Friedel–Crafts Isomerization. XIII.[1a] Aluminum Chloride Catalyzed Isomerization of the Halocumenes

GEORGE A. OLAH,[1b] JOAN C. LAPIERRE, AND GERALD J. MCDONALD

The Eastern Research Laboratory, The Dow Chemical Company, Wayland, Massachusetts, and the Department of Chemistry, Western Reserve University, Cleveland, Ohio

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The water-promoted aluminum chloride catalyzed isomerization of the isomeric *o*-, *m*-, and *p*-fluorocumenes, chlorocumenes, and bromocumenes has been investigated. Fluorocumenes isomerize by exclusive migration of the isopropyl group and chlorocumenes by predominant migration of the isopropyl groups, whereas bromocumenes isomerize by migration of both the isopropyl group and the bromine atom (as positively polarized species). The equilibrium isomer distributions consist in the case of the fluorocumenes of 22% *ortho*, 62% *meta*, and 16% *para* isomer, in the case of the chlorocumenes of 10% *ortho*, 66% *meta*, and 24% *para* isomer, and in the case of the bromocumenes of 9% *ortho*, 66% *meta*, and 25% *para* isomer. The preparation of pure isomeric halocumenes as well as the mechanism of their Friedel–Crafts isomerization is discussed.

In previous work we have discussed the aluminum chloride catalyzed isomerization of the halotoluenes[2] and haloethylbenzenes.[3] No similar investigation of the Friedel–Crafts isomerization of the isomeric halocumenes was reported in the literature. It was therefore felt of interest to extend our investigation to this problem.

Results and Discussion

Preparation of Halocumenes.—All *o*-, *m*-, and *p*-fluoro-, chloro-, and bromocumenes were previously reported in the literature.[4]

p-Bromoisopropenylbenzene, prepared by the method of Ziegler and Tieman[5] from *p*-bromophenylmagnesium bromide and acetone, was hydrogenated to *p*-bromocumene by Copenhaver, Roy, and Marvel.[6] Ellingboe and Fuson[7] hydrogenated *p*-chloroisopropenylbenzene to *p*-chlorocumene.

In view of the fact that we intended to carry out the study of the isomerization of halocumenes using high-resolution gas–liquid partition chromatography (glpc) as the analytical method, we needed highest purity samples of the pure isomers both for standards and for starting materials. Of the isomeric halocumenes only *p*-chlorocumene and *p*-bromocumene are easily available. The reported preparations of the other isomers prove difficult owing to separation of mixtures or difficult preparation of pure starting materials (pure isopropylanilines, for example, are needed for the Schiemann reaction to prepare the corresponding fluorocumenes). We feel it to be of interest to report our preparation of the pure isomeric halocumenes.

The preparation of all the isomeric halocumenes involved the synthesis of the appropriate halophenyldimethylcarbinols. These were dehydrated, and the resulting haloisopropenylbenzenes were hydrogenated to yield the required halocumenes.

The *m*-fluoro-, *p*-fluoro-, *m*-chloro-, and *m*-bromophenyldimethylcarbinols were prepared from the appropriate halobromobenzene by treatment with butyllithium followed by reaction of the resulting halophenyllithium with acetone.

The three *o*-halophenyldimethylcarbinols were prepared by treatment of the appropriate methyl *o*-halobenzoates with methyl magnesium bromide. Unsuccessful attempts had been made to prepare the fluoro compound by treatment of 2-bromofluorobenzene with butyllithium and then reaction of the *o*-fluorophenyllithium intermediate with acetone. It is believed that the intermediate eliminated lithium fluoride to give benzene (dehydrobenzene), which then underwent further reactions.

The most favorable conditions which were found for dehydrating the carbinols involved heating to about 160–180° with sodium bisulfate and phosphorus pentoxide. The olefin and water were distilled from the reaction mixture at reduced pressure through a short column packed with pieces of glass. The column was used to retain the carbinol in the reaction flask. It was noted that the dehydration of *o*-chloro- and *o*-bromophenyldimethylcarbinol proceeded at about 110°. The greater ease of dehydration of these alcohols may be attributed to a steric effect.

Various conditions were employed for the hydrogenations of the various halopropenylbenzenes. Some cleavage of the carbon–halogen bond was observed in the hydrogenations of *o*-chloro- and *o*-bromopropenylbenzene over 10% palladium on carbon. The reduction of the latter compound was found to be especially difficult. Whereas the other olefins were hydrogenated at atmospheric pressure, the reduction of this compound proceeded to completion only very slowly using platinum oxide catalyst at 55 psi pressure in a Parr apparatus. This may also be attributed to a steric effect.

Isomerization.—The isomerization of *o*-, *m*-, and *p*-fluoro-, chloro-, and bromocumenes was investigated under the catalytic effect of water-promoted aluminum chloride at 25°. Experimental conditions were similar

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(1) (a) Part XII: G. A. Olah and J. C. Lapierre, *J. Org. Chem.*, **31**, 1271 (1966). (b) To whom inquiries should be sent: Department of Chemistry, Western Reserve University.

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to those used in the isomerization of halotoluenes and haloethylbenzenes. Results are given as normalized percentages of *ortho*, *meta*, and *para* isomers.

Fluorocumenes.—Tables I–III show the data for the isomerization of the three isomeric fluorocumenes. The equilibrium mixture contained about 22% *o*-, 62% *m*-, and 16% *p*-fluorocumene. There were always formed products of disproportionation (transpropylation) among which fluorobenzene and diisopropylfluorobenzenes are the main ones. At equilibrium these amounted to about 45 mole % of the total amounts present (including some unidentified higher boiling materials). The absence of cumene from all the samples clearly indicates that fluorine is not undergoing migration and the disproportionation involves only the isopropyl groups. Halogen exchange with the catalyst (aluminum chloride) is also observed to some degree, although at the temperature used (25°) this is of no major importance.

TABLE I

ALUMINUM CHLORIDE CATALYZED ISOMERIZATION OF *o*-FLUOROCUMENE

	Normalized % of fluorocumenes		
Time	*ortho*	*meta*	*para*
0 min	100	0	0
5 min	99.5	0	0.5
10 min	98.3	0.7	1.0
15 min	89.0	4.9	6.1
20 min	88.2	5.7	6.1
25 min	72.4	14.6	13.0
30 min	69.9	17.5	12.6
40 min	52.2	31.4	16.4
50 min	34.8	46.2	19.0
1 hr	26.5	54.4	19.1
1.5 hr	23.3	59.8	16.9
2 hr	22.2	61.3	16.5
4 hr	22.3	63.2	14.5
24 hr	22.3	63.3	14.4
48 hr	22.3	63.2	14.5
96 hr	22.4	62.0	15.6

TABLE II

ALUMINUM CHLORIDE CATALYZED ISOMERIZATION OF *m*-FLUOROCUMENE

	Normalized % of fluorocumenes		
Time	*ortho*	*meta*	*para*
0 min	0.2	99.7	0.1
2 min	0.4	99.2	0.4
5 min	1.5	96.0	2.5
10 min	4.0	91.7	4.3
15 min	6.7	86.4	6.9
25 min	7.6	85.8	6.6
30 min	8.1	84.9	7.0
40 min	9.5	82.8	7.7
50 min	10.7	81.1	8.2
1 hr	11.2	79.5	9.3
1.5 hr	13.9	75.2	10.9
2 hr	14.2	74.0	11.8
3 hr	15.4	73.4	11.2
7 hr	16.2	71.0	12.8
24 hr	18.7	66.8	14.5
48 hr	19.7	65.8	14.5
72 hr	20.6	64.5	14.9
96 hr	21.7	62.9	15.4

TABLE III

ALUMINUM CHLORIDE CATALYZED ISOMERIZATION OF *p*-FLUOROCUMENE

	Normalized % of fluorocumenes		
Time	*ortho*	*meta*	*para*
0 min	0	0.8	99.2
2 min	12.5	10.4	77.1
5 min	23.9	23.1	53.0
10 min	29.7	35.6	34.7
15 min	29.7	44.2	26.1
20 min	28.7	48.2	23.1
25 min	27.6	51.5	20.9
30 min	27.0	52.9	20.1
40 min	25.1	55.8	19.1
50 min	24.6	57.8	17.6
1 hr	23.1	59.8	17.1
1.5 hr	22.6	61.1	17.3
2 hr	22.7	60.3	17.0
4 hr	22.2	61.3	16.5
6 hr	22.0	61.5	16.5
24 hr	22.4	61.4	16.2
48 hr	21.9	61.9	16.2
96 hr	22.6	62.2	15.2

Chlorocumenes.—Tables IV–VI show the course of isomerization of *o*-, *m*-, and *p*-chlorocumene. The equilibrium mixture contains about 10% *o*-, 66% *m*-, and 24% *p*-chlorocumene. In the course of the isomerizations chlorobenzene and the diisopropylchlorobenzenes are also formed, indicating transalkylation (disproportionation). No cumene was detected, however, in any significant amount, which points to the isopropyl group as the main migrating entity.

TABLE IV

ALUMINUM CHLORIDE CATALYZED ISOMERIZATION OF *o*-CHLOROCUMENE

	Normalized % of chlorocumenes		
Time	*ortho*	*meta*	*para*
0 min	97.3	0	2.7
2 min	97.3	0	2.7
5 min	97.0	0.1	2.9
10 min	94.9	0.6	4.5
15 min	89.4	4.7	5.9
20 min	67.3	14.8	17.9
25 min	62.8	18.7	18.5
30 min	54.8	24.1	21.1
40 min	39.4	34.4	26.2
50 min	32.9	39.3	27.8
1 hr	29.2	42.5	28.3
1.25 hr	20.0	48.7	31.3
1.5 hr	14.9	54.3	30.8
2 hr	13.3	59.3	27.4
3 hr	10.2	64.8	25.0
4 hr	10.5	64.3	25.2
5 hr	11.7	63.3	25.0
7 hr	10.2	66.0	23.8
24 hr	11.0	65.7	23.3
48 hr	10.0	65.5	24.5
72 hr	9.9	66.1	24.0

Bromocumenes.—Bromocumenes isomerize faster than either fluorocumenes or chlorocumenes. The equilibrium isomer mixture consists of about 9% *o*-, 66% *m*-, and 25% *p*-bromocumene.

Tables VII–IX show the course of isomerization of the bromocumenes at 25°. It is seen that in the isomerization of *o*-bromocumene the formation of the *para* isomer is faster than that of the *meta*, with the *para* going through a maximum. Similarly, in the isomerization of *p*-bromocumene the concentration of the

TABLE V
ALUMINUM CHLORIDE CATALYZED ISOMERIZATION OF *m*-CHLOROCUMENE

Time	Normalized % of chlorocumenes *ortho*	 *meta*	 *para*
0 min	0	99.8	0.2
10 min	1.3	93.1	5.6
30 min	1.1	95.9	3.0
40 min	1.7	94.0	4.3
50 min	2.0	93.0	5.0
1 hr	2.5	90.6	6.9
1.5 hr	4.8	84.5	10.7
2 hr	9.6	66.9	23.5
3 hr	11.2	63.9	24.9
4 min	10.5	64.3	25.2
5 hr	10.9	63.2	25.9
7 hr	10.5	63.7	25.8
24 hr	10.9	63.5	25.6
48 hr	9.3	67.0	23.7
72 hr	9.4	66.4	24.2

TABLE VI
ALUMINUM CHLORIDE CATALYZED ISOMERIZATION OF *p*-CHLOROCUMENE

Time	Normalized % of chlorocumenes *ortho*	 *meta*	 *para*
0 min	0	1.1	98.9
2 min	1.5	1.3	97.2
5 min	4.7	3.4	91.9
20 min	5.5	3.7	90.8
30 min	7.7	7.3	85.0
40 min	7.9	14.8	77.3
50 min	9.4	22.0	68.6
1 hr	11.3	30.6	58.1
1.25 hr	13.0	39.6	47.4
1.5 hr	12.7	47.3	40.0
1.75 hr	10.7	51.9	37.4
2 hr	12.1	55.9	32.0
2.5 hr	9.6	59.9	30.5
3 hr	9.2	61.8	29.0
6 hr	9.4	64.0	26.6
8 hr	9.4	66.1	26.5
48 hr	9.3	66.3	24.4

TABLE VII
ALUMINUM CHLORIDE CATALYZED ISOMERIZATION OF *o*-BROMOCUMENE

Time	Normalized % of bromocumenes *ortho*	 *meta*	 *para*
0 min	99.9	0	0.1
2 min	99.2	0.3	0.5
5 min	99.4	0.2	0.4
10 min	97.1	1.0	1.9
15 min	91.3	3.4	5.3
17 min	74.1	10.7	15.2
20 min	70.7	12.6	16.7
25 min	66.9	13.9	19.2
30 min	63.9	15.5	20.6
40 min	54.9	20.2	24.9
50 min	41.7	24.5	26.8
1 hr	39.8	29.0	31.2
1.25 hr	27.8	38.1	34.1
1.5 hr	11.3	50.2	38.5
2 hr	9.6	53.7	36.7
3 hr	7.8	57.2	35.0
5 hr	7.8	62.5	29.7
24 hr	8.9	64.7	26.4
72 hr	8.2	66.5	25.3

TABLE VIII
ALUMINUM CHLORIDE CATALYZED ISOMERIZATION OF *m*-BROMOCUMENE

Time	Normalized % of bromocumenes *ortho*	 *meta*	 *para*
0 min	0	100	0
2 min	4.7	80.1	15.2
5 min	6.2	75.7	18.1
10 min	6.1	73.5	20.4
15 min	6.7	72.5	20.8
20 min	6.9	72.4	20.7
25 min	6.5	73.1	20.4
30 min	7.6	91.9	20.5
40 min	6.5	72.3	21.2
50 min	7.2	73.0	19.8
1 hr	6.9	71.7	21.4
2 hr	6.8	71.2	22.0
3 hr	7.9	70.6	21.5
5 hr	7.1	70.5	22.4
7 hr	8.3	68.9	22.8
24 hr	10.7	67.1	22.2
96 hr	12.8	65.4	24.8

TABLE IX
ALUMINUM CHLORIDE CATALYZED ISOMERIZATION OF *p*-BROMOCUMENE

Time	Normalized % of bromocumenes *ortho*	 *meta*	 *para*
0 min	3.0	0.5	96.5
0.5 min	12.0	0.9	87.1
1 min	12.2	3.6	84.2
2 min	15.4	6.5	78.1
5 min	13.9	13.1	73.0
10 min	11.7	18.4	69.9
15 min	11.3	22.3	66.4
30 min	10.2	33.2	56.6
45 min	9.9	40.9	49.2
1 hr	9.9	46.3	43.8
1.25 hr	9.6	53.1	37.8
1.5 hr	10.2	54.7	35.1
2 hr	9.6	57.7	32.7
6 hr	9.3	59.6	31.1
24 hr	9.1	63.8	27.1
96 hr	8.7	65.4	25.9

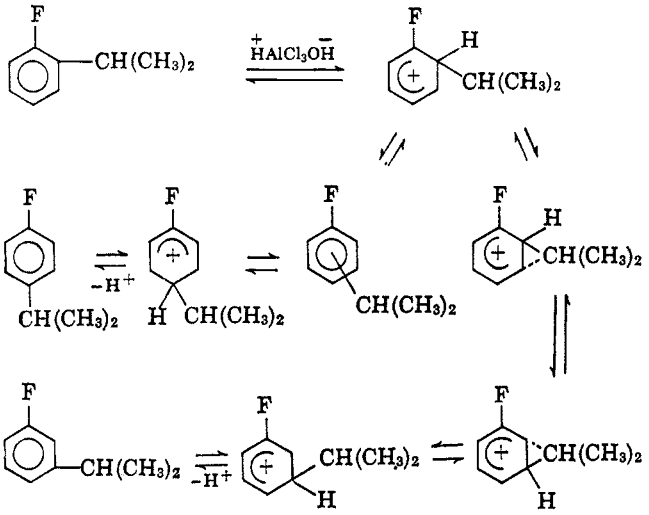
ortho isomer goes through a maximum. The isomerizations are always accompanied by disproportionation. Varying amounts of cumene and bromobenzene, as well as higher boiling materials (diisopropylbromobenzenes and dibromocumenes), were found, indicating that both the isopropyl group and bromine atoms migrate.

Mechanism.—In the isomerization of *o*-chloro- and *o*-fluorocumene, as well as in the case of *o*-bromocumene, it is observed that the formation of the *para* isomers goes through a maximum. Similarly the isomerization of *p*-chloro- and *p*-fluorocumene (as that of *p*-bromocumene) also goes through a maximum of the corresponding *ortho* isomers. Products of disproportionation from the fluoro- and chlorocumenes include fluorobenzene and chlorobenzene (as well as diisopropylhalobenzenes) but *not* cumene. Thus the migrating group in these cases is the isopropyl group. In the isomerization of bromocumenes both the isopropyl group and the bromine atom migrates, indicated by the presence of both bromobenzene and cumene in the products of disproportionation.

The migration of the isopropyl groups (and that of bromine) is in our view both *inter-* and *intramolecular*, indicated by the fact that isomerization when carried out in excess benzene shows not only transpropylation (forming cumene) and transbromination (forming bromobenzene), but also, even if much slower, positional migration.

It is possible to suggest that the isopropyl cation, when formed through cleavage of the σ complex, is remaining associated in the form of a π complex with the same substrate molecule, thus the dealkylation–alkylation can be still intramolecular. This mechanism would also account for the fast *ortho–para* conversion of isomers, followed probably by further isomerization involving intramolecular alkyl shifts in the benzonium ions. (See Scheme I.)

SCHEME I



Experimental Section

p-Chlorocumene (Eastman Kodak) and *p*-bromocumene (K and K Laboratories) were commercially available and were purified.

***m*-Fluorocumene.**—A solution of 1.61 *N* (180 ml, 0.29 mole) of *n*-butyllithium (Foote Chemical Co.) in hexane was placed in a 1-l., three-necked, round-bottomed flask equipped with a paddle stirrer, pressure-equalizing addition funnel, thermometer well, and a bubbler bypass system for maintaining a nitrogen atmosphere. The glassware had been flamed out under a stream of nitrogen, and a nitrogen atmosphere was maintained throughout the course of the reaction. Ether (150 ml, Mallinckrodt anhydrous, dried over calcium hydride) was added, and stirring was begun. The flask was immersed in a Dry Ice bath, and the solution was maintained at −40° while a solution of 50.7 g (0.29 mole) of 3-bromofluorobenzene (Aldrich) in anhydrous ether was added dropwise over a 15-min period. The solution gradually acquired an orange color. It was stirred at −40° for an additional 15 min, and then a solution of 20.3 g (0.35 mole) of acetone (Baker reagent grade) in 50 ml of anhydrous ether was added dropwise over a 15-min period while still maintaining the reaction mixture at −40°. Near the end of the addition the orange color faded to a light yellow. The cold bath was then removed, and the solution was allowed to warm to 20° with stirring over a 2.5-hr period. Then 30 ml of water was added dropwise, and the mixture was stirred for 45 min. The organic phase was decanted off, and the solid residue was dissolved in additional water. The solution was extracted with ether, and the extracts were added to the original organic phase which was then dried over anhydrous magnesium sulfate.

Solvent was distilled off, and the residual *m*-fluorophenyldimethylcarbinol was treated with a catalytic amount of iodine in refluxing toluene in an apparatus designed for the continuous removal of water. This treatment appeared not to effect dehydration of the carbinol, for no water separated out. Likewise, treating the carbinol with 0.2 g of Dowex 50 cation-exchange resin in refluxing benzene in the same apparatus did not result in the formation of water. The carbinol was finally dehydrated by heating it with 0.3 g of Dowex 50 in a flask equipped with a 10-cm Vigreux column. The olefin and water distilled out of the reaction mixture at 76–83° (50 mm) as the pot temperature was slowly increased from 130 to 165° by heating in an oil bath. The collected distillate was 13.5 g. Prior to this cut, an earlier one was collected at 75–78° (36 mm) while increasing the pot temperature from 110 to 120°. This material was dry and weighed 13 g. It was more of the olefin which apparently had been formed by the prior treatments of the carbinol. Also, although it was not suspected at this point, this material undoubtedly contained some of the by-product which is believed to have been formed in the preparation of the carbinol. The two cuts were combined for hydrogenation.

Hydrogenation was conducted in a Brown² hydrogenator following the directions for a 500-mmole run with external generation of hydrogen as described in "Operating Directions for the Brown² Hydrogenator" (Delmar Scientific Laboratories). The procedure involved the preparation of a platinum-on-carbon catalyst in the reaction flask by the reduction of chloroplatinic acid with sodium borohydride solution. The hydrogenation was carried out at atmospheric pressure in a setup designed for the generation of hydrogen as needed by the dropwise addition of a sodium borohydride solution to acetic acid in a separate flask. After hydrogen uptake had ceased, the catalyst was filtered off, and most of the ethanol (solvent) was distilled off. The pot residue still contained acetic acid and inorganic salts. It was poured into 50 ml of water, and potassium hydroxide pellets were added until the aqueous phase was strongly basic. The phases were separated, and the aqueous phase was extracted with several portions of methylene chloride. The combined organic phases were extracted with two 20-ml portions of water and dried over anhydrous magnesium sulfate. Solvent was distilled off, and the residual material was vacuum distilled through a 10-cm Vigreux column prior to careful fractional distillation to give 16.7 g (42% over-all yield) of material collected at 60–70° (50 mm), and 2 g collected by vacuum stripping at about 0.1 mm. The latter material was mostly the carbinol, which apparently had been carried over with the olefin in its preparation. The *m*-fluorocumene was fractionated through a 1 ft × 0.5 in. column packed with HeliPak. Numerous cuts were taken and analyzed by vpc. Those which were pure by this method of analysis were combined, and calcium hydride was added to remove traces of water. The liquid was then transferred to a clean dry flask and vacuum transferred to a second flask cooled in a Dry Ice bath in order to remove stopcock grease which had been picked up in the receiving apparatus of the vacuum distillation setup. *m*-Fluorocumene (10.9 g, 27% over-all yield) was obtained and stored over calcium hydride: bp 87.5° (88 mm), $n^{25}\text{D}$ 1.4690.

Anal. Calcd for $C_9H_{11}F$: C, 78.23; H, 8.02; F, 13.75. Found: C, 78.31; H, 8.12; F, 13.57.

***p*-Fluorocumene** was prepared by the same sequence as the *meta* isomer starting with 50.7 g (0.29 mole) of 4-bromofluorobenzene (Aldrich). In the preparation of the intermediate *p*-fluorophenyllithium, no color was noted, which was in contrast to the orange color observed in the preparation of the *meta* isomer. The carbinol which was obtained upon treatment of the organolithium intermediate with 20.3 g (0.35 mole) of acetone was not isolated, but was dehydrated directly after distilling off solvent from the solution in which it was isolated. Heating the carbinol with Dowex 50 cation-exchange resin under reduced pressure in a flask equipped with a 10-cm Vigreux column resulted in the distillation of a liquid at 87° (81 mm) as the pot temperature rose from 150 to 190°. However, a water phase did not separate out in the distillate. It was later shown by vpc analysis that the distillate was largely the desired olefin, but at the time it appeared as though the dehydration reaction was not taking place. The remainder of the carbinol was stripped out of the reaction flask at 0.1 mm pressure into a new receiver. It was dehydrated by heating with 2 g of sodium bisulfate and 0.5 g of phosphorus pentoxide in the same type of setup. The olefin and water distilled out of the reaction mixture at a convenient rate at 91° (62 mm) by maintaining the reaction mixture at about 180°. Vpc analysis showed that the major peak in both samples had the same retention times, indicating that both were the desired olefin. Both samples of the olefin were combined and hydrogenated in the Brown² hydrogenator. After hydrogen uptake had ceased, the reaction mixture was worked up as in the case of the *meta* isomer. The methylene chloride solution of the *p*-fluorocumene was concentrated by distillation, and the concentrate was then distilled in a short-path apparatus prior to careful distillation. Fractionation was carried out using a 1 ft × 0.5 in. column packed with HeliPak. Twenty-two cuts were collected and analyzed by vpc. The *p*-fluorocumene (3.9 g, nine early cuts) was contaminated with traces of olefin and was set aside. The remainder (13.6 g, total crude yield was 17.5 g or 44% over-all yield) of the most pure *p*-fluorocumene was dried over calcium hydride and then vacuum transferred in clean dry apparatus to remove stopcock grease. This gave 13.2 g (33% over-all yield) which was collected and stored over calcium hydride: bp 88.5° (91 mm), n^{25}_{D} 1.4678 (lit.[4] bp 153–155°, n^{20}_{D} 1.4733).

Anal. Calcd for $C_9H_{11}F$: C, 78.23; H, 8.02; F, 13.75. Found: C, 78.26; H, 8.10; F, 13.64.

m-**Chlorocumene** was prepared by the same reaction sequence as for the previous two halocumenes. 3-Bromochlorobenzene (55.5 g, 0.29 mole, Aldrich) was converted to *m*-chlorophenyldimethylcarbinol with butyllithium and acetone. After distilling off solvent from the solution in which the carbinol had been isolated, 7 g of sodium hydrogen sulfate and 2 g of phosphorus pentoxide were added to the concentrate, and the carbinol was dehydrated by heating under reduced pressure and distilling out the olefin and water through a 7 × 0.5 in. column packed with small pieces of glass. This column was used to retain the carbinol in the pot more effectively, since some carbinol had been observed to come overhead with the olefin in the previous two preparations in which only a 10-cm Vigreux column had been used. While heating the reaction flask from 130 to 155°, 16.7 g distilled at 89° (16 mm). No more distillate was collected until the flask temperature reached 170°. Then an additional 14 g of the olefin–water mixture was collected at the same head temperature while heating the flask from 170 to 180°. The olefin was dissolved in 100 ml of ethyl acetate and hydrogenated over 1.5 g of a 5% rhodium-on-alumina catalyst at atmospheric pressure and ambient temperature. This catalyst was chosen because it had previously been shown to be ineffective in reducing chlorobenzene. After the hydrogenation had proceeded about half way, the rate of hydrogen uptake became very slow. The catalyst was filtered off, a fresh sample was added, and the hydrogenation then proceeded to completion as indicated by vpc analysis. After filtering off the catalyst, the solution was dried over anhydrous magnesium sulfate, and solvent was distilled off. The concentrate was vacuum distilled using a 1 ft × 0.5 in. column packed with glass helixes. Eighteen cuts were collected and analyzed by vpc. The over-all yield of *m*-chlorocumene was 22 g (49%), of which 15.3 g was highly pure. This latter material was vacuum transferred to remove stopcock grease; 15 g (33% over-all yield) was collected and stored over calcium hydride: bp 65° (7 mm), n^{25}_{D} 1.5103 [lit.[5] bp 66–68° (8 mm), n^{20}_{D} 1.5136].

Anal. Calcd for $C_9H_{11}Cl$: C, 69.90; H, 7.17; Cl, 22.93. Found: C, 70.05; H, 7.04; Cl, 23.10.

m-**Bromocumene** was prepared in a similar manner as the preceding three compounds starting with 68.4 g (0.29 mole) of *m*-dibromobenzene (Eastman White Label). The reactions with butyllithium and acetone in the preparation of the *m*-bromophenyldimethylcarbinol were carried out at −65°. A yellow color developed as the halide was added to the butyllithium solution, and by the time the addition was completed, the solution was a very dark brown or black color. After the acetone had been added, the solution was yellow. Upon warming, a solid precipitated. The reaction mixture was hydrolyzed and worked up as before. The carbinol was dehydrated in the same manner as the *m*-chlorophenyldimethylcarbinol, except that the column was packed with HeliPak. About 26 g of the olefin-water mixture distilled at about 93° at 3 mm while heating the reaction flask slowly to 190°. When no more liquid could be forced overhead, the column was removed, and a short-path distillation yielded 19 g more of the dry olefin coming overhead at about 110° at 3.5 mm. The combined cuts of the olefin were dissolved in 80 ml of ethyl acetate, and two attempts were made to hydrogenate it over 1.3-g samples of 5% rhodium on alumina at 1 atm pressure. In both cases the catalyst soon became poisoned. The reduction was completed using 1 g of 10% palladium-on-carbon catalyst at atmospheric pressure. The yellow solution obtained upon filtering off the catalyst was not decolorized upon boiling with charcoal. Solvent was distilled off, and the concentrated solution was fractionated using a 1 ft × 0.5 in. column packed with glass helices. Twenty-five cuts were collected and analyzed by vpc. The latter method gave better resolution of the *m*-bromocumene from the residual *m*-bromo-α-methylstyrene. The total yield was 30 g (52% over-all yield), of which 26 g was taken as pure *m*-bromocumene and vacuum transferred to remove stopcock grease. This material (25.5 g, 44% over-all yield) was collected and stored over calcium hydride: bp 65.8° (2.7 mm), n^{25}_{D} 1.5352 [lit.[6] bp 71–74° (2.5 mm), n^{20}_{D} 1.5370].

Anal. Calcd for $C_9H_{11}Br$: C, 54.29; H, 5.57; Br, 40.14. Found: C, 54.20; H, 5.57; Br, 40.19.

o-**Fluorocumene.**—After two unsuccessful attempts to prepare this compound from 2-bromofluorobenzene by the procedure used for the previous four halocumenes, it was prepared through the reaction of methyl *o*-fluorobenzoate with methylmagnesium bromide. The carbinol resulting from this reaction was dehydrated and hydrogenated to yield the desired *o*-fluorocumene.

An approximately 3 *M* solution (250 ml, 0.75 mole, 25% excess) of methylmagnesium bromide (Arapahoe) in ether was placed in a 1-l. three-necked round-bottomed flask equipped with a paddle stirrer, pressure-equalizing addition funnel, condenser, and drying tube. Methyl *o*-fluorobenzoate (46.2 g., 0.3 mole, Eastman practical grade) in 60 ml of anhydrous ether was added dropwise over 15 min while cooling the reaction flask in an ice bath. The ice bath was removed, and after stirring for 0.5 hr, the mixture was refluxed for 1 hr. It was then treated first with 20 ml of water and then a solution of 30 ml of sulfuric acid (96%) in 100 ml of water. The mixture was stirred overnight, and the organic phase was decanted from the solid and aqueous phases. The solid was filtered off, and both it and the aqueous phase were washed with ether. The ether extracts were added to the original organic phase, and the solution was extracted with water, potassium bicarbonate solution, and water again. The solution was dried over anhydrous magnesium sulfate, and ether was distilled off. The carbinol was dehydrated without isolation by heating with 7 g of sodium bisulfate and about 2 g of phosphorus pentoxide. The olefin and water were distilled out of the reaction mixture through a 7 × 0.5 in. column packed with small pieces of glass at about 67° at 58 mm to give 30 g of the mixture. In addition, 4.3 g of an oil was also obtained which distilled in a short-path apparatus at about 103° at 0.1 mm: n^{25}_{D} 1.5391. Most of the water was separated from the olefin, and it was hydrogenated at atmospheric pressure in 70 ml of ethyl acetate over 1 g of 10% palladium on carbon. The catalyst was filtered off, and the solution was dried over anhydrous magnesium sulfate. Distillation through a 1 ft × 0.5 in. column packed with HeliPak yielded 17 g (41% over-all yield) of *o*-fluorocumene. The most pure cuts, as judged by vpc analysis, were combined and vacuum transferred to remove stopcock grease. The product (11.3 g, 27% over-all yield) was collected and stored over calcium hydride: bp 89° (about 100 mm), n^{25}_{D} 1.4710.

Anal. Calcd for $C_9H_{11}F$: C, 78.23; H, 8.02; F, 13.75. Found: C, 78.28; H, 8.28; F, 13.88.

o-**Chlorocumene** was prepared by the same reaction sequence that was used for the preparation of *o*-fluorocumene. Methyl *o*-chlorobenzoate (51.2 g, 0.3 mole, Eastman White Label) was used in the Grignard reaction with methylmagnesium bromide. The reaction mixture was hydrolyzed with 20 ml of water, and then a solution of 75 ml of hydrochloric acid in 50 ml of water was added. The phases were separated, and the aqueous phase was extracted with ether. The combined organic phases were extracted numerous times with water, sodium bicarbonate solution, and water again. The final water wash always remained acidic to litmus. The ethereal solution was dried over anhydrous magnesium sulfate, and solvent was removed with a water aspirator. The carbinol was dehydrated without isolation by heating with 7 g of sodium bisulfate and 2 g of phosphorus pentoxide in the same setup as was used for the corresponding fluoro compound. The dehydration proceeded at a considerably lower temperature than all of the previous dehydration reactions. The olefin and water distilled at about 75–110° at about 50 mm (uncertain owing to an air leak in the system) while heating the reaction flask at only 115°. The greater ease of dehydration may be attributed to a relief of steric strain accompanying the elimination reaction. About 29 g of the olefin–water mixture was collected and added to 50 ml of ethyl acetate, and the water layer was separated. The olefin solution was hydrogenated at atmospheric pressure over 1 g of

10% palladium on carbon. The rate of hydrogen uptake was slower than in the reduction of the corresponding fluoro compound, possibly reflecting a steric effect in the hydrogenation reaction. The catalyst was filtered off, and the orange-yellow solution was dried over anhydrous magnesium sulfate and distilled through a 1 ft × 0.5 in. column packed with glass helices. Seventeen cuts were collected with a relatively constant boiling point of 80° (19 mm). However, vpc analysis showed that all of the cuts were contaminated with residual olefin and also with *m*- and/or *p*-chlorocumene. The concentration of the olefin remained constant in all of the cuts, indicating that its boiling point is nearly identical with that of *o*-chlorocumene at 19 mm. The concentration of the isomeric impurity increased in the last two cuts, indicating a slightly higher boiling point. The combined cuts were again hydrogenated at atmospheric pressure in 70 ml of ethyl acetate over 2 g of 10% palladium on carbon. This time the reduction was allowed to proceed too far. Upon filtering off the catalyst, the solution smelled strongly of HCl, and vpc analysis showed a large peak for cumene. The yellow solution was stirred with anhydrous potassium carbonate, which rapidly decolorized it, and was distilled as before. About 5.5 g of cumene was collected at 54° (23 mm). The *o*-chlorocumene distilled at 83.5° (22 mm). It was contaminated with the isomeric impurity (*ca.* 5%) and was purified by preparative-scale vpc (using an F and M Model 770 preparative-scale Fractometer). This isomeric impurity presumably arose from the corresponding methyl chlorobenzoate present as an impurity in the starting material.

***o*-Bromocumene** was prepared by the same reaction sequence as the other two *o*-halocumenes starting with 64.5 g (0.3 mole) of methyl *o*-bromobenzoate (Eastman White Label). The Grignard reaction with methylmagnesium bromide was hydrolyzed with a total of 100 ml of water and 100 ml of saturated ammonium chloride solution. The ether phase was decanted off, and the residual solid was dissolved in a solution of 50 ml of hydrochloric acid in 100 ml of water. The aqueous solution was extracted with ether, the extracts were added to the original ether phase, and the ethereal solution was extracted with water and dried over anhydrous magnesium sulfate. After removing much of the ether with a water aspirator, the residual carbinol was dehydrated by heating with 7 g of sodium bisulfate and about 2 g of phosphorus pentoxide. The dehydration took place readily at 105–110°. Most of the water distilled out of the reaction mixture before the olefin through a 7 × 0.5 in. column packed with glass pieces. The olefin (41.6 g, 71% over-all yield) was collected at about 93–99° (11 mm).

Hydrogenation of the *o*-bromo-α-methylstyrene proceeded with difficulty. A solution of 41.6 g (0.211 mole) in 65 ml of ethyl acetate was subjected to atmospheric pressure hydrogenation over 1 g of 10% palladium on carbon. Hydrogen uptake was very sluggish. More catalyst (4.5 g) was added with little helpful effect. After about 28% of the calculated amount of hydrogen had been taken up, the reaction stopped. The catalyst was filtered off. The presence of HBr fumes and vpc analysis showed the presence of cumene already at this stage of the reduction. Hydrogenation was then continued in ethyl acetate solution over 4 g of 10% palladium on carbon at 55-psi pressure using the Parr apparatus. The hydrogen uptake was still very slow. After running the reaction overnight, vpc analysis showed that the reduction still had not proceeded half way. The catalyst was filtered off, and 4 g of fresh catalyst was added. At 55-psi pressure no further hydrogen uptake occurred. Catalyst was filtered off, and the mixture was distilled in an effort to remove any poison that might be present. Only 25 g of the bromo olefin–bromocumene mixture was obtained. A solution of this material in 35 ml of ethyl acetate over 4 g of 10% palladium on carbon did not absorb hydrogen at 55-psi pressure. The catalyst was filtered off and replaced with 0.3 g of platinum oxide. Reduction on the Parr apparatus was carried out over 2 days. Vpc analysis showed about 5% olefin still remaining. However, little if any further formation of cumene was noted. The catalyst was filtered off and replaced with 0.3 g of fresh platinum oxide. Hydrogenation overnight at 55-psi pressure reduced the amount of residual olefin to about 1%. Again, no appreciable further formation of cumene was noted. The catalyst was filtered off, and the yellow solution was decolorized by stirring with anhydrous potassium carbonate.

Distillation through a 1 ft × 0.5 in. column packed with glass helices afforded about 17.5 g (29% over-all yield) of *o*-bromocumene. The early cuts were contaminated with cumene. The material (13.5 g) collected at 87° (14 mm) was contaminated only with about 1% of *o*-bromo-α-methylstyrene. An additional 1.7 g was collected upon stripping out the column at 0.1 mm. This material was contaminated only with about 0.2% of the olefin. Stopcock grease was removed from these samples by vacuum transfers. Separate samples (13.1 and 1.6 g) were collected and stored over calcium hydride. The total yield of purified *o*-bromocumene was 14.7 g (25% over-all yield), $n^{25}D$ 1.5382 [lit.[7] bp 83.0° (10 mm), $n^{25}D$ 1.5385].

Anal. Calcd for $C_9H_{11}Br$: C, 54.29; H, 5.57; Br, 40.14. Found: C, 54.2; H, 5.7; Br, 40.1.

General Procedure of Isomerization.—The ratio of substrate and catalyst in all isomerizations was 0.15 mole of aluminum chloride/mole of halocumene. One milliliter of water was added as promoter. All isomerizations were carried out in stoppered reaction flasks magnetically stirred and thermostated at 25 ± 0.5°. Samples were withdrawn periodically; the reaction was stopped by quenching with water. The organic material was extracted with ether. The extracts were dried with anhydrous magnesium sulfate and analysed by gas–liquid partition chromatography.

Gas–Liquid Partition Chromatographic Analysis.—All analyses were carried out on a Perkin-Elmer Model 226 Fractometer equipped with a 150-ft polypropylene glycol coated open-tubular (Golay) column, using a hydrogen flame-ionization detector. Helium carrier gas pressure of 30 psi was used, columns being operated at 80–120°. Peak areas were directly determined by the use of a high-speed Infotronics Model CRS-1 electronic integrator. Characteristic retention times and column conditions used are summarized in Table X.

Table X

Retention Times of Halocumenes

Compd	Temp, °C	Retention time, min
Fluorobenzene	80	4.5
o-Fluorocumene		11.5
m-Fluorocumene		12.4
p-Fluorocumene		13.8
Chlorobenzene	100	4.5
o-Chlorocumene		11.8
m-Chlorocumene		13.0
p-Chlorocumene		13.9
Cumene	120	3.5
Bromobenzene		4.2
o-Bromocumene		9.6
m-Bromocumene		10.6
p-Bromocumene		11.4

The accuracy of the gas–liquid partition chromatographic analytical method, as established from the analysis of isomer mixtures of known composition, was ±5 relative % for all isomers.