(i) the anomalies are displayed by the primary alkyl substituents which have large numbers of hydrogens in the 7 position and (ii) the number of hydrogens in the 7 position has a direct, although small, effect on electron densities near the nitrogen.

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(5) All substituent groups R′ are where possible in a fully staggered conformation, with the exception of those with an odd number of α'-hydrogens (1, 6, 7, and 10), in which the oxygen is eclipsed. The *i*-Bu substituent conformation places the β'-H cis to the amide hydrogen. In *s*-Bu conformations, the γ'-C is nearly cis to the nonadjacent β'-C, being 15° above the β', α', β'-C plane. Finally, in *i*-PrMeCH, one γ'-C is trans to the nitrogen and the other trans to the α'-H.
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(13) The range of the ^{13}C chemical shift of the carbonyl carbon is only 2.1 ppm. We thank Dr. George Levy of Florida State University for making available this preliminary data (private communication).
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Stereospecific Formation of 1,3,3-Trimethyl-2-*endo*-acetoxynorbornane in the Reaction of Acetylsulfoacetic Acid on Terpinolene

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The acetoxylation of terpinolene by acetylsulfoacetic acid in acetic anhydride seems to take place through the formation of an intimate ion pair which leads stereospecifically to the 1,3,3-trimethyl-2-*endo*-acetoxynorbornane.

Ethylenic ketones and alkylacetates are obtained[1,2,3] by addition of acetylsulfoacetic acid[4] to olefins. In this reaction both acetylation and acetoxylation seem to take place in a two-step pathway, as checked with open-chain and cyclic alkenes (unpublished work, to be submitted to this journal). In all cases the structure of the acetylation products fits with the hypothesis of electrophilic addition of an acetylium ion, followed by a proton elimination during a second stage. On the other hand the acetoxylation can be interpreted as a proton addition followed by that of an acetate ion.

Yet a problem arises in the acetoxylation of terpinolene which leads exclusively to the 1,3,3-trimethyl-2-*endo*-acetoxynorbornane, instead of the expected 1-acetoxy-4(8)-*p*-menthene or 8-acetoxy-1-*p*-menthene (Figure 1). At first sight, if the reaction takes place through a carbocation, terpinolene and limonene should give rise to a common acetoxylation product. As we can report, this is not the case. Next we must notice that, whereas in the acetoxylation of terpinolene the only product is a stereospecific bicyclic acetate, we obtained exclusively monocyclic acetates in the case of limonene. As previously observed,[5-8] limonene seems not to bicyclize under acid-catalysis conditions. In order to explain this behavior of limonene, Sorensen[9] assumes that the *p*-menth-1-en-8-yl cation, created in the first reaction step by addition of a proton to the C-9 atom, shows an equatorial disposition of the isopropylium substituent at the C-4 atom. Such a spatial arrangement disfavors overlapping between the empty 2p orbital at the C-8 atom and the π bond on C-1,C-2 atoms. The situation is quite different in the case of terpinolene, where the spatial disposition of the substituent on the C-4 atom is altered during the proton approach. By the rehybridization process the isopropylium is pushed in an axial disposition that facilitates the overlapping of the concerned orbitals and accordingly the bicyclization.

The last point to be considered is the nature of the reaction medium. As Whittacker et al.[10] showed, in anhydrous acetic acid solutions sulfuric acid adds in its undissociated form to ethylenic bonds, as does acetic acid itself. To our mind acetic anhydride is a bad ionizing solvent too, leading to the formation of an intimate ion pair during the primary attack of the alkene substrate, put forth by the un-ionized acid B–H.[11,12] Whatever the accurate structure of the counterion of the intimate ion pair would be, it seems to contribute so adequately to its stabilization that rearrangement[13] would take place before any capture by an external nucleophile.

Keeping these arguments in mind, the stereospecific formation of 1,3,3-trimethyl-2-*endo*-acetoxynorbornane can be anticipated as follows (Figure 2):

The approach of B–H initiates the formation of a bond between the C-4 atom of terpinolene and H which is paralleled by a movement of the C-4 substituent toward axial disposition, as indicated; the C-8 atom acquires a cationic character. Simultaneous overlapping of the C-8 $2p_z$ orbital with the π orbital resting on C-1,C-2 begins. The structure of an intimate ion pair is attained.

Because of unfavorable steric interactions between the substituents of C-1 and C-8, the orbital overlapping seems to strengthen the attraction between C-8 and C-2, the C-1 atom moving at the same time in the opposite direction. Overlapping of C-3 and C-1 orbitals begins by neighboring group

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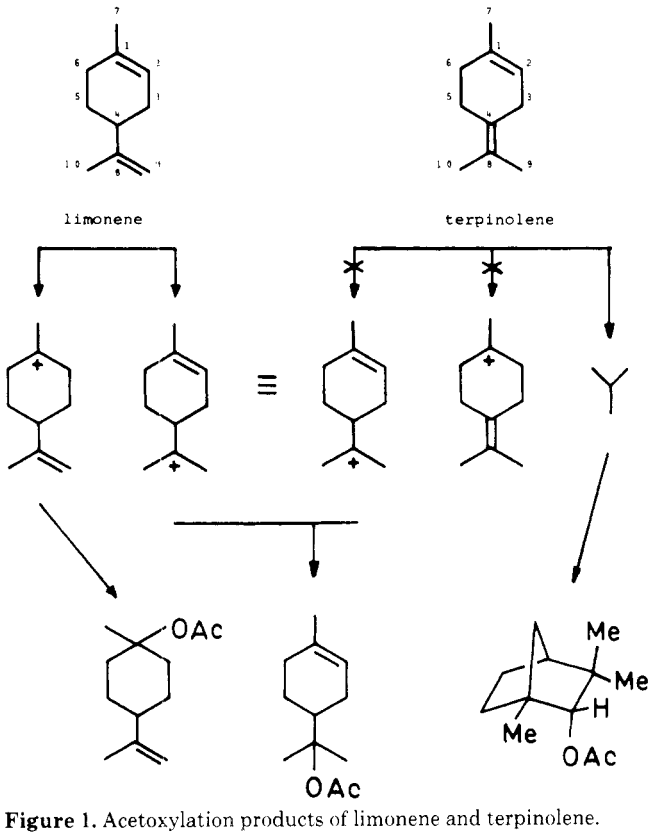

Figure 1. Acetoxylation products of limonene and terpinolene.

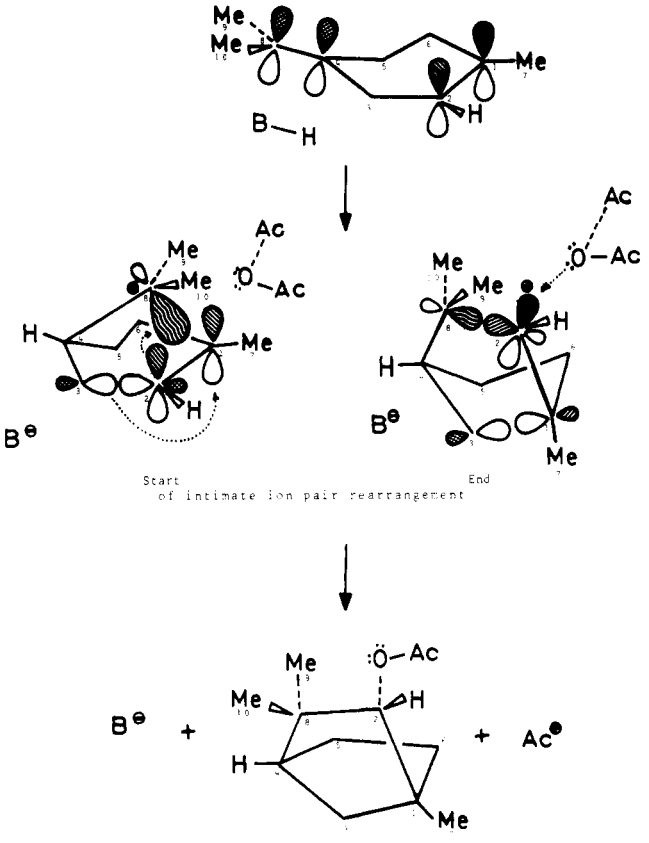

Figure 2.

participation, whereas simultaneously the C-2,C-3 bond is weakened. At the end of the rearrangement (Figure 2) the cation of the intimate ion pair has a structure analogous to one of those intervening in the acid[10,12,14] or basic[15] solvolysis of pinenes; the cationic character rests on the C-2 atom.

A solvent molecule (acetic anhydride) approaches the C-2 atom and releases the acetate group which is stereospecifically attached in the endo position. The global process is a trans addition.

Experimental Section

Preparation of Acetylsulfoacetic Acid (ASA). A solution of pure sulfuric acid in acetic anhydride (H_2SO_4/Ac_2O less than 1/5) is reluxed for 15 min. The liquid turns dark red and changes into an Ac_2O solution of ASA.

Reaction between ASA and Terpinolene. Ac_2O solutions of ASA and of terpinolene are cooled separately below 0 °C, mixed by adjusting them in such a way as to reach a molar fraction value of terpinolene/Ac_2O equal to 3/20. The mixture is stirred on an ice bath for 2 h. After hydrolysis and extraction of the aqueous layer, the organic fractions are collected, dried, and separated by preparative GLC (stationnary phase carbowax 20 M). As an example, we give the results obtained when the molar fraction ASA/terpinolene/Ac_2O was 0.73/3/20: recovered terpinolene 10%, *p*-cymene 17%, 2-acetyl-*p*-cymene 18%, 8-acetyl-*p*-cymene 18%, 4-acetyl-1,8-*p*-menthadiene + 6-acetyl-α-terpinene 26%, 1,3,3-trimethyl-2-*endo*-acetoxynorbornane 11%. No formation of the latter compound is observed when the ASA molar fraction is taken below 0.55/3 terpinolene/20Ac_2O.

Spectroscopic Data. Terpinolene (1,4(8)-*p*-Menthadiene) and *p*-Cymene (*p*-Me, *i*-PrBz). The IR and the NMR of the proton spectra are identical with the literature data.

1,3,3-Trimethyl-2-*endo*-acetoxynorbornane: IR (CCl_4) 2990, 2900, 1735, 1250 cm^{-1}; NMR (CCl_4) δ 0.72 (s, 3 H), 1.05 (d, J = 3, 5 Hz, 6 H), 1.62 (t, J = 2 Hz, 2 H), 1.97 (s, 3 H), 4.28 (d, J = 2 Hz, 2 H).

4-Acetyl-1,8-*p*-menthadiene: IR (CCl_4) 3120, 1710, 1640, 900, 865 cm^{-1}; NMR (CCl_4) δ 1.60 (m, 6 H), 1.95 (s, 3 H), 4.93 (m, 2 H), 5.30 (m, 1 H).

2-Acetyl-*p*-cymene: IR (CCl_4) 2980, 1685, 1560, 1495, 1380, 1350, 1260, 820 cm^{-1}; NMR (CCl_4) δ 1.20 (d, J = 7 Hz, 6 H), 2.44 (s, 3 H), 2.47 (s, 3 H), 2.90 (sept, J = 7 Hz, 1 H), 7.25 (3 H, ABC system).

8-Acetyl-*p*-cymene: IR (CCl_4) 2990, 2930, 1710, 1510, 1350 cm^{-1}; NMR (CCl_4) δ 1.33 (s, 6 H), 1.75 (s, 3 H), 2.26 (s, 3 H), 7.01 (s, 4 H).

These spectra were performed with the aid of Beckman IR 8 and Varian A 60 spectrometers.

Registry No.—ASA, 29721-78-6; terpinolene, 586-62-9; *p*-cymene, 99-87-6; 2-acetyl-*p*-cymene, 1202-08-0; 8-acetyl-*p*-cymene, 25570-48-3; 4-acetyl-1,8-*p*-menthadiene, 68475-34-3; 6-acetyl-2-terpinene, 68475-35-4; 1,3,3-trimethyl-2-*endo*-acetoxynorbornane, 4057-31-2; sulfuric acid, 7664-93-9; acetic anhydride, 108-24-7.

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