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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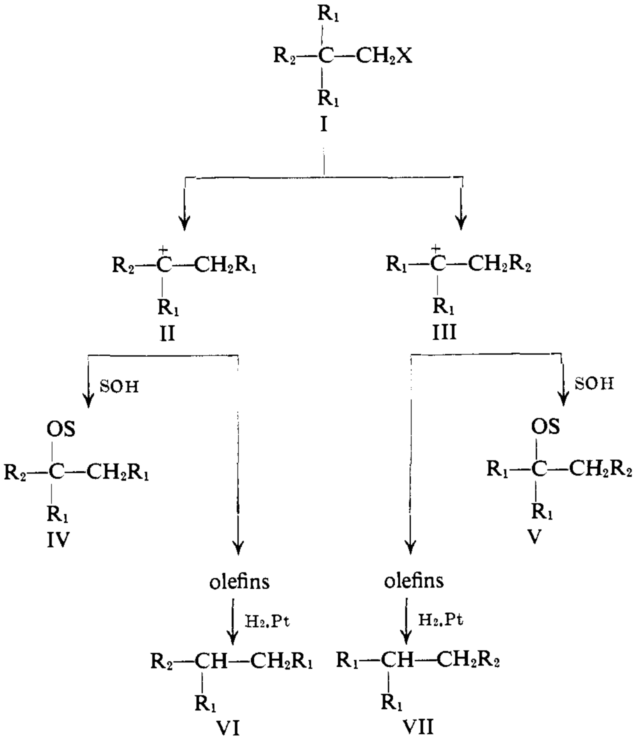
**Abstract:** Rates of acetolysis at 100 and 110° were determined for neopentyl (Ia), neohexyl (Ib), 2-ethyl-2-methyl-1-butyl (Ic), and 2,2-diethyl-1-butyl (Id) brosylates. The products of acetolysis were found to be almost entirely rearranged olefins, accompanied by *ca.* 1% of acetate esters which 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]

**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

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

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[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).

Ib ranged from 56 to 98%, while the higher boiling olefins from Ic were less completely recovered (26–52%). Controls in both cases demonstrated that the compositions of the olefin mixtures were independent of the percentage recovery. In another set of controls, analyzed olefin samples from Ib and Ic were found to be changed less than 1% (in the proportions of methyl- and ethyl-migrated products) by exposure to the reaction conditions.

Acetate esters were shown to constitute less than 1% of the product in acetolysis of Ib and Ic. A special effort was made to detect unrearranged acetate (I, X = OAc). Traces of material corresponding in retention time to the unrearranged acetate were obtained in the products from Ib and Id; the products from Ic contained 0.3% of material corresponding in retention time to the unrearranged acetate. These experiments do not, of course, constitute positive identification of unrearranged acetates, but the demonstration that such small quantities of acetate ester can be detected establishes that rearrangement must be at least several hundred times as fast as direct substitution.

Table I reports average rate constants and methyl: ethyl migration aptitudes, corrected for the statistical preference for methyl in Ib and ethyl in Ic. If ionization and rearrangement are concerted, the rates and product analyses can be combined to obtain partial rates of methyl and ethyl migration ($k_p^{CH_3}$ and $k_p^{C_2H_5}$). These partial rates are presented in Table I and should be examined with the reservation in mind that they are physically meaningless unless ionization and migration are concerted.[3] The final column of Table I presents *migration tendencies*[5] of ethyl relative to methyl, calculated as $k_p^{C_2H_5}:k_p^{CH_3}$, with each group migrating from an atom bearing the same nonmigrating groups (two methyls, a methyl and an ethyl, and two ethyls, respectively).

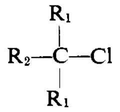
**Table I.** Rates and Migration Aptitudes in Acetolysis of Neopentyl-Type *p*-Bromobenzenesulfonates

| Compd | $10^5 k_1$,[a] $\sec^{-1}$ | $CH_3$: $C_2H_5$[b] | $k_p^{C_2H_5}$[c] | $k_p^{C_2H_5}$[c] | $k^{C_2H_5}$: $k_p^{CH_3}$ |
|---|---|---|---|---|---|
| | | | Results at 110° | | |
| Ia | 1.68 | | 0.560 | | |
| Ib | 2.92 | 1.79 | 1.14 | 0.639 | 1.14[d] |
| Ic | 6.22 | 2.01 | 3.15 | 1.55 | 1.36[e] |
| Id | 9.64 | | | 3.21 | 1.03[f] |
| | | | Results at 100° | | |
| Ia | 0.631 | | 0.210 | | |
| Ib | 1.18 | 1.93 | 0.467 | 0.242 | 1.15 |
| Ic | 2.24 | 2.08 | 1.14 | 0.549 | 1.18 |
| Id | 3.45 | | | 1.15 | 1.01 |

[a] Acetolysis in anhydrous acetic acid, substrate *ca.* 0.05 *M*, sodium acetate *ca.* 0.10 *M*. Each figure is the average of at least two runs, with average deviation usually *ca.* 1%, and never above 2%. [b] Product ratios, corrected for the statistical factor. [c] Partial rates per methyl or ethyl group. For example, $k_1$ for Ia is $3k_p^{CH_3}$, for Ib is $2k_p^{CH_3} + k_p^{C_2H_5}$, etc. [d] Ratio of $k_p^{C_2H_5}$ for Ib to $k_p^{CH_3}$ for Ia. [e] Ratio of $k_p^{C_2H_5}$ for Ic to $k_p^{CH_3}$ for Ib. [f] Ratio of $k_p^{C_2H_5}$ for Id to $k_p^{CH_3}$ for Ic.

## Discussion

The variation in rate of acetolysis over the series is considerable, Id reacting nearly six times as fast as Ia. This variation becomes more striking when compared with that found in ethanolysis of the tertiary chlorides, VIIIa–d, at 25°.[9] In spite of the lower temperature and the greater proximity of the substituent change to the reaction center, VIIId reacts only three times as fast as VIIIa. This rate increase has been attributed to relief of steric strain on ionization,[6] an explanation which seems less likely to be applicable to the solvolyses of Ia–d. While the rate increases about twofold from Ia to Ib and from Ib to Ic, it increases only about 50% from Ic to Id. Yet Ib and Ic can ameliorate ground-state strain by adopting favorable rotational conformations, and Id cannot, so that the steric explanation would predict the greatest rate increase between Ic and Id. The observed behavior seems more consistent with the electron-releasing inductive effect of ethyl substitution, though the failure of the third ethyl group to produce as large an effect as the first two is still somewhat puzzling. While a saturation effect is possible, it is unexpected with differences in inductive effect as small as that between methyl and ethyl. More will be said on this point later.



$R_2C(R_1)_2Cl$

VIIIa, $R_1 = R_2 = CH_3$
b, $R_1 = CH_3, R_2 = C_2H_5$
c, $R_1 = C_2H_5, R_2 = CH_3$
d, $R_1 = R_2 = C_2H_5$

Clearly, the increased rate along the series cannot be explained simply by increased rate enhancement due to ethyl participation, for the migration aptitude of ethyl is less than that of methyl. Fritz[8] uses this fact as evidence against a mechanism in which ionization and rearrangement are concerted, arguing that a rate decrease on substituting ethyl for methyl would be expected. This reasoning is essentially a qualitative application of the approach used by Gudmundsen and McEwen[10] and depends for its validity on the assumption that nonmigrating groups have at most a small effect on the migration aptitude of the migrating group. We have pointed out the doubtfulness of this assumption before[3] and also note that it is demonstrably incorrect in a reaction where concerted ionization and rearrangement are highly likely: the acetolysis of 2,2-diarylethyl tosylates.[11,12]

Even though the argument against a concerted process is not compelling, the argument for it is not without difficulties. Examination of the partial rate factors in Table I leads to the conclusion that the migration aptitude is determined primarily by the nature of the *nonmigrating* group, for the migration tendencies[5] ($k_p^{C_2H_5}:k_p^{CH_3}$ when the nonmigrating groups are identical) are slightly in favor of ethyl migration. One could argue that such a result is unreasonable, and that the partial rate factors are meaningless because the reaction is not concerted.

We feel that such a conclusion would be premature, for it would then leave one with the equally difficult task of explaining why methyl migrates better than ethyl in a discrete neopentyl-type carbonium ion. The order of migration aptitudes is, of course, that expected for

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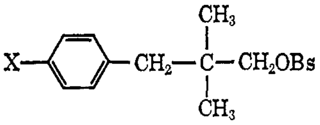
(9) H. C. Brown and R. S. Fletcher, *J. Am. Chem. Soc.*, **71**, 1845 (1949).

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

(11) J. G. Burr, Jr., *ibid.*, **75**, 5008 (1953).

(12) J. G. Burr, Jr., *Chem. Ind.* (London), 850 (1954).

hyperconjugative electron release,[8] but it is not at all clear why this order should control in the present case. Hyperconjugation is generally most obvious in cases where the electron demand is large, yet ethyl migrates better than methyl in the pinacol rearrangement, where a greater degree of alkyl participation in the rearrangement step is expected because of the much greater stabilization of positive charge on the migration origin by the hydroxyl oxygen. In addition, the *inductive* effect of the migrating group is clearly important in determining the migration aptitudes of substituted benzyl groups in a system, IX, closely related to the present one.[3]



IX

For these reasons, we consider that ionization and migration may well be concerted in the solvolyses of Ia–d. The degree of participation by the migrating group must be quite small, so that the electron demand on the migrating group calls into play very little of the electron-repelling effect of ethyl relative to methyl. When discrimination between two migrating groups is feeble, it is not unreasonable to expect the nonmigrating groups to exert a controlling effect. The migrating group may, in fact, bear less positive charge in the transition state than does the migration origin, for the weakening of the bond between the group and the migration origin is being compensated by the formation of the bond to the migration terminus. No comparable effect tends to reduce the charge borne by the migration origin. This argument is not necessarily in conflict with our previous observation[3] in solvolyses of IX that a substituent on a migrating benzyl group exerted a greater effect than on a nonmigrating benzyl group, for there the nonmigrating *methyl* group was undoubtedly responsible for much of the stabilization of the fractional positive charge on the migration origin in the transition state.

A final argument may be based on the relative rates. We noted earlier that the third ethyl group (from Ic to Id) had a smaller effect on the rate than either of the first two. This observation can be reconciled with a concerted process as follows. Let us assume, as is indicated by the partial rate factors, that the migration tendencies of ethyl and methyl are practically the same, and that the rate increments are essentially entirely the result of changes in the nonmigrating group. Since Ic gives about a 50:50 mixture of ethyl- and methyl-migrated products, the change from Ic to Id means that only *half* of the total reaction increases in rate, for the other half already involves a migration origin bearing two ethyl groups. In contrast, from Ia to Ib 80% of the total reaction (80:20 ratio of methyl- to ethyl-migrated product) is accelerated by a change from a migration origin bearing two methyl groups to one bearing one ethyl and one methyl group. Similarly, from Ib to Ic, 70% of the reaction is accelerated by addition of one nonmigrating ethyl group (50% changes from one ethyl and one methyl to two ethyls, and 20% changes from two methyls to one methyl and one ethyl).

One can, of course, produce *ad hoc* explanations of the nonadditivity of the effect of ethyl substitution. One plausible alternative is that the third ethyl group causes steric hindrance of solvation of the incipient carbonium ion, thereby partially counteracting the favorable inductive effect. As noted above, a saturation effect is another possibility. A dependence of the inductive effect of ethyl on conformation might also result in nonadditivity.

While no firm conclusions are possible from the present data, we have argued previously that results in solvolyses of IX are better accommodated by a concerted mechanism,[3] and it seems highly unlikely that I and IX would undergo solvolytic rearrangement by different mechanisms. The high rearrangement:substitution ratio is also difficult to explain with a probably unselective primary carbonium ion. In the absence of positive evidence for such an ion, we prefer to regard neopentyl-type rearrangements as concerted processes, though with too small a degree of participation to have unmistakable effects on the rate.[13]

A minor point deserves brief comment. Three derivatives of 2-ethyl-2-methyl-1-butanol which we report in the Experimental Section have melting points in singularly unanimous disagreement with the literature values. Yet analyses of the derivatives, the nmr spectrum of one of them (the tetrachlorophthalate), and the products of solvolysis of the brosylate all demonstrate that we must have 2-ethyl-2-methyl-1-butanol. We can only surmise that errors of tabulation must be present in the references quoted on the derivatives.

## Experimental Section[14]

**Starting Alcohols.** Neopentyl alcohol was from the Aldrich Chemical Co., and neohexyl (2,2-dimethyl-1-butyl) alcohol was from Eastman Chemical Products. The remaining two alcohols were prepared as follows.

**2-Ethyl-2-methyl-1-butanol.** To a stirred solution of 0.20 mole of lithium aluminum hydride in 400 ml of anhydrous ether was added dropwise 0.10 mole of crude 2,2-diethyl-3-hydroxyl-1-propyl tosylate (see below for preparation) in 200 ml of anhydrous ether. The mixture was refluxed for 8 hr and decomposed with 28 ml of saturated sodium chloride, and the ether solution was filtered through Celite and dried. Fractionation gave 5.4 g (50%) of product, bp 86–88° (50 mm), $n^{23}\text{D}$ 1.4287 (lit.[15] $n^{25}\text{D}$ 1.4288); acid tetrachlorophthalate, mp 150–152° (lit.[15] 144–145°) (*Anal.* Calcd for $C_{15}H_{16}Cl_4O_4$: C, 44.88; H, 4.02. Found: C, 44.88; H. 4.00); acid phthalate, mp 66–67° (lit.[15] 44.5–45.5°) (*Anal.* Calcd for $C_{15}H_{20}O_4$: C, 68.18; H, 7.63. Found: C, 68.35; H, 7.45); 3,5-dinitrobenzoate, mp 64–67° (lit.[16] 144–146°) (*Anal.* Calcd for $C_{14}H_{18}N_2O_6$: C, 54.24; H, 5.85. Found: C, 54.40; H, 5.77).

**2,2-Diethyl-1-butanol** was prepared in 48% yield by reduction of triethylacetic acid with lithium aluminum hydride in the usual manner. The product had bp 87–88° (22 mm), $n^{24}\text{D}$ 1.4393 (lit.[15] bp 92° (25 mm), $n^{25}\text{D}$ 1.4411).

**Brosylate Esters.** To 0.2 mole of the alcohol and 0.8 mole of dry pyridine, cooled to −5° in an ice–salt bath, was added with stirring 0.22 mole of *p*-bromobenzenesulfonyl chloride over 2 hr, keeping the temperature below 0°. The mixture was stirred another 12 hr at a temperature of 5–10°. It was then added to 533 ml of ice-cold 3 *N* hydrochloric acid and the resulting mixture was kept at 5–10° for 12 hr. The precipitated brosylate was removed by suction filtration and dissolved in 100 ml of petroleum ether, and

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(13) For arguments against the concerted mechanism, see J. E. Nordlander, S. P. Jindal, P. von R. Schleyer, R. C. Fort, Jr., J. J. Harper, and R. D. Nicholas, *J. Am. Chem. Soc.*, 88, 4475 (1966).

(14) Melting and boiling points are uncorrected. Analyses are by Mr. A. Revilla and Micro-Tech Laboratories, and nmr spectra are by Dr. L. D. Colebrook.

(15) S. Sarel and M. S. Newman, *J. Am. Chem. Soc.*, 78, 5416 (1956).

(16) R. V. Rice, G. L. Jenkins, and W. C. Harden, *ibid.*, 59, 2000 (1937).

the solution was washed with water, 5% sodium bicarbonate, and water. It was then concentrated (rotary evaporator) until crystallization began, and the brosylate was collected and crystallized once more from petroleum ether. **Neopentyl brosylate** had mp 67.5–68.5° (lit.[7] 69–70°), yield 96%; **2,2-dimethyl-1-butyl brosylate,** mp 33.8–34.8° (lit.[7] 35°), yield 92%.

**2-Ethyl-2-methyl-1-butyl brosylate** was a liquid at room temperature and had to be extracted from the acidic aqueous solution with petroleum ether. The solution was washed and dried as above, and the brosylate was crystallized by cooling in a Dry Ice–acetone bath and quickly filtered. Residual solvent was removed under vacuum and the liquid forced through a column of alumina (1 g of activity grade 2 alumina per 5 g of brosylate); $n^{22}\mathrm{D}$ 1.5243. *Anal.* Calcd for $C_{13}H_{19}SO_3Br$: C, 46.57; H, 5.71. Found: C, 46.85; H, 5.75.

**2,2-Diethyl-1-butyl brosylate** had mp 38.8–39.2°, yield 88%. *Anal.* Calcd for $C_{14}H_{21}SO_3Br$: C, 48.14; H, 6.06. Found: C, 47.92; H, 6.04.

**2,2-Diethyl-3-hydroxy-1-propyl Brosylate and Tosylate.** The procedure in both cases was essentially as above, using 1.0 mole of 2,2-diethyl-1,3-propanediol in 11.8 moles of dry pyridine and 0.65 mole of the appropriate sulfonyl chloride. A crystalline brosylate resulted from extraction in a continuous extractor with petroleum ether of the crude liquid brosylate. After recrystallization from petroleum ether the product had mp4 5–46°. *Anal.* Calcd for $C_{13}H_{19}SO_4Br$: C, 44.45; H, 5.45. Found: C, 44.60; H, 5.63. The tosylate could not be crystallized, and the material obtained in the extraction by petroleum ether was used directly.

**Rearranged Alcohols. 2-Methyl-2-pentanol** was obtained in 63% yield by the reaction of methylbutyrate with methylmagnesium bromide,[17] bp 120–122°, $n^{25}\mathrm{D}$ 1.4070 (lit.[18] bp 120.5–121°, $n^{25}\mathrm{D}$ 1.4089).

**3-Methyl-3-pentanol** was obtained in 80% yield by the reaction of 2-butanone with ethylmagnesium bromide,[19] bp 117–120°, $n^{25}\mathrm{D}$ 1.4164 (lit.[20] bp 120°, $n^{25}\mathrm{D}$ 1.4161).

**3-Methyl-3-hexanol** was prepared in 54% yield by the reaction of 3-hexanone with methylmagnesium bromide, bp 140–141°, $n^{22}\mathrm{D}$ 1.4200 (lit.[19,21] bp 141°, $n^{20}\mathrm{D}$ 1.4231).

**3-Ethyl-3-pentanol** was commercial material (Distillation Products Industries), $n^{22}\mathrm{D}$ 1.4272 (lit.[19] $n^{20}\mathrm{D}$ 1.4294).

**Acetate esters** were prepared by a standard procedure for *t*-alkyl acetates.[22] Those prepared were neohexyl, 2-methyl-2-pentyl, 3-methyl-3-pentyl, 3-methyl-3-hexyl, 3-ethyl-3-pentyl, and 2-ethyl-2-methyl-1-butyl acetates. In most cases there was no attempt to obtain highly purified product. Infrared spectra and gas chromatography showed that the only contaminant was unreacted alcohol, which did not interfere with the use of the acetates as standards for identification in gas chromatographic analyses.

**Olefins** were mostly available commercially: 2-ethyl-1-butene, 2-methyl-1-pentene (K and K Laboratories); *cis-* and *trans*-3-methyl-3-hexenes, *cis*-3-methyl-2-hexene (American Petroleum Institute); 3-ethyl-2-pentene (Distillation Products Industries). The remainder were prepared as described below.

**3-Methyl-2-pentene** was obtained by heating on a steam bath equimolar amounts of 3-methyl-3-pentanol and anhydrous zinc chloride in a flask surmounted by a 6-in. Vigreux column. Analysis of the distillate by gas chromatography showed three peaks, one due to 2-ethyl-1-butene (comparison with commerical sample, see above), and the other two presumed to be *cis-* and *trans*-3-methyl-2-pentenes.

***trans*-3-Methyl-2-hexene and 2-ethyl-1-pentene** were obtained by dehydration of 3-methyl-3-hexanol by the procedure described above for 3-methyl-3-pentanol. Attempts to isolate and identify positively these compounds from the mixture of five olefins were unsuccessful. That all of the products had the proper carbon skeleton was demonstrated by hydrogenation to a single product identified by gas chromatography as 3-methylhexane.

**Saturated Hydrocarbons.** 2-Methylpentane and 3-methylhexane were commercially available (Phillips Petroleum Co.). 3-Ethylpentane and 3-methylhexane were obtained by hydrogenation of olefins from the dehydration of 3-ethyl-3-pentanol and 3-methyl-3-hexanol, respectively. The procedure employed was essentially that of Brown and Brown.[23] The hydrogenations were carried out on a 4-g scale and 10 ml of pure *n*-pentane was added to facilitate handling of the product. The *n*-pentane solution was dried over phosphorus pentoxide and used directly in gas chromatographic comparisons.

**Kinetics and Products of Acetolysis.** Anhydrous sodium acetate (Baker A.R. grade) was dried at 130° before use. Anhydrous acetic acid was prepared by refluxing 4 l. of glacial acetic acid (Mallinckrodt A.R. grade) with 2 moles of triacetyl borate[24] for 8 hr, followed by distillation through a Vigreux column.

The apparatus consisted of a 500-ml three-neck round-bottom flask fitted with a serum cap, a sealed stirrer, and a distilling head fitted with a nitrogen inlet tube reaching into the flask in place of the thermometer. The distilling head was connected to a condenser with a small trap at the end followed by a tube packed with sodium hydroxide pellets so as to remove any uncondensed acetic acid vapor. The outlet of the sodium hydroxide tube led to a Dry Ice–acetone trap to collect the olefins.

The flask was immersed to just below the side arms in a constant-temperature bath (±0.10°) and flushed with dry nitrogen (10–15 ml/min) for 24 hr. Into a 500-ml volumetric flask was weighed sufficient sodium acetate to give a 0.1 *M* solution and sufficient brosylate to give a 0.05 *M* solution. The flask was filled to the mark with anhydrous acetic acid. When the solutes had dissolved, about 450 ml of the solution was transferred to the reaction flask, and the nitrogen flow was adjusted to 10–11 ml/min. Aliquots (*ca.* 8 ml) were withdrawn by syringe at 1.5–2.0 hr and appropriate intervals (0.5–3.0 hr) thereafter. The aliquots were cooled in ice to 25°, and from each an accurately measured 5-ml aliquot was taken with a calibrated syringe and titrated with standard perchloric acid in acetic acid with crystal violet indicator. Reactions were followed to at least 35% completion and rate constants determined by the method of least squares. Duplicate runs agreed within 1–2%.

**Analysis of Products.** Analyses were performed by gas chromatography on Wilkens Aerograph A-110-C or A-600-B instruments. The columns used were a 45-ft × 1/4-in. 20% dimethylsulfolane on 30–60 mesh Chromosorb (Johns-Manville Corp.), a 20-ft × 1/16-in. 28% di-*n*-decyl phthalate on 30–60 mesh Chromosorb, and a 20-ft × 1/4-in. 25% Ucon Polar on 80–90 mesh Anakrom (ABS).

The olefins from neohexyl brosylate solvolysis were analyzed on the dimethylsulfolane column. The five peaks were identified by comparison of retention times and by peak-enhancement experiments with authentic samples. The order of elution agreed with published data.[25] The olefin yield was almost quantitative (98%) when the solvolysis was run to 99% completion, but only 56 for 48% completion, presumably because the olefins were produced faster than they were removed in the early stages of the reaction. There was no significant difference in the composition of products between the two runs, however. To test the effect of reaction conditions on the product, vapors of an analyzed olefin mixture were carried slowly by nitrogen into a reaction vessel containing acetic acid and 0.01 *M* sodium acetate. The olefin mixture collected in the Dry Ice trap (60% of the material introduced) after 12 hr had the same composition within experimental error as the original sample. As another check on the procedure, an analyzed olefin mixture was hydrogenated to a mixture of 2-methylpentane and 3-methylpentane, which showed within 1% the same proportions of methyl- and ethyl-migrated products as the olefin analysis.

In one run, the acetate ester product was isolated by pouring the reaction mixture into ice water and extracting with four 100-ml portions of petroleum ether. Careful fractionation of the extract gave 1.80 g of residue boiling above 60°. Gas chromatographic analysis on the Ucon Polar column showed that 98.4% of the residue was high-boiling material from the petroleum ether, and only 1.6% had retention times in the region expected for acetate esters. Consequently, acetate esters can constitute less than 1% of the acetolysis product. A trace of material having the same retention time as neohexyl acetate was noted.

The olefins from 2-ethyl-2-methyl-1-butyl brosylate could not be completely separated by gas chromatography, and were hydro-

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(17) M. Willcox and R. F. Brunel, *J. Am. Chem. Soc.*, **38**, 1821 (1916).

(18) F. Hovorka, H. P. Lankelma, and C. K. Naujoks, *ibid.*, **55**, 4820 (1933).

(19) F. C. Whitmore and D. E. Bodertsch, *ibid.*, **55**, 1559 (1933).

(20) F. H. Norton and H. B. Hass, *ibid.*, **58**, 2147 (1936).

(21) "Handbook of Chemistry and Physics," 44th ed, The Chemical Rubber Publishing Co., Cleveland, Ohio, 1962, p 1034.

(22) C. R. Hauser, B. E. Hudson, B. Abramovitch, and J. C. Shivers, *Org. Syn.*, **24**, 19 (1944).

(23) H. C. Brown and C. A. Brown, *J. Am. Chem. Soc.*, **84**, 2829 (1962).

(24) W. C. Eichelberger and V. K. LaMer, *ibid.*, **55**, 3633 (1933).

(25) R. A. Hively, *J. Chem. Eng. Data*, **5**, 237 (1960).

genated to a mixture of 3-methylhexane and 3-ethylpentane. This mixture was analyzed on the di-*n*-decyl phthalate column. The olefin yields varied from 26 to 52%, being higher in the runs at 110 than at 100°. A control experiment in which an analyzed olefin sample was carried by nitrogen into a simulated reaction mixture (see above) resulted in a 70% recovery of material which, on hydrogenation, gave a saturated hydrocarbon mixture analyzing within 0.7% of that obtained by hydrogenating the original olefin mixture. The validity of the hydrogenation procedure was demonstrated by hydrogenating and analyzing a synthetic mixture of olefins. The analysis was within 1% of the calculated composition.

Isolation of acetate ester was attempted in the same manner as in the neohexyl brosylate acetolysis. In the residue from fractionation of the petroleum ether was detected 0.3% of material having the same retention time as 2-ethyl-2-methyl-1-butyl acetate, along with *ca.* 0.6% of rearranged acetates. A control experiment with 3-ethyl-3-pentyl acetate showed the method of isolation was capable of extracting less than 0.04 g (corresponding to 1% yield) of ester.

A run with 2,2-diethyl-1-butyl brosylate was worked up so as to obtain any acetate ester formed. A trace of 2,2-diethyl-1-butyl acetate was noted.

# The Mechanism of the Periodate Oxidation of Aromatic Systems. III. A Kinetic Study of the Periodate Oxidation of Catechol

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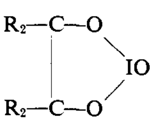
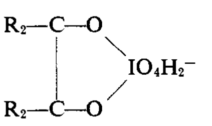
**Abstract:** The kinetics of the periodate oxidation of catechol have been investigated over the pH range 0–10. An intermediate was directly observable on a stopped-flow apparatus over the pH range 0.45–7.26. The kinetics of intermediate formation were found to be second order (first order in each reactant concentration), and were adequately explained on the basis of differing reactivities of the various periodate and catechol species present in solution over the pH range 0–10. The intermediate was found to decompose to products in a first-order fashion which was independent of the catechol and periodate concentrations. The observed kinetics of intermediate decomposition were explained by the assumption of a combination of uncatalyzed, specific hydrogen ion and specific hydroxide ion catalyzed paths. Since the maximum half-life of the intermediate was only 2.9 sec, it was not possible to isolate and characterize it. While the assumption of a cyclic diester of periodic acid as the structure of the intermediate is logical in light of the proposed mechanism of periodate oxidation of $\alpha$-glycols, this postulate does not appear to be supported by all of the experimental evidence now in hand.

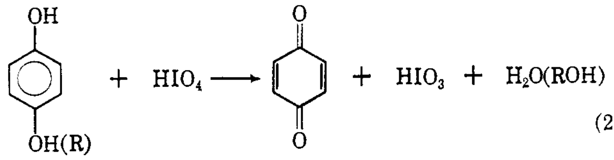
The kinetics of the oxidative cleavage of $\alpha$-glycols by periodic acid have been studied extensively.[3,4] The observed kinetics were satisfactorily explained by assuming that an intermediate is first formed in a rapid and reversible step and that the rate-determining step is the breakdown of this intermediate to the products (reaction 1). Using this assumption, the equilibrium constant for intermediate formation, $K$, and the rate constant for its breakdown to products, $k$, could be calculated from the kinetic data. From the effect of pH on these two quantities, it was concluded that the intermediate was a cyclic diester of periodic acid (I or a hydrated form, II). The formation of the intermediate is, for most glycols, faster than the irreversible decomposition of the intermediate to products. Therefore, it was possible to follow the kinetics of intermediate formation with negligible interference from the decomposition to products. In this manner checks were made on the equilibrium constants for intermediate formation obtained from the kinetic form of the over-all reaction.

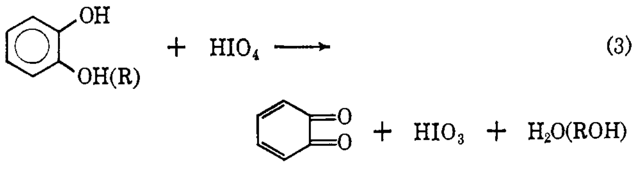
$$\text{glycol} + \text{periodate} \overset{K}{\rightleftharpoons} \text{intermediate} \xrightarrow[\text{slow}]{k} \text{products} \qquad (1)$$


I


II

The periodate oxidations of aromatic diols and their monoethers (reactions 2 and 3) have not, until recently, been subjected to thorough kinetic investigation. In a previous paper we reported the results of a kinetic study of the periodate oxidation of hydroquinone and *p*-methoxyphenol in acidic solution.[5] The oxidation reactions showed a first-order dependence on the substrate concentration and a first-order dependence on the total periodate concentration. No evidence for the formation of appreciable concentrations of intermediates was found even with stopped-flow methods.


(2)


(3)

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[3] G. J. Buist and C. A. Bunton, *J. Chem. Soc.*, 1406 (1954); 4580 (1957).

[4] G. J. Buist, C. A. Bunton, and J. H. Miles, *ibid.*, 4567, 4575 (1957); 743 (1959); and references cited therein.

[5] E. T. Kaiser and S. W. Weidman, *J. Am. Chem. Soc.*, **86**, 4354 (1964).