The dry material weighed 1.2 g. and melted at 166–167°. An additional 1.0 g. was obtained by evaporating the filtrate to dryness under reduced pressure. The two fractions were combined and recrystallized from benzene. The yield of pure Piperidide B was 2.0 g., melting at 187–188°. Boiling pyridine also converted the low melting isomer to the higher melting compound. In a similar way the low melting Morpholide A was converted to the higher melting Morpholide B.

Summary

1. A series of α-benzoylamino-N,N-disubstituted hydrocinnamamides has been prepared by the reaction of 2-phenyl-4-benzyl-5-oxazolone with dimethylamine, diethylamine, methylaniline, ethylaniline, piperidine and morpholine.

2. A series of α-benzoylamino-N,N-disubstituted cinnamamides has been prepared by the reaction of 2-phenyl-4-benzal-5-oxazolone with the same secondary amines. Each of these compounds was catalytically hydrogenated to the corresponding hydrocinnamamide.

3. Piperidine and morpholine were found to react with 2-phenyl-4-benzal-5-oxazolone to yield two isomeric products in each case. The isomeric piperidides were both hydrolyzed to the same α-benzoylaminocinnamic acid, and reduced to α-benzoylaminohydrocinnamapiperidide and morpholide, respectively.

4. Diphenylamine, indole and carbazole failed to react with 2-phenyl-4-benzyl-5-oxazolone or 2-phenyl-4-benzal-5-oxazolone under the conditions employed in this work.

BLOOMINGTON, INDIANA
IOWA CITY, IOWA RECEIVED NOVEMBER 10, 1947

[CONTRIBUTION FROM THE PURDUE RESEARCH FOUNDATION AND THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Monomers and Polymers. III. A New Synthesis for α-Methylstyrenes[1,2]

BY G. BRYANT BACHMAN AND HENRY M. HELLMAN

Most α-methylstyrenes so far described have been prepared by two general types of syntheses. The first involves the conversion of carbonyl or carbalkoxyl groups to isopropenyl groups, *e. g.*

$$\begin{array}{l}(1)\ \mathrm{R{-}COCH_3}\\ \xrightarrow[\text{(2) acid}]{\text{(1) }\mathrm{CH_3MgX}} \mathrm{R{-}C(CH_3)_2OH} \xrightarrow{-\mathrm{H_2O}} \mathrm{R{-}C(CH_3){=}CH_2}\\ (2)\ \mathrm{R{-}CO_2CH_3}\end{array}$$

The method is limited to intermediates which contain no other groups affected by Grignard reagents and is impractical for large scale production. The second type involves the conversion of isopropyl groups to isopropenyl groups, *e. g.*

$$(3)\quad \mathrm{R{-}CH(CH_3)_2} \xrightarrow{\mathrm{Al_2O_3}} \mathrm{R{-}C(CH_3){=}CH_2 + H_2}$$

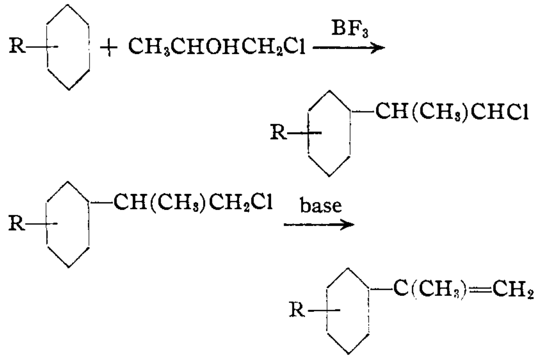
$$(4)\quad \mathrm{R{-}CH(CH_3)_2} \xrightarrow{\mathrm{Cl_2}} \mathrm{R{-}C(CH_3)_2Cl} \xrightarrow{\text{base}} \mathrm{RC(CH_3){=}CH_2}$$

It is better suited for commercial production but is also limited as to other groups which may be present. Thus alkyl substituents are especially troublesome because of their indiscriminant attack by the dehydrogenation catalyst or by the halogen. Furthermore, the tertiary halides produced (Equation 4) tend to dehydrohalogenate during distillation giving difficulty separable mixtures.

We have sought for and found a synthesis which can be applied more or less generally to substitute α-methylstyrenes, especially of the types difficultly obtainable by previously known methods, and which might be adapted to large scale production. The synthesis is illustrated by the following equations in which R represents one or more nuclear substituents.

(5)

(6)



Aromatic compounds have been alkylated before with alcohols and with alkyl halides[3] but never apparently with halohydrins. We have found that secondary alcohols react so much more readily than primary halides in this synthesis that condensation with two aryl nuclei to form diarylpropanes may be made of minor importance. Positional isomers are formed but the para derivative (with monosubstituted benzenes) is the chief product.

In Table I are shown the haloalkylation products of a number of substituted benzenes. The method appears to work especially well with alkylated benzenes, probably because the alkyl group activates the nucleus to further substitution.

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(1) From the Ph.D. thesis of H. M. Hellman, Purdue University, June, 1947. Present address: Department of Chemistry, New York University, New York.

(2) For previous papers in this series see THIS JOURNAL, **69**, 2022 (1947); **70**, 622 (1948), and others to be published.

(3) For a general review see C. C. Price, "The Alkylation of Aromatic Compounds by the Friedel–Crafts Method," in "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1946, Vol. III, Chapter 1.

TABLE I

HALOALKYLATED BENZENES

Reactants		Yield, %[a]	Products B. p. °C.	Mm.	d^{25}_{25}	$n^{25}\mathrm{D}$	Analyses Calcd.	Found
$CH_3CHOHCH_2Cl$	Benzene[b]	37	79–80	9	1.047	1.5210	Cl, 23.0	23.3
$CH_3CHOHCH_2Cl$	Toluene[c]	36	80–82	5	1.028	1.5205	Cl, 21.0	20.9
$CH_3CHOHCH_2Cl$	Chlorobenzene[b]	29	116–122	15	1.181	1.5384	Cl, 37.5	37.5
$CH_3CHOHCH_2Cl$	Cumene	48	103–109	3	0.995	1.5130	Cl, 18.0	18.0
$CH_3CHOHCH_2Cl$	*o*-Xylene	27	78–79	2	1.027	1.5260	Cl, 19.4	19.6
$CH_3CHOHCH_2Cl$	*o*-Chlorotoluene	30	95–97	2	1.164	1.5392	Cl, 34.9	34.9
$CH_3CHOHCH_2Cl$	*o*-Bromotoluene	30	109–112	1	1.389	1.5595	Cl, 14.4	14.2
							Br, 32.3	32.0
$CH_3CHOHCH_2Cl$	*o*-Dichlorobenzene	7	116–120	2	1.304	1.5556	Cl, 47.7	46.9
$CH_3CHOHCH_2Cl$	Anisole	5	108–110	5	1.095	1.5281	Cl, 19.2	18.7
$CH_3CHOHCH_2Cl$	2,6-Dichlorotoluene	4	110–112	1	1.265	1.5553	Cl, 44.8	43.4
$CH_3CHOHCH_2Cl$	1-Chloronaphthalene	20	130–135	1	1.232	1.6168	Cl, 29.7	29.4
$CH_3CHOHCH_2Br$	Cumene	32	98–99	1	1.192	1.5290	Br, 33.2	33.3
$CH_3CHOHCH_2Br$	*o*-Fluorotoluene	17	72–74	2	1.334	1.5233	Br, 34.6	34.4
							F, 8.2	8.1
$C_2H_5CHOHCH_2Cl$	Toluene	41	80–83	3	1.011	1.5140	Cl, 19.4	19.4
$C_2H_5CHOHCH_2Br$	Toluene	51	89–90	1	1.224	1.5332	Br, 35.2	35.0

[a] Based on halohydrin. [b] Truffault, *Compt. rend.*, **202**, 1286 (1936). [c] Truffault, *Bull. soc. chim.*, **6**, 726 (1939).

TABLE II

α-METHYLSTYRENES

Substituents	Yield, %	B. p. °C.	Mm.	d^{25}_{25}	$n^{25}\mathrm{D}$	Br. No.	Percentage composition E[e]	Calcd.	Found	E[e]	Calcd.	Found
None[a]	77	72–72	30	0.910	1.5350	...	..	..	..	..	..	..
4-CH_3[a]	60	76–78	19	0.898	1.5290	...	..	..	..	..	..	..
4-Cl[a,b]	16	80–83	10	1.079	1.5529	106	Cl	23.3	23.4	..	..	..
4-$CH(CH_3)_2$	73	76–77	5	0.889	1.5204	98	C	90.0	89.5	H	10.0	9.9
2,3-di-CH_3	8	54–55	3	0.895	1.5170	111	C	90.4	90.5	H	9.6	9.8
3,4-di-CH_3	72	72–73	4	0.908	1.5362	109	C	90.4	90.0	H	9.6	9.6
3-Cl-2-CH_3	26	64–65	4	1.043	1.5340	106	Cl	21.3	21.4	..	..	..
3-Cl-4-CH_3	48	73–74	4	1.056	1.5520	99	Cl	21.3	21.3	..	..	..
3-Br-2-CH_3	18	89–90	7	1.295	1.5555	76	Br	37.8	38.0	..	..	..
3-Br-4-CH_3	45	102–103	7	1.311	1.5757	77	Br	37.8	38.1	..	..	..
Chlorobenzo[c]	10	119–121	1	1.150	1.6210	78	Cl	17.5	17.8	..	..	..
3-F-2-CH_3+ 3-F-4-CH_3	83	72–90	10	0.996	1.5128–1.5187	100	C	80.0	80.0	F	12.6	12.4
4-CH_3[a,d]	18	78–81	10	0.890	1.5202	110	C	90.4	90.0	H	9.6	10.0

[a] Known compound, *cf.* Beilstein or indicated reference. [b] Reported recently by Mowry, Huber and Ringwald, THIS JOURNAL, **69**, 851 (1947), b. p. 88–89° (15); $n^{25}\mathrm{D}$ 1.5543. [c] From chloroisopropylated α-chloronaphthalene. [d] An α-ethylstyrene, *cf.* Griskevich–Trokhimovskii, *C. A.*, **5**, 3799 (1911). [e] E represents element analyzed for.

Boron trifluoride alone as catalyst is satisfactory, but the yields of condensation products are often improved (5–10%) by the addition of dehydrating agents such as sulfuric acid or phosphorus pentoxide. The low yields with anisole may be attributed to combination between the ether oxygen and the boron trifluoride molecule creating a group-complex ($-\overset{+}{O}R \rightarrow \overset{-}{B}F_3$) whose dipolar character is such as to deactivate the nucleus. Haloalkylation of thiophene was unsuccessful, probably for similar reasons, and because of cleavage of the thiophene ring.

In attempting to extend the utility of the reaction to homologs of propylene halohydrins it was found that the halohydrin of 1-butene (1-bromo-2-butanol) reacted very satisfactorily with toluene. There appears to be no reason why α-alkylstyrenes generally should not be readily available by this synthesis.

The α-methylstyrenes prepared by dehydrohalogenation (Table II) showed evidence of being mixtures of positional isomers not completely separated by distillation through a 42-cm. glass helices packed column. The products boiled over a range and showed varying refractive indices, but the several cuts gave correct bromine numbers and correct analyses. The styrenes were therefore redistilled through a 3-foot, 1/4 inch tantalum spiral column with an efficiency of about 10 theoretical plates. The separated isomers were then oxidized with 6 molar nitric acid to the corresponding substituted benzoic acids. Comparison of the m. p.'s of these acids with values reported in the literature led to a determination of the structures of the original styrenes.

An advantage of this synthesis is that the haloisopropylated benzene obtained as an intermediate may easily be further substituted nuclearly before

TABLE III

1,2-DIPHENYLPROPANES

Phenyl substituents	Yield	B. p. °C.	Mm.	n^{25}_D	d^{25}_{25}	Analyses, % Calcd. Carbon	Hydrogen	Found Carbon	Hydrogen
None[a]	4.3	90–91	1	1.5593	0.989	91.8	8.2	91.68	8.36
4-CH_3	35.5	106–110	1	1.5525	.970	91.0	9.0	91.00	8.94
4-CH_3[b]	16.0	115–117	1	1.5476	.960	90.7	9.3	90.4	9.2
3,4-di-CH_3	30.0	150–155	2	1.5560	.971	90.4	9.6	90.1	9.5
4-$CH(CH_3)_2$	2.0	104–106	0.5	1.5238	.979	90.0	10.0	89.52	9.66

[a] Reported by Klages and Heilmann, *Ber.*, **37** 1450 (1904), b. p. 285–286°; d^{17}_4 0.9857; n^{17}_D 1.5635. [b] 1,2-ditolylbutane.

dehydrohalogenation. Thus *p*-(chloroisopropyl)-toluene was brominated and then dehydrohalogenated to give 3-bromo-4-methyl-α-methylstyrene. In this way products with substituents in the meta and para positions rather than in the ortho positions are obtained, and even deactivating (electron-withdrawing) groups may be introduced without interfering with the subsequent styrene formation.

All of the styrenes prepared except those with ortho substituents copolymerized satisfactorily with butadiene in emulsion systems to give rubber-like materials similar to GR-S in appearance. They also copolymerized with styrene, methyl methacrylate and maleic anhydride, but they did not polymerize alone with peroxide catalysts.

Acknowledgment.—The authors are indebted to the General Tire and Rubber Company and the Purdue Research Foundation for financial assistance in the form of a fellowship.

Experimental[4,5]

1-Halo-2-arylpropanes.—The chloroalkylation of *o*-chlorotoluene is typical for all of the compounds in this series. A cooled, stirred solution of 1920 g. (15 moles) of *o*-chlorotoluene and 520 g. (5.5 moles) of freshly distilled propylene chlorohydrin was saturated with boron trifluoride at temperatures below 10°, and then 196 g. (1.4 moles) of phosphorus pentoxide was added. The resulting two phase mixture was heated at 75° for four hours. During the heating period boron trifluoride was evolved and vented into a water trap. The layers were separated after cooling, the top layer was washed several times with water, dried, and rectified through a 43-cm. Fenske column; yield 358 g. (32%), b. p. (2 mm.) 95–97°, d^{25}_{25} 1.164, n^{25}_D 1.5392. It is interesting to note that the narrow b. p. range and constant n_D values give no evidence of the presence of isomers, although the styrenes later obtained by dehydrohalogenation separated into fractions on distillation and were definitely shown to contain positional isomers by oxidation to known isomeric benzoic acids. In Table I are listed the haloalkylated aromatic compounds together with their physical constants and analyses.

1,2-Diarylalkanes.—The chloroalkylation of benzene, isopropylbenzene, *o*-xylene, and toluene led to 1,2-diarylalkanes as by-products. The yields and properties of these compounds are shown in Table III.

Bromination of Chloroisopropylated Toluene.—Chloroisopropylated toluene (250 g., 1.5 moles) was mixed with 0.6 g. of iodine, and 76 ml. (1.5 moles) of bromine was added dropwise to the cooled, stirred mixture which was shielded from light. After twenty-four hours, the color of bromine was still apparent; hence, about 0.1 g. of iron filings was added and the mixture was allowed to stand at room temperature for an additional twenty-four hours, after which it was washed with water, dilute sodium hydroxide, twice again with water, distilled, washed with sodium thiosulfate solution, and rectified. There was obtained 257 g. of product b. p. (2 mm.) 108–113°; n^{25}_D 1.5590; d^{25}_{25} 1.3896. It is interesting to compare these properties with those of chloroisopropylated *o*-bromotoluene which were: n^{25}_D 1.5592; d^{25}_{25} 1.3893; b. p. (1–2 mm.) 109–112°. The yield on the bromination was 70%.

Substituted α-Methylstyrenes.—The preparation of 3-chloro-2-methyl- and 3-chloro-4-methyl-α-methylstyrenes is typical. Chloroisopropylated *o*-chlorotoluene (2 moles) was refluxed with a filtered solution of 466 g. (7 moles) of 85% potassium hydroxide in 1850 ml. of methanol. Most of the methanol was removed by distillation and the residual liquid was washed with water, dried with calcium chloride, and rectified through an efficient column giving 90 g. (26%) of 3-chloro-2-methyl-α-methylstyrene (I) (b. p. (4 mm.) 64–65°; n^{25}_D 1.5340; d^{25}_{25} 1.043) and 152 g. (48%) of 3-chloro-4-methyl-α-methylstyrene (II) (b. p. (4 mm.) 73–74°; n^{25}_D 1.5520; d^{25}_{25} 1.056).

Anal. Calcd. for $C_{10}H_{11}Cl$: Cl, 21.3; bromine number, 96. Found: (I) Cl, 21.4; bromine number, 96. Found: (II) Cl, 21.3; bromine number, 99.

Oxidation of (I) and (II) with dilute nitric acid gave respectively 3-chloro-2-methylbenzoic acid (m. p. 152–153°; neutral equivalent 172)[6] and 3-chloro-4-methylbenzoic acid (m. p. 205–206°; neutral equivalent 171).[7]

In Table II are listed the substituted α-methylstyrenes together with their physical constants and analyses.

Preparation of Copolymers.—Copolymers of the substituted α-methylstyrenes with methyl methacrylate, maleic anhydride and styrene were made at 65–70° in small stoppered test-tubes, using 0.5% benzoyl peroxide as catalyst. Copolymers with butadiene[8] were made at 40° in small sealed tubes, using the following formula: butadiene 7.5 parts, substituted α-methylstyrene 2.5 parts, water 18 parts, soap 0.5 part, a peroxide 0.03 part and lauryl mercaptan 0.06 part. Copolymers were obtained from all of the alpha-methylstyrenes except those with ortho substituents (*e. g.* 3-chloro-2-methyl-alpha-methylstyrene). None of the alpha-methylstyrenes copolymerized with vinyl acetate.

Summary

A new synthesis of α-methylstyrenes has been developed which involves the catalytic condensation of aromatic compounds with propylene chlorohydrin and the dehydrohalogenation of the resulting halopropylated derivatives. Several new α-methylstyrenes have been prepared and copolymerized with butadiene, methyl methacrylate, styrene and maleic anhydride.

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[4] All melting points and boiling points are corrected.

[5] Analyses by Mr. A. M. Ribley and Miss L. Roth of the Purdue Department of Chemistry.

[6] Kruger, *Ber.*, **18**, 1758 (1885), reports m. p. 154°.

[7] Von Gerichten, *Ber.*, **11**, 365 (1878), reports m. p. 199–201°.

[8] These copolymers were made by Dr. L. J. Filar of the Purdue Department of Chemistry.