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THE SYNTHESIS AND ACETOLYSIS OF BENZONORBORNENYL-1-CARBINYL TOSYLATE. A MODEL COMPOUND FOR THE STUDY OF AROMATIC INDUCTIVE EFFECTS IN NEOPHYL SYSTEMS

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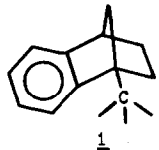
The -I inductive effect of the aromatic ring in β-aralkyl sulfonates should retard solvolysis, but its true value is masked in these substances by the concomitant +R effect of the ring which, via anchimeric participation, accelerates solvolysis, often dramatically. Compounds of partial structure 1 should prove valuable in the study of this heretofore unseparated and unmeasured inductive* effect. Thus, in tosylate 10 (see later), scale models indicate that the overlap of the aromatic pi cloud with the developing cationic site at the carbinyl carbon atom is definitely precluded by the geometry of the molecule. Therefore, the acetolysis of 10 should provide an example of an inductively controlled (-I) process, since anchimeric participation (+R) is effective only when such overlap of the aromatic pi cloud



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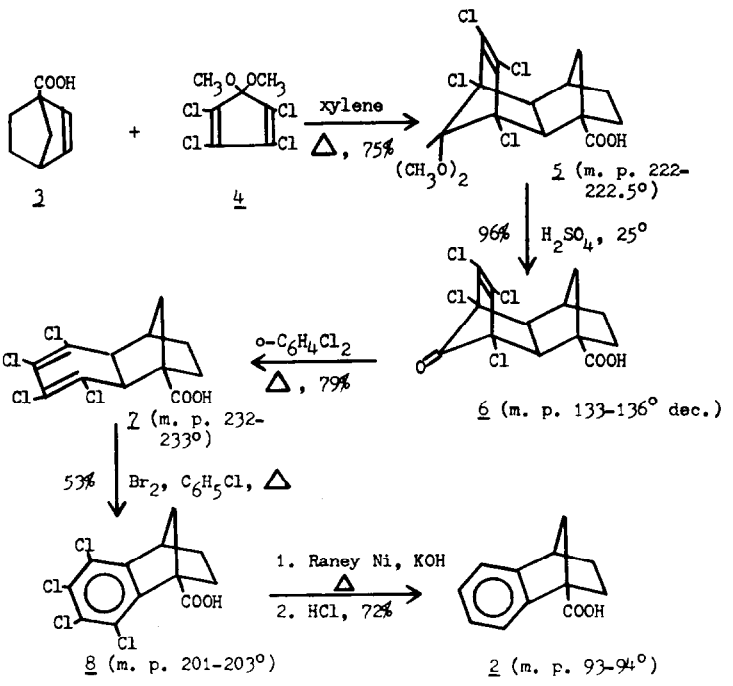
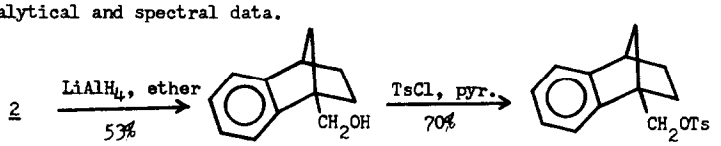
*A distinction must be made between such an effect transmitted through space (a field effect) or through sigma bonds (classical induction). The present study, however, makes no attempt to ascribe the rate retardation observed with 10 (see text) to one rather than the other of these effects.

with the reaction site is possible.

Our previous work in this area has given two relevant results: first, the rearrangement of an aromatic ring in the neophyl radical rearrangement, which depends upon the overlap of the aromatic pi cloud with the free radical site, can be decreased by employing a more rigid molecule (1); and second, the double bond in norbornenyl-1-carbinyl tosylate occasioned a five-fold rate retardation in solvolysis compared to norbornyl-1-carbinyl tosylate (2). These findings led to our interest in compounds of structure 1, which are in reality neophyl-type compounds. The synthesis of benzonorbornene-1-carboxylic acid 2, the key compound of this class, was achieved as shown.

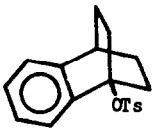


The synthesis of 3 has been described (3). The conversions shown proceeded quite acceptably, as indicated. A more extended discussion of this synthetic sequence will be reserved for the later full paper. The structures of the intermediates 5 - 8 were confirmed spectrally (IR, UV and NMR) and by combustion analysis for 5 and 8. Acid 2 gave a correct combustion analysis, as did its S-benzylisothiuronium salt (m. p. 146-147°), and its IR, UV and NMR spectra were consonant with the structure given. Acid 5 was also characterized via methylation as the ester (b. p. 163-164° at 0.1 mm.), which, curiously, could not be formed from the methyl ester of 3 and diene 4. Acid 2 was reduced with lithium aluminum hydride to benzonorbornenyl-1-carbinol 9 and thence to its tosylate 10 by reaction with tosyl chloride in pyridine at room temperature. The structures of 9 and 10 were supported by analytical and spectral data.



9 (m. p. 58-59°) 10 (m. p. 95-96°)

Acetolysis of 10 was complicated by isomerization to an inert tosylate. First order rate plots showed considerable drift with longer reaction times and acetolysis ended after 65-70% completion. The rate constant was calculated from the initial slope before the complications from the return process became serious. The rearranged tosylate (>20%) was separated from the acetate ester products of the acetolysis by chromatography. While it has not been fully characterized, its spectra indicate it to be either benzobicyclo-[2.2.2] octen-1-yl tosylate 11, 6,7-benzobicyclo[3.2.1] octen-1-yl tosylate 12, or possibly a mixture of them. Structure 12 is more likely because migration of the ethylene bridge appears to be favored over the methylene bridge in norbornenyl-1-carbinyl compounds (2).



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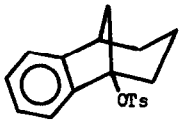

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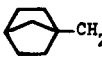
The pertinent rate data for the acetolysis of 10 and other compounds of interest are gathered in the table. The comparisons in the table show

TABLE

Acetolysis Data

Tosylate	k_1 (133°, sec.$^{-1}$)	k_{rel} (133°)
10[a]	$5.8 \pm 0.2 \times 10^{-6}$	1
$(CH_3)_3C\text{-}CH_2\text{-}$[b, c]	$6.8 \pm 0.1 \times 10^{-5}$	12
 [a]	$2.7 \pm 0.1 \times 10^{-4}$	47
$C_6H_5C(CH_3)_2CH_2\text{-}$[b, d]	$4.7 \pm 0.2 \times 10^{-3}$	800

[a]This work. Carried out in purified, anhydrous acetic acid in the presence of sodium acetate. [b]Extrapolated from data at other temperatures. [c]S. Winstein and H. Marshall, J. Am. Chem. Soc., 74, 1120 (1952). [d]S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber and J. Corse, ibid., 74, 1113 (1952).

that the aromatic ring in 10 definitely retards acetolysis, its rate being even less than that of neopentyl tosylate! The difference in rate between 10 and the parent neophyl tosylate is even more striking (over 800-fold). Tosylate 10 is, actually, the first slow neophyl-like substrate ever reported in solvolysis. The data sustain the belief that anchimeric participation by the aromatic ring is cancelled in 10. Moreover, for the first time, a definite experimental value can now be given for the inductive retardation by the aromatic ring in the acetolysis of neophyl compounds. Relative to

the acyclic model, neopentyl tosylate, the aromatic ring retards acetolysis 12-fold at 133°, an effect that would be considerably greater at 70° than the estimate of an 8-fold retardation at this temperature made by Streitwieser for a 3-phenyl group in the 2-butyl system (4) (5). Relative to norbornyl-1-carbinyl tosylate, where some participation by the endomethylene bridge produces a slight acceleration in acetolysis compared to neopentyl tosylate, the incorporation of the aromatic ring of 10 slows acetolysis more dramatically by nearly 50-fold.

All these matters will be discussed at more length in the later publication wherein the behavior of 10 at other temperatures and in other solvents, as well as the synthesis and behavior of other compounds of structure 1, will be described.

Acknowledgement. We appreciate very much the support given this work by National Science Foundation Grant GP-1968.

References. 1. J. W. Wilt and C. A. Schneider, J. Org. Chem., 26, 4196 (1961).

2. J. W. Wilt, C. A. Schneider and C. A. Parsons, Abstracts of Papers, 148th National Meeting of the American Chemical Society, Chicago, September, 1964, p. 44S.

3. J. W. Wilt and C. A. Schneider, Chem Ind. (London), 951 (1963).

4. A.Streitwieser, Chem. Rev., 56, 675 (1956).

5. Such rate differences become more pronounced at lower temperatures. For example, the neophyl/neopentyl rate ratio at 133° is ca. 70, while at 50° it is nearly 500!