C	KOR	50	90	42	1
A	None	75	45	21	5

[a] A and C refer to anisole and *o*-cresyl methyl ether, respectively. [b] KOR signifies potassium isopropoxide. The NaCl was Wurtz sodium chloride. One-half mole of these added salts was used. [c] A fraction (1.6%) corresponding to diamylanisole was obtained also.

Examination of the Reacting System, *o*-Sodioanisole and Organic Halide.—*o*-Sodioanisole was prepared at 35° by dropwise addition of one-half mole of *n*-amyl chloride to one gram atom of sodium metal and one-half mole of anisole in heptane in the usual way, followed by one-half hour of stirring. *n*-Amyl chloride (0.5 mole) was then added and the mixture was stirred together for the time recorded in Table I. The reactants were then transferred to 2 one-liter centrifuge bottles and centrifuged for 25 minutes at 20,000 r.p.m. The clear hydrocarbon layer was decanted, and the surface of the solid was rinsed gently with two 100-ml. portions of dry (over sodium) pentane. The washings were added to the original hydrocarbon layer. The upper solid or fines was loosely packed and was suspended in 200 ml. of pentane by swirling the bottle gently. This portion was removed by decantation under nitrogen and was carbonated. The lower solid, or coarse particles, was tightly packed but

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[14] O. Hönigschmid, *Monatsh.*, **22**, 561 (1901).

[15] W. Borsche and B. G. B. Scholten, *Ber.*, **50**, 601 (1917).

[16] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 259.

[17] F. Jannasch and C. Kölitz, *Ber.*, **31**, 1745 (1898).

[18] W. E. Bachmann and H. T. Clarke, THIS JOURNAL, **49**, 2089 (1927).

was broken up by vigorous shaking with pentane and was carbonated.

The usual analysis[9] for *o*-anisic acid showed the amount of *o*-sodioanisole which had been present. The sodium halide was determined by means of silver nitrate with an aliquot and titration of the excess nitrate with potassium thiocyanate against ferric nitrate as an indicator. The alkyl or aryl chloride was determined by digesting an aliquot from the hydrocarbon layer with sodium sand and then analyzing for halide ion in the above way with silver nitrate.

In a few cases, the fines and coarse particles were scarcely distinguishable. The control experiment, no. 1, contained no true fines, but a few of the most finely divided particles were analyzed. The last two reactions listed in the table proceeded too rapidly for isolation of any especially reactive fraction.

Adsorption of Amyl Chloride on Sodium Chloride and Potassium Isopropoxide.—Wurtz sodium chloride (one mole) was prepared from amyl chloride and sodium metal in pentane. The mixture was centrifuged, the pentane layer was removed by decantation and the sodium chloride was transferred to a flask which contained heptane. Amyl chloride, one mole, was then added, the mixture was stirred together for 45 minutes with the high-speed stirring apparatus. The mixture was then centrifuged. The solid appeared homogeneous, but as much as possible of an upper portion was removed by swirling and was analyzed.

In a similar way, the adsorption of a mole of amyl chloride on a mole of potassium isopropoxide (from potassium metal and isopropyl alcohol) and the adsorption of two moles of amyl chloride on a mixture of a mole each of sodium chloride and potassium isopropoxide were measured.

In Table IV the adsorptions on the fines and the coarse particles are given but there was no differentiation in physical appearance possible between the two grades. The results show more adsorption on the alkoxide than on the chloride. In the mixture the halide salt appears to repress the adsorption on the alkoxide. All adsorption values are less than those on *o*-sodioanisole shown in Table I.

TABLE IV

ADSORPTION OF AMYL CHLORIDE ON SODIUM CHLORIDE AND POTASSIUM ISOPROPOXIDE

Solid	Mole ratio of amyl chloride to solid, Fines	Coarse
Wurtz sodium chloride	2.00/10.4 = 0.192	85.8/778 = 0.110
Potassium isopropoxide	21.4/41.3 = .518	127/390 = .328
NaCl + KOC_3H_7-*i*	23.4/72.4 = .323	93.0/849 = .109

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, STANFORD UNIVERSITY]

Peroxides. I. *n*-Alkyl Hydroperoxides

BY HOMER R. WILLIAMS[1] AND HARRY S. MOSHER

RECEIVED JANUARY 8, 1954

A new and practical synthesis for the pure *n*-alkyl hydroperoxides (*n*-propyl through *n*-decyl) by the reaction of *n*-alkyl methane sulfonates with 30% hydrogen peroxide has been developed. These compounds are now readily available as analytically pure materials. These primary alkyl hydroperoxides exhibit the same order of stability as *t*-butyl hydroperoxide.

Although the tertiary alkyl hydroperoxides have been readily available by the reaction of the tertiary alcohol with hydrogen peroxide in the presence of strong acid,[2] and many allylic types are formed by air oxidation,[3] only the methyl, ethyl, *n*-propyl and *n*-butyl members of the normal saturated series have been described. These have been prepared in the past by the method of Baeyer and Villiger,[4,5] using the reaction of hydrogen peroxide with dialkyl sulfates; the yields were generally unsatisfactory[6] and the methyl and ethyl hydroperoxides were dangerously unstable. Recently Lindstrom[7] has added the *n*-butyl hydroperoxide to the list of pure saturated normal hydroperoxides which have been made by the method of Baeyer and Villiger. By the use of methanol solvent the yield was greatly improved. A recent communication by Walling and Buckler[8] reports the preparation of hydroperoxides by the action of oxygen on Grignard reagents.[9] This shows promise of being a useful and general method.

The use of alkyl methanesulfonates as alkylating agents for hydrogen peroxide has not been previously reported. Rieche[4] was actively engaged in a search for new alkylating agents for hydrogen peroxide but failed to mention alkyl methanesulfonates in any of his publications. Medwedew and Alexjewa[6d] stated that they were unsuccessful in attempts at making alkyl hydroperoxides by alkylation of hydrogen peroxide with alkyl toluenesulfonates or by the alkylation of sodium or barium peroxide with alkyl halides. Harris and Egerton[6c] concluded after extensive studies that the strongly alkaline reaction mixture required to bring about the alkylation of hydrogen peroxide rapidly decomposed the alkyl hydroperoxide as formed and consequently appreciable yields by this general method were unlikely.

We have now found that acceptable yields of *n*-alkyl hydroperoxides result from the alkylation of 30% hydrogen peroxide by alkyl methanesulfonates in aqueous methanol solvent in the presence of potassium hydroxide at room temperature. We chose to study the reaction of alkyl methanesulfo-

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[1] Shell Development Co., Agricultural Division, Denver, Colorado.

[2] N. A. Milas, U. S. Patent 2,223,807 (Dec. 3, 1940).

[3] W. A. Waters, Oxidation Processes, in Gilman's "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 1120.

[4] (a) A. Rieche, "Alkyl Peroxyde und Ozonide," Verlag von T. Steinkopff, Dresden und Leipzig, 1931; (b) W. Eggersglüss, "Organische Peroxyde," Verlag Chemie, Weinheim, 1951; (c) R. Criegee, "Peroxyde, in Houben-Weyl, Methoden der Organischen Chemie," Vol. VIII, Georg Thieme Verlag, Stuttgart, 1952, Chapt. 1.

[5] A. Baeyer and V. Villiger, *Ber.*, **23**, 3387 (1900); **34**, 738 (1901).

[6] (a) Methyl hydroperoxide, 12% yield, ref. 5; (b) ethyl hydroperoxide, 21% yield, A. Rieche and Hitz, *Ber.*, **62**, 2458 (1929); (c) *n*-propyl hydroperoxide, 1.3% yield, E. J. Harris and A. C. Egerton, *Proc. Roy. Soc.* (*London*), **A173**, 126 (1939); (d) S. S. Medwedew and E. N. Alexejewa, *Ber.*, **85B**, 133 (1952), report the preparation of the *n*-propyl hydroperoxide in 27% solution (determined by titration) but they were unable to isolate any of the pure substance.

[7] E. G. Lindstrom, THIS JOURNAL, **75**, 5123 (1953).

[8] C. Walling and S. A. Buckler, *ibid.*, **75**, 4372 (1953).

[9] J. Schmidlin, *Ber.*, **39**, 631, 4184 (1906), reported a 54% yield of triphenylmethyl hydroperoxide by the action of oxygen on triphenylmethylmagnesium chloride.