[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Isomer Distribution and Partial Rate Factors in the Gallium Bromide Catalyzed Alkylation of Benzene and Toluene. The Selectivity Factor, S_f, in Electrophilic Substitution[1,2]

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Isomer distributions have been determined for the gallium bromide catalyzed alkylation of toluene with methyl, ethyl, isopropyl and *t*-butyl bromides. The following values were obtained: methylation, 55.7% *ortho*, 9.9% *meta* and 34.4% *para*; ethylation, 38.3% *ortho*, 21.1% *meta* and 40.6% *para*; isopropylation, 26.2% *ortho*, 26.6% *meta* and 47.2% *para*; and *t*-butylation, 0.0% *ortho*, 32.1% *meta* and 67.9% *para*. These isomer distributions were combined with the relative rates of reaction with benzene and toluene in order to calculate the "activities" of the attacking species. The log of the ratio of the *para* to *meta* partial rate factors for toluene, p_f/m_f, is defined as the Selectivity Factor, S_f, and provides a convenient measure of the "activity" of the reaction. The available data indicate that a linear relationship exists between S_f and the log of the partial rate factors for substitution in the *para* and *meta* positions, and for substitution in the *ortho* positions where steric factors are small or absent. Analysis of the alkylation data indicates the order of "activities" to be methylation < ethylation < isopropylation > *t*-butylation. This order supports the conclusion that the nature of the transition state changes markedly with increasing branching of the alkyl halide. Values of the reaction constants, ρ, for these four aromatic alkylation reactions are calculated. The established linear relationship between S_f and the log of the *para* and *meta* partial rate factors for toluene provides the basis for calculation of partial rate factors and reaction constants in cases where these have not been directly determined. A method is presented whereby these quantities can be determined using only the observed isomer distribution.

The relatively high proportion of *meta* isomer obtained in Friedel–Crafts alkylation of toluene has been attributed to the high "activity" and low "selectivity" of the attacking species.[4] It has been demonstrated that a linear relationship exists between the log of the *para* partial rate factors (p_f), taken as a measure of the "activity" of the reaction, and the log of the *para* to *meta* partial rate factors (p_f/m_f), taken as a measure of the "selectivity" of the reaction.[5] The slope of the resulting straight line has been accurately fixed and, thus far, all electrophilic reactions of toluene for which accurate data are available have been shown to follow this proposed relationship within the experimental uncertainty.

While this proposed relationship has been highly successful in accounting for variations with different reactions in *para* to *meta* substitution. it may prove even more valuable in the study of the mechanisms of aromatic substitution. Since the activity of a reacting species can be expressed in quantitative terms the results can be used to explore the question as to the nature and structure of the intermediates and transition state involved in the reaction.

For example, in the alkylation of an aromatic by the alkyl halides, methyl, ethyl, isopropyl and *t*-butyl, the reaction might proceed by a carbonium ion mechanism,[6] by a displacement mechanism[7] or by a displacement mechanism in the case of the primary halides with a shift to a carbonium ion mechanism in the more highly branched halides.[8] If the reaction proceeded by an ionization mechanism, the order of selectivities would be expected to parallel the order of stabilities of the carbonium ions: methyl < ethyl < isopropyl < *t*-butyl.[4] In a displacement mechanism, the opposite order would be anticipated, with a much smaller difference in the selectivities of the different alkyl groups. A change in mechanism in the series would be expected to result in a change from one sequence to the other, such as methyl < ethyl > isopropyl > *t*-butyl or methyl < ethyl < isopropyl > *t*-butyl.

In order to apply this diagnostic tool to the Friedel–Crafts alkylation reaction, a study was made of the relative reactivities and isomer distributions in the gallium bromide catalyzed reactions of benzene and toluene with methyl, ethyl, isopropyl and *t*-butyl bromides.

Results

The absolute rate constants for the gallium bromide catalyzed reactions of methyl and ethyl bromides with benzene and toluene were reported previously.[9] The rate constants and relative rates with benzene and toluene are summarized in Table I.

TABLE I

RATE CONSTANTS FOR THE REACTIONS OF METHYL AND ETHYL BROMIDES WITH BENZENE AND TOLUENE UNDER THE INFLUENCE OF GALLIUM BROMIDE

Alkyl bromide	Temp., °C.	Rate constants[a] Benzene, Benzene, k_B	Toluene, Toluene, k_T	Ratio k_T/k_B
Methyl	15	0.137	0.86	6.25
Methyl	25	.300	1.71	5.70
Methyl	40	.785	4.60	5.85
Ethyl	15	4.52	11.5	2.55
Ethyl	25	9.55	23.5	2.47
Ethyl	40	25.5	61.2	2.39

[a] All rate constants are k_2 (l. mole^{-1} min.$^{-1}$) values.

Isomer distributions were determined for the reactions of methyl, ethyl, isopropyl and *t*-butyl bromides with toluene at 25°.

The reactions with methyl and ethyl bromides were performed under the same conditions as those used in the kinetic measurements. In the case of

(1) The Catalytic Halides. XX. Directive Effects in Aromatic Substitution. VIII.

(2) Based upon the thesis submitted by Charles R. Smoot in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Standard Oil Co. (Indiana) Fellow at Purdue University, 1952–1954.

(4) H. C. Brown and K. L. Nelson, THIS JOURNAL, **75**, 6292 (1953).

(5) H. C. Brown and C. W. McGary, *ibid.*, **77**, 2300 (1955).

(6) C. C. Price, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, Chapt. I.

(7) L. Schmerling, *Ind. Eng. Chem.*, **45**, 1462 (1953).

(8) (a) H. C. Brown, H. W. Pearsall, L. P. Eddy, W. J. Wallace, M. Grayson and K. L. Nelson, *ibid.*, **45**, 1462 (1953); (b) H. C. Brown and M. Grayson, THIS JOURNAL, **75**, 6285 (1953).

(9) C. R. Smoot and H. C. Brown, *ibid.*, **78**, 6249 (1956).

ethyl bromide, a doubling of the reaction time from 40 to 80 min. did not produce any measurable change in the isomer distribution. It was concluded that in this case isomerization of the reaction product was not a complicating factor. In the case of the isopropylation reaction, isomerization was affecting the isomer distribution even with a reaction time of but 1 min. Consequently, the reactions with isopropyl and *t*-butyl bromides were performed in a flow apparatus with reaction periods of the order of 0.005 sec. In order to test this procedure, pure *p*-*t*-butyltoluene was treated with gallium bromide and hydrogen bromide in the flow apparatus under conditions identical with those of the alkylation reactions. Only 3% isomerization was observed. In view of the far greater rate of isomerization of *t*-butyl groups,[10] it is believed that the isopropyl results must be free of this complication, while the yield of *meta* isomer in the *t*-butyl reaction may be too high by approximately 2%.

The results are summarized in Table II.

TABLE II

ISOMER DISTRIBUTIONS IN THE ALKYLATION OF TOLUENE WITH ALKYL BROMIDES UNDER THE INFLUENCE OF GALLIUM BROMIDE AT 25°

Product $RC_6H_4CH_3$	Alkyltoluene *Ortho*	*Meta*	*Para*	Ratio p_f/m_f
Methyl	55.7	9.9	34.4	6.94
Ethyl[a]	38.3	21.1	40.6	3.86
Ethyl[b]	38.4	21.0	40.6	3.85
Isopropyl[a]	28.4	33.4	38.2	2.29
Isopropyl[b,d]	26.2	26.6	47.2	3.55
Isopropyl[b,d]	29.6	25.2	45.2	3.60
t-Butyl[d]	0.0	32.1	67.9	4.23
p-*t*-Butyltoluene[c,d]	0.0	3.2	96.8	

[a] Longer reaction period. [b] Shorter reaction time. [c] Pure hydrocarbon treated under alkylation conditions. [d] Flow apparatus with 0.005 sec. reaction time.

Discussion

It has been pointed out that a linear relationship exists between the "activity" of a substituting reaction, as measured by log p_f, and its "selectivity," as measured by log p_f/m_f. It is convenient to define the Selectivity Factor, S_f, as equal to the log of the ratio of the *para* to *meta* partial rate factors for toluene.

In cases where the partial rate factors are not known, S_f can be calculated from the *meta* and *para* isomer distribution.

$$S_f = \log (2 \times \%\ para/\%\ meta) \qquad (1)$$

In Table III are listed the S_f values for the alkylation reactions along with the available data on electrophilic substitution reactions of toluene.

It is apparent that the numerical values for S_f for the four alkylation reactions vary in the order: methylation > ethylation > isopropylation < *t*-butylation. Since lower values of S_f correspond to lower selectivity, or greater "activity," it appears that the attacking species in the isopropylation reaction is the most active in the series. This result precludes an ionization mechanism for the reactions of methyl and ethyl bromide. As was pointed out, the methyl- and ethylcarbonium ions would be expected to be much more reactive than the isopropylcarbonium ion and in an ionization mechanism the S_f values would be expected to vary in the opposite manner to that observed.

(10) D. A. McCaulay and A. P. Lien, THIS JOURNAL, **74**, 6246 (1952).

TABLE III

SELECTIVITY FACTORS AND PARTIAL RATE FACTORS FOR A SERIES OF ELECTROPHILIC SUBSTITUTION REACTIONS OF TOLUENE

Reaction	Partial rate factors o_f	m_f	p_f	S_f[b]
Chlorination	600	5.0	870	2.241
Chloromethylation	117	4.37	430	1.993
Basicity, HF	145	3.6	414	2.061
Basicity, $HF-BF_3$	103	3.1	145	1.670
Nitration, 45°	42	2.5	58	1.366
Mercuration, 25°	4.98	2.25	32.9	1.165
Detrimethylsilylation	17.5	2.0	16.5	0.917
Sulfonylation	5.44	1.67	7.99	.680
Alkylation (Ga_2Br_6)				
Methylation[a]	9.51	1.70	11.8	.841
Ethylation[a]	2.84	1.56	6.02	.586
Isopropylation[a]	1.45	1.47	5.20	.548[c]
t-Butylation[a]	0.0	1.56	6.57	.624[c]

[a] Present study. Other data from summary in ref. 5. [b] Calculated from partial rate factors except where otherwise indicated. [c] Calculated from the isomer distribution (eq. 1).

On the other hand, the increase in S_f in going from isopropylation to *t*-butylation is in the direction to be expected for a carbonium ion reaction.

It appears, therefore, that the methylation and ethylation reactions probably involve a displacement reaction with the aromatic component contributing to the breaking of the carbon–bromine bond. On the other hand, *t*-butylation in all probability involves an ionization mechanism with the aromatic not involved in the breaking of the carbon–bromine bond. From the selectivity factor it is not possible to say whether the isopropylation reaction should be classed primarily as a displacement or as an ionization mechanism. However, the large difference in the rate of isopropylation and *t*-butylation (about 10^5) as compared to methylation and ethylation argues strongly for a predominantly ionization mechanism here also.

In summary, the reactions with methyl and ethyl bromide are believed to proceed by way of a nucleophilic attack by the aromatic on the polarized addition compound of the alkyl bromide with gallium bromide. In the transition state the carbon atom undergoing attack develops a partial positive charge and may therefore be said to have considerable carbonium ion character. With isopropyl and *t*-butyl bromides the carbonium ion character is considered to dominate the transition state with only minor nucleophilic participation by the aromatic component.

In terms of this picture, the Friedel–Crafts alkylation reaction with alkyl halides and Lewis acid proceeds *via* a transition state which has both ionization (SN1) and displacement (SN2) character. The relative contributions of each to the transition state will be dependent primarily upon the structure of the alkyl group, but also on the halide used, the catalyst, the aromatic component and the reaction medium.

It should be pointed out that this interpretation of the Friedel–Crafts reaction is closely related to

those proposed by Winstein and Swain for other substitution reactions of alkyl halides.[11,12] It differs primarily in that the Lewis acid catalyst is covalently bonded to the halide on which it is exerting a pull.

Calculation of Partial Rate Factors from the Selectivity Factor.—The alkylation data fit the linear relationship which has been shown to exist between log p_f and the quantity S_f (Fig. 1). A similar linear relationship exists between log m_f and S_f (Fig. 2). The scatter of points is well within the relatively large experimental uncertainties in the analyses for small quantities of the *meta* isomers.

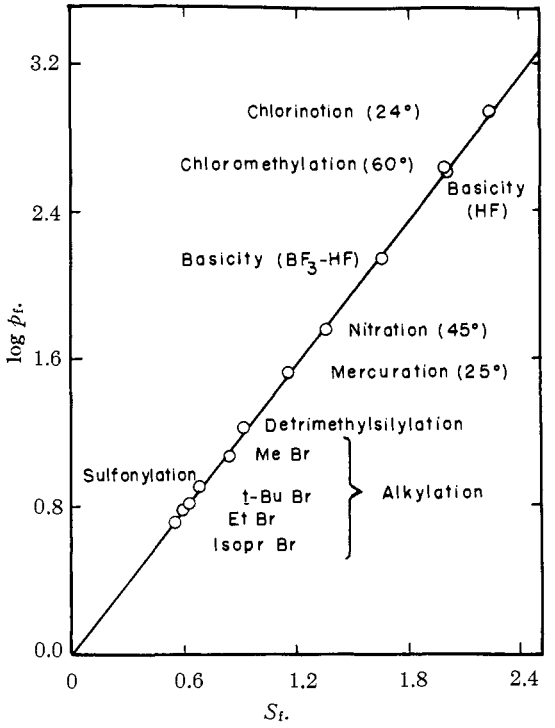


Fig. 1.—Relationship between log p_f and S_f, the Selectivity Factor.

A similar plot of log o_f *vs.* S_f is shown in Fig. 3. It is apparent that a considerable number of reactions, such as chlorination, basicity with hydrogen fluoride–boron trifluoride, nitration, detrimethylsilylation and methylation, follow the proposed relationship. However, a number of other reactions deviate from the line. These deviations are attributed to steric effects. The phenomenon will be discussed later in this paper.

From a consideration of Figs. 1 and 3, it is apparent that the slopes of the lines are quite similar. Presumably this arises from the similarity in resonance effects in the *ortho* and *para* positions. In the absence of steric effects, the following relationship holds.

$$\log p_f = 1.08 \log o_f \qquad (2)$$

It is apparent from this relationship that resonance effects are slightly greater in the *para* position than in the *ortho*. Equation 2 is merely a quantitative expression of a phenomenon which has been noted frequently.[12a]

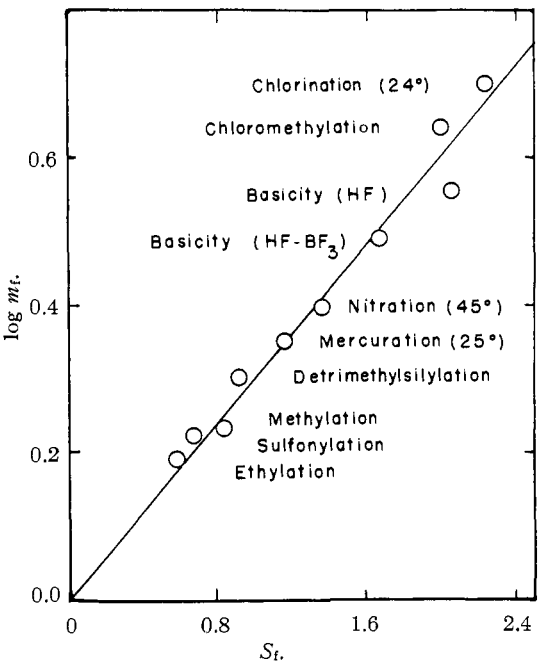


Fig. 2.—Relationship between log m_f and S_f, the Selectivity Factor.

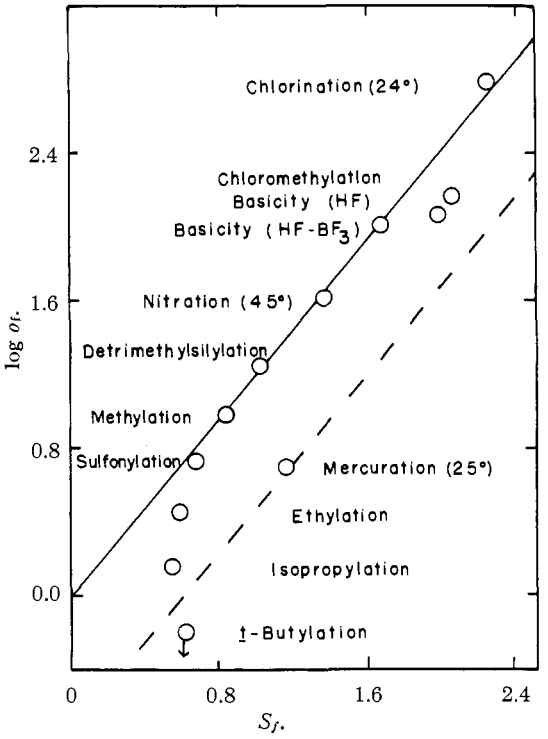


Fig. 3.—Relationship between log o_f and S_f, the Selectivity Factor.

(11) S. Winstein, E. Grunwald and H. W. Jones, THIS JOURNAL, **73**, 2700 (1951).

(12) C. G. Swain and W. P. Langsdorf, *ibid.*, **73**, 2813 (1951).

(12a) NOTE ADDED IN PROOF.—Partial rate factors have been reported recently for bromination of toluene by hypobromous acid in the presence of perchloric acid [P. B. D. de la Mare and J. T. Harvey, *J. Chem. Soc.*, 36, (1956)]. The reaction is believed to involve an attack by bromonium ion, Br^+. The values of p_f and m_f agree with the Selectivity Relationship. However, the value of o_f would place this point considerably above the solid line in Fig. 3. We hope to examine this exception to the treatment.

A considerable number of electrophilic aromatic substitution reactions have been studied and *all* such reactions, for which accurate data are available, have been shown to follow the log p_f–S_f relationship. *It is therefore proposed that this relationship is general and that all such reactions follow this relationship.* With this assumption it becomes possible to calculate the partial rate factors for any substitution reaction of toluene solely from the isomer distribution.

The following equations define the linear relationships shown in Figs. 1–3

$$\log p_f = 1.310S_f \quad (3)$$

$$\log m_f = 0.309S_f \quad (4)$$

$$\log o_f = 1.215S_f \quad (5)$$

Equation 5 should be applied only to reactions which are not susceptible to steric effects, *i.e.*, to reactions which do not deviate from the relationship. A more general expression for the *ortho* partial rate factor, applicable to all reactions, may be derived.[13]

$$\log o_f = 1.310S_f + \log \frac{\%\ ortho}{2 \times \%\ para} \quad (6)$$

Since S_f is equal to log $[(2 \times \%\ para)/(\%\ meta)]$, all of the partial rate factors are defined in terms of the isomer distribution in the reaction of toluene.[14]

In the methylation and ethylation of toluene it was possible to obtain accurate values both for the rates of the reaction and the isomer distributions. In these reactions the S_f values were calculated from the partial rate factors (Table III). In the case of isopropylation and *t*-butylation the reactions were too fast to obtain accurate rate data. Consequently, the S_f values and partial rate factors were calculated from the isomer distributions with the aid of equations 3, 4 and 6.

Steric Effects in Substitution Reactions.—In the plot of log o_f *vs.* S_f (Fig. 3), it is apparent that certain reactions fail to obey the relationship. The observation that methylation obeys the relationship while ethylation, isopropylation and *t*-butylation show increasing deviation from the line suggests that steric effects may be responsible for the deviation. Moreover, the deviation from the line for chloromethylation and ethylation are quite close and plausible arguments exist that the steric requirements of the two intermediates involved should be quite similar.

Holleman[15] pointed out that the size of the attacking group was quite important in determining the extent of *ortho* substitution. For example, in the chlorination, nitration, bromination and sulfonation of chlorobenzene, the percentage *ortho* isomer decreased in the order 45, 30.1, 12.8 and 0%, respectively. He pointed out that these data could not be explained in terms of polar factors and must be attributed to steric factors. Similarly, it was observed in the nitration of toluene, ethyl-, isopropyl- and *t*-butylbenzene that the *ortho*/*para* ratio decreased from 1.57 in toluene to 0.217 in *t*-butylbenzene, an effect attributed to the increasing steric requirements of the alkyl substituent.[16]

It appears reasonable, therefore, that the deviations from the log o_f–S_f line be attributed to steric strains in the transition state between the attacking species and the methyl group of toluene. On this basis, the extent of the deviation from the line should provide a measure of these steric strains in the transition state.

The mathematical relationship for any reaction is therefore

$$\log o_f = 1.215\ S_f - \frac{\Delta E_{act}}{2.3RT} \quad (7)$$

where ΔE_{act} is the difference in the energies of activation at the *ortho* and *para* positions due to steric effects. The dotted line in Fig. 3 represents a displacement resulting from 1 kcal. of steric strain.[17]

Of the alkylation reactions studied in the present paper, only methylation appears to be free of any appreciable steric effect. The points for ethylation and isopropylation fall below the line and represent 400 and 740 calories of strain, respectively. With *t*-butylation no detectable amount (<1%) of the *ortho* isomer was obtained. This suggests that a much larger steric strain must be involved (2 kcal. or greater).

These results are quite similar to those observed in the reactions of 2-alkylpyridines with methyl iodide.[18] In this system the observed increases in the energies of activation, in going from 2-methyl- to 2-ethyl- to 2-isopropyl- to 2-*t*-butylpyridine, are 0.24, 0 86 and 3.5 kcal., respectively.

Reaction Constants for the Alkylation Reactions.—An extension of the Hammett $\rho\sigma$ relationship to electrophilic substitution recently has been proposed.[19] In this extension it was assumed that aromatic electrophilic substitution obeys a linear free energy expression of the Hammett type

$$\log k_f = \rho\sigma^+ \quad (8)$$

where k_f is the partial rate factor, ρ is the reaction constant and σ^+ is a substituent constant applicable to electrophilic aromatic substitution. Utilizing the σ^+ values for *m*- and *p*-methyl,[19] it is possible to calculate ρ values for the alkylation reactions. These are summarized in Table IV.

It should be possible to utilize these ρ values with considerable accuracy in predicting the rates and isomer distribution in the alkylation of alkyl aromatics. In applying the method to other monosubstituted organics which are capable of coördinating

(13) From the definition of partial rate factors, p_f = % *para* × relative rate × 6/100, and o_f = % *ortho* × relative rate × 3/100. It is now possible to obtain o_f as a function of p_f and the isomer distribution.

$$o_f = 1/2\ (\%\ ortho/\%\ para)\ p_f$$

$$\log o_f = \log\ [\%\ ortho/(2 \times \%\ para)] + \log p_f$$

Substituting for log p_f (eq. 3), we obtain eq. 6.

(14) In a similar manner, the relative rate of reaction of benzene and toluene may be defined in terms of the isomer distribution: log $(k_T/k_B) = 1.310\ S_f - \log\ (6 \times \%\ para)/100)$.

(15) A. F. Holleman, *Chem. Revs.*, **1**, 218 (1926).

(16) H. C. Brown and W. H. Bonner, THIS JOURNAL, **76**, 605 (1954).

(17) This expression assumes that the entropies of activation at the *ortho* and *para* positions are identical. While this will not be true (L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapt. IV), there is increasing evidence that in the reactions of sterically hindered molecules the effects on the energy of activation are considerably greater than the effects on the entropy term (*e.g.*, ref. 18). Consequently, the errors introduced by the neglect of the entropy factor should not be large.

(18) H. C. Brown and A. Cahn, THIS JOURNAL, **77**, 1715 (1955).

(19) C. W. McGary, Y. Okamoto and H. C. Brown, *ibid.*, **77**, 3037 (1955).

TABLE IV

REACTION CONSTANTS FOR THE GALLIUM BROMIDE CATALYZED ALKYLATION REACTIONS

Reaction	Reaction constants ρ_m	ρ_p	ρ
Methylation	−3.43	−3.61	−3.52 ± 0.09
Ethylation	−2.88	−2.62	−2.75 ± .13
Isopropylation	−2.49	−2.41	−2.45 ± .04
t-Butylation	−2.87	−2.75	−2.81 ± .06

with gallium bromide, caution should be observed. Such coördination will probably alter the activity of the catalyst and may change the reaction mechanism. It is not possible at this time to estimate the effect of such changes on the isomer distribution.

Experimental Part

Materials.—The purification and physical properties of all materials were reported in previous papers of this series.[9,20]

Isomer Distributions.—A 0.042 *M* solution of gallium bromide in toluene was prepared. To 25 ml. of this catalyst solution was added 0.0195 mole of methyl bromide in 25 ml. of toluene. The reaction was continued for 13 hours at 25° and by titration for hydrogen bromide it was ascertained that 58% reaction had occurred. In similar experiments 25 ml. of the catalyst solution was added to 25 ml. of toluene containing 0.0202 mole of ethyl bromide and reaction periods of 40 to 80 minutes were used. For the 40-minute reaction period, 55% reaction was observed, and in the 80-minute reaction period, 75–80% reaction was obtained. Toluene was treated with isopropyl bromide in a similar manner using 0.0205 mole of the halide. Complete reaction was obtained upon mixing. The reactions of isopropyl and *t*-butyl bromides in a flow apparatus were described previously.[9]

A pure sample of *p*-*t*-butyltoluene was passed through the flow reactor under the same conditions as the alkylations except that hydrogen bromide was added. It was analyzed in a similar manner as in other experiments.

All of the reactions were performed in toluene solution to correspond to the conditions used in the kinetic studies. The dried products were partially rectified in an efficient column with a small hold-up. Most of the excess toluene was removed. When the pot temperature began to rise, the rectification was discontinued. The column was washed down with toluene and the material remaining in the distillation flask was then analyzed by infrared analyses.[21] Since a considerable quantity of toluene remained in the sample, a "blanking out" technique was used for the analyses. Thus, as a double beam instrument was being used, toluene was added to the reference cell in order to compensate for that present in the sample. In this manner 70 to 90% of the absorption due to toluene in the sample was "blanked out."

The results of the infrared analyses were summarized in Table II.

Acknowledgment.—It is a pleasure to acknowledge our appreciation to the Bureau of Standards for providing the samples of pure hydrocarbons used as infrared standards and to Mr. P. Kinsey for his coöperation in determining the infrared spectra for this study.

(20) C. R. Smoot and H. C. Brown, THIS JOURNAL, **78**, 6245 (1956).

(21) For further details concerning the infrared analyses of alkyltoluenes, consult the Ph.D. thesis of C. R. Smoot, Purdue University Library.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

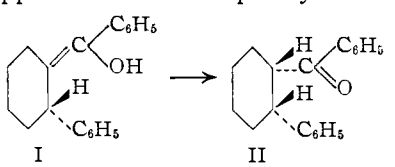
The Stereochemistry of the Ketonization Reaction of Enols. III[1,2]

BY HOWARD E. ZIMMERMAN AND HARRY J. GIALLOMBARDO

RECEIVED JUNE 5, 1956

A study has been made of the stereochemistry of decarboxylation of 4-phenylcyclohexane-1,1-dicarboxylic acid. Maximum specificity was observed in collidine where an average of 61% *cis*-4-phenylcyclohexanecarboxylic acid resulted. This is contrasted with 11% *cis*-isomer required for thermodynamic control.

Previously[3] it has been demonstrated that ketonization of exocyclic cyclohexane enols proceeds by prototropic attack from the less hindered side of the enolic double bond to yield the less stable stereoisomeric product. For example, ketonization of the enol I appeared to be completely stereospecific,



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leading to *cis*-1-phenyl-2-benzoylcyclohexane (II). In addition it was suggested[3] that decarboxylation of substituted cyclohexane-1,1-dicarboxylic acids involves such an enolic intermediate which ketonizes to yield the less stable isomer, in which the remaining carboxyl is axial. One case cited was the decarboxylation of 2-methylcyclohexane-1,1-dicarboxylic acid which had been reported by Perkin[4] and much more recently by Golmov[5] to yield *cis*-2-methylcyclohexanecarboxylic acid. In disagreement with this picture was the report by Perkin[6] that the decarboxylation of 2-phenylcyclohexane-1,1-dicarboxylic acid yielded 2-phenylcyclohexanecarboxylic acid of m.p. 104°, the isomer now known[7] to be *trans*.

It seemed clear that a quantitative study of decarboxylation of cyclohexane-1,1-dicarboxylic acids would not only clarify the situation but also would provide further examples of ketonization. To this end a study of the decarboxylation of the 2-phenyl and the 4-phenylcyclohexane-1,1-dicarboxylic acids was initiated. The present paper deals with the latter system.

The investigation of the 4-phenylcyclohexane-1,1-dicarboxylic acid (III) required first its synthesis,

(1) Paper II of this series: H. E. Zimmerman, THIS JOURNAL, **78**, 1168 (1956).

(2) Abstracted from the Master's thesis of Harry J. Giallombardo, presented to Northwestern University.

(3) H. E. Zimmerman, *J. Org. Chem.*, **20**, 549 (1955).

(4) W. Goodwin and W. Perkin, *J. Chem. Soc.*, 119 (1895).

(5) V. Golmov, *J. Gen. Chem.*, **23**, 1221 (1953).

(6) F. Kipping and W. Perkin, *J. Chem. Soc.*, 304 (1890).

(7) C. Gutsche, THIS JOURNAL, **70**, 4150 (1948).