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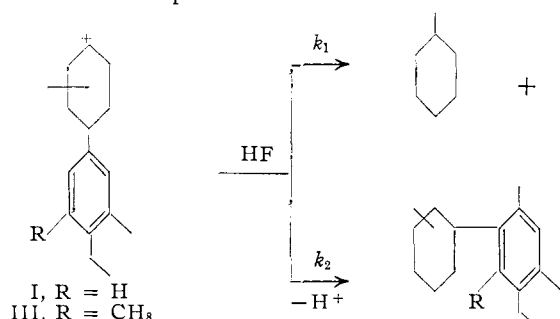
Hydrogen Transfer. VI.¹ Reaction of 1,3-Dimethyl-4-ethylbenzene and Ethylmesitylene with Methylcyclohexene. Transaralkylation Reaction of Diarylethanes²

BY HERMAN PINES AND JOSEPH T. ARRIGO³

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The reactions of 1,3-dimethyl-4-ethylbenzene (I) and ethylmesitylene (III) with 4-methylcyclohexene in hydrogen fluoride were carried out under conditions previously used with *p*-ethyltoluene, in order to evaluate the effect of increasing *o*-substitution on the hydrogen transfer process. It was found that although cycloalkylation remained about the same (5–8%) throughout the series, the mole % of arene converted to hydrogen transfer products decreased markedly in the case of the di-*o*-methyl substituted arene. The results are discussed in terms of the steric and polar effects of substituents on the reactions involved. Of significance was the formation of *m*-xylene and 1,5-dimethyl-2,4-diethylbenzene in the above reaction of I. It was found that these arenes arose not by conventional transalkylation of I, but by alternate cleavage of the hydrogen transfer product, 1-(2,4-dimethylphenyl)-1-(2,4-dimethyl-5-ethylphenyl)-ethane (II), in the reverse reaction. The transaralkylation of several additional diarylethanes to form monocyclic arenes and triaryldiethanes was studied. The ratios of the various arenes formed were compared with calculated values obtained by means of "partial relative basicity" factors. There was reasonably good agreement except in cases in which steric factors prevailed. An ionic mechanism for the transaralkylation reaction is discussed.

In previous studies in this series,^{1,4} it was shown that certain alkyltoluenes undergo hydrogen transfer and subsequent self-condensation on treatment

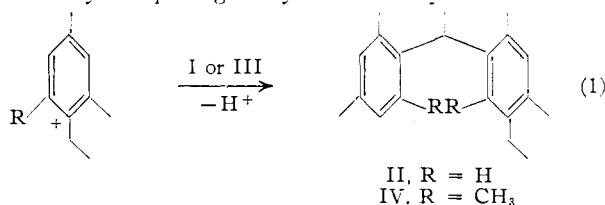


with 4-methylcyclohexene in sulfuric acid or hydrogen fluoride. Thus, *sec*-alkyltoluenes (*e.g.*, *m*- and *p*-cymene) yielded substituted indans, while *p*-*prim*-alkyltoluenes afforded 1,1-diarylethanes. Only conventional cycloalkylation was observed with *o*-cymene and *p*-xylene.

It was the purpose of the present investigation to ascertain and evaluate the effects of *o*-methyl substitution on the course of the hydrogen transfer and cycloalkylation reactions by studying 1,3-

dimethyl-4-ethylbenzene (I) and ethylmesitylene (III) as shown in equations 1 and 2.

By comparing the yields of diarylethanes and cy-



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(2)

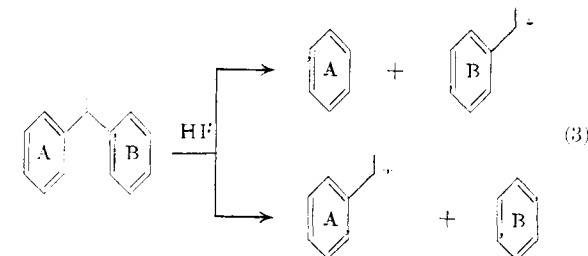
cloalkylarenes (as a measure of rates k_1 and k_2) with those found with *p*-ethyltoluene^{4c} under comparable conditions, it was hoped that the desired information could be obtained.

During the course of the investigation, it was found that II was unstable under the reaction conditions. This observation led to a study of the direction of cleavage of II and other unsymmetrical diarylethanes in hydrogen fluoride according to the generalized equation 3, where A and B are alkylbenzene molecules.

Results

The reaction of 1.00 mole of ethylxylene (I) and 0.50 mole of 4-methylcyclohexene in 125 g. of hydrogen fluoride at 0–10° led to the products shown in Table I.

The structures of the products in Table I were proved by comparison with authentic samples as described in the Experimental section. It is assumed that 1,3-dimethyl-5-(1-methylcyclohexyl)-benzene was formed on the basis of spectral evidence and the reported orientation on *t*-butylation of *m*-xylene.⁵ The corresponding product from I is presumably 1,5-dimethyl-2-ethyl-4-(*x*-methylcyclohexyl)-benzene, a secondary cycloalkylate. Although the analogous alkylations of benzene^{6,7}



(1) For paper V of this series see H. Pines, D. R. Strehlau and V. N. Ipatieff, *THIS JOURNAL*, **72**, 5521 (1950).

(2) Taken in part from a dissertation submitted by J. T. Arrigo to the Graduate School in partial fulfillment of the requirements for the Ph.D. degree, October, 1956.

(3) Universal Oil Products Co. Predoctoral Fellow, 1953–1956.

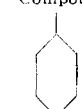

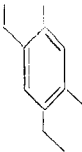


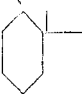
(4) (a) V. N. Ipatieff, H. Pines and R. C. Olberg, *THIS JOURNAL*, **70**, 2123 (1948); (b) H. Pines, A. Weizmann and V. N. Ipatieff, *ibid.*, **70**, 3859 (1948); (c) H. Pines, D. R. Strehlau and V. N. Ipatieff, *ibid.*, **71**, 3534 (1949); (d) **72**, 1563 (1950).

(5) M. J. Schlatter, *ibid.*, **76**, 4952 (1954).

(6) V. N. Ipatieff, E. E. Meisinger and H. Pines, *ibid.*, **72**, 2772 (1950).

(7) J. Linsk, *ibid.*, **72**, 4257 (1950).

TABLE I
PRODUCTS OF THE REACTIONS OF I AND III WITH 4-METHYL-
CYCLOHEXENE

Compound <i>f</i>	Yield ^a		Compound	Yield ^a	
	R = H	R = CH ₃		R = H	R = CH ₃
	32 ^b	15 ^b		..	20 ^{b,v}
<i>m</i> -C ₆ H ₄ (CH ₃) ₂ I and III	5.9 41 ^c	.. 88 ^d	a II and IV	7.5 26 ^h	5.6 6.4
	11 ^e	..	(II)	5	..
	8 ^b	16 ^{b,f}		..	25 ⁱ
	3.9	..			

^a Mole % yields based on arene charged as calculated on a loss-free basis. Although the total of I accounted for in the material balance was somewhat high by this method, the interrelations are more evident. ^b Mole % yields based on olefin charged. ^c About 1% appeared to be 1,3-dimethyl-5-ethylbenzene. ^d No isomerization or transalkylation products of III were detected. ^e A negligible amount of an isomeric tetraalkylbenzene seemed to be present. ^f Approximately a 1:1 mixture of saturated and mono-unsaturated dimer, as determined by chromatographic and infrared analysis. ^g Methylcyclohexene trimer; it was not further investigated. ^h The diarylethane fractions apparently contained two other isomers; II was proved to be the major component. ⁱ Physical properties and infrared spectra indicated that the high boiling cuts were methylcyclohexene polymers. Yield is expressed in terms of molar equivalent of methylcyclohexene. ^j Structural formulas shown in eq. 1 and 2 if not shown in the table.

and toluene⁸ are known to yield the tertiary cycloalkylate, *i. e.*, the (1-methylcyclohexyl)-arene, only secondary isomers were obtained from *p*-xylene.^{8,9}

1-(2,4-Dimethylphenyl)-1-(2,4-dimethyl-5-ethylphenyl)-ethane (II) was synthesized by the previously reported procedure^{4c}; subsequently, a larger amount was needed, so the xylyllithium compound was used in preference to the Grignard reagent, affording a threefold increase in yield of the 1,1-diarylethanol, which was then hydrogenolyzed directly to II in the presence of copper chromite. This result is in agreement with the reported superiority of aryllithium compounds in similar condensations in which steric hindrance prevailed.¹⁰

It was necessary to purify a commercial sample of mesitylene in order to prepare pure ethylmesitylene. In view of the nature of the arene contaminants present, this was accomplished conveniently

(8) B. S. Friedman, F. L. Morrirtz and C. J. Morrissey, *THIS JOURNAL*, **79**, 1465 (1957).

(9) The alternate possibility that compound I yielded a tetramethyltetrahydrofluorene isomeric to that formed from *p*-cymene⁸ is not favored by the experimental data, but cannot be categorically excluded without further study.

(10) L. H. Schwartzman and B. B. Corson, *THIS JOURNAL*, **76**, 78: (1951).

by the procedure of Schlatter,^{5,11} *i. e.*, by selective alkylation with isobutylene, chosen as the most convenient of several olefins tested. The mesitylene, unable to undergo *t*-butylation,¹² was recovered by distillation.

The reaction of 0.60 mole of ethylmesitylene (III) and 0.30 mole of 4-methylcyclohexene in 75 g. of hydrogen fluoride afforded the products shown in Table I.



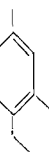
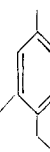
The (methylcyclohexyl) derivative of III must be 1,3,5-trimethyl-2-ethyl-4-(*x*-methylcyclohexyl)-benzene, a secondary cycloalkylate. In this case the formation of a tertiary cycloalkylate or a tricyclic hydrocarbon is precluded by steric considerations.

The synthesis of 1-(2,4,6-trimethylphenyl)-1-(2,4,6-trimethyl-3-ethylphenyl)-ethane (IV) was not attempted by the previously applied methods, as it was anticipated that steric factors would be prohibitive. It was prepared by the hydrogen fluoride-catalyzed alkylation of III with methylmesitylcarbinol. A very low yield of crystalline hydrocarbon identical with IV from the hydrogen transfer reaction was separated from what appeared to be vinylmesitylene dimers by distillation, chromatography and recrystallization.

Discussion

Steric Effects of *o*-Substitution.—The effects of *o*-substitution on the hydrogen transfer reaction may be seen by comparing the pertinent data in Table II.

TABLE II
SUMMARY OF RESULTS OF THE HYDROGEN TRANSFER REACTIONS

				
Yield, mole % ^a				
Arene reacted (total)	62	56	59	12
Arene converted to diarylethanes ^d	49 ^g	50 ^f	31	6.4
Arene cycloalkylated	13	5.4	7.5	5.6
Arene transalkylated	0.6	0	21	0
Ratio of hydrogen transfer ^g to cycloalkylation	1.9	4.6	3.5	0.57

^a Based on arene charged (loss-free basis). ^b Arene: olefin ratio in charge was 5:4; all others 2:1. ^c Results from ref. 4c as recalculated on a loss-free basis. ^d Includes cycloalkylated diarylethane derivatives. ^e 29 mole % of the diarylethane was isolated as such. ^f 45 mole % isolated as the diarylethane. ^g As shown in a later section, transalkylation by way of cleavage of diarylethanes followed by hydrogen transfer consumes a portion of the latter.

Since the diarylethane formed in the *p*-ethyl-toluene reaction was required for a reaction discussed below, it was of interest to prepare it by the hydrogen transfer reaction. In an attempt to increase the yield of the latter, a higher concentration of olefin was used in the charge; the effect of this change is shown by comparing the data (col-

(11) M. J. Schlatter, "Symposium on Petrochemicals in the Postwar Years," Publication No. 28, Division of Petroleum Chemistry of the American Chemical Society, 1953, p. 79.

(12) M. S. Carpenter and W. M. Easter, *J. Org. Chem.*, **19**, 77 (1954).

umn 1) with that previously reported^{4c} (column 2). The amount of arene reacting by all paths was slightly increased, while the total amount converted to diarylethanes and their cycloalkylates was about the same. However, the net result was a sizable decrease in diarylethane isolated, due to its undergoing secondary reactions with the larger amount of olefin present. The amount of arene cycloalkylated also increased. It is noteworthy that a small amount of transalkylation occurred in the present case, as indicated by the toluene formed.

Comparison of the results in the last three columns indicates the following trends caused by methyl substitution *ortho* to the ethyl group, the site of the hydride transfer which precedes self-condensation of the arene: 1, The amount of arene reacted by all paths is approximately unchanged by a single *o*-methyl group, but decreases sharply due to the double *o*-substitution in ethylmesitylene.

2, The conversion of arenes to diarylethanes and their cycloalkylates is markedly decreased by double *o*-methyl substitution. The apparent decrease in the case of the ethylxylene is probably largely due to diversion of the initially-formed diarylethane to transalkylation products and their derivatives (as discussed in point 4), rather than to steric effects of the *o*-methyl group.

3, The extent of cycloalkylation is essentially constant throughout the series; consequently, any steric hindrance to cycloalkylation due to increasing substitution must be counteracted by the polar effects involved. It is of interest to note that the usual cycloalkylate yields with unhindered arenes are of the order of 70–80% based on olefin charged,^{6,8} because competing hydrogen transfer reactions are comparatively unimportant.

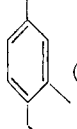
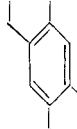
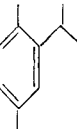



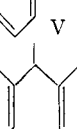
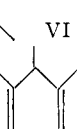
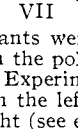
4, Little or no transalkylation was detected with *p*-ethyltoluene or ethylmesitylene, while it occurred to the extent of about 70% as much as the diarylethane isolated in the case of the ethylxylene. It should be noted that, as demonstrated in a later section, the transalkylation products (*m*-xylene and its cycloalkylate and the tetraalkylbenzene) arose by alternate cleavage of diarylethane II (see equation 3) followed by hydrogen transfer in a reaction analogous to the reverse of equation 1. The extent of cleavage in the corresponding reactions of *p*-alkyltoluenes is practically indistinguishable, since it occurs almost exclusively by a reversal of equation 1. Therefore, it is difficult to draw any clear-cut conclusions as to the effects of one *o*-methyl substituent from the net amount of diarylethane formation.

5, The ratio of arene which underwent hydride abstraction (half of the total of diarylethanes and their transalkylates and derivatives thereof formed) to that cycloalkylated by the attacking methylcyclohexyl carbonium ion is seen to decrease from 4.6 to about 0.6 with increasing substitution. In the latter case, the generally unfavored cycloalkylation reaction is relatively more facile than diarylethane formation.

It is of interest to contrast the polar and steric effects of increasing substitution in the present reactions. The preferred orientation in the electrophilic substitution of *p*-alkyltoluenes is *ortho* to the

methyl group.¹³ Increasing methyl substitution *ortho* to the ethyl group should have the twofold effect of enhancing the electron density of the remaining positions toward nuclear attack and, in addition, should stabilize the incipient α -arylethyl carbonium ion.¹⁴ On the other hand, especially

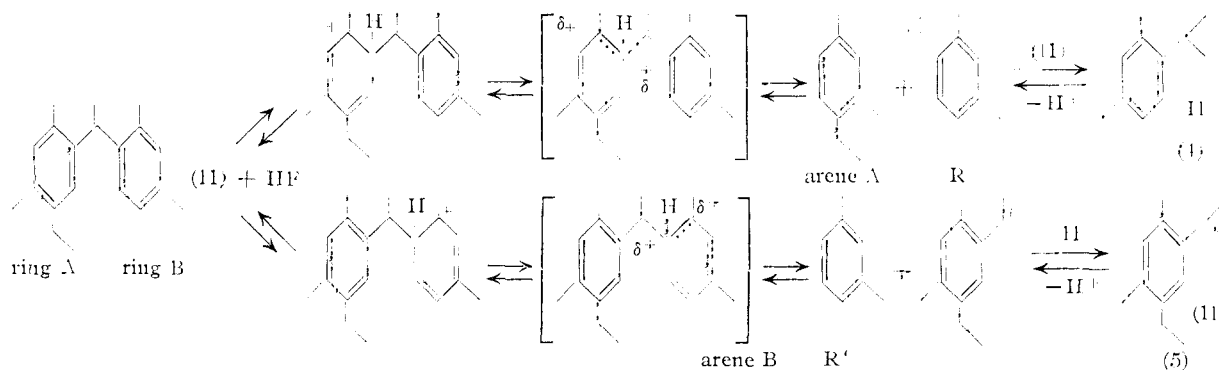
TABLE III
RESULTS OF TRANSALKYLATION REACTIONS

Expt. ^a	Compound charged ^b	Cleavage % ^c	Cleavage ratio, A/B ^d	Remarks
A-1	 (I)	0	..	No transalkylation or isomerization
A-2		0	..	No transalkylation, small amt. isomerization.
B-1	 II	15	5	Some isomerization of II
B-2	II + 	20	7	Cycloalkylation of arenes occurred
B-3	II + 	20	5	Chiefly V formed rather than triaryldiethanes
B-4	II + 	40	3	Cycloalkylation rather than triaryldiethane formation occurred
C	 V	10	All A	Small amount of V isomerized
D	 VI	20	30	No isomzn. of VI nor of <i>p</i> -ethyltoluene formed
E	 VII	10	10	No isomzn. of VII; negligible amt. of <i>m</i> -xylene found

^a Reactants were stirred one hour with excess hydrogen fluoride in the polyethylene apparatus at ice-bath temperature; see Experimental section for details. ^b "Ring A" is written on the left side of the ethylidene bridge, "ring B" on the right (see equation 3). ^c Based on loss-free moles of mononuclear arene formed by both paths divided by moles diarylethane charged. ^d Based on moles A/B using notation defined in footnote b. ^e Molar ratio of II:olefin charged was 2:1. ^f Molar ratio of II:benzene charged was 1:4.4. ^g Molar ratio of II:cyclohexane charged was 1:1.

(13) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 258.

(14) H. C. Brown, J. D. Brady, M. Grayson and W. H. Bonner, THIS JOURNAL, 79, 1897 (1957).



in the case of di-*o*-substitution, the accessibility of the hydrogen which is to undergo hydridic transfer is more limited, and the resulting ion is probably destabilized by steric inhibition of resonance. Examination of the Fisher-Hirschfelder models of the diarylethanes produced in this series indicated that while the first two exhibited essentially free rotation around the connecting carbon of the ethylidene bridge, IV could be assembled only with difficulty and had severe steric restriction to such rotation, indicative of the extreme hindrance to nuclear alkylation in this case. The results in Table II are in accord with the well known generalization that steric effects increase markedly with increasing steric requirements. Apparently polar effects are of secondary importance in such reactions.

Transaralkylation of Diarylethanes.—The isolation of *m*-xylene (and its cycloalkylate) and 1,5-dimethyl-2,4-diethylbenzene from the reaction of ethylxylene (I) above indicated that the latter underwent a typical transalkylation reaction. However, under the conditions employed, ethyl group transfer was unanticipated. The previously reported reactions of *p*-alkyltoluenes in this series^{3,4} were not complicated by analogous transfers and, in addition, it is known that the *t*-butyl group can be transferred from 1,3-dimethyl-2-ethyl-5-*t*-butylbenzene to toluene or *m*-xylene in hydrogen fluoride at 0° without affecting the ethyl group.^{3,11} In order to eliminate the possibility of conventional ethyl group transfer, compound I was treated with hydrogen fluoride under identical conditions as in the alkylation reaction except the olefin was omitted (expt. A-1, Table III).

The arene was found to be completely stable. Similarly, it was observed that 1,5-dimethyl-2,4-diethylbenzene underwent no transalkylation under the same conditions (expt. A-2).

In view of these results, diarylethane II was similarly treated (expt. B-1). In this case, both *m*-xylene and the tetraalkylbenzene were isolated in addition to I.¹⁵ Infrared spectra of the recovered diarylethane cuts showed that II had undergone partial isomerization. A higher boiling fraction was also isolated which was shown to correspond to a triaryldiethane. The reaction may be visualized as illustrated in equations 4 and 5.

(15) Schlatter (ref. 11) found di-*t*-butylbenzenes in the product formed from the exhaustive *t*-butylation of an ethylbenzene-isomeric xylene mixture; 1-(*t*-butylphenyl)-1-xylethanes also were identified. He suggested that the former arenes probably were formed by *t*-butylation of cleavage products of these diarylethanes.

Cleavage probably proceeds *via* the σ -complexes¹⁶ shown,¹⁷ and depending on whether the ring A- or B-ethylidene bridge juncture is attacked by the proton, either arene A or B is formed (I or *m*-xylene in this case). The α -arylethyl cations R and R' react chiefly with the excess II to yield triaryldiethane products. Formation of α -complexes is further indicated by the intense color formation which occurs on contacting diarylethanes with hydrogen fluoride. Such nuclear-side chain scission is analogous to the mechanism postulated for the acid-catalyzed dealkylation¹⁸ or cracking^{19,20} of alkylbenzenes.

The results of treatment of II with 4-methylcyclohexene in hydrogen fluoride indicated that the olefin had little effect on the direction and extent of cleavage, the net result being cycloalkylation of I, II and *m*-xylene (expt B-2).

Cleavage of II in the presence of a 4-molar excess of benzene proceeded to about the same extent as in experiments B-1 and B-2, and the cleavage ratio was about the same (expt. B-3). In this case, the excess benzene served as the acceptor rather than II and 1-phenyl-1-(2,4-dimethylphenyl)-ethane (V) was formed, along with a small amount of what appeared to be 1-phenyl-1-(3,5-dimethylphenyl)-ethane (the latter was probably formed by isomerization of V; see below).

The reversibility of equation 1 was tested by contacting equimolar amounts of II and methylcyclohexane in the presence of hydrogen fluoride (expt. B-4). As would be expected, the cleavage ratio was little changed, while the amount was increased. Thus, diarylethane formation is reversible and little or no triaryldiethane formation occurred; instead, the methylcyclohexyl carbonium ions which formed appeared in the products as the usual cycloalkylates. Analogous alkyl group interchange between a saturated hydrocarbon and an alkylbenzene previously has been reported to occur in the presence of either hydrogen fluoride¹¹ or aluminum chloride.^{21,22}

These results resolve the apparently anomalous

(16) H. C. Brown and J. D. Brady, *THIS JOURNAL*, **74**, 3570 (1952).

(17) Of the numerous other possible σ -complexes which may be formed, each with its usual number of resonance forms, only those shown can lead to the observed results.

(18) L. Schmerling, *Ind. Eng. Chem.*, **45**, 1447 (1953).

(19) B. S. Greensfelder, H. H. Voge and G. M. Good, *ibid.*, **41**, 2573 (1949).

(20) C. L. Thomas, *ibid.*, **41**, 2561 (1949).

(21) L. Schmerling, R. W. Welch and J. P. West, *THIS JOURNAL*, **78**, 5406 (1956).

(22) V. N. Ipatieff and H. Pines, *ibid.*, **59**, 56 (1937).

transfer of the ethyl group of I under non-trans-ethylating conditions and demonstrate the intermediacy of diarylethane II, which itself was shown to undergo transaralkylation in the absence of a saturated hydrocarbon.

In connection with the reactions in Table III, certain minor points should be noted. Although the reactions were performed on a small scale and the data rounded off, the over-all balances were quite good in most cases. In certain of the more complex runs (expts. B-1 to B-4), the relationship of the yields of *m*-xylene and the tetraalkylbenzene were not as clear-cut as might be desired, and it is felt that this is in part due to secondary reactions of cation R' (equation 5). Even in the reaction of I with methylcyclohexene, it is somewhat surprising that R' did not react in part with the excess of I present in the reaction mixture.²³ Apparently the relatively stable R' can preferentially abstract a hydride from ethylarenes rather than alkylating them. One further point that cannot be readily explained is the apparent absence of ethyl group transfer in the reaction of III with methylcyclohexene. This may be due in large part to the fact that a relatively small quantity of IV was actually formed in the reaction, making the detection of transfer products difficult.

Substituent Effects on Transaralkylation of Diarylethanes. The results of the transaralkylation reactions of II suggested the possibility that the procedure might be used to estimate the effect of substituents in electrophilic displacements. Consequently, several other diarylethanes synthesized during the course of this study were subjected to hydrogen fluoride treatment. The results are given in Table III.

Transaralkylation of 1-phenyl-1-(2,4-dimethylphenyl)-ethane (V) proceeded to the extent of 10% of the charged V, and *m*-xylene was the exclusive mononuclear arene formed (expt. C). The recovered diarylethane cuts contained a small amount of an isomeric phenylxylylene, the infrared spectrum of which indicated it to be identical to that formed in expt. B-3. Chromatography of a high boiling cut yielded product corresponding to a triaryldiethane formed by α -phenylethylation of V, in an amount equimolar to *m*-xylene.

Acid treatment of 1-*p*-tolyl-1-(2-methyl-5-ethylphenyl)-ethane (VI) effected 20% cleavage of the latter with the ratio of *p*-ethyltoluene to toluene formed equal to 30 (expt. D). This explains why no toluene or its alkylation products were found in the previous studies^{4c,4d} of the hydrogen transfer reaction of *p*-alkyltoluenes.

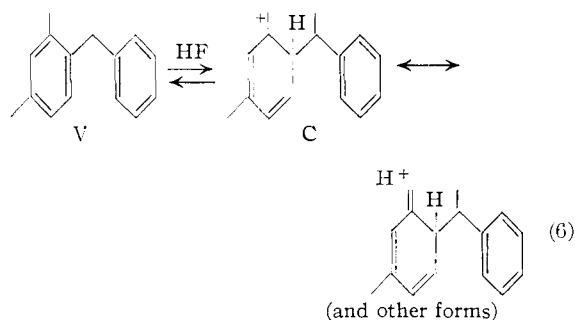
It was of interest to study the effects of an *o*- vs. a *p*-methyl group; to this end, 1-(3,4-dimethylphenyl)-1-(2,5-dimethylphenyl)-ethane (VII) was synthesized and subjected to cleavage. Although the ideal compound would be 1-*p*-tolyl-1-*o*-tolyl-ethane, identification would have necessitated labeling with radioactive carbon. Compound VII might be expected to react very much like the latter in the reaction under consideration, for presumably the substitution of a methyl group on each ring

(23) The experimental data preclude the presence of significant amounts of "cross-products" formed by condensation of arene A or B with R' or R, respectively.

meta to the ethylidene bridge should have little net effect on the cleavage ratio.

Compound VII, on contacting with hydrogen fluoride, underwent 10%²⁴ transaralkylation; ring A with the *o*-methyl substituent was attacked in 10:1 preference to the *p*-substituted ring B (expt. E). Only a trace of *m*-xylene was detected, indicating that isomerization during the reaction was negligible.

In the cleavage mechanism given for II in equations 4 and 5, it is evident that the course of the transaralkylation reaction depends on the relative stability of the σ -complexes formed in the protonation step. Thus, one would expect a predominance of *m*-xylene formation from V due to the possibility of simultaneous hyperconjugative stabilization of σ -complex C (equation 6), in contrast to the corresponding complex of the phenyl group, which lacks such stabilization. It was of interest



to attempt to correlate the cleavage ratios with the "partial relative basicities"²⁵ at the ethylidene bridge-substituted nuclear carbon atoms using the method of Condon²⁵ and "partial relative basicity" factors calculated by Brown and co-workers²⁶ from the data on the relative basicity of polymethylbenzenes in hydrogen fluoride.²⁷ The methyl values were used for the ethyl groups, which is a fair approximation, since the latter appear only at weakly activating *m*-positions in II and VI. The data are given in Table IV.

The data in Table IV show that the observed cleavage ratio and that calculated from basicity data are in good agreement for compounds II and V, but the correlation fails by a large margin for VI and VII. In the latter cases, the ring with a methyl group *ortho* to the reaction site is cleaved to a much greater extent than predicted from the calculations (such an effect would be undetectable with V due to the magnitude of the cleavage ratio). Such anomalous behavior of *o*-substituted compounds in electrophilic displacement reactions is not unique. It has been encountered previously in studies of the acid-catalyzed decarboxylation,²⁸

(24) Although all the transaralkylation reactions were carried out under the same conditions, the amount of acid in excess varied. Consequently, no conclusion could be drawn on the effect of structure on the extent of cleavage (which varied from 10–20%), for presumably solubility effects could alter the latter to some degree. Differences in solubility in hydrogen fluoride should not, however, affect the direction of cleavage significantly.

(25) F. E. Condon, *THIS JOURNAL*, **74**, 2528 (1952).

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

(27) M. Kilpatrick and F. E. Luborsky, *ibid.*, **75**, 577 (1953).

(28) W. M. Schubert, *ibid.*, **71**, 2639 (1949).

TABLE IV

CORRELATION OF CLEAVAGE RATIOS IN THE TRANSALKYLATION OF DIARYLETHANES

Compound	Structure ^a	Monocyclic cleavage products	Calcd. "part. rel. basicity" ratio A/B	Obsd. cleavage ratio A/B
V	V	<i>m</i> -C ₆ H ₄ (CH ₃) ₂	6.0 × 10 ⁴	All A
VI	VI	<i>p</i> -C ₂ H ₅ C ₆ H ₄ CH ₃ , C ₆ H ₅ CH ₃	1.3 (37) ^a	30
VII	VII	<i>p</i> -C ₆ H ₄ (CH ₃) ₂ , <i>o</i> -C ₆ H ₄ (CH ₃) ₂	0.35	10
II	II	I, <i>m</i> -C ₆ H ₄ (CH ₃) ₂ , 1,5-(CH ₃) ₂ -2,4-(C ₂ H ₅) ₂ C ₆ H ₂	3.6	5

^a Corrected for a single *o*-substituent on ring A by using the factor (10/0.35) derived from results with compound VII. ^b Although both arenes from ring B attack were isolated, values for the observed cleavage ratio were in quite good agreement in 4 reactions. ^c For structural formulas see Table III.

deacylation²⁹ and detrimethylsilylation³⁰ of substituted aromatic compounds.

In the case of VII, ring A with the *o*-methyl substituent was cleaved in 10:1 preference to the *p*-methyl-substituted ring B. This caused the observed ratio to be about 30 times greater than the calculated one. By application of this factor, the low value from VI gave a corrected ratio of 37, which is of the order of magnitude of the observed one. The use of the correction factor is justified in that the steric situation at the reaction site should be quite similar in VI and VII; consequently, any enhancement of cleavage by the relief of steric strain should be of the same magnitude in both cases.

It is seen that the general method shows some promise in competitive cleavages of variously substituted diarylalkanes in order to gain additional data on the relative steric and polar properties of functional groups in the reaction of electrophilic displacement by hydrogen.

In conclusion, the present results seem to favor a carbonium ion process for the transfer of α -arylethyl groups, in accordance with the view of Burwell and Shields³¹ on the mechanism of the transfer of secondary and tertiary alkyl groups. This would parallel the findings of Brown and co-workers³² on the mechanism of arene alkylation with alkyl halides. The recently suggested modification³³ of the McCaulay-Lien Sn² transalkylation mechanism³⁴ wherein a localized π -complex is proposed as the species involved in the rate-determining nucleophilic displacement step offers a more detailed picture of what may occur, but does not clearly explain why certain structural types of localized π -complexes can undergo hydride transfer with the solvent, while other types do not enjoy sufficient free carbonium ion character to allow rearrangement of the migrating group.

(29) W. M. Schubert and H. K. Labourette, *THIS JOURNAL*, **74**, 1829 (1952).

(30) R. A. Benkeser and H. B. Fryzak, *ibid.*, **76**, 6353 (1954).

(31) R. L. Burwell, Jr., and A. D. Shields, *ibid.*, **77**, 2766 (1955).

(32) H. Jungk, C. R. Smoot and H. C. Brown, *ibid.*, **78**, 2185 (1956).

(33) H. C. Brown and C. R. Smoot, *ibid.*, **78**, 2176 (1956).

(34) D. A. McCaulay and A. P. Lien, *ibid.*, **75**, 2411 (1953).

Experimental³⁵

I. The Reaction of 1,3-Dimethyl-4-ethylbenzene with 4-Methylcyclohexene in Hydrogen Fluoride. A. Synthesis of Reactants. 1. 1,3-Dimethyl-4-ethylbenzene (I).—2,4-Dimethylacetophenone was prepared from 3.80 moles of aluminum chloride, 3.50 mole of acetyl chloride and 3.00 moles of *m*-xylene (*n*_D²⁰ 1.4973, 98% purity estimated by infrared spectroscopy), using 1 l. of carbon disulfide as solvent. The ketone was obtained in 92% yield, b.p. 118–120° at 20 mm., *n*_D²⁰ 1.5342 (lit.³⁶ b.p. 92–94° at 5 mm., *n*_D²⁰ 1.5340). One ml. was subjected to hypodermic cleavage by a modification of the procedure of Shriner and Fuson³⁷; the product yielded white needles of 2,4-dimethylbenzoic acid, m.p. 123.5–125° (lit.³⁸ m.p. 126–127°), on recrystallization from Skellysolve C.

The ketone (202 g.) was hydrogenolyzed³⁹ in 200 ml. of pentane at about 180–200° and initial hydrogen pressure 132 atm. in the presence of copper oxide–alumina catalyst⁴⁰ (20 g.). The arene was obtained in 73% yield; redistillation through an efficient column afforded material boiling at 184.0–185.2° at 748 mm., *n*_D²⁰ 1.5029 (lit.⁴¹ b.p. 188.4° at 760 mm., *n*_D²⁰ 1.5038). The infrared spectrum was essentially identical to the published one (A.P.I. No. 738).⁴² The viscous bottoms from the initial distillation deposited 5 g. of crystals on standing. The crude solid was treated with Norit and recrystallized from pentane; it melted at 105–106°. This product may have arisen by hydrogenolysis of the dypnone condensation product of the ketone, leading ultimately to bis-1,3-(2,4-dimethylphenyl)-butane.

Anal. Calcd. for C₂₀H₂₆: C, 90.16; H, 9.84. Found: C, 90.58; H, 10.00.

2. 4-Methylcyclohexene.—The olefin was prepared by dehydration of 4-methylcyclohexanol on alumina at 420°. The product (77% yield) had b.p. 100–104°, *n*_D²⁰ 1.4418 (lit.^{43a} 102.7°, *n*_D²⁰ 1.4414), and its infrared spectrum was identical to the published one (A.P.I. No. 899).⁴²

B. The Alkylation Reaction.—The reaction was carried out by the previously described procedure,⁴⁴ using 134 g. (1.00 mole) of I and 48 g. (0.50 mole) of 4-methylcyclohexene in 125 g. of hydrogen fluoride. The organic product (174 g.) was subjected to a total of nine distillations using Vigreux, Podbielniak⁴⁴ Hypercal and Whirling Band and Piro-Glover⁴⁵ columns. The composition of the individual cuts was determined by infrared spectral analysis after the compounds were identified⁴⁶ and characterized as follows. Yield data are given in Table I.

1. Methylcyclohexane boiled at 41° at 98 mm. (99° cor. to 760 mm.), *n*_D²⁰ 1.4233 (lit.^{43b} b.p. 100.9°, *n*_D²⁰ 1.4231) (IR).

2. *m*-Xylene had b.p. 74.5° at 95 mm. (139° cor. to 760 mm.), *n*_D²⁰ 1.4893 (lit.^{43c} b.p. 139.1°, *n*_D²⁰ 1.4972) (IR). The index was lowered by the presence of 8% of methylcyclohexane as determined by infrared analysis. A sample

(35) Infrared spectral analyses were performed on a double beam recording infrared spectrophotometer (Baird Associates, Inc., Cambridge, Mass.) by the base-line method of N. Wright, *Ind. Eng. Chem., Anal. Ed.*, **13**, 1 (1941). Additional details and spectrograms of a number of the hydrocarbons used in this study are given in the Ph.D. thesis of J. T. Arrigo, Northwestern University Library.

(36) C. S. Marvel, J. H. Saunders and C. G. Overberger, *THIS JOURNAL*, **68**, 1085 (1946).

(37) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 138.

(38) N. A. Lange, "Handbook of Chemistry," 7th ed., Handbook Publishers, Inc., Sandusky, Ohio, 1949, p. 478.

(39) Hydrogenations were performed in a rotating autoclave or a Magne-Dash autoclave (Autoclave Engineers, Inc., Erie, Pa.).

(40) V. N. Ipatieff and V. Haensel, *THIS JOURNAL*, **64**, 520 (1942).

(41) S. F. Birch, R. A. Deau, F. A. Fidler and R. A. Lowry, *ibid.*, **71**, 1362 (1949).

(42) American Petroleum Institute Research Project 44, Catalog of Selected Infrared Absorption Spectrograms.

(43) (a) S. W. Ferris, "Handbook of Hydrocarbons," Academic Press, Inc., New York, N. Y., 1955, p. 150; (b) p. 151; (c) p. 152; (d) p. 180; (e) p. 158.

(44) Podbielniak, Inc., Chicago, Ill.

(45) H. S. Martin and Co., Evanston, Ill.

(46) The notation "IR" indicates that the infrared spectrum of the particular component was identical with that of an authentic reference sample.

was acetylated⁴⁷ and the 2,4-dinitrophenylhydrazone of the ketone prepared, m.p. 173–175° (lit.⁴⁷ 174.5–176°).

3. **Compound I** boiled at 117° at 94 mm. (186° cor. to 760 mm.), n_D^{20} 1.5033–1.5041. The infrared spectrum was almost identical to that of the starting material except for the presence of a weak band at 11.83 μ , probably due to slight isomerization to 1,3-dimethyl-5-ethylbenzene (lit.⁴⁸ analytical band 11.83 μ).

4. **1,5-Dimethyl-2,4-diethylbenzene** had b.p. 78.9° at 4.5 mm. (224° cor. to 760 mm.), n_D^{20} 1.5075, d_4^{20} 0.8818; MR_D calcd. 54.02, obsd. 54.82 (IR). The preceding intermediate cut contained a negligible amount of an isomeric arene with a very weak band at 11.70 μ , possibly 1,5-dimethyl-2,3-diethylbenzene.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 89.04; H, 11.09.

Nitration failed to yield a characterizable derivative, and acetylation gave a ketone which formed no 2,4-dinitrophenylhydrazone under ordinary conditions, in accordance with reported behavior of di-*o*-substituted acetophenones such as 2,6-dimethylacetophenone.¹⁰ Benzoylation yielded a white crystalline solid, m.p. 125–126.5° (IR). Oxidation⁴⁹ of 1 ml. of arene with dilute nitric acid in a sealed tube, followed by refluxing of the recrystallized acid 5 hours with 3 ml. of thionyl chloride (excess reagent was then distilled off), then esterification by refluxing 2 hours with 10 ml. of methanol, afforded, after the usual work-up, lustrous, white leaflets of tetramethyl pyromellitate, m.p. 143–143.5° (lit.⁵⁰ m.p. 143–144°).

Synthesis of 1,5-Dimethyl-2,4-diethylbenzene.—Acetylation of I (0.50 mole) was carried out with 0.58 mole of acetyl chloride and 0.64 mole of aluminum chloride in 167 ml. of carbon disulfide. The yield of ketone was 86%, b.p. 147.5–149° at 25 mm., n_D^{20} 1.5334; it formed white needles on cooling, m.p. 26.5–27° (lit.⁵¹ b.p. 140–150° at 20 mm., m.p. 27°). Hydrogenolysis of 0.18 mole of ketone in 30 ml. of pentane with 4 g. of copper oxide–alumina at 200–260° and initial hydrogen pressure 117 atm. gave a 10.2 g. (36%) yield of redistilled arene, b.p. 107° at 17 mm. (224° cor. to 760 mm.), n_D^{20} 1.5078, d_4^{20} 0.8793; MR_D calcd. 54.02, obsd. 54.86 (lit.⁵¹ b.p. 105° at 15 mm., which is 225° cor. to 760 mm.). Benzoylation afforded a white crystalline solid, m.p. 125–126.5°.

Anal. Calcd. for $C_{18}H_{22}O$: C, 85.66; H, 8.33. Found: C, 85.33; H, 7.97.

5. **Dimethyldicyclohexyl** boiled at 120–122° at 9 mm., n_D^{20} 1.4803, d_4^{20} 0.8806; MR_D calcd. 62.45, obsd. 62.69 (lit.⁴⁶ 96–98° at 5 mm., n_D^{20} 1.4860, d_4^{20} 0.8858). The cut contained olefinic components (see ethylmethylene section where dimers were further characterized).

6. **1,3-Dimethyl-5-(1-methylcyclohexyl)-benzene** had b.p. 137.5–140° at 8.5 mm., n_D^{20} 1.5254, d_4^{20} 0.9350; MR_D calcd. 65.67, obsd. 66.34. The infrared spectrum exhibited the characteristic pattern of a 1,3,5-trisubstituted benzene⁵² in the 5–6 μ region (IR).

Anal. Calcd. for $C_{15}H_{22}$: C, 89.04; H, 10.96. Found: C, 88.57; H, 10.90.

Acetylation yielded no characterizable product, but benzoylation gave lustrous white crystals, m.p. 80.5–82°.

Anal. Calcd. for $C_{22}H_{26}O$: C, 86.24; H, 8.55. Found: C, 86.61; H, 8.26.

Synthesis of 1,3-Dimethyl-5-(1-methylcyclohexyl)-benzene.—*m*-Xylene (0.10 mole) was alkylated with 0.050 mole of 4-methylcyclohexene in 5 g. of hydrogen fluoride. The cycloalkylate cuts were redistilled to yield 4.4 g. (44%) of arene, b.p. 154.5° at 26 mm., n_D^{20} 1.5257, d_4^{20} 0.9328; MR_D calcd. 65.67, obsd. 66.60. Benzoylation afforded lustrous white plates, m.p. 80–81°.

7. **1,5-Dimethyl-2-ethyl-4-(*x*-methylcyclohexyl)-benzene** had b.p. 142° at 4 mm., n_D^{20} 1.5332 (after chromatography

(47) H. Pines and A. Shaw, *J. Org. Chem.*, **20**, 373 (1955).

(48) R. B. Williams, S. H. Hastings and J. A. Anderson, Jr., *Anal. Chem.*, **24**, 1911 (1952).

(49) H. Pines, A. V. Grosse and V. N. Ipatieff, *This Journal*, **61**, 640 (1939).

(50) D. E. Read and C. B. Purves, *ibid.*, **74**, 116 (1952).

(51) E. Philippi, R. Seka and N. Froeschl, *Ann.*, **428**, 300 (1922).

(52) C. W. Young, R. B. DuVall and N. Wright, *Anal. Chem.*, **23**, 709 (1951).

on silica gel^{53–55}, d_4^{20} 0.9525; MR_D calcd. 74.91, obsd. 75.04. The infrared spectrum in the 5–6 μ region was not clearly defined enough to allow a choice between a 1,2,4,5- or 1,2,3,5-tetrasubstituted benzene structure.

Anal. Calcd. for $C_{17}H_{26}$: C, 88.62; H, 11.38. Found: C, 88.90; H, 10.98.

Acetylation, benzoylation, nitration and sulfonamide⁵⁶ and aroylbenzoic acid⁵⁷ preparation reactions all failed to yield a characterizable derivative. Oxidation with dilute nitric acid followed by esterification afforded a low yield of tetramethyl pyromellitate, m.p. 141.5–142.5°, mixed m.p. with the authentic sample prepared above was undepressed.

8. **1-(2,4-Dimethylphenyl)-1-(2,4-dimethyl-5-ethylphenyl)-ethane (II)** had b.p. 174° at 4 mm., n_D^{20} 1.5543, d_4^{20} 0.9682; MR_D calcd. 87.34, obsd. 88.22 (IR). The usual methods failed to yield characterizable derivatives of the diarylethanes encountered in this study.

Anal. Calcd. for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found: C, 90.35; H, 9.70.

Synthesis of II.—2,4-Dimethylbromobenzene was prepared⁵⁸ from 1.61 moles of *m*-xylene, 1.66 moles of bromine and 1 g. of iron powder. The product, 193 g. (64%; worked up according to the method of Smith⁵⁹), boiled at 105–106° at 33 mm. (205–206° cor. to 760 mm.), n_D^{20} 1.5514, d_4^{20} 1.361; MR_D calcd. 43.31, obsd. 43.41 (lit.⁶⁰ b.p. 205–207°). Oxidation⁶¹ of the halide with chromic acid yielded 4-bromo-3-methylbenzoic acid, m.p. 207–208° (lit.⁶² m.p. 209°).

Compound IIa was prepared by condensing the above halide with 2,4-dimethyl-5-ethylacetophenone by the Grignard method and also by the addition of the aryllithium compound to the ketone. The yields of carbinol were 15 and 47%, respectively (Tables V–VII). While dehydration and subsequent selective hydrogenation of the resulting diarylethene were facile, it was found to be more convenient to hydrogenolyze the carbinol directly (76% yield) to II.

9. **Isomeric Diarylethanes.**—In the diaryl boiling range, two compounds presumably isomeric to II were detected in minor amounts. The higher boiling one was found chiefly in a cut of b.p. 184° at 3.5 mm., n_D^{20} 1.5452, d_4^{20} 0.9546; MR_D calcd. 87.34, obsd. 88.28. The main band of II at 12.22 μ was present only to a small extent in the infrared spectrum of this cut, while a medium intensity 11.84 μ band characteristic of the isomer also was exhibited.

Anal. Calcd. for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found: C, 90.30; H, 10.09.

The lower boiling compound was found in highest concentration in a cut having b.p. 167° at 4.5 mm., n_D^{20} 1.5536, d_4^{20} 0.9716; MR_D calcd. 87.34, obsd. 87.82. Chromatography yielded a purified fraction (n_D^{20} 1.5548) which exhibited infrared bands of rather low intensity at 11.70 and 11.80 μ , and a sharper, more intense characteristic band at 12.20 μ .

Anal. Calcd. for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found: C, 90.09; H, 10.09.

In order to exclude the possibility that the lower boiling compound was bis-1,1-(2,4-dimethylphenyl)-ethane (VIII) the latter was synthesized by the usual methods (Tables V–VII). The infrared spectrum of VIII had a main band at 12.27 μ , with a medium intensity band at 11.50 μ , and was readily distinguishable from that of the unidentified lower boiling compound above.

(53) B. J. Mair and A. F. Forziatti, *J. Research Natl. Bur. Standards*, **32**, 151, 165 (1944).

(54) B. J. Mair, *ibid.*, **34**, 435 (1945).

(55) B. J. Mair, J. W. Westhaver and F. D. Rossini, *Ind. Eng. Chem.*, **42**, 1279 (1950).

(56) Reference 37, p. 194.

(57) N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," Thomas Y. Crowell Co., New York, N. Y., 1947, p. 316.

(58) Ng. Ph. Buu-Hoi and P. Cagniant, *Bull. soc. chim.*, [5] **10**, 151 (1943).

(59) L. I. Smith, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 95.

(60) Reference 38, p. 405.

(61) Reference 37, p. 198.

(62) I. M. Heilbron, "Dictionary of Organic Compounds," Vol. I, Oxford University Press, New York, N. Y., 1934, p. 207.

TABLE V
 SYNTHESSES OF 1,1-DIARYLETHANOLS

Halide	Reactants	Ketone	Carbinol, ^a ethanol	Yield, %	B.P., °C.	Mm.	n_D^{20}
Bromobenzene		2,4-Dimethylacetophenone	1-Phenyl-1-(2,4-dimethylphenyl)- (Va)	43 ^c
2,4-Dimethylbromobenzene		2,4-Dimethylacetophenone	Bis-1,1-(2,4-dimethylphenyl)- (VIIIa)	6 ^c
2,5-Dimethylbromobenzene		3,4-Dimethylacetophenone	1-(3,4-Dimethylphenyl)-1-(2,5-dimethylphenyl)- ^{d,e} (VIIa)	70	164-165	3	1.5746
2,4-Dimethylbromobenzene		2,4-Dimethyl-5-ethylacetophenone	1-(2,4-Dimethylphenyl)-1-(2,4-dimethyl-5-ethylphenyl)- ^{d,f} (IIa)	15	183	4	1.5673

^a Synthesized from equimolar amounts of organic reactants on a 0.2-0.5 mole scale by the Grignard method. ^b Based on ketone charged. ^c Although the products were hydrolyzed with aqueous ammonium chloride and distilled from a small amount of potassium carbonate, partial dehydration occurred and the yields of crude carbinol are approximate. ^d Carried out under nitrogen using lithium rather than magnesium. No density was determined on the extremely viscous carbinol. ^e Calcd. for C₁₈H₂₀O: C, 85.00; H, 8.72. Found: C, 85.12; H, 8.29. ^f Obsd. d_{20}^{25} 1.003; *M*R_D calcd. 88.86, obsd. 92.01. The infrared spectrum indicated the presence of a small amount of olefin. Calcd. for C₂₀H₂₆O: C, 85.08; H, 9.28. Found: C, 85.68; H, 8.88. ^g The organolithium method afforded a 47% yield of IIa, n_D^{20} 1.5644.

 TABLE VI
 SYNTHESSES OF 1,1-DIARYLETHENES

Carbinol charged	Product, ^a ethene	Yield, %	B.P., °C.	Mm.	n_D^{20}	d_{20}^{25}	<i>M</i> R _D obsd.	Analyses, % found	C	H
Va	1-Phenyl-1-(2,4-dimethylphenyl)- ^c (Vb)	89	136	5	1.5896	0.9886	71.07	92.32	7.47	
VIIIa	Bis-1,1-(2,4-dimethylphenyl)- ^d (VIIIb)	84	147	4	1.5796	0.9784	80.15	91.87	8.51	
VIIa	1-(3,4-Dimethylphenyl)-1-(2,5-dimethylphenyl)- ^d (VIIb)	92	147-148	3	1.5859	0.9780	81.16	91.62	8.32	
IIa	1-(2,4-Dimethylphenyl)-1-(2,4-dimethyl-5-ethylphenyl)- ^e (IIb)	85	178	8	1.5747	0.9673	90.26	91.05	8.69	

^a The carbinols were dehydrated with anhydrous oxalic acid in refluxing benzene. ^b Based on carbinol charged. ^c Calcd. for C₁₆H₁₆: C, 92.26; H, 7.74; *M*R_D 68.43. ^d Calcd. for C₁₈H₂₀: C, 91.47; H, 8.53; *M*R_D 77.67. ^e Calcd. for C₂₀H₂₄: C, 90.85; H, 9.15; *M*R_D 86.87.

 TABLE VII
 SYNTHESIS OF 1,1-DIARYLETHANES

Olefin charged	Product, ^a ethane	Yield, %	B.P., °C.	Mm.	n_D^{20}	d_{20}^{25}	<i>M</i> R _D obsd.	Analyses, % found	C	H
Vb	1-Phenyl-1-(2,4-dimethylphenyl)- ^{d,e} (V)	76	142	5	1.5663	0.9806	70.03	91.71	8.21	
VIIIb	Bis-1,1-(2,4-dimethylphenyl)- ^{e,f} (VIII)	40	140-142	3.5	1.5613	0.9690	79.65	91.14	9.42	
VIIb	1-(3,4-Dimethylphenyl)-1-(2,5-dimethylphenyl)- ^e (VII)	95	145-146.5	3	1.5630	0.9680	80.10	90.77	9.03	
IIb	1-(2,4-Dimethylphenyl)-1-(2,4-dimethyl-5-ethylphenyl)- ^{e,h} (II)	56	147-148.5	1	1.5567	0.9403	89.27	90.54	9.84	

^a The olefins were hydrogenated with copper chromite in pentane at 125-170° and 80-130 atm. initial hydrogen pressure. ^b Based on olefin charged. ^c Calcd. for C₁₆H₁₈: C, 91.38; H, 8.62; *M*R_D 68.90. Chromatography of the amorphous 2,4-dinitrophenylhydrazone of the acetylated V failed to give any crystalline derivative. ^d "1-Phenyl-1-*m*-xylylene" has been reported to have b.p. 150-160° at 10 mm., n_D^{20} 1.5590 and d_{20}^{25} 0.9801; L. N. Petrova and O. V. Shvarts, *J. Gen. Chem. (U.S.S.R.)*, **20**, 2168 (1950); *C. A.*, **45**, 7075 (1951). ^e Calcd. for C₁₈H₂₂: C, 90.69; H, 9.31; *M*R_D 78.14. ^f R. Anschutz, *Ann.*, **235**, 299 (1886), reported b.p. 169-172° at 11 mm., d_{20}^{25} 0.966. ^g Calcd. for C₂₀H₂₆: C, 90.16; H, 9.84; *M*R_D 87.34. ^h II was also made in 76% yield by the hydrogenolysis of carbinol IIa in absolute ethanol with copper chromite at 220-240° and 110 atm. initial hydrogen pressure.

10. Higher boiling products above the diaryl range were assumed to be mainly cycloalkylated diaryl isomers along with minor amounts of methylcyclohexene polymers.

11. The Reaction of Ethylmesitylene with 4-Methylcyclohexene in Hydrogen Fluoride. A. Synthesis of Ethylmesitylene (III).—A commercial mesitylene sample was obtained and infrared analysis showed it to contain 68% mesitylene⁶³ accompanied by the isomeric ethyltoluenes and trimethylbenzenes. Hypercal fractionation over sodium yielded distillate equal to 90 wt.-% of the charge, boiling 163.0-165.5°. Rather than purification through mesitylenesulfonic acid,⁶⁴ an alternate method was used. Five small-scale alkylations were carried out using 0.10 mole of an impure cut containing 90% mesitylene, 0.050 mole of olefin and 6-10 g. of hydrogen fluoride, with 1 hour stirring time. The composition of the recovered C₉-arene distillation cuts was determined by infrared analysis. The results are summarized in Table VIII.

(63) A reference sample of 99.7% pure mesitylene was obtained through the courtesy of the Indol Chemical Co., Chicago, Ill.

(64) L. I. Smith and O. W. Cass, *This Journal*, **64**, 1603 (1932).

 TABLE VIII
 PURIFICATION OF MESITYLENE

Olefin used	Recov. C ₉ -range cuts, wt.-% ^a	Purity of recov. C ₉ -cuts
Cyclohexene	38	Isomeric C ₉ -arenes removed
4-Methylcyclohexene	48	^b
4-Methylcyclohexene ^c	54	...
Diisobutylene	67	^{b,d}
Isobutylene	61	^b

^a Based on weight of impure arene charged. ^b Isomeric arenes essentially completely removed. ^c Purified mesitylene was charged. ^d C₉ cuts contaminated by minor amounts of non-aromatic impurities.

Since isobutylene gave the highest yield of uncontaminated mesitylene, it was used in the large-scale purification. The remaining Hypercal cuts (256 g., 73% mesitylene) were combined and treated with 1.07 moles of isobutylene in the

presence of hydrogen fluoride (5 moles). The product (284 g. after work-up) was roughly distilled and all mesitylene-containing fractions were combined (184 g.) and fractionated through the Hypercal. The purified mesitylene (151 g., 59%) was used in the synthesis below (IR).

2,4,6-Trimethylacetophenone was prepared by a modification of the method of Noller and Adams.⁶⁵ It was obtained in 83% yield, b.p. 133–134° at 31 mm., n_D^{20} 1.5169 (lit.⁶⁶ b.p. 134.5–135° at 31 mm., n_D^{20} 1.5158). The ketone (160 g., 0.99 mole) was hydrogenolyzed at 190–215° with 15 g. of copper chromite and initial hydrogen pressure of 119 atm. The purified III boiled at 121–123° at 47 mm. (211–213° cor. to 760 mm.), n_D^{20} 1.5102 (lit.^{43d} b.p. 212.4°, n_D^{20} 1.5074) and amounted to 89 g. (62% yield).

The bottoms from the initial rough distillation was fractionated to yield 19.4 g. (12%) of methylmesitylcarbinol, b.p. 120–123.5° at 8 mm., m.p. after recrystallization from ethanol 71.5–73° (lit.⁶⁷ b.p. 93° at 2 mm., m.p. 72–72.5°).

B. The Alkylation Reaction.—Arene III (89 g., 0.60 mole), 4-methylcyclohexene (28.8 g., 0.30 mole) and hydrogen fluoride (75 g.) were contacted and worked up following the usual procedure, yielding 111 g. of product. Five distillations and subsequent infrared analysis allowed the identification of the following products. Yield data are given in Table I.

1. Methylcyclohexane boiled at 98–102°, n_D^{20} 1.4220–1.4232 (IR).

2. Compound III had b.p. 136° at 85 mm. to 83° at 9 mm. (210–212° cor. to 760 mm.), n_D^{20} 1.5091–1.5103; no isomerization was detected (IR).

3. Methylcyclohexene dimers were separated into two types by chromatography of cuts boiling in the range of 104° at 5 mm. to 128° at 4 mm., n_D^{20} 1.4881 and 1.4948. The saturated dimer had n_D^{20} 1.4777, d_4^{20} 0.8750; *MRD* calcd. 62.45, obsd. 62.86. The unsaturated dimer was more strongly adsorbed on silica gel, but yielded no index plateau. The separations were conveniently followed by the permanganate test for unsaturation.⁶⁸ Approximately equal amounts of both types were found to be present. The cuts had n_D^{20} 1.5023–1.5067 and were distilled free of solvent to yield the main portion with n_D^{20} 1.5032, d_4^{20} 0.9010; *MRD* calcd. 61.98, obsd. 63.15. The infrared spectrum indicated the presence of a *cis*-disubstituted double bond absorbing at 14.24 μ .⁶⁹

4. 1,3,5-Trimethyl-2-ethyl-4-(*x*-methylcyclohexyl)-benzene boiled at 155–158.5° at 3 mm. and after chromatographic removal of cycloolefinic impurities, an analytical sample had n_D^{20} 1.5383, d_4^{20} 0.9824; *MRD* calcd. 74.32, obsd. 77.85.

Anal. Calcd. for $C_{18}H_{22}$: C, 88.46; H, 11.54. Found: C, 88.20; H, 11.40.

Nitration yielded no characterizable derivative.

5. Methylcyclohexene trimers boiled chiefly at 158.5–181° at 3 mm., n_D^{20} 1.5247–1.5291. Chromatography of the lower index cut yielded a small saturated cut, n_D^{20} 1.5038, followed by 8 cuts with n_D^{20} increasing to 1.5307, which gave positive permanganate tests. The infrared spectrum of the first cut resembled that of dimethylcyclohexyl, while subsequent fractions exhibited a 14.14 μ band due to *cis*-disubstituted olefins.

6. 1-(2,4,6-Trimethylphenyl)-1-(2,4,6-trimethyl-3-ethylphenyl)-ethane (IV) was found in highest concentration in a cut boiling at 181–196° at 3 mm., n_D^{20} 1.5410. Chromatography of the 1.96-g. cut freed it of olefin trimer and IV was desorbed; it was mixed with absolute ethanol in the later fractions. These were freed of solvent and had n_D^{20} 1.5502–1.5521 (negative test for unsaturation). Stirring with cold absolute ethanol caused a solid to deposit, which, after decolorization with Norit and several recrystallizations from ethanol, yielded white needles, m.p. 78.5–79.0°. The infrared spectrum (carbon disulfide solvent) was identical to that of the authentic sample described below, and a mixed melting point with the latter was undepressed.

Anal. Calcd. for $C_{22}H_{30}$: C, 89.74; H, 10.26. Found: C, 89.31; H, 10.08.

(65) C. R. Noller and R. Adams, *THIS JOURNAL*, **46**, 1889 (1924).

(66) R. T. Morrison and M. Wishman, *ibid.*, **76**, 1059 (1954).

(67) D. V. Nightingale and H. D. Radford, *J. Org. Chem.*, **14**, 1089 (1949).

(68) V. N. Ipatieff, W. W. Thompson and H. Pines, *THIS JOURNAL*, **70**, 1658 (1948).

(69) H. L. McMurry and V. Thornton, *Anal. Chem.*, **24**, 318 (1952).

Synthesis of IV.—Arene III (0.35 mole) was stirred with methylmesitylcarbinol (0.12 mole) in the presence of 84 g. of hydrogen fluoride by the usual procedure. The worked-up, blue fluorescent organic product yielded 90% of unreacted arene along with a small amount of mesitylene, 8.75 g. of high-boiling, viscous liquid and 6 g. of resinous bottoms. The product cuts were carefully refractionated and the lower boiling fractions (158–181° at 1 mm., n_D^{20} 1.5638–1.5658) gave a positive test for unsaturation. Their infrared spectra had bands at 10.40, 11.24, 12.54 and 14.29 μ and a main 11.75 μ band. These were consistent with olefin structures of the type formed by dimerization of the substituted styrene arising by dehydration of the carbinol, *i.e.*, 1,3-bis-mesityl-*x*-butenes. The cuts boiling at 181–185° at 1 mm., n_D^{20} 1.5651, were chromatographed and deposited crystals on standing. Filtration after cooling yielded a filtrate which gave a positive test for unsaturation. Decolorization and recrystallization of the solid gave about 0.5 g. of white needles, m.p. 78.5–79° (negative test for unsaturation). The infrared spectrum had main bands at 11.55 and 11.82 μ . Nitration failed to yield a crystalline derivative.

7. Higher boiling products above the diaryl range gave a positive test for unsaturation, and after infrared examination it was concluded that they consisted mainly of methylcyclohexene polymers.

III. Transaralkylation of Diarylethanes and Related Reactions.—The reactions were carried out on a small scale in a 75-ml. polyethylene bottle equipped with small bore polyethylene addition and vent tubes and a stainless steel stirrer in a bored Teflon stopper. The reactants and hydrogen fluoride were stirred for one hour at ice-bath temperatures and the mixtures were worked up as usual using pentane solvent to minimize losses.

A. Mononuclear Arenes in Hydrogen Fluoride. 1. 1,3-Dimethyl-4-ethylbenzene (I), 20 g., and 28 g. of hydrogen fluoride yielded 13.9 g. of recovered product, b.p. 181–182°, n_D^{20} 1.5033–1.5037. Its infrared spectrum was identical to that of the charged arene.

2. 1,5-Dimethyl-2,4-diethylbenzene, 2.0 g., was treated with 5 g. of hydrogen fluoride. The recovered product (1.15 g.) had b.p. 112° at 22 mm. (223° cor. to 760 mm.), n_D^{20} 1.5073, and its infrared spectrum indicated that apparently minor isomerization occurred (weak 12.74 μ band), but no 1,3-dimethyl-4-ethylbenzene could be detected.

B. 1-(2,4-Dimethylphenyl)-1-(2,4-dimethyl-5-ethylphenyl)-ethane (II) Reactions.—1. Compound II (9.32 g., 35 mmol.), was treated with 8 g. of hydrogen fluoride and the deep pink complex, after working up, yielded 7.51 g. of recovered arenes (see Table IX for product distribution).

The triaryldiethane components were extremely viscous and strongly blue fluorescent under ultraviolet light (probably due to the presence of small amounts of condensed ring aromatics) and boiled in the range of 211–216° at 1 mm. Chromatography on silica gel (using benzene solvent and absolute ethanol as desorbing agent) yielded center cuts having n_D^{20} 1.5713. The infrared spectrum was qualitatively very similar to that of II.

Anal. Calcd. for $C_{30}H_{38}$: C, 90.39; H, 9.61. Found: C, 90.04; H, 9.30.

2. Compound II (20.0 g., 75 mmol.), 3.6 g. (37 mmol.) of 4-methylcyclohexene and 5 g. of hydrogen fluoride yielded 22.6 g. of product which was first roughly distilled and the cuts subjected to three careful fractionations. The results are given in Table IX.

3. Compound II (6.0 g., 22 mmol.), 7.5 g. (96 mmol.) of benzene and 8 g. of hydrogen fluoride yielded the products listed in Table IX. Phenylxylylethane cuts were combined and redistilled to give a heart cut boiling at 138–142° at 5 mm., n_D^{20} 1.5577. The infrared spectrum was qualitatively identical to that of authentic V (synthesis and physical constants given in Tables V–VII), having main bands at 12.18 and 14.35 μ . There was one significant difference in that the spectrum exhibited a weak 11.78 μ band absent from that of the reference sample (see part C below).

4. Compound II (4.72 g., 18 mmol.), 1.74 g. (18 mmol.) of methylcyclohexane and 12 g. of hydrogen fluoride gave 4.85 g. of distilled product (Table IX). No cuts of n_D^{20} greater than 1.5546 were obtained, hence little or no formation of tricyclics occurred.

C. 1-Phenyl-1-(2,4-dimethylphenyl)-ethane (V) in Hydrogen Fluoride.—Compound V (13.5 g., 64 mmol.), was treated with 8 g. of hydrogen fluoride and afforded 11.6 g.

of distillate composed of the following products: *m*-xylene (7 mmol.), V recovered (49 mmol.) and triaryls (7 mmol.). Recovered V had b.p. 144–150° at 7 mm., n_D^{20} 1.5640–1.5657. Its infrared spectrum was identical to that of the starting material except for a relatively weak 11.78 μ band which decreased in intensity in the higher boiling cuts.

TABLE IX
REACTIONS OF II IN HYDROGEN FLUORIDE
Experiment B

Product (mmol. ^a)	1	2 ^b	3	4 ^c
<i>m</i> -Xylene	0.1	..	0.6	2
1,3-Dimethyl-4-ethylbenzene (I)	5 ^d	13	3	9
1,5-Dimethyl-2,4-diethylbenzene	1	3	0.2	0.7
1,3-Dimethyl-5-(1-methylcyclohexyl)-benzene	..	3	..	0.2
1,5-Dimethyl-2-ethyl-4-(<i>x</i> -methylcyclohexyl)-benzene	..	9	..	3
II recovered	21 ^e	50	14	11
Methylcyclohexyl-(II)	..	6
Triaryldiethanes	7	6
1-Phenyl-1-(2,4-dimethylphenyl)-ethane (V)	3 ^f	..

^a Products on loss-free basis except in expt. B-3. ^b One mmol. of methylcyclohexene dimer also formed. ^c Methylcyclohexane (12 mmol.) was recovered. ^d Contained a small amount of the 5-ethyl isomer. ^e A minor amount of II underwent isomerization. ^f Includes a small amount of the 3,5-dimethyl isomer.

It is probable that some isomerization to 1-phenyl-1-(3,5-dimethylphenyl)-ethane occurred, the latter being responsible for the appearance of the 11.78 μ band (1,3,5-trisubstituted arenes are known to have bands in the 11.75–12.05 μ region⁶⁹). The triaryl components boiled about 185° at 2 mm.; chromatography yielded purified material having n_D^{20} 1.5858. It was of interest that the infrared spectrum had a 5–6 μ pattern resembling that of a monosubstituted arene.

Anal. Calcd. for C₂₄H₂₆: C, 91.66; H, 8.34. Found: C, 91.70; H, 8.35.

D. Synthesis and Cleavage of 1-*p*-Tolyl-1-(2-methyl-5-ethylphenyl)-ethane (VI). 1. **Synthesis of VI.**—*p*-Methylacetophenone was prepared in 77% yield by the acetylation of toluene⁴⁶; it had b.p. 116–118° at 27 mm., n_D^{20} 1.5342 (lit.⁴⁶ b.p. 108° at 18 mm., n_D^{20} 1.5348). The ketone was hydrogenolyzed in pentane at 230–260° and 101 atm. initial hydrogen pressure. Hypercal redistillation

afforded a 78% yield of *p*-ethyltoluene, b.p. 161–162°, n_D^{20} 1.4948 (lit.⁴⁶ b.p. 162.0°, n_D^{20} 1.4950), essentially free of the small amounts of *o*- and *m*-isomers (main bands at 13.27 and 12.80 μ ,⁴⁸ respectively) initially detected in the roughly distilled product.

The reaction of *p*-ethyltoluene (60 g., 0.50 mole) with 4-methylcyclohexene (38.4 g., 0.40 mole) in the presence of 104 g. of hydrogen fluoride was carried out and the products isolated as previously reported.⁴⁶ The physical constants of the individual products corresponded well with the recorded values.⁴⁶ The following distribution was obtained (with moles in parentheses): methylcyclohexane (0.16), toluene (0.0032), *p*-ethyltoluene (0.20), dimethylcyclohexyl (0.028), mono-unsaturated methylcyclohexene dimer (0.013), 4-ethyl-2-(*x*-methylcyclohexyl)-toluene (0.074), VI (0.080), methylcyclohexyl derivative of VI (0.031) and triaryls (0.016). The infrared spectrum of VI was identical to the published one.⁴⁶

2. **VI in Hydrogen Fluoride.**—Compound VI (11.9 g., 50 mmol.) was stirred with 8 g. of hydrogen fluoride and yielded the following products (total 10.9 g.): toluene (0.3 mmol.), *p*-ethyltoluene (10 mmol.), VI recovered (34 mmol.) and triaryls (7 mmol.). No isomerization of *p*-ethyltoluene or VI was detected. The highest boiling fraction (160–195° at 1 mm., n_D^{20} 1.5693) deposited a minute amount of yellow solid which melted in the range of 136–145° after recrystallization from ethanol. It was intensely yellow fluorescent in ultraviolet light and its infrared spectrum exhibited a strong 12.56 μ band (carbon disulfide solvent). The small amount precluded any further characterization of this compound which was probably an alkylanthracene. Chromatography of the distillation bottoms (n_D^{20} 1.582) failed to effect any separation of the triaryl components.

E. Synthesis and Cleavage of 1-(3,4-Dimethylphenyl)-1-(2,5-dimethylphenyl)-ethane (VII). 1. **Synthesis of VII.**—The compound was prepared in good over-all yield via the organolithium method followed by the usual steps (Tables V–VII).

2. **VII in Hydrogen Fluoride.**—Compound VII (23.8 g., 100 mmol.) was stirred with 10 g. of hydrogen fluoride and yielded 22.9 g. of distilled product consisting of the following compounds: *o*-xylene (0.8 mmol.), *p*-xylene (9 mmol.), VII recovered (79 mmol.) and bis-(α -xylylethyl)-xylenes (10 mmol.). Only a trace of *m*-xylene was detected in the xylene fraction and recovered VII cuts had infrared spectra identical to that of the starting material. The triaryl cut boiled at 190–195° at 1 mm. and the chromatographed material had n_D^{20} 1.5842. Its infrared spectrum strongly resembled that of VII.

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Base-catalyzed Hydrocarbon Cleavage Reactions: A Novel Wurtz-type Reaction^{1,2}

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The major products of the reaction of 3-methyl-3-phenyl-1-chlorobutane with potassium were found to be 2,5-dimethyl-2,5-diphenylhexane and ethylene which were formed by an elimination reaction followed by a Wurtz-type condensation. 3-Phenyl-1-chloropropane gave a much smaller yield of 1,4-diphenylbutane. Diarylalkanes such as 2-methyl-2,4-diphenylpentane and 2-methyl-2-phenyl-4-*p*-tolylpentane were cleaved by potassium at 180° to yield cumene and cumene with *p*-cymene, respectively, but were not cyclized to form indans. The mechanisms of the reactions are discussed.

The potassium-catalyzed ethylation of arylalkanes was previously reported to yield indans in addition to the expected ethylated products.⁴ These probably were formed by the attack of the primary carbanion produced in the reaction on the aromatic nucleus as illustrated for the reaction of cumene.

In the course of the investigation of the cyclization reaction, 3-methyl-3-phenyl-1-chlorobutane (VI) was treated with potassium in refluxing cyclo-

tion to the expected ethylated products.⁴ These probably were formed by the attack of the primary carbanion produced in the reaction on the aromatic nucleus as illustrated for the reaction of cumene.

In the course of the investigation of the cyclization reaction, 3-methyl-3-phenyl-1-chlorobutane (VI) was treated with potassium in refluxing cyclo-

(1) Paper XIV of the series of Base-catalyzed Reactions. For paper XIII see H. Pines and L. Schaap, *THIS JOURNAL*, **80**, 3076 (1958).

(2) Taken in part from a dissertation submitted by L. Schaap in partial fulfillment of the requirements for the Ph.D. degree, August, 1957.

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(4) L. Schaap and H. Pines, *THIS JOURNAL*, **79**, 4967 (1957).