was determined by weighing the product after chromatography.

The yields of isolated products were essentially the same in all experiments: benzpinacol, 24%; tertiary alcohol, 48–60%; and hydrocarbon, 24%.

Procedures.—The general photochemical procedure was described earlier.[2] In the latter part of the work the photoreduction of benzophenone by isopropyl alcohol was used for actinometric measurements. It was found that the rates of reduction were reproducible and easily measured by spectrophotometric analysis for residual benzophenone. In fact, the best evidence to support the assignment of the quantum yield one to the photoreduction is found in the comparison of the quantum yields in the reduction of toluene based on uranyl oxalate actinometry with those based on the isopropyl alcohol reaction (Table I). The values determined by the isopropyl alcohol reduction are slightly higher than those measured by the oxalate method. Obviously we could assign a value of more than one to the alcohol reaction and bring the values into agreement; however, we do not have sufficient confidence in the precision of the oxalate procedure to justify such a correction.

Analyses.—Pinacols were determined by titration with lead tetraacetate[2] except in the work with cumene. The method was not applicable in that case because it was found that the tertiary alcohol produced in the reaction was also cleaved by the reagent. In the cumene work the yield of benzpinacol was determined gravimetrically after isolation by a procedure essentially the same as that described for the batch reactions. Residual ketone concentrations were determined spectrophotometrically. Readings of the absorbance of the analytical solutions (prepared by dilution of aliquots) were taken at several wave lengths and compared directly with samples of the original solutions which had not been irradiated.

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[CONTRIBUTION FROM THE POLYMER RESEARCH LABORATORY, THE DOW CHEMICAL COMPANY, MIDLAND, MICHIGAN]

Kinetics of Three-Compound Equilibrations. V. Concurrent Alkylation and Isomerization

BY ROBERT H. ALLEN AND LARRY D. YATS

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A study has been made of the monoalkyltoluene isomer distributions obtained by the Friedel–Crafts methylation, ethylation and isopropylation of toluene using a variety of catalysts and alkyl derivatives. All of the isopropyltoluene isomer distributions could have been obtained by alkylation to produce a mixture containing 42% *o*-, 21.5% *m*- and 36.5% *p*-isopropyltoluene and isomerization of this mixture. With the possible exception of ethylation with ethylene, all the ethyltoluene isomer distributions could have been obtained by alkylation to produce an initial mixture containing 48% *o*-, 18% *m*- and 34 % *p*-ethyltoluene and isomerization of this mixture. Ethylation with ethylene appears to produce an initial isomer distribution somewhat lower in *p*-ethyltoluene than the above. Methylation of toluene with methyl chloride, methyl bromide or methyl alcohol produces a mixture containing 60% *o*-, 14% *m*- and 26% *p*-xylene. These results indicate that in the methylation, ethylation and isopropylation of toluene, the particular catalyst and derivative used influences only the extent of isomerization that accompanies the alkylation. For the above series of initial isomer distributions, the ratio of *p*-substitution to *m*-substitution is constant within experimental error so that methylation, ethylation and isopropylation have the same positional selectivity. Since equal selectivity implies equal reactivity, the enormous increase in absolute rates in the above series probably result from the quantity of activated alkyl derivative involved in each reaction and not the reactivity of the activated alkyl derivative involved in each reaction.

Introduction

Only rather recently has the Friedel–Crafts alkylation of alkylaromatics come to be considered a typical electrophilic aromatic substitution. Previously the alkylation reaction was believed to produce atypical isomer distributions. There were three major reasons for this belief.

1. Before the use of infrared and Raman spectroscopy, the methods used for the analysis of alkylaromatic isomers were tedious, unreliable or both. Thus, the propylation of toluene was frequently reported to yield *p*-cymene uncontaminated by *o*- or *m*-cymene.[1] As late as 1954 this claim was made.[2]

2. Several alkylations were reported in which the proportion of *meta* substitution obtained was anomalously large for an electrophilic reaction.[3] Recently, Brown has shown that the substantial proportion of *m*-isopropyltoluene obtained by the propylation of toluene is due to the low selectivity of the reaction for the activated *ortho* and *para* positions of toluene.[4]

3. An isomer distribution obtained by alkylation can change due to positional isomerization under the Friedel–Crafts reaction conditions. Indeed, since the intermediate σ-complex postulated for alkylation is identical to that postulated for isomerization,[5] it is questionable that alkylation exclusive of isomerization is possible.

For some time the alkylation of aromatics was believed to involve formation of the alkyl carbonium ion, which then attacked the aromatic ring.[3a] More recently, evidence has been accumulating which indicates that many alkylations involve displacement by the aromatic ring on the α-carbon of the alkyl derivative catalyst complex.[6] In contrast to the carbonium ion mechanism, the displacement mechanism implies the possibility

(1) (a) J. H. Simons and H. Hart, *J. Am. Chem. Soc.*, **66**, 1309 (1944); (b) J. H. Simons and H. Hart, *ibid.*, **69**, 979 (1947); (c) T. M. Berry and E. E. Reid, *ibid.*, **49**, 3142 (1927); (d) B. W. Malishev, *ibid.*, **57**, 883 (1935).

(2) N. M. Cullinane and D. M. Leyson, *J. Chem. Soc.*, 2942 (1954).

(3) (a) C. C. Price, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946; C. C. Price, *Chem. Revs.*, **29**, 37 (1941); (b) F. E. Condon, *J. Am. Chem. Soc.*, **71**, 3544 (1949).

(4) H. C. Brown and K. L. Nelson, *ibid.*, **75**, 6292 (1953); L. M Stock and H. C. Brown, *ibid.*, **81**, 3323 (1959).

(5) K. L. Nelson and H. C. Brown in "The Chemistry of Petroleum Hydrocarbons," Vol. III, edited by B. T. Brooks, S. S. Kurtz, C. E. Boord and L. Schmerling, Reinhold Publ. Corp., New York, N. Y., 1955.

(6) (a) H. C. Brown and M. Grayson, *J. Am. Chem. Soc.*, **75**, 6285 (1953); (b) L. Schmerling, *Ind. Eng. Chem.*, **45**, 1447 (1953); (c) H. C. Brown and H. Jungk, *J. Am. Chem. Soc.*, **77**, 5584 (1955); (d) H. Jungk, C. R. Smoot and H. C. Brown, *ibid.*, **78**, 2185 (1956); (e) C. R. Smoot and H. C. Brown, *ibid.*, **78**, 6249 (1956).

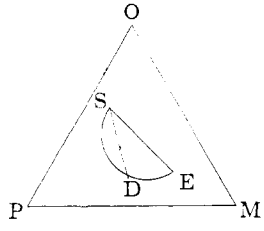
that the group being displaced can affect the selectivity of the alkylation for the various positions of the toluene ring. In order to investigate the possibility of controlling the isomer distribution obtained in a given alkylation by the choice of alkyl derivative and catalyst, we have studied the monoalkyltoluene isomer distributions produced by methylation, ethylation and isopropylation of toluene using a variety of alkyl derivatives and catalysts. The results of previously reported isomerization studies on these alkyltoluenes have been used to determine if the variety of isomer distributions obtained can be due to isomerization.[7]

Theoretical

Alkylation and Isomerization.—The relative rate constant sets obtained by the aluminum chloride–hydrogen chloride catalyzed interconversion in toluene of the three xylene isomers,[7b] of the three ethyltoluene isomers[7c] and of the three isopropyltoluene isomers[7a] have been reported. Each alkyltoluene rate constant set makes possible calculation of the isomer distributions that are produced by isomerization of any starting distribution of isomers. If the starting isomer distribution S is obtained by the alkylation of toluene under conditions similar to those used in the appropriate isomerization study, then by means of the equations

$$O(t) = O^* + Ae^{-\alpha t} + Be^{-\beta t}$$
$$P(t) = P^* + Ce^{-\alpha t} + De^{-\beta t} \qquad (1)$$

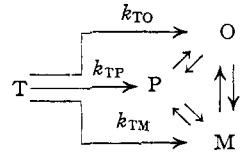
where $O(t)$ is the concentration of *ortho* isomer at time t, O^* is the equilibrium concentration of *ortho* isomer, A and B are determined by the starting isomer distribution, and α and β from the rate constant set, the locus of the line SDE on the triangular isomer composition diagram may be calculated. This line represents the isomer distributions that will be obtained by alkylation followed by isomerization. Since any mixture of distribution S and distribution D must result in an isomer distribution on the line SD, then the area SDE includes all possible isomer distributions that can be obtained from isomer distribution S by isomerization.[8] Thus, any isomer distribution outside the area SDE that is produced by alkylation conditions that involve the same isomerization relative rate constants must indicate a different alkylation selectivity than that which produced isomer distribution S.



(7) (a) R. H. Allen, T. Alfrey, Jr., and L. D. Yats, *J. Am. Chem. Soc.*, **81**, 42 (1959); (b) R. H. Allen and L. D. Yats, *ibid.*, **81**, 5289 (1959); (c) R. H. Allen, L. D. Yats and D. S. Erley, *ibid.*, **82**, 4853 (1960).

(8) This and the following discussion do not include the high *meta* compositions that are obtained when large quantities of strong Friedel–Crafts catalysts are used. See D. A. McCaulay and A. P. Lien, *Tetrahedron*, **5**, 186 (1959).

Concurrent Alkylation and Isomerization.—If an alkyltoluene is concurrently forming and isomerizing according to the pattern



then the isomer mole fractions formed in the interval dt' would be $O_0 = k_{TO}/k_T$, $P_0 = k_{TP}/k_T$, $M_0 = k_{TM}/k_T$, where $k_T = k_{TO} + k_{TP} + k_{TM}$. If this substitution distribution concurrently isomerized till time t, and the isomerization rate steps were first order, then according to equations

$$O(t) = O^* + Ae^{-\alpha(t-t')} + Be^{-\beta(t-t')}$$
$$P(t) = P^* + Ce^{-\alpha(t-t')} + De^{-\alpha(t-t')}$$

where $O(t)$ is the mole fraction of *ortho* isomer at time t, O^* is the equilibrium mole fraction of *ortho* isomer, A and B are determined by the substitution distribution of isomer mole fractions, and α and β from the isomerization rate constants. If G is the rate of formation of all three isomers, then the concentration of each of the three isomers resulting from concurrent formation and isomerization can be obtained from

$$O(t) = \int G[O^* + Ae^{-\alpha(t-t')} + Be^{-\beta(t-t')}]dt'$$
$$P(t) = \int G[P^* + Ce^{-\alpha(t-t')} + De^{-\beta(t-t')}]dt'$$

If G is a constant, then integration of the above equations between $t' = 0$ and $t' = t$ gives

$$O(t) = G\{O^*t + A[1 - e^{-\alpha t}]/\alpha + B[1 - e^{-\beta t}]/\beta\}$$
$$P(t) = G\{P^*t + C[1 - e^{-\alpha t}]/\alpha + D[1 - e^{-\beta t}]/\beta\}$$

dividing these equations by Gt yields

$$O(t) = O^* + A[1 - e^{-\alpha t}]/\alpha t + B[1 - e^{-\beta t}]/\beta t$$
$$P(t) = P^* + C[1 - e^{-\alpha t}]/\alpha t + D[1 - e^{-\beta t}]/\beta t \qquad (2)$$

These last equations contain only those terms present in equations 1 for isomerization by first-order rate steps and are independent of the absolute rate of alkylation. Thus using the same set of terms permits calculation of the isomer distributions expected from alkylation followed by isomerization and concurrent alkylation and isomerization. Although experimental alkylation conditions generally differ significantly from those assumed for derivation of the above equations, the equations do appear to correlate the data reported in the present work. These correlations imply that within experimental error the trajectories of isomer compositions are insensitive to the catalyst used,[8] the temperature variation involved and the absolute relation between the alkylation rate and the isomerization rate.

Results

Methylation of Toluene.—In Table I are summarized the methylations carried out in the present work.

The *m*- to *p*-xylene isomer ratio was determined by differential infrared spectroscopy, the ratio of *o*-xylene to the other xylene isomers was determined by vapor phase chromatography.[7b] The isomer distributions are plotted as the closed circles on Fig. 1.

TABLE I

ISOMER DISTRIBUTIONS IN THE METHYLATION OF TOLUENE

Methyl derivative	Catalyst	Catalyst, mole %	Temp., °C.	Rx. time, min.	Conversion, mole %	Isomer distribution, % p-	m-	o-
MeBr	$AlBr_3$	3	15	10	1.8	26	14	60
MeCl	$AlCl_3$	3	15	15	6.0	26	15	59
MeOH	$BF_3 \cdot P_2O_5$	3	60	300	2.0	26	14	60
MeI	$AlBr_3$	3	15	10	4.4	34	11	56
MeI	$AlBr_3$	1.5	20	5	0.7	34	11	56

TABLE II

ISOMER DISTRIBUTION IN THE METHYLATION OF TOLUENE

Methyl halide	Catalyst	Catalyst, mole %	Av. temp., °C.	Rx. time, min.	Isomer distribution, % p-	m-	o-
MeI	$AlBr_3$	25	0.5	11	40	11	49
MeI	$AlBr_3$	25	1	19	40	13	48
MeBr	$AlBr_3$	25	−1.5	1	28	17	55
MeBr	$AlBr_3$	25	5	1	30	18	53
MeBr	$AlBr_3$	25	29	1	29	21	50

In Table II are summarized methylations reported by Brown and Jungk.[6c]

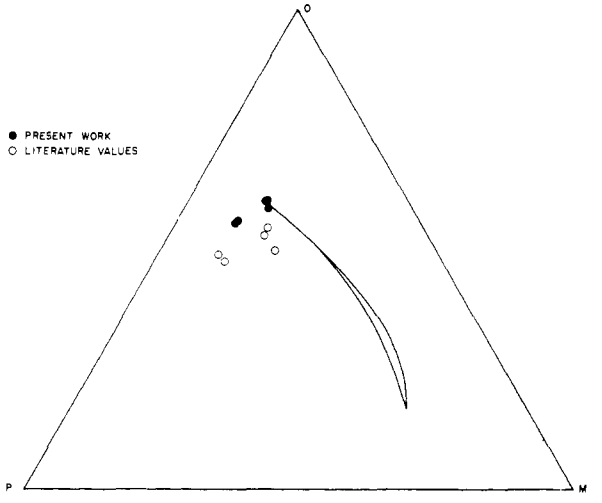


Fig. 1.—Xylene isomer distributions obtained by methylation of toluene.

The above isomer distributions were determined by differential infrared spectroscopy and are plotted as the open circles in Fig. 1.

If 26% *p*-, 14% *m*- and 60% *o*-xylene is taken as the starting distribution, and the xylene isomerization results used,[7b] equations 1 become

$$O(t) = 17.1 + 37.0e^{-4.1\tau} + 5.9e^{-8.6\tau}$$
$$P(t) = 21.5 - 19.3e^{-4.1\tau} + 23.8e^{-8.6\tau}$$

for the isomer distributions produced by alkylation and subsequent isomerization. Use of the same constants in equations 2 permit calculation of the isomer distributions expected from concurrent methylation at a constant rate and isomerization by first-order rate steps. The two equation sets are plotted on Fig. 1.[9] The curves differ by less than 2 mole %.

The difference in the isomer distributions reported by Brown and Jungk and those reported here are undoubtedly due to the different analytical method used for the determination of the *o*-xylene composition.

Whether a C–O bond, a C–Br bond or a C–Cl bond is ruptured does not affect the selectivity of the methylation of toluene under the reaction conditions reported. These data offer no support for a displacement mechanism. In contrast, the methyl iodide reaction proceeds comparatively slowly[7b] and with greater selectivity. This one alkylation system offers definite evidence of a displacement mechanism.

Ethylation of Toluene.—In Table III are summarized the ethylations carried out in the present work. The isomer distributions, as determined by differential infrared spectroscopy are plotted as the points on Fig. 2.

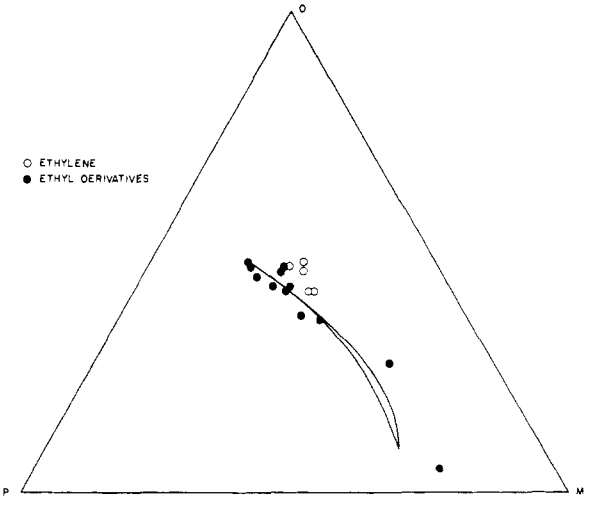


Fig. 2.—Ethyltoluene isomer distributions obtained by ethylation of toluene.

If 34% *p*-, 18% *m*- and 48% *o*-ethyltoluene is taken as the starting distribution and the ethyltoluene isomerization results used,[7c] equations 1 become

$$O(t) = 9.0 + 36.3e^{-44.2\tau} + 2.7e^{-88.6\tau}$$
$$P(t) = 26.2 - 18.7e^{-44.2\tau} + 26.5e^{-88.6\tau}$$

for the isomer distributions produced by ethylation and subsequent isomerization. Use of the

(9) Whenever the two equation sets have the same constants and are plotted on the same figure, equations 1 produce the more curved trajectory, equations 2 the less curved trajectory.

TABLE III
ISOMER DISTRIBUTIONS IN THE ETHYLATION OF TOLUENE

Ethyl derivative[a]	Catalyst	Catalyst, mole %	Temp., °C.	Rx. time, min.	Isomer distribution, % p-	m-	o-[b]
EtBr	$GaBr_3$	0.04	25	20	..	..	..[c]
				40	34	18	48[c]
				60	34	19	47[c]
EtBr	$GaBr_3$	.04	25	40	28	25	47
EtBr	$GaBr_3$	.04	25	40	34	21	45
EtBr	$AlBr_3$	.03	0	10	33	25	43
EtBr	$AlBr_3$	.03	15	10	27	37	36
EtBr	$AlBr_3$	.03	30	195	21	74	5
EtCl	$AlCl_3$	.03	20	14	30	28	42
EtCl	$AlCl_3$	.03	15	7	29	28	43
EtI	$AlBr_3$	.03	0	7	30	33	37
EtI	$AlBr_3$	.03	15	21	19	54	27
EtOH	$BF_3{\cdot}P_2O_5$	.03	90	350	30	25	46
C_2H_4	$AlCl_3$	.03	15	20	24	28	48
C_2H_4	$AlCl_3$	.03	−78	60	27	26	47
C_2H_4	$AlBr_3$	.017	15	20	25	29	46
C_2H_4	HF	2.0	0	40	25	33	42
C_2H_4	HF	1.6	0	45	26	32	42

[a] The molar ratio of toluene to ethyl derivative was from 10/1 to 20/1. [b] A few reaction mixtures were analyzed for *o*-ethyltoluene by vapor phase chromatography. The v.p.c. analyses for % *ortho* were 1 to 3% higher than the infrared analyses. [c] One reaction mixture sampled at three different times. After 20 minutes there was no evidence for ethyltoluene formation.

same constants in equations 2 permit calculation of the isomer distributions expected from concurrent ethylation at a constant rate and isomerization by first-order rate steps. The two equation sets are plotted in Fig. 2.[9] The two curves differ by less than 2 mole %.

Table III and Fig. 2 lead to four principal conclusions. First, the precision of the isomer analyses is rather poor. Analysis of ethyltoluene isomer mixtures involves serious analytical difficulties.[7c] Second, isomerization is taking place in several of these alkylations. Third, in at least the two ethyltoluene isomer distributions lowest in *o*-ethyltoluene, selective complexing by catalyst is evident. The ethyltoluene isomer distribution lowest in *o*-ethyltoluene actually has a *m*-ethyltoluene composition higher than the thermodynamic equilibrium composition. Fourth, within experimental error all the isomer distributions obtained could have been produced by ethylation to yield the same ethyltoluene isomer distribution and isomerization of this distribution. A possible exception would be those ethylations in which ethylene was used as the ethylating agent. They invariably involve isomer distributions low in *p*-ethyltoluene.

In Table IV are summarized ethylations reported in the literature. These isomer distributions are plotted on Fig. 3. The ferric pyrophosphate–boron trifluoride produced distribution was reported as only approximate. The $GaBr_3$ produced isomer distribution is not consistent with that obtained in the present work. The $BF_3(P_2O_5)$ produced distribution is the same within experimental error as that obtained in the present work.

It is remarkable how the isomer distributions reported by Kutz, *et al.*, may be correlated by the concurrent alkylation and isomerization equation reported in the present work. If 22% *p*-, 30% *m*- and 48% *o*- are taken as the substitution distribution, the following equations result.

TABLE IV
ISOMER DISTRIBUTIONS IN THE ETHYLATION OF TOLUENE

Ethyl derivative	Catalyst	Isomer distribution, % p-	m-	o-	Ref.
C_2H_4[a]	Al_2O_3–SiO_2	21	50	29	10
C_2H_4[a]	H_3PO_4	22	32	46	10
C_2H_4[a]	$FePO_4$	22	30	48	10
C_2H_4	$AlCl_3$	25	64	11	10
C_2H_4	$Fe(P_2O_7)_3(BF_3)$	20	20	60	11
C_2H_4	$CdSO_4{\cdot}H_2O{\cdot}BF_3$	27	26	47	12
EtBr	$GaBr_3$	41	21	38	13
EtOH	$BF_3(P_2O_5)$	25	30	45	14

[a] Continuous alkylations.

$$O = 9.0 + \frac{37.5}{44.2\tau}[1 - e^{-44.2\tau}] + \frac{1.5}{88.6\tau}[1 - e^{-88.6\tau}]$$

$$P = 26.2 - \frac{19.3}{44.2\tau}[1 - e^{-44.2\tau}] + \frac{15.1}{88.6\tau}[1 - e^{-88.6\tau}]$$

These equations are plotted as the curve on Fig. 3.

The substitution distribution used to correlate the isomer distributions of Kutz, *et al.*, is 12 mole % lower in *p*-ethyltoluene than the substitution distribution used to correlate the distributions reported in the present work. Since the ethylations reported by Kutz, *et al.*, were all carried out with ethylene, it again appears that toluene ethylations by ethylene produce a substitution distribution lower in *p*-ethyltoluene than ethylations by other ethyl derivatives.

Isopropylation of Toluene.—In Table V are summarized the propylations carried out in the present work.

The first eleven isomer distributions are plotted as the closed circles on Fig. 4. The *o*-isopropyl-

(10) W. M. Kutz, J. E. Nichels, J. J. McGovern and B. B. Corson, *J. Org. Chem.*, **16**, 699 (1951).
(11) J. T. Kelly and H. M. Knight, U. S. Patent 2,824,146 (1958).
(12) H. M. Knight and J. T. Kelly, U. S. Patent 2,824,150 (1958).
(13) H. C. Brown and C. R. Smoot, *J. Am. Chem. Soc.*, **78**, 6255 (1956).
(14) M. J. Schlatter and R. D. Clark, *ibid.*, **75**, 361 (1953).

TABLE V

ISOMER DISTRIBUTIONS IN THE ISOPROPYLATION OF TOLUENE

Isopropyl derivative	Catalyst	Catalyst, mole %	Temp., °C.	Rx time, min.	Conversion, mole %	Isomer distribution, % p-	m-	o-[a]
i-PrOH	$TiCl_4$	50.0	90	180	25	28	70	2
i-PrI	$AlBr_3$	0.25	25	1	9	37	25	38
i-PrI	$AlBr_3$	.25	25	10	10	43	36	21
i-PrI	$AlBr_3$	.25	25	40	13	43	50	7
i-PrTs[b]	...	...	116	240	8	37	21	42
C_3H_6	$AlCl_3$	.1	100	40	25	42	42	16
C_3H_6	$AlCl_3$	.2	60	55	30	41	54	5
C_3H_6	$AlCl_3 \cdot 2H_2O$	1.3	55	90	26	37	57	7
C_3H_6	$AlCl_3$	5.0	r.t.	240	36	30	68	2
C_3H_6	90% H_2SO_4	9	0	60	10	39	19	42
C_3H_6	90% H_2SO_4	9	0	30	10	38	19	43
C_3H_6	$AlCl_3 \cdot 4(CH_3NO_2)$	1.0	40	23	23	36	23	41
C_3H_6	$AlCl_3 \cdot 4(CH_3NO_2)$	0.5	40	17	25	37	23	40
C_3H_6	$FeCl_3$	5.0	35	1070	3.3	38	20	42
C_3H_6	$AlBr_3$	0.1	40	95	4.8	39	23	37
C_3H_6	$TiCl_4$	1.0	80	50	25	35	22	42
C_3H_6	$AlCl_3$	1.0	25	25	22	37	25	38
C_3H_6	$AlCl_3$	1.0	25	13-22	22	34	26	39
C_3H_6	$AlCl_3$	0.5	40	12	31	36	37	27
C_3H_6	$AlCl_3$	.1	40	35	?	37	25	38
C_3H_6	$AlCl_3$	.1	70	103	15	40	28	32
C_3H_6	$AlCl_3$	1.2	0	17	16	37	23	40
C_3H_6	$AlCl_3$	0.1	40	40	29	40	28	33
C_3H_6	$AlCl_3$	.1	60	40	30	43	33	24
C_3H_6	$AlCl_3$	.1	80	40	20	40	17	43
C_3H_6	$AlCl_3$	.1	100	40	25	42	42	16
C_3H_6	$AlCl_3$	.2	40	55	23	41	32	27
C_3H_6	$AlCl_3$	.2	80	55	23	39	38	23
C_3H_6	$AlCl_3$	.2	100	55	17	41	30	29
C_3H_6	$AlCl_3$	.2	40	17	26	38	29	32
C_3H_6	$AlCl_3$	.2	40	40	26	41	33	26
C_3H_6	$AlCl_3$	.2	40	58	28	40	36	24
C_3H_6	$AlCl_3$	.2	40	135	19	39	32	29
C_3H_6	$AlCl_3$	.2	40	264	27	39	39	22
C_3H_6[c]	$AlCl_3$	.2	40	205	16	38	16	46
C_3H_6[c]	$AlCl_3$	.2	40	16	28	40	29	32
C_3H_6	$AlCl_3 \cdot 2.3(H_2O)$	1.3	40	45	21	38	26	36
C_3H_6	$AlCl_3 \cdot 4(H_2O)$	0.8	40	50	18	38	26	36
C_3H_6	$AlCl_3 \cdot 5(H_2O)$	1.2	40	39	13	36	17	48

[a] Determined by infrared spectroscopy. [b] Isopropyl-*p*-toluenesulfonate. [c] The toluene was saturated with water at room temperature.

toluene composition in the remaining twenty-nine isomer distributions ranged from 22 to 48%. These isomer distributions are correlated by the equation

$$55.4 - 0.81O = M$$

with a standard deviation of 1.7. The location of this straight line is indicated by the dotted line on Fig. 4.

On Table VI are summarized isopropylations reported in the literature.

These isomer distributions are plotted as the open circles on Fig. 4.

If 36.5% *p*-, 21.5% *m*- and 42% *o*-isopropyltoluene is taken as the starting distribution and the isopropyltoluene results used,[7a] equations 1 become

$$O(t) = 1.5 - 0.4e^{-8.9\tau} + 40.9e^{-66.7\tau}$$

$$P(t) = 29.8 + 18.9e^{-8.9\tau} + 12.3e^{-66.7\tau}$$

for the isomer distributions produced by alkylation and subsequent isomerization. Use of the same constants in equations 2 permit the calculation of the isomer distributions expected from concurrent alkylation at a constant rate and isomerization by first-order rate steps. These theoretical isomer composition trajectories are plotted as the curves on Fig. 4.[9]

Tables V and VI and Fig. 4 lead to two principal conclusions. First, that isomerization of the isopropyltoluene isomer distribution obtained by the propylation of toluene is likely with many propylation systems. Second, within experimental error all the isopropyltoluene isomer distributions obtained could have been produced by propylation to yield one isopropyltoluene isomer distribution and isomerization of this distribution. This view is strongly supported by the agreement between the empirical straight line correlation of isomer distributions and the theoretical trajectory of isomer distributions. In the cases of the isomer distributions that deviate most seriously from the theoretical trajectory, the $GaBr_3$·*i*-PrBr alkylations and the HCl·*i*-PrCl alkylations, the devia-

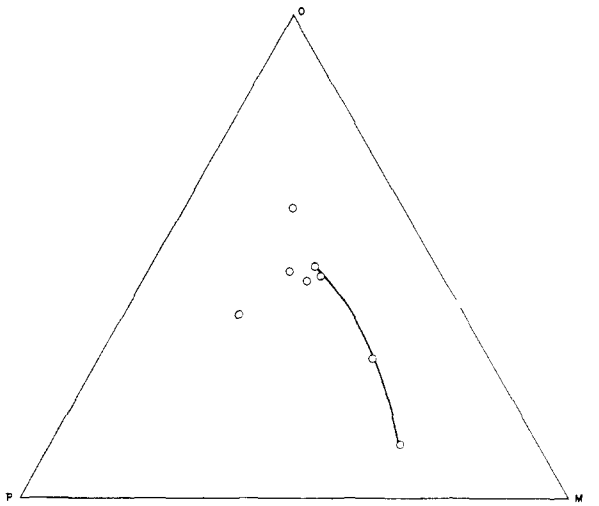


Fig. 3.—Ethyltoluene isomer distributions obtained by ethylation of toluene.

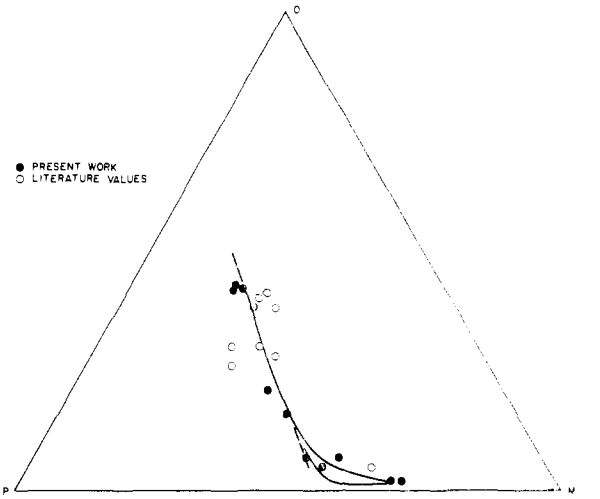


Fig. 4.—Cymene isomer distributions obtained by propylation of toluene.

tion of the experimental distributions from one another is as large as the deviation from the theoretical trajectory. Thus, in spite of the great variety of catalysts and alkylating agents used for the propylation of toluene, the isomer distributions obtained may all be explained by the hypothesis that in all cases a cymene mixture containing 36.5% *p*-, 21.5% *m*- and 42.0% *o*-isopropyltoluene[17]

TABLE VI

ISOMER DISTRIBUTIONS IN THE ISOPROPYLATION OF TOLUENE

Isopropyl derivative	Catalyst	Isomer distribution, % *p*-	*m*-	*o*-	Ref.
C_3H_6	U.O.P. #2	35	25	40	14
C_3H_6	HF	33	26	41	14
C_3H_6[a]	$BF_3 \cdot Et_2O$	34	29	38	3[b]
C_3H_6[b]	$AlCl_3 \cdot CH_3NO_2$	34	29	38	3[b]
C_3H_6	Montmorillonite	32	63	5	15
C_3H_6	$CuSO_4 \cdot 5H_2O \cdot nH_2O$	40	30	30	16
i-PrOH	BF_3	41	30	29	14
i-PrOH	P_2O_5	41	30	29	14
i-PrOH	$CuSO_4 \cdot 5H_2O \cdot nH_2O$	35	25	40	16
i-PrCl	HCl	37	25	38[c]	1[b]
		53	22	25[d]	
		42	27	31[d]	
i-PrBr	$GaBr_3$	38	33	28	13
		47	27	26	
		45	25	30	

[a] Average of results for four runs. [b] Average of results for six runs. [c,d] Replicate analyses of the same reaction mixture, [c] was done by Raman spectroscopy and [d] by infrared spectroscopy. Since the precision was poor, these distributions were not plotted.

is produced by the alkylation reaction, and the isomer distributions actually obtained differ only in the extent of isomerization that accompanies the alkylation.

Tertiary Butylation of Toluene.—Unfortunately the *t*-butylation of toluene cannot be studied by the technique used in the present work since only two isomers are produced. Schlatter and Clark have reported several *t*-butylations under a variety of conditions,[14] and all the isomer distributions produced contain 93% *p*- and 7% *m*- *t*-butyltoluene, 33% *p*- and 67% *m*- *t*-butyltoluene or an intermediate distribution. In view of the results of the present work, it would seem probable that the first isomer distribution is the substitution distribution and the second the thermodynamic equilibrium. Indeed, the first distribution is produced by mild catalysts such as sulfuric acid and aqueous hydrofluoric acid, the second by strong catalysts such as aluminum chloride, and isomerization of *t*-butyltoluenes in this Laboratory indicated that the second distribution is the thermodynamic equilibrium.

A tertiary butylation of toluene result that appeared to conflict with the above view was reported by Brown and Smoot,[13] but recently the interpretation of the above result was found to be in error.[18]

Discussion

The mechanism for the Friedel–Crafts alkylation of toluene basically appears to be

$$RX + CAT. \rightleftharpoons R^{\delta\oplus}X\ CAT.^{\delta\ominus}$$

$$R^{\delta\oplus}X\ CAT.^{\delta\ominus} + \text{C}_6\text{H}_5\text{CH}_3 \rightarrow \text{R(H)C}_6\text{H}_4\overset{\oplus}{\text{C}}\text{H}_3 + X\ CAT.^{\ominus}$$

The catalyst complexes with the alkyl derivative to form a polarized complex,[19] this polarized complex then reacts with toluene to form a σ-complex, loss of proton from the σ-complex yields alkyltoluene. This mechanism indicates that the alkyltoluene isomer distribution obtained, and therefore the selectivity of the reaction for the activated positions of the toluene ring, will be significantly affected by the amount of polarization of the RX bond that precedes reaction with the

(15) J. E. Mahan, U. S. Patent 2,564,488 (1951).

(16) W. G. Tolland, Jr., U. S. Patent 2,793,239 (1957).

(17) Since experimental isomer distributions containing more *o*-isopropyltoluene were obtained, this distribution may be too low in o-isopropyltoluene.

(18) S. U. Choi and H. C. Brown, *J. Am. Chem. Soc.*, **81**, 3315 (1959).

(19) Actually, probably more than one complex is involved in the reaction.

aromatic ring. If the polarization of the RX bond is nearly complete before reaction with the aromatic ring, the reaction will exhibit a low selectivity for the activated *ortho* and *para* positions and the selectivity of the reaction will be relatively independent of the nature of the X and catalyst involved. Previous studies of the methylation, ethylation and isopropylation of toluene[4] show the former to be true; the present study shows the latter to be true.

In Table VII are summarized the alkylation isomer distributions obtained in the present work and pertinent data of Brown and co-workers.

TABLE VII

ALKYLATION OF TOLUENE

	Isomer distribution, %					
	p-	*m*-	*o*-	$\frac{2p}{m}$	ΔS^{*}[a]	Relative rates[a]
Methylation	26	14	60	3.7	−20.0	1.0
Ethylation	34	18	48	3.8	−21.5	13.7
Isopropylation	36.5	21.5	42	3.4	−19.3	20,000
t-Butylation	93	7	0	26.6	...	...

[a] Obtained for $GaBr_3$ alkyl bromide alkylations.

The constancy of the entropy of activation for the $GaBr_3$ catalyzed methylation, ethylation and isopropylation of toluene has been taken to indicate that no significant change in mechanism is involved. The constancy of the ratio of *p*-isomer composition to *m*-isomer composition indicates that no significant change in the selectivity of the polarized alkyl species is involved. Since equal selectivity implies equal reactivity,[4] the enormous increase in relative rates of alkylation cannot be due to increase in reactivity of the polarized alkyl species but must be due to the relative quantities or rates of formation of polarized alkyl species.

The high ratio of *p*-isomer composition to *m*-isomer composition for the *t*-butylation of toluene indicates a high selectivity and therefore a low reactivity. Therefore, the rapid rate of *t*-butylation of toluene must be due to the relative quantities or rates of formation of polarized alkyl species. Since the rate of reaction of polarized *t*-butyl species with toluene must be slower than the corresponding rate for methylation, ethylation and isopropylation, if the rate of reaction with toluene is rate determining in the latter three reactions,[6,18] it must also be rate determining in the *t*-butylation reaction.

Experimental

Materials.—The toluene used was plant grade. The $GaBr_3$ used was prepared as described in ref. 20. The remaining catalysts were commercial materials and were used without purification. Their purity or grade, if specified, and their manufacturers were: $TiCl_4$, Amend Drug and Chemical Company; $AlCl_3$, C.P. anhydrous, General Chemical Division, Allied Chemical; $AlBr_3$, C.P. anhydrous, Fisher and Amend Drug and Chemical Company, Inc.; HF anhydrous, The Matheson Company; BF_3 anhydrous, The Matheson Company; P_2O_5 A.C.S., General Chemical Division, Allied Chemical.

The alkylating agents used were also commercial materials used without purification. Their grade or purity, if specified, and their manufacturers were: CH_3I, reagent, General Chemical Division, Allied Chemical; CH_3Cl, b.p. −24.6 to −23.6°, The Dow Chemical Company; CH_3Br, 100%, The Dow Chemical Company; CH_3OH, du Pont; CH_3CH_2I, white label, Distillation Products Industries; CH_3CH_2OH, U.S.P. absolute, U.S. Industrial Chemical Corporation; CH_3CH_2Cl, technical (b.p. 12 to 13°), The Dow Chemical Company; CH_3CH_2Br, 99.5%, The Dow Chemical Company; C_2H_4, C.P., The Matheson Company or Ohio Chemical and Surgical Equipment Company; C_3H_6 C.P., The Matheson Company; *i*-C_3H_7I, Matheson, Coleman and Bell; *i*-C_3H_7OH, U.S. Industrial Chemical Corporation; isopropyl *p*-toluenesulfonate, Fine Organics Inc.

Alkylation Procedures.—The apparatus used was a 500-ml. 3-necked creased flask equipped with a thermometer, a stirrer and a gas exhaust tube connected through a drying tube to a water trap. Generally two moles of toluene was added and then catalyst. If the toluene was to be alkylated with olefin, using unmodified metal halide as catalyst, hydrogen halide was first passed through the stirred mixture for a few minutes. When the alkylating agent was a gas at room temperature, it was added gradually through a gas inlet tube; when the alkylating agent was a liquid at room temperature, it was added dropwise through a dropping funnel, either neat or in toluene solution. The reaction mixture was then washed with water until the washing was neutral, dried over Drierite, filtered and analyzed.

Monel equipment was used for the hydrogen fluoride catalyzed alkylations.

Acknowledgments.—The authors are indebted to T. Alfrey, Jr., of the Dow Polymer Research Laboratory for derivation of the concurrent alkylation and isomerization equations and to D. S. Erley of the Dow Chemical Physics Laboratory for the infrared data.

(20) C. R. Smoot and H. C. Brown, *J. Am. Chem. Soc.*, **78**, 6245 (1956).