its methioide which, after two recrystallizations from acetonitrile–ether, melted at 263–264°.

Anal. Calcd for $C_{23}H_{30}INO$: C, 61.60; H, 6.20; N, 2.87. Found: C, 61.77; H, 6.13; N, 2.93.

Cyclization of methiodide XV was effected by treating 9.75 g (0.02 mole) of XV with silver oxide essentially as described for the methiodide of 2-(dimethylaminomethyl)triphenylmethanol.[24] The oily residue resisted crystallization and was chromatographed on alumina eluted with hexane. Removal of solvent afforded, after recrystallization from hexane, 1.15 g (20%) of 3,4-dimethyl-1,1-diphenylphthalan (XVI), mp 105.5–106.5°. The infrared spectrum of XVI exhibited a peak for a cyclic ether[25] at 1010 cm^{-1} and peaks at 813, 759, and 799 cm^{-1}, consistent with the structure having two and five adjacent aromatic hydrogens.[7] The nmr spectrum of XVI showed singlets at 126 and 134 ± 1 cps, assigned to the ring methyl protons, and at 303 ± 1 cps, assigned to the benzylic protons. The aromatic multiplet was centered at approximately 430 cps.

Anal. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 88.00; H, 6.67.

(24) R. L. Vaulx, R. N. Jones, and C. R. Hauser, *J. Org. Chem.*, **29**, 505 (1964).

(25) See ref 7, p 119.

The Migration Aptitude of Substituted Benzyl *vs.* Methyl in Carbonium Ion Reactions of the 2,2-Dimethyl-3-aryl-1-propyl System. The Question of Alkyl Participation[1]

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Abstract: A series of 2,2-dimethyl-3-(*p*-X-phenyl)-1-propyl *p*-toluenesulfonates (X = CH_3O, CH_3, H, Cl, CF_3) was prepared and subjected to solvolysis in acetic and formic acids. The rates of solvolysis were determined along with the yields of methyl- and benzyl-migrated products. Methyl migrated faster than benzyl in all cases, but the methyl:benzyl migration aptitude (corrected for the statistical factor) varied from 4.6 for X = CF_3 down to 1.4 for X = CH_3O in acetic acid at 109.58°, and a similar variation was noted in formic acid. The rates also varied with the substituent, being about four times faster for X = CH_3O than for X = CF_3. The rates, migration aptitudes, and partial rate factors for methyl and benzyl migration all follow the Hammett equation. Earlier results on the migration aptitude of unsubstituted benzyl were shown to be too high. Whether the ionization and rearrangement are concerted or stepwise is discussed. While firm conclusions cannot be drawn, the concerted process seems more likely.

We undertook a study of relative migration aptitudes of methyl and substituted benzyl groups as a continuation of earlier work on methyl *vs.* benzyl[2] and methyl *vs.* phenyl[3] migration aptitudes in neopentyl-like systems. The substituted benzyl group offered the opportunity of varying the electronic character of an alkyl group without simultaneously changing its steric requirements. We also hoped that a careful study of the relation between rate and migration aptitude would permit a decision on whether the ionization and migration were stepwise or concerted.

Results

The starting materials (I; see Scheme I) were easily prepared from the appropriate benzyl halide and methyl isobutyrate with sodium hydride,[2,4] followed by reduction and tosylation. The major synthetic task was preparation of reference samples of the expected products.

The esters IV and V are expected from capture of solvent by the carbonium ions II and III, and our earlier work[2] revealed that VIII is also produced, presumably by addition of solvent to the conjugated olefin from II. The alcohols corresponding to IV, V, and VIII were obtained by Grignard additions which, in most cases, employed readily available starting materials. Details are given in the Experimental Section.

Our former studies on Ic employed analysis of the rearranged olefin mixture as a part of the determination of product proportions.[2] Reduction of the olefins to the alkylbenzenes VI and VII had seemed a very attractive way of simplifying the analytical problem, but we found no way of separating VI and VII. In the present work, we found several gas chromatographic columns capable of separating VI and VII (see the Experimental Section). Authentic samples were readily prepared by dehydrating the alcohols corresponding to IV and V and hydrogenating the resulting olefin mixtures.

Some difficulty was encountered in preparing VId and VIId, for the hydrogenation conditions (palladium on charcoal in ethanol) partially dechlorinated the aromatic ring. A pure sample of VId was obtained by gas chromatography and of VIId by Wolff–Kishner reduction of 3-methyl-1-(*p*-chlorophenyl)-2-butanone. Rather than suffer the complication of a four-component hydrocarbon mixture, however, we usually converted the olefin mixture obtained in the solvolyses to VIc and VIIc by hydrogenation over palladium on charcoal in alkaline ethanol. This procedure gives quantitative dechlorination.

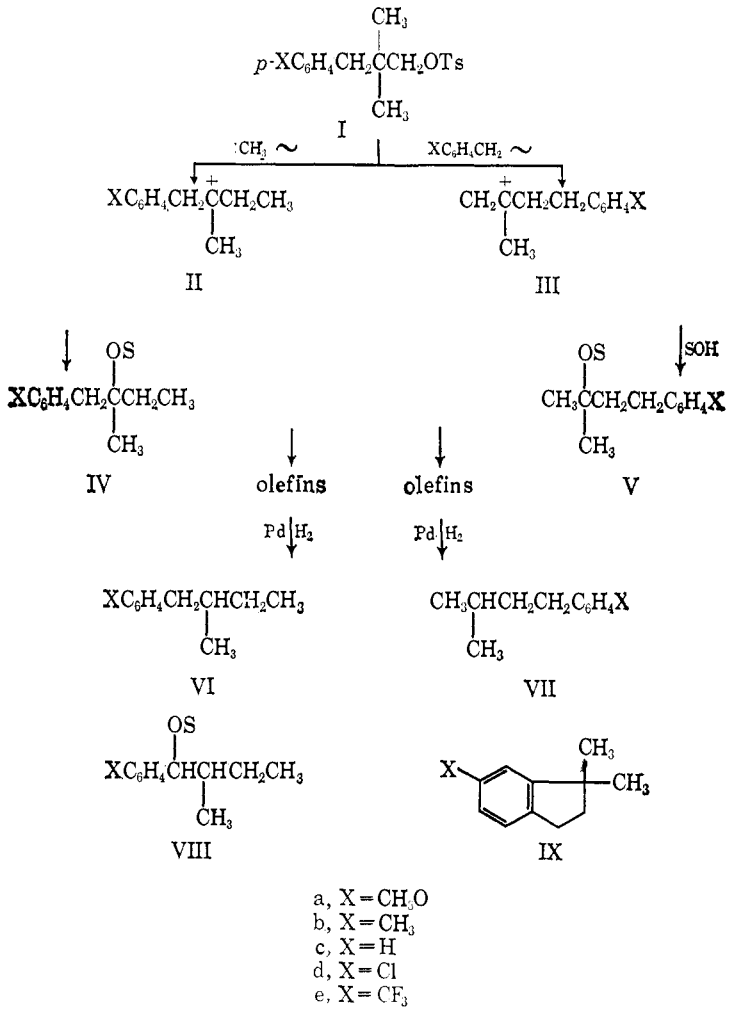
(1) This work was supported by the U. S. Army Research Office (Durham). J. R. O. received an American Cyanamid Fellowship in 1963–1964, and an Eastman Kodak Award in 1963.

(2) P. Warrick, Jr., and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **84**, 4095 (1962).

(3) W. H. Saunders, Jr., and R. H. Paine, *ibid.*, **83**, 882 (1961).

(4) B. E. Hudon and C. R. Hauser, *ibid.*, **62**, 2457 (1940).

Scheme I



a, X = CH_3O
b, X = CH_3
c, X = H
d, X = Cl
e, X = CF_3

Finally, the indan IXc had been found as a product of the formolysis of Ic.[2] We also observed IXc, as well as indans IXa and IXb in the corresponding reactions. No indans were obtained in solvolyses of Id and Ie. Comparison samples of IXa–c resulted from cyclization of the corresponding 2-methyl-4-aryl-2-butanol.

Rates of solvolysis of Ia–e were determined in acetic acid at 100 and 110°, and in formic acid at 90 and 70°, by titrating with perchloric acid in acetic acid the unconsumed sodium acetate or sodium formate. Reactions were followed to at least 50% completion. Rate constants are recorded in Table I.

Runs for product analysis were carried out under the same conditions as the rate studies for at least three half-lives. The crude product was chromatographed on alumina to separate it into olefin and ester fractions, and the latter was separated into acetate (or formate) and unreacted tosylate by crystallization from petroleum ether. Yields were excellent (around 80–90%), and recoveries in the separation procedure were usually above 90%. The olefin fraction was hydrogenated, and the acetate or formate was reduced to the alcohol with lithium aluminum hydride prior to analysis. Either a Golay (capillary) column or a packed column of 0.2–0.5% benzoquinoline on Chromosorb P was used for the hydrocarbons, and a packed column of Ucon Polar on Anakrom ABS was used for the alcohols. Details are given in the Experimental Section. Migration aptitudes, corrected for the statistical preference for

Table I. Rates, Migration Aptitudes, and Partial Rate Factors for Solvolyses of 2,2-Dimethyl-3-(*p*-X-phenyl)-1-propyl *p*-Toluenesulfonates

X	10^6k, sec^{-1} [a]	Migration aptitude, Me:Bz [b]	$10^6k_p^{Me}$, sec^{-1} [c]	$10^6k_p^{Bz}$, sec^{-1} [d]
	Acetic Acid, 109.58°			
OCH_3	4.36	1.36	1.59	1.17
CH_3	3.59	1.68	1.38	0.823
H	2.90	1.83	1.14	0.622
Cl	1.72	3.30	0.747	0.226
CF_3	1.09	4.62	0.492	0.106
	Acetic Acid, 99.58°			
OCH_3	1.44	1.38	0.528	0.383
CH_3	1.23	1.72	0.476	0.277
H	0.986	1.86	0.388	0.209
Cl	0.580	3.43	0.253	0.0738
	Formic Acid, 90.07°			
OCH_3	6.60	*e*		
CH_3	6.75	1.93	2.68	1.39
H	5.18	2.55	2.16	0.849
Cl	2.82	4.13	1.26	0.304
CF_3	1.78	6.38	0.825	0.129

[a] Average of three runs with average deviation 1–2%. [b] Average of three or more runs. Average deviation 1–2% in the acetolyses except for 2.4 and 5.8% for the *p*-Cl compound at 109.58 and 99.85°, respectively. Average deviation 1–4% in the formolyses. Corrected for the statistical preference for methyl. [c] $k \times 0.5 \times$ fraction of methyl migration. [d] $k \times$ fraction of benzyl migration. [e] Could not be measured because product was not stable to reaction conditions (see text).

methyl, are recorded in Table I. The only exception to the high yields noted above was the formolysis of Ia, where the products appeared to be polymerizing to a gum under the reaction conditions. Consequently, no reliable product analysis was possible in this case.

Control experiments in which both methyl-migrated and benzyl-migrated olefins were subjected to the reaction conditions demonstrated that there was no carbon-skeleton isomerization of the products. As noted before,[2] there was some interconversion of olefin and ester. Another control demonstrated that unrearranged acetate, none of which was observed in the products, would have survived the reaction conditions. Synthetic mixtures were used to calibrate the gas-chromatographic analyses whenever separation of adjacent peaks was not completely clean.

Discussion

One immediately apparent observation is that our migration aptitudes for unsubstituted benzyl do not agree with those of Warrick and Saunders.[2] We find a considerably smaller methyl:benzyl ratio, especially in the acetolysis, though the direction of the effect is unchanged. The earlier work ignored the small (*ca.* 4%) acetate fraction, which we find to consist mainly of benzyl-migrated product, but less than 10% error in the migration aptitude could arise from this source. Consequently, we reexamined the olefin fraction from acetolysis using the Golay and the benzoquinoline columns, both of which gave better separation than had previously been possible. Referring now to Table I of Warrick and Saunders,[2] we could separate peak 5 into its two components, but not peak 3. We were, however, able to isolate peak 3 by preparative-scale gas chromatography, hydrogenate it, and determine the methyl:benzyl ratio of the hydrogenation products.

The results show that peak 5 in the earlier work must have been incorrectly analyzed or extensively contaminated with peak 4 since we find it to be essentially entirely benzyl-migrated material. By comparison, the differences in results on peak 3 are minor. An error from this source would explain why our results in the formolysis are closer to those of Warrick and Saunders, for peak 5 constituted much less of the total product in formolysis than in acetolysis. We did not recheck the deamination products, but here peak 5 constituted only 2.6% of the mixture, and an error in analysis of the peak could at most reduce the methyl:benzyl migration aptitude from 2.1 to 1.8. Unless there are other unsuspected errors, the selectivity of the deamination remains rather higher than one would expect.[5]

The main point of interest is whether our results can be adduced as evidence for or against concerted ionization or rearrangement. The simplest piece of evidence is the complete absence of unrearranged product. Our analytical methods could detect *ca.* 0.1% of such material, and a control experiment showed it would survive, so rearrangement must be at least 10^3 faster than direct substitution. The 4–5-kcal difference in activation energies that this represents seems to us unreasonable for rearrangement *vs.* substitution in a primary carbonium ion, which should be of high energy and relatively unselective toward the paths of reaction open to it.

If we assume that ionization and rearrangement are concerted, we can divide the total rate of solvolysis[6] into a rate of ionization with methyl migration and a rate of ionization with benzyl migration. The partial rate factors, k_p^{Me} and k_p^{Bz}, in Table I are the results of this operation (k_p^{Me} is the rate for *one* methyl group, so $k = k_p^{Bz} + 2k_p^{Me}$). If the ionization and migration are *not* concerted there is no necessary relationship between rates and product proportions, and the partial rate factors are without physical significance. In order to decide whether the reaction is concerted, we might first ask whether these quantities based on that assumption are reasonable.

To get the data in a form permitting convenient objective judgment on this point, we examined the correlation of the rate constants, migration aptitudes, and partial rate factors with the Hammett equation. The least-squares procedure of Jaffé[7] was used. The substituent constants were the σ° values of Taft,[8] which are appropriate when there is no direct conjugation between the reaction site and the substituent. The results are shown in Table II.

Table II. Hammett Correlations of Rates and Partial Rate Factors for Solvolyses of 2,2-Dimethyl-3-(*p*-X-phenyl)-1-propyl *p*-Toluenesulfonates[a]

Quantity correlated	Temp, °C	Solvent	ρ	s^b	r^c
k	109.58	HOAc	−0.801	0.055	0.993
Me:Bz[d]	109.58	HOAc	0.717	0.073	0.984
k_p^{Me}	109.58	HOAc	−0.680	0.038	0.995
k_p^{Bz}	109.58	HOAc	−1.398	0.105	0.992
k	99.85	HOAc	−0.851	0.087	0.990
Me:Bz[d]	99.85	HOAc	0.818	0.149	0.968
k_p^{Me}	99.85	HOAc	−0.701	0.055	0.994
k_p^{Bz}	99.85	HOAc	−1.519	0.196	0.984
k	90.07	HCOOH	−0.829	0.032	0.998
Me:Bz[d]	90.07	HCOOH	0.743	0.021	0.999
k_p^{Me}	90.07	HCOOH	−0.746	0.033	0.998
k_p^{Bz}	90.07	HCOOH	−1.490	0.050	0.999

[a] Data from Table I. Correlation by the least-squares method of Jaffé, using the σ° constants of Taft.[8] [b] Standard deviation of ρ. [c] Correlation coefficient. [d] Migration aptitude of methyl relative to benzyl, corrected for the statistical factor.

If the reaction is a two-step process, the only effect the *para* substituent could exert is an inductive effect on the formation of the carbonium ion. We might ask, then, whether the ρ value for the over-all rate is reasonable for a simple inductive effect operating over this distance. No close analogies are available in the literature, but we were able to find two rough indications. Phenylacetate ion has, like the unrearranged carbonium ion in our system, two carbon atoms between the ring and the charged atoms. The ρ value for ionization of phenylacetic acids in water at 25° is +0.489. More closely related, because the charge is localized on one atom, would be the ionization of phenylethylamines. No figure is available, but appli-

(5) A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957).

(6) In neopentyl-like systems, there should be no rate disturbance from ion-pair return, and the rate of solvolysis should equal the rate of ionization. See A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2763 (1956).

(7) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(8) R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

cation of a transmission factor of 0.410 for the extra methylene group[9a] to the ρ value of -0.723[7] for benzylamines in water at 25° gives a ρ of -0.296. We conclude that the ρ values for the over-all reaction are substantially larger than expected for simple ionization without participation. The validity of these crude comparisons is difficult to judge. Allowance for the temperature difference would make the disparity even wider (ρ generally decreases with increasing temperature[7]), but allowance for the difference in dielectric constants of the solvents would produce a change in the opposite direction.

A referee has cited the work of Peterson[9b] as evidence that simple ionizations to carbonium ions can have large substituent effects. They report rather large Taft ρ_I values for secondary tosylate solvolyses (-7.79 at 25° for formolysis and -5.72 at 70° for acetolysis). Closer examination of their data, however, reveals that only moving the functional group closer to the center of the molecule has any large effect (2-pentyl *vs.* 3-pentyl, for example). There is virtually no change in rate when there is a structural change at least two atoms removed from the reaction site (2-butyl *vs.* 2-pentyl and 2-hexyl, for example). In contrast, we find a 30% increase in formolysis rate at 90° when we replace phenyl by *p*-tolyl. Since the added methyl group in our case would have to exert its inductive effect over a distance of two carbon atoms plus a benzene ring, we still conclude that our substituent effects are larger than expected for simple ionization.

A correlation between the over-all rates of reaction and the migration aptitudes is to be expected if the reaction is concerted, but is not required if it is not. Such a correlation necessarily exists in our work because both rates and migration aptitudes follow the Hammett equation, which requires that

$$\log (\mathrm{Me/Bz}) - \log (\mathrm{Me/Bz})_0 = \rho' \log k/k_0 \qquad (1)$$

where ρ' is the ratio of ρ for the migration aptitude (ρ_{MA}) and ρ for the over-all reaction (ρ_R). Even if the ionization and migration are separate steps, however, both might reasonably be expected to correlate with σ values, for both should be aided by electron release and hindered by electron withdrawal. While eq 1 is consistent with a concerted process, it does not require it. We also considered the approach of Gudmundsen and McEwen,[10] but a key assumption of their correlation, that the group which remains constant over a series of reactants (in their case an unsubstituted phenyl and in ours a methyl) migrates at a rate unaffected by the changing substituents on the other group, is demonstrably untrue in our system. The k_p^{Me} values depend markedly on the substituent in the benzene ring.

Turning now to the Hammett correlations of the k_p values, we find that ρ_{Bz} is considerably greater in magnitude than ρ_{Me}. This situation is entirely reasonable for a concerted process where the substituent on the benzene ring would be expected to have a greater effect when the benzyl group is actually migrating than when it is merely one of the two groups influencing inductively the migration of methyl. It is possible that these values could appear fortuitously in a two-stage reaction. It is also, however, possible that entirely unreasonable values would result. Suppose the variation in over-all rate were very small, but the variation in migration aptitudes as large as ours. Then our definition of the k_p's would require that k_p^{Bz} and k_p^{Me} vary in the *opposite* direction. It seems very unreasonable to expect that methyl migration could be aided by electron withdrawal, so such a result would constitute evidence that the k_p's were physically meaningless. Again, the data are consistent with a concerted process but do not require it.

A change to a more ionizing solvent, such as the present change from acetic to formic acid, is predicted to *increase* neighboring-group participation.[11] Such an increase should result in greater sensitivity of reaction rate to the nature of the participating group. The ρ values for our over-all rates are the same, within experimental error, in both solvents. The ρ in formic acid may be slightly low because of an anomalous rate for the *p*-methoxy compound (less than *p*-methyl) in formic acid. Even so, the predicted effect of solvent either does not exist, or is too small to be unequivocally apparent.

One indication that selectivity is somewhat greater in formic acid is that all the methyl:benzyl ratios are higher in formic than in acetic acid. This fact alone would be consistent with either a one- or two-stage process. The slightly greater spread in k_p^{Me} values in formic acid than in acetic acid might be taken as evidence for increased methyl participation in formic acid, but the change is still within experimental error. Neither ρ_{MA} nor ρ for the partial rate of benzyl migration changes appreciably from one solvent to the other.

The relatively low sensitivity of the migration aptitude to *para* substituents is expected, since $\rho_{MA} = \rho_{Me} - \rho_{Bz}$, where ρ_{Me} and ρ_{Bz} are the ρ values for the partial rates of methyl and benzyl migration, respectively.[12] Such a relationship holds even in a two-stage process, if the rate constants are those for the product-determining stage. Unless ρ_{Me} is very small, which it is not here, ρ_{MA} will be substantially smaller than ρ_{Bz}.

A more sensitive measure of the inherent ability of a group to migrate is the *migration tendency* as defined by Stiles and Mayer.[13] This quantity is an intermolecular comparison intended to eliminate the effect of a variable nonmigrating group. In our system it may be defined as the ratio of the rate constant for migration of a methyl group in the corresponding neopentyl derivative (which will be simply one-third of the solvolysis rate constant if the ionization and migration are concerted) to k_p^{Bz}. Thus, we are comparing the abilities of methyl and benzyl groups to migrate from a migration origin which in both cases bears two nonmigrating methyl groups. Migration tendencies were calculated using our data in combination with rate constants for solvolysis of neopentyl tosylate reported by Winstein and co-workers.[11,14] The results are recorded in Table III.

Migration tendencies of substituted benzyl groups cover a range more than twice as wide in formic as in

(9) (a) H. H. Jaffé, *J. Chem. Phys.*, **21**, 415 (1953); (b) P. E. Peterson, R. E. Kelley, Jr., R. Belloli, and K. A. Sipp, *J. Am. Chem. Soc.*, **87**, 5169 (1965).

(10) C. H. Gudmundsen and W. E. McEwen, *ibid.*, **79**, 329 (1957).

(11) S. Winstein and H. Marshall, *ibid.*, **74**, 1120 (1952).

(12) R. Heck and S. Winstein, *ibid.*, **79**, 3432 (1957).

(13) M. Stiles and R. P. Mayer, *ibid.*, **81**, 1497 (1959).

(14) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *ibid.*, **74**, 1113 (1952).

Table III. Migration Tendencies of Methyl Groups Relative to Substituted Benzyl Groups in Solvolysis of 2,2-Dimethyl-3-(*p*-X-phenyl)-1-propyl *p*-Toluenesulfonates

X	Migration tendencies[a] in HOAc, 109.58°	HOAc, 99.85°	HCOOH, 90.07°
OCH_3	1.41	1.49	
CH_3	2.00	2.06	2.40
H	2.49	2.73	3.92
Cl	7.30	7.72	11.0
CF_3	9.90		25.8

[a] The ratio of one-third of the rate of solvolysis of neopentyl *p*-toluenesulfonate to k_p^{Bz} (Table I) under the same conditions.

acetic acid. The comparison of migration tendencies thus reveals an important trend that was obscured by competing effects in the comparison of migration aptitudes. We believe that this trend, and the greater preference for methyl migration in formic acid, constitute the most persuasive evidence that ionization and migration are concerted. While none of the evidence obtained in our work is explicable only by a concerted process, we believe it unlikely that such a self-consistent set of results would have been obtained for a two-stage reaction.

Experimental Section[15]

***p*-Methoxybenzyl chloride** was obtained by the dropwise addition of 63 g (0.53 mole) of thionyl chloride to 70 g (0.51 mole) of *p*-methoxybenzyl alcohol. The temperature was kept below 40°, the mixture was stirred for an additional 1.5 hr, and a vacuum of 50 mm was applied for a final 0.5 hr to remove the remaining gaseous products. The mixture was taken up in ether, washed with 10% sodium carbonate and water, dried over sodium sulfate, and distilled to yield 69 g (88%) of product, bp 87–88° (2.5 mm) (lit.[16] bp 125–127° (25 mm)). It was stored in the cold as a 50% solution in anhydrous ether to retard decomposition.

***p*-Trifluoromethylbenzoic acid** was obtained from *p*-bromobenzotrifluoride *via* carbonation of the Grignard reagent and melted at 215–217° (lit.[17] mp 212–213°).

***p*-Trifluoromethylbenzyl alcohol** was obtained by slowly adding, with stirring, *p*-trifluoromethylbenzoic acid, suspended in anhydrous ether, to an excess of lithium aluminum hydride in anhydrous ether. The mixture was worked up in the usual fashion to yield 88% of *p*-trifluoromethylbenzyl alcohol, bp 59–60° (0.5 mm), $n^{22}D$ 1.4611 (lit.[18] bp 78.5–80° (4 mm), $n^{26}D$ 1.4600).

***p*-Trifluoromethylbenzyl chloride** was obtained by treating 0.40 mole of the alcohol with a twofold excess of thionyl chloride, followed by 4 hr of refluxing. Distillation at 20 mm revealed that conversion was still incomplete, so the residue was treated twice again with 5-ml portions of thionyl chloride and a few drops of pyridine, followed each time by distillation at 20 mm. The total yield was 87% of product, bp 86–87° (20 mm), $n^{24}D$ 1.4366.

Preparation of Methyl 2,2-Dimethyl-3-(*p*-X-phenyl)propionates. The procedure of Warrick and Saunders[2] was used. Reaction of the appropriate benzyl chloride with methyl isobutyrate and sodium hydride gave the desired esters in 60–70% yields, with the following properties: **methyl 2,2-dimethyl-3-phenylpropionate,** bp 76–81° (1.4 mm), $n^{21.5}D$ 1.4939; **methyl 2,2-dimethyl-3-(*p*-methoxyphenyl)propionate,** bp 116–120° (1.5 mm), $n^{22.3}D$ 1.5019; **methyl 2,2-dimethyl-3-(*p*-tolyl)propionate,** bp 105–109° (2.9 mm), $n^{22.7}D$ 1.4932; **methyl 2,2-dimethyl-3-(*p*-chlorophenyl)propionate,** bp 104–107° (0.6 mm), $n^{22}D$ 1.5073; **methyl 2,2-dimethyl-3-(*p*-trifluoromethylphenyl)propionate,** bp 74–77° (0.4 mm), $n^{22}D$ 1.4512.

Preparation of 2,2-Dimethyl-3-(*p*-X-phenyl)propanols. Reduction of the corresponding methyl 2,2-dimethyl-3-(*p*-X-phenyl)propionates with lithium aluminum hydride[2] gave the desired alcohols in 90–95% yields and with the following properties: **2,2-dimethyl-3-phenylpropanol,** bp 77–78° (0.6 mm), mp 36.1–36.7° (lit.[2] bp 120–124° (14 mm)), mp 34–35°); **2,2-dimethyl-3-(*p*-methoxyphenyl)propanol,** bp 115–116° (1.2 mm), mp 48.8–49.8° (*Anal.* Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.26; H, 9.39); **2,2-dimethyl-3-(*p*-tolyl)propanol,** bp 106–110° (2.3–3.0 mm), mp 34.9–35.2° (lit.[19] mp 37°); **2,2-dimethyl-3-(*p*-chlorophenyl)propanol,** bp 107° (0.6 mm), mp 33–35° (*Anal.* Calcd for $C_{11}H_{15}ClO$: C, 66.49; H, 7.61. Found: C, 66.54; H, 7.65); **2,2-dimethyl-3-(*p*-trifluoromethylphenyl)propanol,** bp 94° (1.6 mm), mp 68.9–69.5°.

Preparation of 2,2-Dimethyl-3-(*p*-X-phenyl)propyl *p*-Toluenesulfonates. The preparation followed the procedure of Marvel and Sekera[20] except that the product obtained on pouring the reaction mixture into cold hydrochloric acid was taken up in ether and the ether solution washed with 10% hydrochloric acid, 10% sodium carbonate, and water. The solution was dried over sodium sulfate, the ether removed, and the product recrystallized from a mixture of ether and petroleum ether. Yields ranged from 66 to 88% of materials having the following properties: **2,2-dimethyl-3-phenylpropyl *p*-toluenesulfonate,** mp 71.4–71.9° (lit.[2] 71.4–71.8°); **2,2-dimethyl-3-(*p*-methoxyphenyl)propyl *p*-toluenesulfonate,** mp 62.8–63.2° (*Anal.* Calcd for $C_{19}H_{24}O_4S$: C, 65.49; H, 6.64. Found: C, 65.32; H, 6.91); **2,2-dimethyl-3-(*p*-tolyl)propyl *p*-toluenesulfonate,** mp 73.8–74.3° (*Anal.* Calcd for $C_{19}H_{24}O_3S$: C, 68.64; H, 7.28. Found: C, 68.73; H, 7.30); **2,2-dimethyl-3-(*p*-chlorophenyl)propyl *p*-toluenesulfonate,** mp 89.7–90.5° (*Anal.* Calcd for $C_{18}H_{21}O_3ClS$: C, 61.27; H, 6.00. Found: C, 61.33; H, 5.92); **2,2-dimethyl-3-(*p*-trifluoromethylphenyl)propyl *p*-toluenesulfonate,** mp 117.5–118.0° (*Anal.* Calcd for $C_{19}H_{21}O_3F_3S$: C, 59.05; H, 5.48. Found: C, 58.90; H, 5.54).

Comparison Samples of Expected Products of the Rearrangements. I. 2-Methyl-1-(*p*-X-phenyl)-1-butanols. Four of these alcohols were obtained by treating the Grignard reagent from 0.1–0.2 mole (g-atom) each of 2-bromobutane and magnesium with the appropriate *para*-substituted benzaldehyde. Yields were around 40–60%, and the products were identified by oxidation to the corresponding ketone with chromium trioxide, followed by preparation of the 2,4-dinitrophenylhydrazone.

2-Methyl-1-(*p*-methoxyphenyl)-1-butanol. Purification was by molecular distillation at 0.05 mm because the alcohol underwent elimination during ordinary vacuum distillation. Gas chromatography indicated greater than 97% purity; 2,4-dinitrophenylhydrazone, mp 101.5–102.2°. *Anal.* Calcd for $C_{18}H_{20}N_4O_5$: C, 58.06; H, 5.42. Found: C, 58.43; H, 5.52.

2-Methyl-1-(*p*-tolyl)-1-butanol had bp 91.0–92.5° (1.1 mm), $n^{23}D$ 1.5083; 2,4-dinitrophenylhydrazone, mp 108.0–108.7. *Anal.* Calcd for $C_{18}H_{20}N_4O_4$: C, 60.67; H, 5.68. Found: C, 60.74; H, 5.50.

2-Methyl-1-(*p*-chlorophenyl)-1-butanol had bp 80–83° (0.5 mm), $n^{22.3}D$ 1.5259; 2,4-dinitrophenylhydrazone, mp 126.8–127.6°. *Anal.* Calcd for $C_{17}H_{17}ClN_4O_4$: C, 54.19; H, 4.55. Found: C, 54.51; H, 4.53.

2-Methyl-1-(*p*-trifluoromethyl)-1-butanol. A different procedure was followed in this case, the addition of 2-methylbutyraldehyde with a Grignard reagent made from *p*-bromobenzotrifluoride. The product, obtained in 70% yield, had bp 74–76° (0.5 mm), $n^{22.5}D$ 1.4615; 2,4-dinitrophenylhydrazone, mp 102.1–102.7°. *Anal.* Calcd for $C_{18}H_{17}F_3N_4O_4$: C, 52.68; H, 4.18. Found: C, 52.91; H, 4.46.

II. 2-Methyl-4-(*p*-X-phenyl)-2-butanols. The addition of the appropriate *p*-X-benzylacetone to methylmagnesium bromide gave the desired alcohols in 85–90% yield. The substituted benzylacetones were unavailable for X = CH_3, Cl, and CF_3, and were prepared *via* the reaction of the substituted benzyl chloride with the sodium salt of acetoacetic ester, followed by hydrolysis and decarboxylation. The procedure is illustrated below for X = CH_3.

2-Methyl-4-phenyl-2-butanol had bp 96.0–96.5° (3.2 mm), $n^{25.3}D$ 1.5063 (lit.[2] bp 120–121° (13 mm); $n^{25}D$ 1.5080); phenylurethan, mp 138.8–139.2 (lit.[2] 139.3–140.1°).

2-Methyl-4-(*p*-methoxyphenyl)-2-butanol had bp 121° (0.5 mm), mp 37.4–38.4° (*Anal.* Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.18; H, 9.41); *p*-nitrobenzoate, mp 60.4–61.7°.

2-Methyl-4-(*p*-tolyl)-2-butanol had bp 83.5–84.5° (0.4 mm), mp 42.5–43.1° (*Anal.* Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.79; H, 9.98); phenylurethan, mp 95.8–96.3°.

(15) Melting points and boiling points are uncorrected. Microanalyses are by Mr. V. Landeryou and Microtech Laboratories.

(16) A. L. Buckle, A. McGooken, and A. Robertson, *J. Chem. Soc.*, 3981 (1954).

(17) R. G. Jones, *J. Am. Chem. Soc.*, 69, 2346 (1947).

(18) H. B. Hass and M. L. Bender, *ibid.*, 71, 1767 (1949).

(19) A. Haller and E. Bauer, *Ann. Chim.*, [9] 9, 5 (1918).

(20) C. S. Marvel and V. C. Sekera, *Org. Syn.*, 20, 50 (1940).

2-Methyl-4-(*p*-chlorophenyl)-2-butanol had bp 92–93° (0.4 mm), mp 37.1–38.5° (*Anal.* Calcd for $C_{11}H_{15}ClO$: C, 66.49; H, 7.62. Found: C, 66.45; H, 7.63); phenylurethan, mp 100–100.6°.

2-Methyl-4-(*p*-trifluoromethylphenyl)-2-butanol had bp 74–75° (0.5 mm), $n^{23}D$ 1.4597; phenylurethan, mp 91.0–91.6°. *Anal.* Calcd for $C_{19}H_{20}F_3NO_2$: C, 64.94; H, 5.74. Found: C, 65.11; H, 5.86.

α-(*p*-Methylbenzyl)acetoacetic Ester. To 0.4 mole of a dispersion of sodium hydride in 300 ml of anhydrous tetrahydrofuran was added over 2.5 hr 0.4 mole of ethyl acetoacetate in anhydrous tetrahydrofuran. To the resulting solution was added 0.4 mole of *p*-methylbenzyl chloride in 100 ml of anhydrous tetrahydrofuran, and the mixture was refluxed for 38 hr. Addition of 20 ml of water coagulated the sodium chloride, which was removed by filtration. More water was added to the filtrate, followed by extraction with ether. The extracts were washed with water, 10% hydrochloric acid, 5% sodium carbonate, and water, and then dried over anhydrous potassium carbonate. Distillation gave 60.4 g (64%) of product, bp 110–112° (0.25 mm), $n^{20.3}D$ 1.4961.

***p*-Methylbenzylacetone.** To 17 ml of water and 8 ml of concentrated sulfuric acid in 300 ml of acetic acid was added 58.7 g (0.25 mole) of α-(*p*-methylbenzyl)acetoacetic ester, and the resulting solution was refluxed for 3 hr. After addition of an excess of water the solution was extracted with petroleum ether. The combined extracts were washed with water, 5% sodium carbonate, and again with water, and then dried over anhydrous potassium carbonate. Distillation yielded 35.8 g (90%) of product, bp 87–89° (0.9 mm), $n^{21.5}D$ 1.5058.

III. 2-Methyl-1-(*p*-X-phenyl)-2-butanols. Essentially the same procedure was used for X = H, CH_3, CH_3O, and Cl. A Grignard reagent was prepared from the appropriate benzyl chloride and a twofold excess (threefold for X = CH_3O) of an equal mixture (by weight) of magnesium turnings and 40-mesh magnesium powder. Slow addition of the benzyl chloride and fairly large volumes of ether (*ca.* 400–500 ml of 0.2–0.3 mole of halide) were used to minimize coupling. To the Grignard reagent was added 2-butanone, and the complex was decomposed with saturated ammonium chloride to yield, after distillation, 60–80% of product.

The reaction using the benzyl Grignard reagent was unsuccessful for X = CF_3, so the reaction of ethylmagnesium chloride with 1-(*p*-trifluoromethylphenyl)-2-propanone (the preparation of which is described below) was used to obtain an 86% yield of the desired product. The properties of the alcohols were as follows: **2-methyl-1-phenyl-2-butanol**, mp 122–124° (20 mm), $n^{25.3}D$ 1.5097 (lit.[2] bp 110–112° (14 mm), $n^{24}D$ 1.5097); phenylurethan, mp 83.1–83.9° (lit.[2] 83.5-84.0°); **2-methyl-1-(*p*-methoxyphenyl)-2-butanol**, bp 107–109° (0.9 mm), $n^{23.5}D$ 1.5180; 3.5-dinitrobenzoate, mp 88.3–88.9° (*Anal.* Calcd for $C_{19}H_{20}N_2O_7$: C, 58.78; H, 5.19. Found: C, 58.78; H, 5.53); **2-methyl-1-(*p*-tolyl)-2-butanol**, bp 85–87° (1.1 mm), $n^{22}D$ 1.5096 (lit.[21] bp 112.8–113.5° (6.5 mm), $n^{20}D$ 1.5120); **2-methyl-1-(*p*-chlorophenyl)-2-butanol**, bp 107–111° (2.5-2.8 mm), $n^{22.3}D$ 1.5266; phenylurethan, mp 121.9–122.4° (*Anal.* Calcd for $C_{18}H_{20}ClNO_2$: C, 68.01; H, 6.34. Found: C, 68.17; H, 6.00); **2-methyl-1-(*p*-trifluoromethylphenyl)-2-butanol**, bp 65–66° (0.45 mm), $n^{23}D$ 1.4623; phenylurethan, mp 120.0–120.4° (*Anal.* Calcd for $C_{19}H_{20}F_3NO_2$: C, 64.94; H, 5.74. Found: C, 65.19; H, 5.86).

1-(*p*-Trifluoromethylphenyl)-2-propanone. A Grignard reagent was prepared from 0.64 g-atom of magnesium turnings, 0.28 mole of ethyl bromide, and 0.29 mole of *p*-bromobenzotrifluoride. The reagent was treated with 1.1 moles of propylene oxide in anhydrous ether, first at 0° for 3 hr and then at room temperature overnight. The mixture was treated with saturated ammonium chloride and worked up in the usual fashion to obtain 57% of product, bp 75–80° (1.8 mm), which was shown by gas chromatography to contain 84% of the desired 1-(*p*-trifluoromethylphenyl)-2-propanol. The three minor peaks (5, 8, and 3%) were not identified.

This product (0.14 mole), dissolved in 30 ml of acetic acid, was added over 30 min to a solution of 0.25 mole of chromium trioxide in 250 ml of acetic acid and 20 ml of water. After stirring at 70° for 2 hr, the reaction mixture was poured into water and extracted with petroleum ether. The extract was filtered, washed with 10% sodium hydroxide and water, and dried over anhydrous potassium carbonate. Removal of the solvent and distillation on an 18-in. spinning-band column gave a main fraction weighing 9.2 g, bp 76–78° (3.0 mm), which solidified and was finally recrystallized from petroleum ether to give 8.5 g of white flakes, mp 39.1–39.9°.

(21) A. L. Liberman, N. I. Tyun'kina, and B. A. Kazanskii, *Dokl. Akad. Nauk SSSR*, **134**, 603 (1960); *Chem. Abstr.*, **55**, 641*d* (1961).

IV. 2-Methyl-1-(*p*-X-phenyl)butanes. The basic procedure was to dehydrate the 2-methyl-1-(*p*-X-phenyl)-2-butanol with phosphorus oxychloride in pyridine, followed by hydrogenation of the resulting olefin mixture at 25 psi with a palladium–charcoal catalyst. The procedure is illustrated below with 2-methyl-1-phenyl-2-butanol, the properties of all the saturated hydrocarbons being described and two exceptions to the general procedure noted.

Dehydration of 2-Methyl-1-phenyl-2-butanol. A solution of 0.20 mole of the alcohol in 100 ml of dry pyridine was cooled in an ice bath, and 0.10 mole of phosphorus oxychloride in 50 ml of pyridine was added with stirring over 30 min. After an additional 30 min of stirring, the mixture was refluxed for 2 hr and poured into a slurry of crushed ice and 175 ml of concentrated hydrochloric acid. The product was extracted with petroleum ether, and the extracts were washed with 5% sodium carbonate and water and dried over sodium sulfate. Distillation yielded 74% of an olefin mixture, bp 65–72° (4.5 mm). The substituted alcohols (X = CH_3, Cl, CF_3) gave olefin in 78–83% yields by this method.

In one case, X = CH_3O, the alcohol was too unstable to handle conveniently, so the crude product from 2-butylmagnesium bromide and anisaldehyde was refluxed with a mixture of 5% water, 5% concentrated sulfuric acid, and 90% tetrahydrofuran for 4 hr. The mixture was diluted with water and extracted with petroleum ether, and the extracts were washed with 10% sodium carbonate and water before drying over sodium sulfate. Distillation yielded 64% of olefin mixture, bp 60–63° (0.4 mm).

2-Methyl-1-phenylbutane. Hydrogenation of 0.06 mole of the olefin mixture in 60 ml of ethanol was performed in a Parr shaker at 25 psi for 3 hr with 0.3 g of 5% palladium–carbon as catalyst. After filtration and removal of the ethanol a 68% yield of product resulted, having bp 194–197°, $n^{25.3}D$ 1.4846 (lit.[22] bp 194–195°, $n^{20}D$ 1.4873). Gas chromatography showed the product to be free of detectable impurities.

The other olefin mixtures gave 70–85% of saturated hydrocarbon except when X = Cl, in which case partial (18%) dechlorination of the aromatic ring occurred. Preparative gas chromatography was used in this case to obtain 43% of pure product.

2-Methyl-1-(*p*-methoxyphenyl)butane had bp 58–59° (0.25 mm), $n^{21.5}D$ 1.4973 (lit.[23] bp 82–84° (2.0 mm), $n^{20}D$ 1.4998).

2-Methyl-1-(*p*-tolyl)butane had bp 71–72° (3.8 mm), $n^{24}D$ 1.4873 (lit.[21] bp 92.5 (12.5 mm), $n^{20}D$ 1.4899).

2-Methyl-1-(*p*-chlorophenyl)butane was purified by gas chromatography, $n^{21.3}D$ 1.5043, nmr spectrum consistent with expected structure. Dechlorination on a Parr shaker with hydrogen and 5% palladium–charcoal in 1% sodium hydroxide in ethanol yielded 2-methyl-1-phenylbutane, identified as the dinitrophenylhydrazone of the acetylation product, mp 150.0–150.6° (lit.[24] 147–148°).

2-Methyl-1-(*p*-trifluoromethylphenyl)-1-butane had bp 39.0–39.5° (0.6 mm). *Anal.* Calcd for $C_{12}H_{15}F_3$: C, 66.65; H, 6.69. Found: C, 66.98; H, 7.19.

V. 3-Methyl-1-(*p*-X-phenyl)butanes. The procedures followed were precisely analogous to those used for the 2-methyl-4-(*p*-X-phenyl)butanes (see IV, above) using the 2-methyl-1-(*p*-X-phenyl)-2-butanol as starting material. For the case where X = Cl an alternative procedure was devised to obviate the necessity of purifying the partially dechlorinated hydrogenation product. It is described below.

3-Methyl-1-phenylbutane had bp 198–199°, $n^{25.3}D$ 1.4818 (lit.[22,25] bp 198–199, $n^{20}D$ 1.4835).

3-Methyl-1-(*p*-methoxyphenyl)butane had bp 73° (1.1 mm), $n^{21.5}D$ 1.4944 (lit.[26] bp 78° (1.0 mm), $n^{27}D$ 1.4940).

3-Methyl-1-(*p*-tolyl)butane had bp 68–69° (3.2 mm), $n^{20}D$ 1.4850 (lit.[27] bp 85.7° (12 mm), $n^{20}D$ 1.4949). *Anal.* Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.87; H, 11.17.

3-Methyl-1-(*p*-chlorophenyl)butane. To 6.1 g (0.12 mole) of hydrazine hydrate in 20 ml of 95% ethanol was added 5.6 g (0.029 mole) of 3-methyl-1-(*p*-chlorophenyl)-2-butanone in 20 ml of ethanol, and the solution was refluxed for 45 min. The ethanol was removed under vacuum, and the residue was heated with 5.6 g (0.10 mole) of potassium hydroxide in 30 ml of triethylene glycol

(22) V. N. Ipatieff and L. Schmerling, *J. Am. Chem. Soc.*, **60**, 1476 (1938).

(23) A. Mertwoy, M. Trachtman, and H. Gissser, *J. Phys. Chem.*, **64**, 1085 (1960).

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

(25) C. Fischer and R. Wolffenstein, *Ber.*, **37**, 3215 (1904).

(26) G. G. S. Dutton, T. I. Briggs, and E. Merler, *Can. J. Chem.*, **31**, 1138 (1953).

(27) I. Romadane, E. Grikit, and N. I. Shuikin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 507 (1959); *Chem. Abstr.* **54**, 347*d* (1960).

and 6 ml of water. Water was distilled until the temperature rose to 155° and nitrogen evolution began. The solution was then refluxed for 15 hr, poured into excess water, and extracted with petroleum ether. The extract was washed with water, dried over sodium sulfate, and distilled to yield 2.0 g (39%) of product, bp 80° (3.2 mm), $n^{24.3}$D 1.5002. Identification was accomplished by dechlorination on a Parr shaker at 35 psi in 1% sodium hydroxide in ethanol using 5% palladium on charcoal as a catalyst. The hydrocarbon was acetylated and the acetyl derivative converted to a dinitrophenylhydrazone, mp 156.6–157.2° (lit.[24] 151.5–152.0°).

The 3-methyl-1-(*p*-chlorophenyl)-2-butanone used in this procedure was obtained from *p*-chlorobenzylmagnesium chloride and isobutyraldehyde, followed by oxidation of the resulting 3-methyl-1-(*p*-chlorophenyl)-2-butanol with chromium trioxide in acetic acid.

VI. Indans. Treatment of the appropriate 2-methyl-4-(*p*-X-phenyl)-2-butanol with cold 85% sulfuric acid[2,28] gave the desired indans in 60–70% yield except for X = CH_3O, where the yield was only 11%: **1,1-dimethylindan,** bp 40.0–40.2° (1.7 mm), $n^{22.3}$D 1.5126 (lit.[2] bp 71° (8 mm), n^{24}D 1.5136); **1,1,6-trimethylindan,** bp 49.1–49.5° (1.1 mm), $n^{24.3}$D 1.5133 (*Anal.* Calcd for $C_{12}H_{16}$: C, 89.93; H, 10.06. Found: C, 90.08; H, 10.17); **6-methoxy-1,1-dimethylindan,** bp 62–65° (0.4 mm) (removal of 2% of an unknown inpurity by gas chromatography yielded material of $n^{23.5}$D 1.5179. *Anal.* Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.88; H, 9.05).

Reagents. Reagent grade anhydrous sodium acetate and sodium formate were dried at least 12 hr at 110° before use. Acetic acid (1400 g) was distilled from chromium trioxide (15 g) and then from triacetyl borate (60 g). The triacetyl borate was prepared by heating 23 g of boric acid and 115 g of acetic anhydride to 60°. A vigorous reaction ensued and all of the boric acid dissolved. The solution was cooled in an ice bath to precipitate triacetyl borate, which was removed by filtration and used immediately. Eastman 97+% formic acid (1000 g) was refluxed with 60 g of boric anhydride for 8 hr. Another 60 g of boric anhydride was added and the formic acid distilled.

Kinetics in Acetic Acid. The reactor was a 500-ml three-neck round-bottom flask fitted with a nitrogen inlet, a stirrer and a rubber septum cap. Solutions were prepared by dissolving 0.125 mole each of the toluenesulfonate and sodium acetate in anhydrous acetic acid in a 250-ml volumetric flask, and were then transferred to the reactor which had been previously purged with nitrogen and immersed (to within 0.5 in. of the tops of the side arms) in a constant-temperature bath (±0.025°). A 12-ml aliquot was withdrawn with a syringe, cooled quickly in ice water, and then allowed to come to room temperature. Two 5-ml aliquots were then taken with a calibrated constant-volume syringe, and titrated with perchloric acid in anhydrous acetic acid, using crystal violet as indicator. The reaction was followed to at least 50% completion, a total of 10–12 points being taken. Rate constants were calculated graphically and by the Guggenheim method.

Kinetics in Formic Acid. The reactor was a single-neck flask with a glass stopper fitted with a three-way stopcock connecting to a nitrogen supply through the end of the barrel and allowing direct introduction of a syringe needle through a rubber septum into the flask. The procedure was similar to that for the runs in acetic acid except that 0.010 mole each of the toluenesulfonate and sodium formate in 100 ml of formic acid was used. In some cases warming on a stream bath was necessary to bring the toluenesulfonate into solution. The total aliquot for each point was 6 ml, which was divided into two 2-ml aliquots as above. Titration was with 0.04 *N* perchloric acid in acetic acid, using *p*-naphtholbenzein as indicator.

Products in Acetic Acid. The reactor and the quantities of reactants were the same as in the kinetic studies. The reaction was allowed to proceed for at least 3 half-lives (100–400 hr, depending on the reactant and the temperature). The solution was cooled, poured into twice its volume of water, and extracted with two 100-ml portions of petroleum ether. The extract was washed with water, sodium carbonate, and again water, and then dried over potassium carbonate. Evaporation of the petroleum ether left 2.5–3.5 g of yellow oil which was chromatographed on 70–80 g of Merck acid-washed alumina. Olefins were eluted with petroleum ether–benzene, and the acetate esters plus unreacted toluenesulfonate ester were eluted by benzene–ethyl ether.

The olefin fraction was hydrogenated in 20 ml of 95% ethanol with 0.1 g of 5% palladium on carbon in a Parr shaker for several hours at 25 psi. For the *p*-chloro olefins, 20 ml of 1% sodium hydroxide in 95% ethanol and 0.5 g of catalyst were used, and the mixture was hydrogenated at 30 psi for 4 hr so as to remove all of the chlorine from the ring. The catalyst was removed, the ethanol evaporated, and the mixture of alkylbenzenes diluted to 1% with carbon disulfide for analysis by gas chromatography. Control experiments with known olefins established that no isomerization occurred during hydrogenation.

To the second (acetate plus toluenesulfonate) fraction was added 30 ml of petroleum ether, and the solution was cooled in Dry Ice and acetone. The precipitated toluenesulfonate was collected and shown to be pure by melting point and infrared spectrum. The filtrate was evaporated and shown to be free of toluenesulfonate by the absence of bands at 1200 and 1400 cm^{-1} in the infrared. The acetates were converted to the alcohols by treatment with excess lithium aluminum hydride in ether. Water was added to decompose the complex, and the ether was decanted, washed with water, and dried over potassium carbonate. The ether was removed, and the oil was diluted with carbon disulfide for analysis.

Products in Formic Acid. The apparatus and the quantities of reactants were the same as in the kinetic studies. Solutions were heated for 9–35 hr depending upon the reactant. The work-up was identical with that for the product studies in acetic acid.

Gas Chromatographic Analyses. These were performed on an Aerograph A-600-B Hy-Fi or a Perkin-Elmer Model 154 gas chromatograph. Both instruments were equipped with integrators for determining relative peak areas. Columns were 150-ft Golay columns coated with Perkin-Elmer liquid phase "R," or 1/8-in. packed columns with either 30–60 mesh Chromosorb P (Johns-Manville Corp.) or 70–80 mesh Anakrom Type ABS (Analabs Inc.).

The methylphenylbutanes were separated by the Golay column or by a 7.5-ft column of 0.2% benzoquinoline on Chromosorb P, operating around 100–120°. The Golay column also worked well for the methyl(*p*-methoxyphenyl)butanes and the methyl(*p*-tolyl)-butanes. For the latter, a 7-ft column of 15% fluorene–picric acid on Chromosorb P was also used. The benzoquinoline column (see above) was used when 1,1,6-trimethylindan was present (runs in formic acid). The methyl(*p*-chlorophenyl)butanes were analyzed on the 0.2% benzoquinoline column. When the hydrocarbons were dechlorinated prior to analysis, a 0.5% benzoquinoline column was used. This column was also successful with the methyl(*p*-trifluoromethylphenyl)butanes. Finally, the alcohol mixtures were analyzed with a 5- or 10-ft column of 25% Ucon Polar on Anakrom ABS.

Qualitative identification of peaks in the gas chromatograms was tentatively made by comparing retention times of standard and unknown, and confirmed by observing enhancement of the relevant peak when standard was added to unknown. Quantitative analysis was performed by comparing peak areas as determined by the integrator, as mixtures of closely similar isomers were always involved. Where peak separation was not complete, synthetic mixtures of known composition were analyzed and the analyses of the unknowns corrected accordingly. Where two overlapping peaks represented alcohols of the same carbon skeleton, the total area of the two peaks was used to calculate a combined percentage.

Control Experiments. Olefin mixtures of a known single carbon skeleton were subjected to the reaction conditions to determine whether any carbon-skeleton isomerization occurred. In a typical experiment, 0.0050 mole of the olefin mixture from dehydration of 2-methyl-1-phenyl-2-butanol was dissolved in 50 ml of anhydrous formic acid containing 0.0025 mole of sodium formate. The mixture was heated at 90° for 12 hr, worked up, and analyzed as in the solvolyses. The hydrocarbon from hydrogenation of the olefin was pure 2-methyl-1-phenylbutane; the alcohol mixture contained only 2-methyl-1-phenyl-1-butanol, 2-methyl-1-phenyl-2-butanol, and 2-methyl-1-phenyl-3-butanol.

In another control designed to test the stability of any unrearranged acetate that might have formed in the solvolyses, 0.0050 mole of 2,2-dimethyl-3-(*p*-methoxyphenyl)propyl acetate was heated for 100 hr at 110° with 0.0050 mole of sodium acetate in 50 ml of acetic acid. The alcohol obtained on work-up was found to be pure 2,2-dimethyl-3-(*p*-methoxyphenyl)-1-propanol.

Recheck of the Results of Warrick and Saunders on Acetolysis of 2,2-Dimethyl-3-phenylpropyl *p*-Toluenesulfonate. The solvolysis of 2,2-dimethyl-3-phenylpropyl toluenesulfonate at 109.58° was performed and the reaction mixture worked up as described above, except that the hydrogenation was omitted. The alcohols were analyzed as before, and the olefins were examined on the Golay column. Qualitative identification was by comparison with

(28) M. T. Bogert and D. Davidson, *J. Am. Chem. Soc.*, **56**, 185 (1934).

authentic samples prepared by Warrick.[2] Separation was complete except for overlap of the peaks from 2-methyl-4-phenyl-1-butene and 2-methyl-1-phenyl-2-butene. This unresolved peak was separated from the remainder of the mixture using a 15-ft × 1/4-in. column packed with a 7:5 mixture of Bentone 34 and Apiezon L (88% of the weight of the solid phase) on 30–60 mesh Chromosorb P in an Aerograph Autoprep A-700 instrument. The material was then hydrogenated and analyzed on a column of 0.2% benzoquinoline on Chromosorb P. Three runs gave an average methyl:benzyl migration aptitude of 1.72 ± 0.03.

The Migration Aptitude of Ethyl *vs.* Methyl in Solvolyses of Neopentyl-Type Systems[1]

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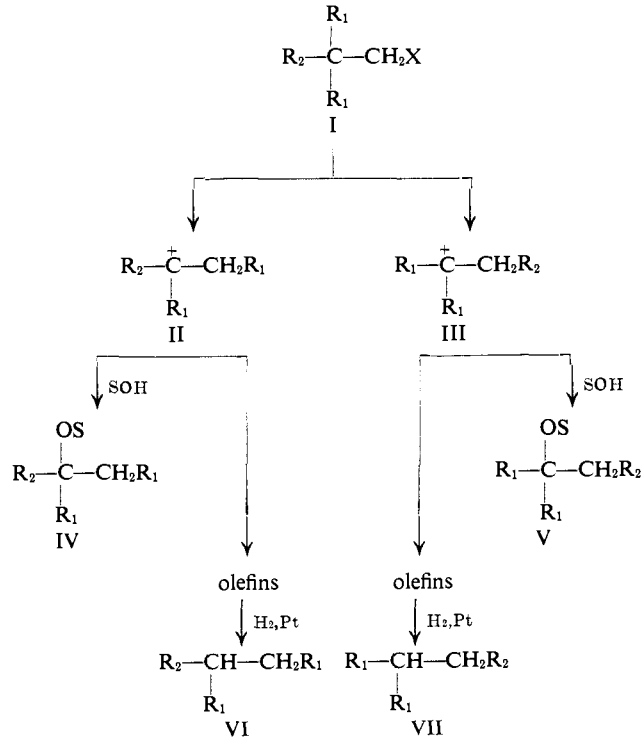
Abstract: Rates of acetolysis at 100 and 110° were determined for neopentyl (Ia), neohexyl (Ib), 2-ethyl-2-methyl-1-butyl (Ic), and 2,2-diethyl-1-butyl (Id) brosylates. The products of acetolysis were found to be almost entirely rearranged olefins, accompanied by *ca.* 1% of acetate esters which included traces of unrearranged acetate. The relative yields of methyl-migrated and ethyl-migrated products were determined for Ib and Ic. Methyl migrates better than ethyl, the migration aptitude running from 1.8 to 2.1 (corrected for the statistical factor). Partial rate factors for methyl and ethyl migration, calculated on the assumption that ionization and migration are concerted, both increase along the series Ia–d. The *migration tendencies* of ethyl relative to methyl (the ratio of partial rate factors when the nonmigrating groups are identical) show a slight preference for ethyl (1.0–1.4). The bearing of these results on whether ionization and migration are concerted is discussed.

Available information on migration aptitudes of simple alkyl groups in carbonium ion rearrangements is still fragmentary and inconclusive. We undertook the careful examination of a number of simple neopentyl-type systems[3] to shed further light on the mechanisms of these rearrangements.

Ethyl migrates more readily than methyl in several pinacol rearrangements.[4,5] On the other hand, methyl migrates better than ethyl in the solvolysis of 3,4-dimethyl-4-phenyl-3-hexyl *p*-bromobenzoate,[6] though the highly ramified nature of the reactant makes the generality of the result doubtful. In another study, which appeared while the present work was in progress, methyl is reported to migrate better than a number of simple alkyl groups in acetolysis of compounds of type I (R_1 = Me, R_2 = other alkyl).[7] Rates were quoted but not migration aptitudes, though the latter are to be found in an unpublished thesis.[8]

In the present work, we studied rates of acetolysis of compounds Ia–d (see Scheme I), and the product distributions from Ib and Ic, at temperatures of 100 and 110°. Identification and analysis of the products were accomplished by gas chromatography, using comparison samples of known structure. The olefin mixture from Ib was analyzed as such and the method checked by hydrogenating the olefins to a mixture of the saturated hydrocarbons VIb and VIIb. The proportions of methyl- and ethyl-migrated products were the same by the two methods within 1%. The olefins from Ic could not be separated completely by gas chromatography, and so were hydrogenated to a mixture of VIc and VIIc for analysis. Control experiments showed that a known olefin mixture analyzed correctly by this procedure. Recoveries of olefins from

Scheme I



a, $R_1 = R_2 = CH_3$, X = *p*-bromobenzenesulfonate
b, $R_1 = CH_3$, $R_2 = C_2H_5$, X = *p*-bromobenzenesulfonate
c, $R_1 = C_2H_5$, $R_2 = CH_3$, X = *p*-bromobenzenesulfonate
d, $R_1 = R_2 = C_2H_5$, X = *p*-bromobenzenesulfonate

(1) This work was supported by the Army Research Office (Durham).
(2) Du Pont Teaching Fellow, 1962–1963.
(3) Previous paper in this series: J. R. Owen and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **88**, 5809 (1966).
(4) W. Reeve and M. Korickhoff, *ibid.*, **78**, 6053 (1956).
(5) M. Stiles and R. P. Mayer, *ibid.*, **81**, 1497 (1959).
(6) D. J. Cram and J. D. Knight, *ibid.*, **74**, 5839 (1952).
(7) E. N. McElrath, R. M. Fritz, C. Brown, C. Y. LeGall, and R. B. Duke, *J. Org. Chem.*, **25**, 2195 (1960).
(8) R. M. Fritz, Ph.D. Thesis, University of Houston, Houston, Texas, 1962; *Dissertation Abstr.*, **23**, 3119 (1963).