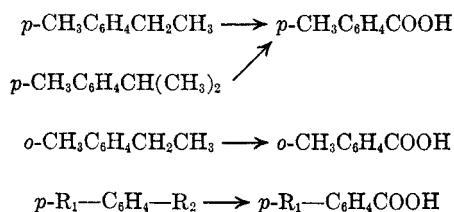


It can be seen that, exclusive of the *t*-butyl groups, the preferential oxidation of these respective alkyl groups decreases in the order, isopropyl, ethyl, methyl. This is the order of increasing electronegativity of the groups and also of the increasing number of *alpha* hydrogens. Hence, to explore further the selectivity shown, groups were chosen which have the same number of *alpha* hydrogens but a third group of varying electronegativity. For example, *p*-isobutylethylbenzene, has a methyl group and an isopropyl group, attached to the *alpha* carbons. In this case, oxidation produced *p*-ethylbenzoic acid. Thus, it appears that the relative ease of oxidation of the alkyl groups, provided there is at least one α -hydrogen atom, is determined by the relative electronegativity of the alkyl groups attached to the *alpha* carbon atoms. To test this idea, *p*-*n*-propylethylbenzene, was oxidized. *p*-Ethylbenzoic acid was obtained, again supporting the idea expressed above. In all cases, mixed melting points and infrared spectra of the oxidation products showed no sign of other *p*-alkylbenzoic acids being present.

The nitric acid oxidations in this study can be summarized as follows:



R_1 = ethyl; R_2 = *n*-propyl, isopropyl, and isobutyl

R_1 = *t*-butyl; R_2 = methyl, ethyl, isopropyl

This generalization about the relative ease of oxidation of carbon-attached side chains only applies to hydrocarbon groups. Once a carbon-oxygen, carbon-nitrogen, or carbon halogen bond is formed, the carbon is easily oxidized. For example, the CH_2OH , $\text{CH}=\text{O}$, and CH_2Cl groups are probably much more easily oxidized than alkyl groups in spite of the fact that there are highly electronegative atoms attached to the α -carbon. To test this idea, *p*-methylbenzyl methyl ether was prepared and oxidized with 15% nitric acid. As expected, the product was *p*-toluic acid.

In summary, it can be generalized that 15% nitric acid will oxidize dialkylbenzenes to alkylbenzoic acids, and with groups containing at least one α -hydrogen atom, the relative ease of oxidation increases with decreasing electronegativity of the groups attached to the α -carbon.

DEPARTMENT OF CHEMISTRY
HOWARD UNIVERSITY
WASHINGTON 1, D. C.

Oxidation of a Secondary Alkyl Tosylate by Dimethyl Sulfoxide

MANUEL M. BAIZER

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In the course of a study of the thermal decomposition of tosylates of secondary alcohols as a route to olefins, we had occasion in one instance to examine the modification reported by Nace.¹ In his procedure dimethyl sulfoxide is used as a medium and sodium hydrogen carbonate is optionally used to protect the olefin formed from the action of the liberated sulfonic acid.

When the tosylate (I) of 1,3-diphenoxy-2-propanol (II) was heated with dimethyl sulfoxide and sodium bicarbonate for six hours at a maximum temperature of 103°, the only product recovered was unchanged starting material. When the reaction temperature was allowed to rise to 150°, 10% of the input of I was recovered as its saponification product II; the remainder was converted to a yellow oil which, after distillation followed by crystallization of the distillate, was found to be 1,3-diphenoxy-2-propanone (III). III showed carbonyl absorption in the infrared; its melting point and that of its 2,4-dinitrophenylhydrazone agreed with the values reported in the literature.²

While the oxidation by dimethyl sulfoxide of phenacyl³ and benzyl halides⁴ and of tosylates of benzyl alcohols⁵ to aldehydes has been reported,⁶ the oxidation of a secondary alkyl tosylate to the corresponding ketone seems not to have been noted before.

Attempts to oxidize II directly by dimethyl sulfoxide were unsuccessful.

EXPERIMENTAL⁷

Dimethyl sulfoxide was obtained from the Stepan Chemical Co. and used without purification.

1,3-Diphenoxy-2-propyl *p*-toluenesulfonate (I) was prepared from the alcohol and *p*-toluenesulfonyl chloride in pyridine according to the usual procedure. The crude yield was 95%, m.p. 117–119°. After recrystallization from 2-propanol the product melted at 121°.

Anal. Calcd. for $\text{C}_{22}\text{H}_{22}\text{O}_6\text{S}$: C, 66.32; H, 5.57. Found: C, 66.08; H, 6.08.

(1) H. R. Nace, *Chemistry & Industry (London)*, 1629 (1958).

(2) J. Munch-Petersen, *Acta Chem. Scand.*, 5, 519 (1951).

(3) N. Kornblum, *et al.*, *J. Am. Chem. Soc.*, 79, 6562 (1957).

(4) H. R. Nace, U. S. Patent 2,888,488, May 26, 1959.

(5) N. Kornblum, *et al.*, *J. Am. Chem. Soc.*, 81, 4113 (1959).

(6) I. M. Hunsberger and J. M. Tien, *Chemistry & Industry (London)*, 88 (1959) also report the oxidation of ethyl bromoacetate to ethyl glyoxylate and propose a mechanism for the reaction.

(7) Melting points were taken on a Fisher-Johns block and are uncorrected.

Attempted preparation of 1,3-diphenoxy-2-propene. A suspension of 19.9 g. (0.05 mole) I and 4.2 g. (0.05 mole) sodium bicarbonate in 75 ml. dimethyl sulfoxide was stirred vigorously and warmed slowly, so that it reached 90° in 63 min. and 100° in 140 min. Carbon dioxide evolution was fairly brisk beginning at the former temperature. After 4 hr. at 100° the reaction mixture was poured onto ice. The gummy solid was broken up, washed thoroughly with water and dried *in vacuo*, wt. 17.3 g. Recrystallization from 2-propanol yielded unchanged I, melting point and mixture m.p. 121–122°.

Oxidation of I by dimethyl sulfoxide. The reaction mixture was prepared as in the experiment above and heated more strongly so that it remained in the range 138–150° for 2 hr. It was then poured onto ice. The precipitated tar was dissolved in benzene and the solution washed several times with water, dried over sodium sulfate and filtered. Evaporation of the benzene at room temperature left 11.6 g. of a brown semisolid residue. Trituration with 2-propanol at room temperature followed by filtration removed 1.2 g. of solid which, after purification, was found to be identical with II. After removal of the propanol from the filtrate, the residual liquid was distilled, b.p. 158–163°/0.30–0.36 mm. Trituration of the distillate with Skellysolve F induced crystallization. The solid after two recrystallizations from 50% 2-propanol melted at 57° (reported² 59–60°). The infrared spectrum showed strong absorption at 5.90 μ .

The 2,4-dinitrophenylhydrazone after recrystallization from ethanol containing a little ethyl acetate melted at 128° (reported² 125–126°).

Anal. Calcd. for C₂₁H₁₇N₃O₆: N, 13.30. Found: N, 13.96.

RESEARCH AND ENGINEERING DIVISION
MONSANTO CHEMICAL COMPANY
DAYTON, OHIO

Crystalline Racemic Bornyl Acetate

WILLIAM J. CONSIDINE

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Although optically pure bornyl acetate has long been known to be a low melting solid with a tendency to supercool, nothing is known about the melting behavior of mixtures of the two optical antipodes. A search of the literature uncovered only a statement by Haller¹ that racemic bornyl acetate did not crystallize, even at -17°. Having samples of pure *d*-bornyl acetate and *l*-bornyl acetate available, the melting point behavior of mixtures of the two was investigated.

When a mixture of equal parts of the dextro and laevo isomers was stored in a freezing chest for a week, crystallization occurred to give a solid mass which had a melting point of 7.0°. With this assurance, a series of mixtures was prepared and the melting points taken: % levo isomer (m.p.); 100%, m.p. 27°; 75%, 18.5°; 62.5%, m.p. 12°; 50%, m.p. 7°; 37.5%, m.p. 12°; 25%, m.p. 17.5°; 0% (i.e. 100% dextro isomer), m.p. 26.5°.

A plot of these melting point data gives a symmetrical fusion curve with a single eutectic point

(1) M. A. Haller, *Comp. rend.*, **109**, 29 (1889).

demonstrating² the formation of a simple conglomerate or racemic mixture. This behavior is to be contrasted with the much more common occurrence of a racemic compound, or, rarely, a solid solution.

EXPERIMENTAL³

The *d*-bornyl acetate, $[\alpha] + 41.2^\circ$, used in this study had a melting point of 26.5° (lit.¹ $[\alpha] + 44.38^\circ$; m.p. 24°). The *l*-bornyl acetate, $[\alpha] - 42.0^\circ$, had a melting point of 27.0° (lit.¹ $[\alpha] - 44.45^\circ$; m.p. 24°). Each sample, and mixture, was originally crystallized by storage in a freezing chest (-10°) for periods up to one week. Thereafter recourse was had to seeding when necessary.

FELTON CHEMICAL COMPANY, INC.
BROOKLYN 37, N. Y.

(2) A. Findlay (ed. Campbell and Smith), *The Phase Rule and Its Applications*, 9th Ed., Dover, New York, 1951, p. 190.

(3) All melting points are uncorrected and rotations (D line) are determined on the supercooled liquid at ambient temperatures. The temperature at which the last crystal disappeared was recorded as the melting point.

Interpretation of Some Reactions on Complex Ionic Bonds^{1a}

HEINZ UELZMANN

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The mechanism of olefin polymerization with Ziegler catalysts has been considered to occur on complex ions, such as $(\text{TiCl}_2)^+(\text{AlR}_3\text{Cl})^-$ from $\text{TiCl}_3/\text{AlR}_3$, with the direct participation of the cation metal and anion metal.^{1b} The initiating step of the polymerization is the activation of the monomer on a cation of a transition element. The second step is the migration of the activated monomer to the anion metal (aluminum for instance, or titanium) which occurs at the moment when the propagation starter (R^- , H^-) neutralizes the cationic transition state of the monomer. The migration can be compared with the addition of a metal alkyl to a Lewis type metal alkyl with the formation of more stable complex ions. The polymerization mechanism of ethylene on $(\text{TiCl}_2)^+(\text{AlR}_3\text{Cl})^-$ complex is formulated below.

