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CONVERSION OF (+)-CAMPHOR TO THE ENANTIOMERIC HYDROCAMPHENYL-ISOBORNYL CATIONS BY THE σ- AND π-ROUTES OF SOLVOLYSIS

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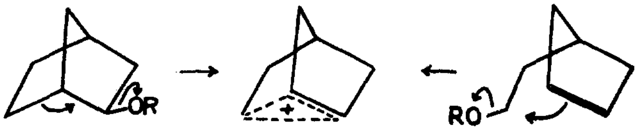
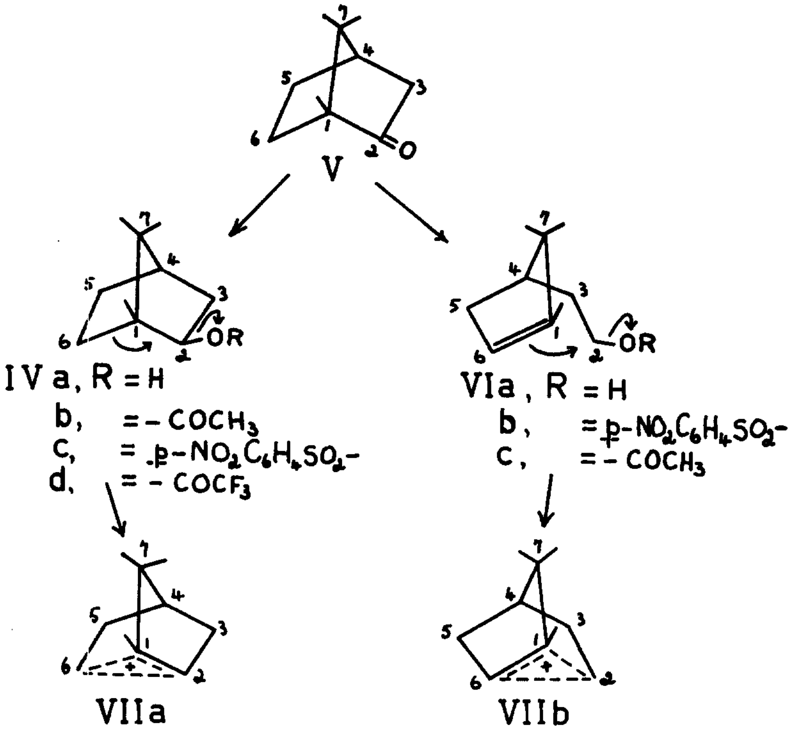
Winstein and Carter (1) have conveniently classified anchimerically assisted ionisations of substrates in which the neighbouring group contributes σ or π electrons as the σ- and π-routes to the corresponding cations. For the norbornyl cation (II), the σ-route may be illustrated by the solvolysis of exo-norbornyl p-bromobenzenesulphonate (I, R = p-bromobenzenesulphonyl) (2), while the π-route is shown by solvolysis of β-(cyclopent-3-enyl)ethyl arenesulphonates (III, R=arenesulphonyl) (3,4)



I II III

We now report the conversion of (+)-camphor (V) to the enantiomeric hydrocamphenyl-isobornyl cations (VIIa and VIIb) by the σ- and π-routes of solvolysis. (+)-α-Campholenyl p-nitrobenzenesulphonate (VIb), m.p. 87-8° (dec.), $[\alpha]_D^{20}$ + 3.4 ($CHCl_3$) was prepared from (+)-α-campholenol (VIa) which was obtained from (+)-camphor via (+)-camphor-10-sulphonic acid by



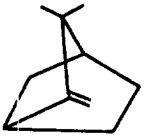
V

IVa, R = H
b, = $-COCH_3$
c, = p-$NO_2C_6H_4SO_2$-
d, = $-COCF_3$

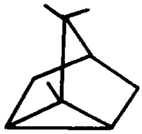
VIa, R = H
b, = p-$NO_2C_6H_4SO_2$-
c, = $-COCH_3$

VIIa

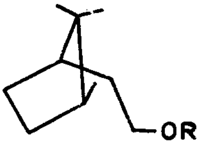
VIIb



VIII



IX



X

known reactions (5). Acetolysis of the sulphonate VIb for 5 hours at 100° in the presence of excess of sodium acetate yielded a mixture consisting of camphene (VIII, 73%), tricyclene (IX, 2%), isobornyl acetate (IVb, 14%), α-campholenyl acetate (VIc, 8%) and an unidentified compound (3%).* The camphene isolated from this reaction had $[\alpha]_D^{21}$ - 98 (benzene), lit. (6) $[\alpha]_D^{25}$ + 107 (benzene).

Using standard techniques (7), good first order kinetics were observed when VIb (ca. 0.02M) was solvolysed in ca. 0.04M acetic acid solution of sodium acetate at various temperatures. The rate constant (4.08×10^{-4} sec^{-1}) at 60° is 3.7 times greater than that reported (3) for β-(cyclopent-3-enyl)ethyl p-nitrobenzenesulphonate (III, R=p-nitrobenzenesulphonyl): this increase undoubtedly is due to the electron-donating methyl group at C_1 in VIb. This rate constant was also 203 times greater than that observed at 60° for the saturated p-nitrobenzenesulphonate (X, R=p-nitrobenzenesulphonyl) m.p. 64-65°, thus indicating a considerable degree of anchimeric assistance by the double bond in the ionisation.

From an Arrhenius plot, k_{VIb} at 100° was found to be 1.26×10^{-2} sec^{-1}, this value being 153 times the one observed with X at 100°. Because of this large ratio, it may be thought that the monocyclic unsaturated acetate VIc is derived by acetate ion attack on C_2 of the bridged ion VIIb. There seems, however, to be no report in the literature of the unsaturated alcohol VIa, or any of its derivatives, having been identified in solvolyses involving the non-classical carbonium ion VIIa. This is consistent with our observation that the unsaturated acetate VIc could not be detected after acetolysis of (-)-isobornyl trifluoroacetate (see below).

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* The analyses were carried out by gas phase chromatography

It would thus seem that the non-classical carbonium ions VIIa and VIIb generated by the σ- and π-routes differ to a small extent, and that one, or maybe both, undergo reactions before the most stable carbonium ion configuration is reached.

We wished to compare the solvolysis products of isobornyl p-nitrobenzenesulphonate (IVc) with those of α-campholenyl p-nitrobenzenesulphonate. All attempts, however, to prepare sulphonic acid esters of isoborneol failed. Reduction of (+)-camphor with lithium tri-tert-butoxyaluminohydride yielded a mixture of (-)-isoborneol (96%) and (+)-borneol (4%) (8). Attempted esterification of this mixture with p-nitrobenzenesulphonyl chloride in pyridine at room temperature for 10 days yielded the expected quantity of bornyl p-nitrobenzenesulphonate m.p. 94-95° (dec.), together with camphene (60%) $[\alpha]_D^{27}$ + 110 (benzene) and unchanged isoborneol (40%). Similar results were obtained when the reaction temperature was 0°, or when p-toluenesulphonyl or methanesulphonyl chlorides were employed. Esterification is apparently very slow due to the hindered nature of the hydroxyl group in isoborneol, but once formed, the sulphonates rapidly solvolyse via the σ-route to yield camphene of high optical purity. The preparation of isobornyl p-toluenesulphonate has been reported by Hückel (9). The remarkable lack of solvolytic reactivity reported for this compound, together with the known great reactivity of isobornyl chloride, make it extremely doubtful that Hückel's compound was in fact a derivative of isoborneol.

A new σ-route to the hydrocamphenyl-isobornyl cation has been provided by acetolysis of (-)-isobornyl trifluoroacetate (IVd), b.p. 87-88°/15 mm, $[\alpha]_D^{19}$ = - 32.5 ($CHCl_3$). Solvolysis of IVd (containing 4%

(+)-bornyl trifluoroacetate) in buffered acetic acid at 100° for 5 hours gave a mixture consisting of camphene (76%), tricyclene (4%), isobornyl acetate (12%), an unidentified compound (3%) and unchanged bornyl trifluoroacetate (5%). The camphene from this reaction had $[\alpha]_D^{21}$ + 103 (benzene).

Of special interest is the fact that the non-classical carbonium ions produced by the σ- and π-routes of solvolysis, VIIa and VIIb respectively, are non-superimposable mirror images. In the formation of VIIa, the C_1-C_6 bond initially present in camphor migrates, resulting in C_6 being partially bonded to both C_1 and C_2. In the preparation of campholenol, however, the C_1-C_2 bond initially present in camphor is broken, resulting ultimately in C_2 being partially bonded to C_1 and C_6 in VIIb. Because of the unique properties of VIIa and VIIb, it has been possible to prepare both (+)- and (-)-camphene of high optical purity from (+)-camphor.

In view of the current interest in the exact nature of carbonium ions such as VIIa, a comparison of the solvolysis products of other isobornyl, bornyl and α-campholenyl derivatives is being made.

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