

stoichiometry of the equilibrium. *p*-Dibromobenzene isomerized at 180° for twelve hours yielded a mixture containing 26% tribromobenzene and only 7% monobromobenzene based on the amount of the remaining dibromobenzenes.

The time requirement of the *ortho* and *para* bromine atoms to reach the fast 1:6.5 quasi-equilibrium *ortho-para* ratio depends somewhat on the nature of the second substituent (and thus the basicity of the compounds) and increases in the order of Br < Cl < F, being about 2, 10, and 20 minutes, respectively, for dibromo-, bromochloro-, and bromofluorobenzene under the investigated experimental conditions at 30°.

Experimental

Materials.—Halobenzenes used were commercially available chemicals of highest purity, which were purified by fractional distillation on an Oldershaw column rated at 50 theoretical plates. Purity of these materials as determined by gas chromatography was 99.5% or higher. Aluminum bromide (Fisher reagent grade) was purified by vacuum sublimation.

Isomerization of Dihalobenzenes.—Aluminum bromide (0.05 mole) and 1 ml. of water were added to 0.5 mole of dihalobenzene in a flask equipped with magnetic stirrer and calcium chloride tube. The reaction mixture was kept in a thermostatically controlled bath with constant agitation. Samples of 1–2 ml. withdrawn at certain intervals were

quenched with ice water, extracted with ether, and the organic layer was washed acid-free.

Gas-Liquid Chromatographic Analysis.—The ethereal solutions of the products after drying with calcium chloride were analyzed by gas-liquid chromatography using a Perkin-Elmer 154C Vapor Fractometer equipped with a Perkin-Elmer Model 194 electronic printing integrator. A four meter by 0.25-in. stainless steel column packed with polypropylene glycol (UCON LB-550-X) on diatomaceous earth was used, employing hydrogen (30 ml./min.) as carrier gas.

The relative response data of the materials investigated were obtained by analyzing synthetic mixtures of mono- and dihalobenzenes of known composition. An error of less than ±2 relative per cent was found for most constituents. The following retention times were observed for the halobenzenes analyzed.

RETENTION TIME OF HALO- AND DIHALOBENZENES

Compound	Column temperature	Retention time, min.
Benzene	145	2.5
Fluorobenzene	145	3
Chlorobenzene	180	4
Bromobenzene	180	6
<i>o</i> -Bromofluorobenzene	145	13
<i>m</i> -Bromofluorobenzene	145	11
<i>p</i> -Bromofluorobenzene	145	12
<i>o</i> -Bromochlorobenzene	180	16
<i>m</i> -Bromochlorobenzene	180	13
<i>p</i> -Bromochlorobenzene	180	14
<i>o</i> -Dibromobenzene	180	24
<i>m</i> -Dibromobenzene	180	21
<i>p</i> -Dibromobenzene	180	22

Friedel-Crafts Isomerization. IV.¹ Aluminum Halide-Catalyzed Isomerization of Halotoluenes

GEORGE A. OLAH AND MAX W. MEYER

Contribution No. 52, Exploratory Research Laboratory, Dow Chemical of Canada, Ltd., Sarnia, Ontario, Canada

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The isomerization of fluorotoluenes, chlorotoluenes, and bromotoluenes has been investigated with water-promoted Al₂Cl₆. *m*- and *p*-fluorotoluene as well as the chlorotoluenes isomerize by an intramolecular 1,2-methyl shift mechanism. Due to the strongly deactivating influence of the fluoro substituent upon the *ortho* position, *o*-fluorotoluene undergoes halogen exchange with the catalyst and Friedel-Crafts type arylation reactions rather than isomerization. *m*-Bromotoluene isomerizes by an apparent 1,2-shift of the bromine while the isomerization of *o*- and *p*-bromotoluene involves an initial fast intermolecular bromine migration followed by a considerably slower rearrangement to the equilibrium mixture.

Many investigations of isomerization and disproportionation reactions of alkylbenzenes and halobenzenes under the influence of Lewis acids have been carried out. Less seems to be known of the behavior of substituted benzenes carrying both an alkyl and a halo substituent.

Norris and Turner² treated *o*-, *m*-, and *p*-chlorotoluene with aluminum chloride at temperatures up to 100° and found isomerization to occur readily, accompanied by some disproportionation. Cryoscopic and ebullioscopic methods were used to determine isomer distributions. An investigation

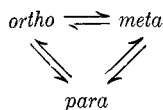
of the aluminum halide-catalyzed isomerization of bromotoluenes over the temperature range –25 to 100° was carried out by Crump and Gornowicz.³

In the present study, fluorotoluenes, chlorotoluenes, and bromotoluenes were isomerized with water-promoted aluminum chloride using infrared analysis to establish isomer distributions. The change of isomer distribution with time allows some insight into the three-compound equilibrium and provides qualitative information regarding the relative velocity with which the individual isomers are formed.

(1) Part III, *J. Org. Chem.*, **27**, 3455 (1962).

(2) J. F. Norris and H. S. Turner, *J. Am. Chem. Soc.*, **61**, 2128 (1939).

(3) J. W. Crump and G. A. Gornowicz, personal communication.



Results

The isomerization of halotoluenes through the catalytic effect of water-promoted Al_2Cl_6 was investigated. Preliminary experiments showed that the rate of isomerization increases with increasing concentration of water as a co-catalyst. To have reproducible conditions, water was added in the same known amount in all experiments. This also eliminated the difficulty of attempting to achieve absolutely anhydrous conditions in a Friedel-Crafts system. The quantity of Al_2Cl_6 used amounted to 9 mole %, and 2 ml. of water was added per mole of organic compound. Isomerization of fluorotoluenes was investigated at 100° and 200° , chlorotoluenes at 100° , and the bromotoluenes at 100° and 30° . Results are given as normalized percentages of *o*-, *m*-, and *p*-isomer as a function of time. As the amount of catalyst employed is relatively small, it is believed that the composition of the final equilibrium mixture is close to the thermodynamic equilibrium, and that complex formation by starting material or products with Al_2Cl_6 does not constitute a determining factor.

Fluorotoluenes.—Figure 1 shows the appearance

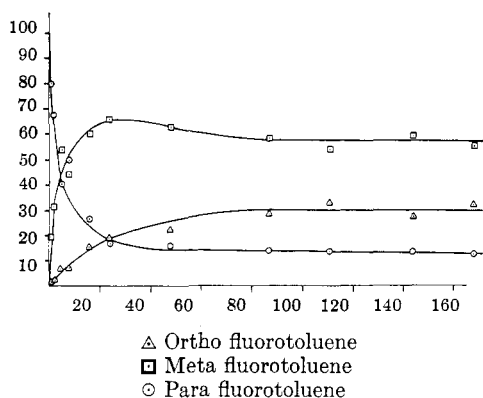
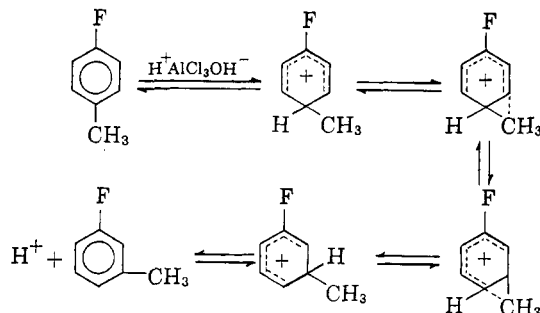


Fig. 1.—Isomerization of *p*-fluorotoluene with $\text{Al}_2\text{Cl}_6 + \text{H}_2\text{O}$ co-catalyst at 100° .

with time of *m*- and *o*-fluorotoluene in the isomerization of *p*-fluorotoluene at 100° . The equilibrium mixture contained 31% *ortho*, 56% *meta*, and 13% *para* isomer. No products of disproportionation could be detected. The percentage of *meta* isomer goes through a maximum after about twenty-five hours (65% *meta*). Formation of *meta* isomer in excess of thermodynamic equilibrium in the early stage of the reaction is in accord with thermodynamics and indicates a kinetically controlled fast conversion of the *para* isomer to the *meta*. Subsequent formation of the *ortho* isomer at the cost of

the *meta* is slower. It is therefore suggested that isomerization of *p*-fluorotoluene proceeds by a 1,2-shift. As discussed previously,⁴ fluorine on the aromatic ring is unable to move under Friedel-Crafts isomerization conditions; therefore it is the methyl group that changes position.



In the course of the intramolecular 1,2-shift the methyl group of the primarily formed σ -complex bridges to two adjacent carbon atoms and then swings over to its final positions, as suggested by Allen⁵ for 1,2-shifts in isomerization of dialkylbenzenes.

The isomerization of *m*-fluorotoluene (Fig. 2)

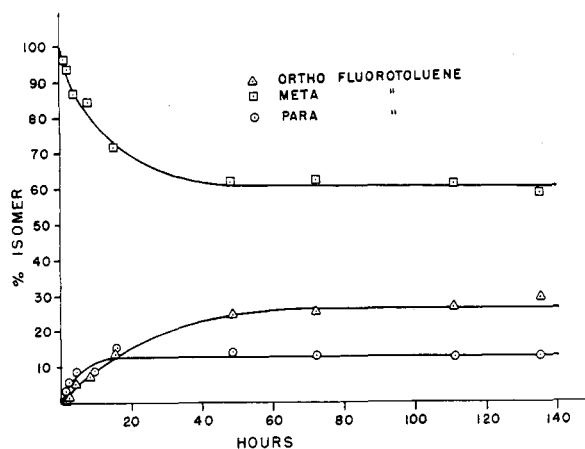


Fig. 2.—Isomerization of *m*-fluorotoluene with $\text{Al}_2\text{Cl}_6 + \text{H}_2\text{O}$ co-catalyst at 100° .

presents a similar picture. Conversion of *meta* to *para* appears to be faster than *meta* to *ortho*. The equilibrium mixture contained 29% *ortho*, 58% *meta*, and 13% *para* which is in fair agreement with the mixture obtained in the isomerization of *p*-fluorotoluene. *m*-Fluorotoluene, too, isomerizes by an intramolecular 1,2-shift of the methyl group.

The behavior of *o*-fluorotoluene is in marked contrast to the smooth rearrangement of *m*- and *p*-fluorotoluene. From Fig. 3 it is seen that *o*-fluorotoluene exhibits a surprising resistance to isomerization. After 400 hours at 100° the decrease in the normalized amount of starting material did not exceed 20%. The rate of isomerization cannot be

(4) G. A. Olah and W. Tolgyesi, Part II, *J. Org. Chem.*, **27**, 3449 (1962).

(5) R. H. Allen, *J. Am. Chem. Soc.*, **82**, 4856 (1960).

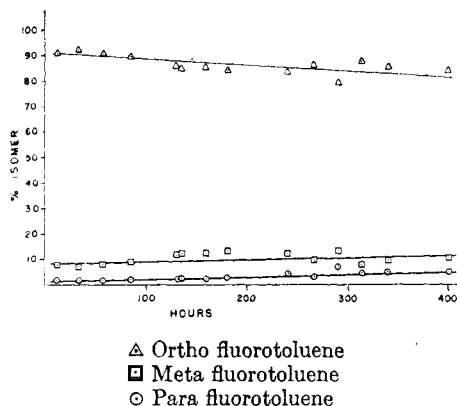
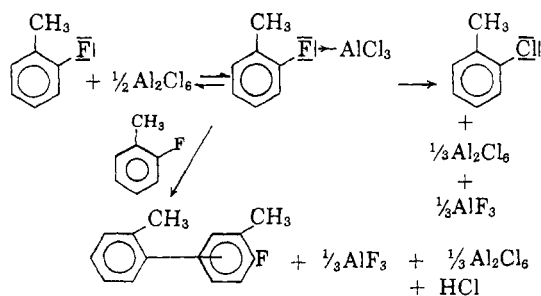


Fig. 3.—Isomerization of *o*-fluorotoluene with $\text{Al}_2\text{Cl}_6 + \text{H}_2\text{O}$ co-catalyst at 100° .

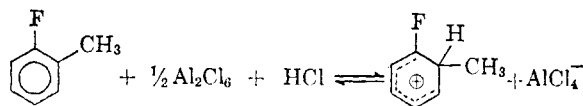
enhanced by an increase in temperature to any appreciable extent, for at 200° halogen exchange with the catalyst Al_2Cl_6 as well as arylation reactions giving methylphenyls are much faster than isomerization. The primarily formed *o*-chlorotoluene partly undergoes rearrangement so that *o*-, *m*-, and *p*-chlorotoluene are the main products after reaction times of up to 260 hours. No *m*- or *p*-fluorotoluene is found but some dimethylfluorobiphenyls are obtained. Both the halogen exchange and the Friedel-Crafts type arylation giving biphenyls are suggested to take place through a mechanism as previously suggested⁶ for fluorobenzene involving an π -complex type intermediate and nucleophilic displacement by another molecule.



Hydrogen bonding between fluorine and the hydrogen atoms of the methyl group cannot be the cause of the resistance of *o*-fluorotoluene to isomerization. Proton magnetic resonance as well as infrared investigations were unable to provide any evidence of hydrogen bonding. A likely explanation might be that the protonation of *o*-fluorotoluene at the carbon atom occupied by the methyl group (e.g., *ortho* to the fluorine) which is necessary for isomerization, takes place only with difficulty due to the strong $-I$ effect of the fluorine affecting mainly the *ortho* position.

The opposed conjugative effect (due to interaction of the unshared electron pair of fluorine)

(6) G. A. Olah, W. S. Tolgyesi, and R. E. A. Dear, *J. Org. Chem.*, **27**, 3441 (1962).



which does not diminish with distance as does the inductive effect, becomes more dominant in the *para* position, thus enabling easy *para* protonation.

If so, a similar although much weaker *ortho* effect might be expected under suitable conditions in the isomerization of *o*-chlorotoluene. Such an effect has been found.

Chlorotoluenes.—Figures 4, 5, and 6 show the

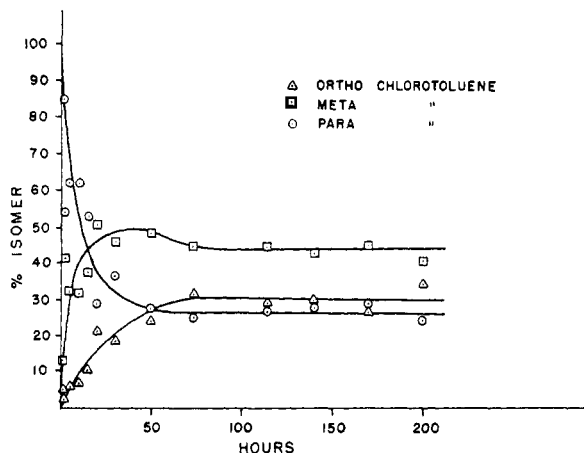


Fig. 4.—Isomerization of *p*-chlorotoluene with $\text{Al}_2\text{Cl}_6 + \text{H}_2\text{O}$ co-catalyst at 100° .

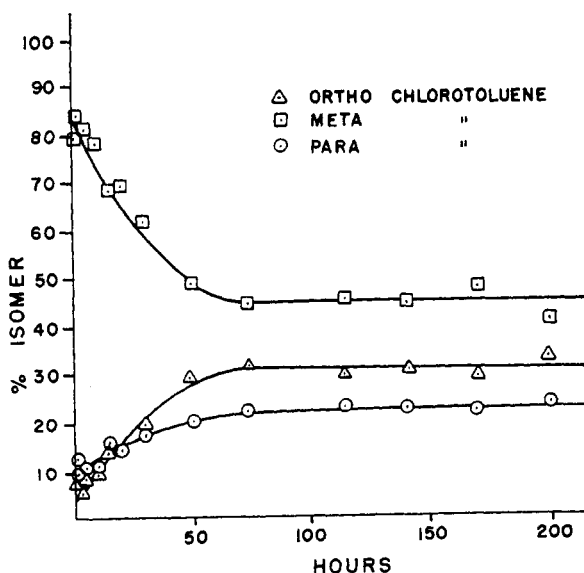


Fig. 5.—Isomerization of *m*-chlorotoluene with $\text{Al}_2\text{Cl}_6 + \text{H}_2\text{O}$ co-catalyst at 100° .

course of isomerization of *p*-, *m*-, and *o*-chlorotoluene. The data suggest the isomerizations to proceed by 1,2-shifts. Rearranged products contained as much as 20% chlorobenzene formed by disproportionation, which points to the methyl group as the migrating entity. The composition of the final equilibrium mixtures (mean equilibrium percent-

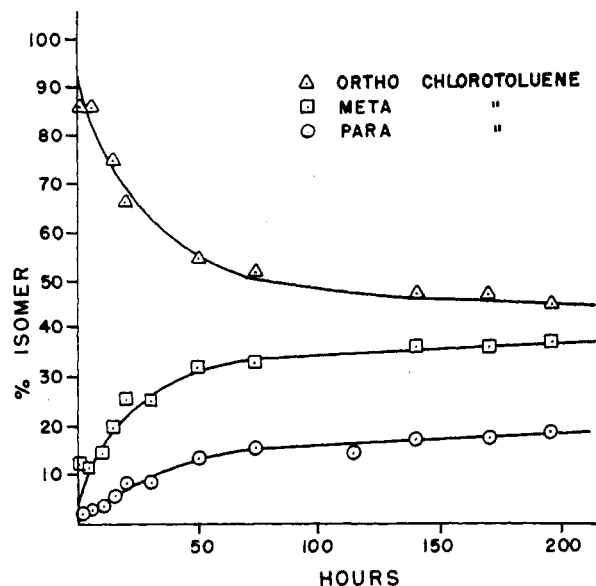


Fig. 6.—Isomerization of *o*-chlorotoluene with $\text{Al}_2\text{Cl}_6 + \text{H}_2\text{O}$ co-catalyst at 100° .

ages of *o*-, *m*-, and *p*-chlorotoluene) was 31% *o*-, 44% *m*-, and 25% *p*-chlorotoluene and agrees with those obtained by Norris and Turner.² As with *p*-fluorotoluene, conversion of *para* to *meta* in the isomerization of *p*-chlorotoluene is faster than *meta* to *ortho*, and the concentration of *meta* goes through a maximum after about fifty hours at 100° .

Figure 6 shows that the isomerization of *o*-chlorotoluene is distinctly slower than that of *m*- and *p*-chlorotoluene. After 200 hours at 100° equilibrium is not yet reached. Like fluorine, the chloro substituent deactivates the *ortho* position. Since the inductive effect decreases in the order $\text{F} > \text{Cl} > \text{Br}$, the deactivating effect is much smaller and is not sufficient to prevent isomerization, but is effective enough to decrease the rate of isomerization as compared to *m*- and *p*-chlorotoluene.

Bromotoluenes.—Bromotoluenes isomerize much faster than either fluoro- or chlorotoluenes. At 100° bromotoluenes reached equilibrium in fifteen minutes, the mixture of isomers consisting of 38% *ortho*, 44% *meta*, and 18% *para*. Prolonged exposure (> fifty hours) of *o*-bromotoluene to a temperature of 100° resulted in the formation of benzene, toluene, the xylenes, and tar, with no detectable amount of starting material left. The composition of the equilibrium mixture is not very sensitive to temperature, for at 30° *o*-, *m*-, and *p*-bromotoluene gave 37% *o*-, 45% *m*-, and 18% *p*-bromotoluene.

Figures 7, 8, and 9 show the course of isomerization of the bromotoluenes at 30° . It is seen that in the isomerization of *o*-bromotoluene (Fig. 9) the formation of the *para* isomer is faster than that of the *meta*, with the *para* going through a maximum. It must be concluded that the *meta* formed from the *para* isomer and from the *ortho*. The isomeriza-

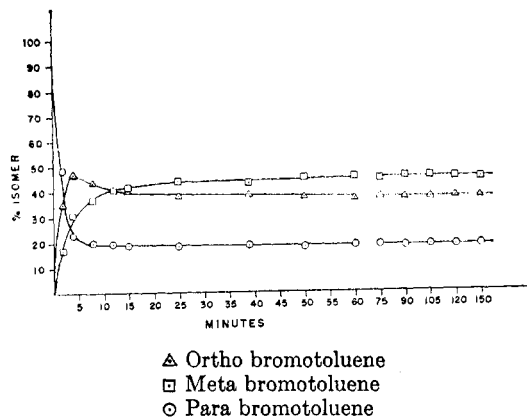


Fig. 7.—Isomerization of *p*-bromotoluene with $\text{Al}_2\text{Cl}_6 + \text{H}_2\text{O}$ co-catalyst at 30° .

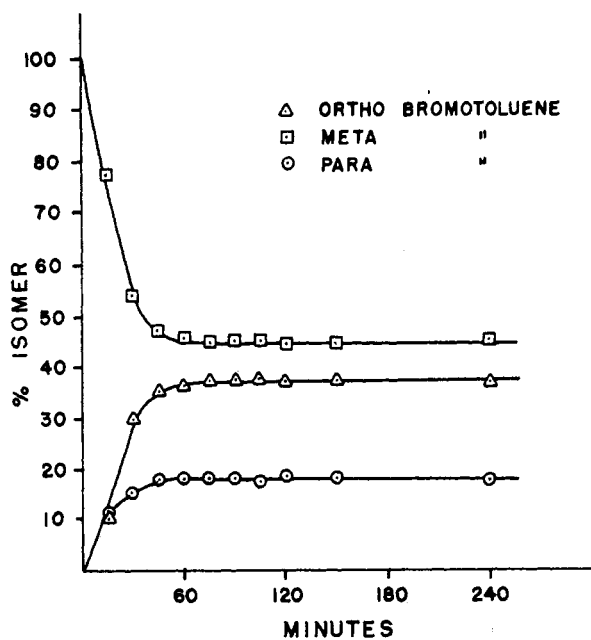


Fig. 8.—Isomerization of *m*-bromotoluene with $\text{Al}_2\text{Cl}_6 + \text{H}_2\text{O}$ co-catalyst at 30° .

tion of *o*-bromotoluene, therefore, does not proceed by a 1,2-shift only but also takes place according to the scheme $\text{ortho} \xrightarrow{\text{fast}} \text{para} \xrightarrow{\text{slow}} \text{meta}$. Similarly, in the isomerization of *p*-bromotoluene (Fig. 7) the concentration of the *ortho* isomer goes through a maximum, and equilibrium is reached by the path $\text{para} \xrightarrow{\text{fast}} \text{ortho} \xrightarrow{\text{slow}} \text{meta}$ as well as a 1,2-shift. *m*-Bromotoluene isomerizes by an apparent 1,2-shift as shown in Fig. 8. The present evidence, however, does not permit differentiation between the intramolecular (1,2-shift) and the intermolecular mechanism in the isomerization of *m*-bromotoluene. Data of Fig. 8 suggest that the *ortho* and *para* isomers are formed simultaneously, which is consistent with either mechanism. Since the conversion *ortho-para* in the isomerization of *o*-bromotoluene as well as *para-ortho* in the rearrangement of *p*-bromotoluene proceed intermolecularly, and

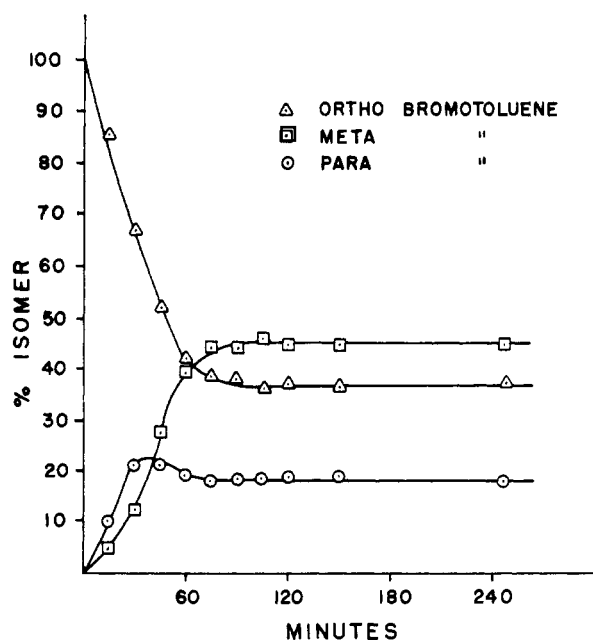


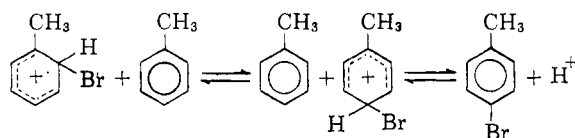
Fig. 9.—Isomerization of *o*-bromotoluene with $\text{Al}_2\text{Cl}_6 + \text{H}_2\text{O}$ co-catalyst at 30° .

since the methyl group is an activating substituent, the isomerization of *m*-bromotoluene might be expected to proceed intermolecularly also. If so, the reverse conversion, *para*-*meta* and *ortho*-*meta* would take place by the same mechanism.

A similar observation was also made by Crump and Gornowicz.³

Isomerization of bromotoluenes under the present conditions is always accompanied by disproportionation. Varying amounts of toluene and dibromotoluenes were formed in each experiment indicating that the bromo substituent moves and not the methyl group. Moreover, it has been known that bromo-substituted aromatic compounds are able to act as brominating agents under Friedel-Crafts conditions.⁷ Accordingly, isomerization of the bromotoluenes in excess benzene led to the formation of appreciable quantities of bromobenzene.

The initial appearance of the *para*-isomer in the isomerization of *o*-bromotoluene suggests that the bromine atom detaches itself from the protonated *o*-bromotoluene, in contrast to the 1,2-shift mechanism, where the migrating group never leaves the aromatic ring. It then rebrinates either excess bromotoluene (resulting in disproportionation) or toluene formed from the debromination. Bromination of toluene takes place according to an electrophilic substitution, where it is not necessary to postulate the presence of a free bromonium ion, because the reaction can take place prior to the bromine being entirely detached as a positive entity, toluene displacing the bromine in the polarized benzenonium ion type activated state



Electrophilic bromination of toluene gives predominantly *ortho*-*para* direction, a typical isomer distribution being: *ortho* 64.6%, *meta* 1.4%, *para* 34.0%.⁸ Transbromination thus easily can explain the fast initial build up of the *para* isomer. The formation of *m*-bromotoluene can take place either in a slower 1,2-shift mechanism from both the *ortho* and *para* isomers, or its build up can result from the fact that the intermolecular bromination-debromination effects preferentially the *ortho* and *para* positions (where it is reversible), but debromination does not effect to any substantial degree the *meta* positions (where protonation is not favored). Differentiation between these two possibilities was not attempted in the present work.

Considerations expressed for the mechanism of isomerization of *o*-bromotoluene must also be valid for the *para* isomer.

In the isomerization of *m*-bromotoluene the rates of formation of both the *ortho* and *para* isomer are of the same order of magnitude. Therefore again from present data no differentiation between an intramolecular (1,2-shift) or an intermolecular mechanism is possible.

Experimental

Material.—The halotoluenes used, with the exception of *m*-chlorotoluene, were Eastman grade. Their purity as determined by infrared analysis was not less than 99%. *m*-Chlorotoluene (The Dow Chemical Co.) was 85% pure containing 10% of the *para* and 5% of the *ortho* isomer. Al_2Cl_6 was reagent grade by Fisher Scientific Co.

Experimental Procedure.—A 0.045-mole sample of bromotoluene (5.0 g., 5.7 g., and 7.7 g. of fluoro-, chloro-, or bromotoluene, respectively) and 0.0045 mole of Al_2Cl_6 (1.2 g.) were weighed into a Pyrex combustion tube of appropriate size. A 0.1-ml. sample of water was added from a syringe. The tube was then sealed; its contents thoroughly mixed by shaking and heated in a thermostated oven with a temperature constancy of $\pm 1^\circ$. The reaction products were poured on ice and the tube rinsed with water and with ether. The organic phase was separated, the aqueous phase extracted with ether, and the extract combined with the organic layer. After drying with calcium chloride and distilling most of the ether, it was analyzed by infrared spectroscopy. With runs involving prolonged heating, the content of the tubes sometimes had a tendency to solidify completely. In such cases the solid was extracted with ether, the extract shaken with water, the phases separated, and proceeded as above. Experiments at room temperature were carried out in glass-stoppered Erlenmeyer flasks with magnetic stirring.

Infrared Analysis.—To analyze halotoluenes for their isomer ratio the characteristic out-of-plane hydrogen deformation absorption bands in the 12-15- μ region were used. Samples were weighed into carbon disulfide at two concentrations (10% and 2% wt./vol.) so that both weak and strong absorption bands could be measured accurately. The solutions were scanned on a double beam infrared spectrom-

(7) G. Baddeley and J. Plant, *J. Chem. Soc.*, 525 (1943).

(8) G. A. Olah, S. J. Kuhn, and S. H. Flood, data to be published.

TABLE I

Compound	—Analytical wave length (μ)—		
	<i>ortho</i>	<i>meta</i>	<i>para</i>
Fluorotoluene	13.3	12.88	12.28
Chlorotoluene	13.4	12.96	12.42
Bromotoluene	13.42	13.0	12.48

eter with sodium chloride optics. Analyses were carried out by the standard base line technique with suitable corrections made for the interference of any isomer on the others by use of an electronic computer. Table I lists the analytical wave lengths used.

When other interfering materials were present (*e.g.* chlorobenzene in the chlorotoluene samples), the base line was sketched into approximate the absorption of the interfering component. Accuracy of the isomer ratios is within ± 3 relative per cent, as checked with mixtures of known composition.

Acknowledgment.—We are indebted to Dr. D. S. Erley and Mr. B. H. Blake of the Chemical Physics Research Laboratory, The Dow Chemical Company, Midland, Michigan, for the infrared analyses.

Reactions of *t*-Butyl Peresters. VI. Pyrolysis of α -Acyloxy Derivatives of Aliphatic Sulfides

GEORGE SOSNOVSKY AND HUGH J. O'NEILL

Armour Research Foundation of Illinois Institute of Technology, Chicago 16, Illinois

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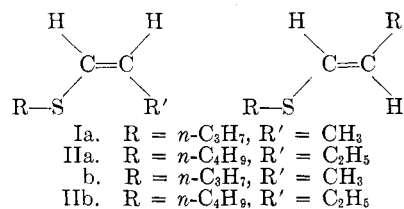
Benzoyloxy-substituted di-*n*-propyl sulfide and acetoxy- and benzoyloxy-substituted di-*n*-butyl sulfides were subjected to pyrolysis. The products in each case were two unsaturated sulfides. The products were analyzed by gas-liquid chromatography, infrared and ultraviolet spectroscopy, and n.m.r. It was concluded that the unsaturated sulfides are the *cis* and *trans* isomers of *n*-propyl 2-methylvinyl sulfide and *n*-butyl 2-ethylvinyl sulfide, respectively.

In preceding communications^{1,2} we reported a method of preparing α -acyloxy derivatives of straight-chain aliphatic and cyclic sulfides. The acyloxy derivatives were produced by the reaction of *t*-butyl peresters with sulfides in the presence of catalytic amounts of cuprous bromide. Similar studies with various sulfides were recently reported by Lawesson, Berglund, and Grönwall.^{3,4}

Until now all workers have assumed that the acyloxy group enters the position which is α to the sulfur atom. However, an alternative is possible. Although the α position may be favored, introduction of the acyloxy group into other positions along the methylene chain cannot be ruled out. If the acyloxy group does enter at other positions, the utility of our method would be seriously decreased. Because of this possibility we analyzed the composition of the products derived from the reaction of *t*-butyl peresters with two straight-chain aliphatic sulfides—namely, the di-*n*-propyl and the di-*n*-butyl sulfides. Since most acyloxy derivatives of aliphatic sulfides are sensitive to heat, they cannot be analyzed successfully by vapor phase chromatography. Therefore, we decided to investigate the composition of the products of pyrolysis of acyloxy derivatives and to make deductions on the basis of

these results about the nature of the initial acyloxy compounds.

If the acyloxy group entered exclusively into the α position, only one positional olefin would result on pyrolysis, with the possibility of both *cis* and *trans* isomers being formed. Di-*n*-propyl and di-*n*-butyl derivatives would then give the *cis* and *trans* isomers, Ia, Ib and IIa, IIb, respectively.



The second possibility is that the entering groups attack the β - or γ -carbon atom as well as the α -carbon and thereby produce a mixture of positional olefinic sulfides on subsequent pyrolysis. To solve this question the products of pyrolysis of the acyloxy derivatives of di-*n*-propyl and di-*n*-butyl sulfide were separated by gas-liquid chromatography and analyzed by infrared and ultraviolet spectroscopy and n.m.r.

The pyrolysis product of benzoyloxy-substituted di-*n*-propyl sulfide was resolved into two components by gas-liquid chromatography at 70°. The first (57% Ia) had a retention time of 5.9 minutes and the second (43% Ib) of 6.8 minutes. The pyrolysis product of the benzoyloxy derivative of di-*n*-butyl sulfide yielded two products by gas-liquid chromatography at 90°. The first (61% IIa) had a retention time of 12.8 minutes and the

(1) G. Sosnovsky, Abstracts of Papers presented at the 138th Meeting of the American Chemical Society, New York, September, 1960, p. 78P.

(2) G. Sosnovsky, *J. Org. Chem.*, **26**, 281 (1961); *Tetrahedron*, in press.

(3) S. O. Lawesson and C. Berglund, *Acta Chem. Scand.*, **15**, 36 (1961).

(4) S. O. Lawesson, C. Berglund, and S. Grönwall, *ibid.*, **15**, 249 (1961).