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MIGRATION OF ELECTRONEGATIVE SUBSTITUENTS II.

AN EXTREMELY FACILE DECARBETHOXYLATION OF 4,4-DICARBETHOXYCYCLOHEXADIENONE.[1]

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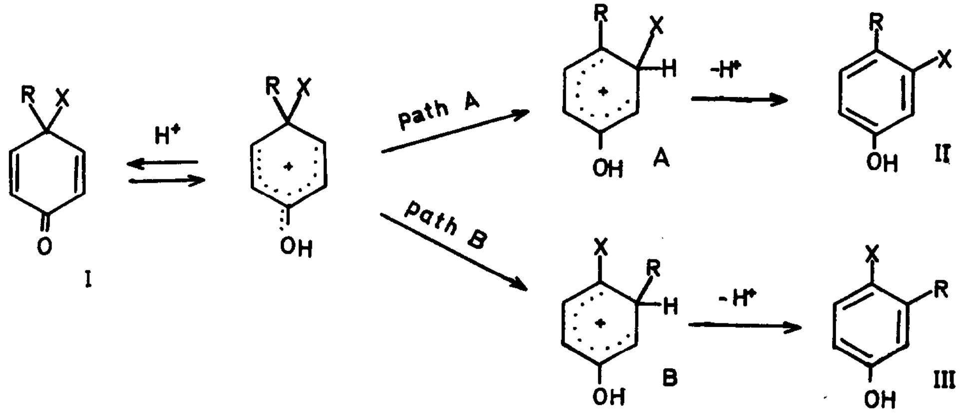
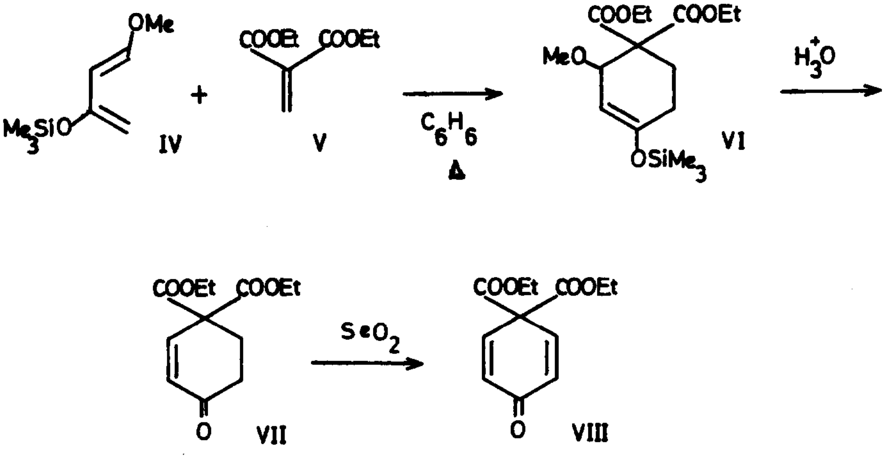
Electronegative substituents undergo surprisingly facile 1,2-shifts in carbonium ion reactions in certain systems. For example, the carbethoxy group migrates in preference to a phenyl group in the dienone-phenol rearrangement.[1] Yet the electronegative groups are polarized such that the atom actually migrating is relatively positive and should be poor in stabilizing further positive charge in the transition state.

It is now clear, from work by ourselves[1] and others,[2] that the group remaining behind is the major factor that decides which group migrates. As applied to the dienone-phenol rearrangement, path a is favored, and the electronegative substituent X migrates primarily by default, since X would show a strong destabilizing influence on ion B and hence the transition state leading to it.

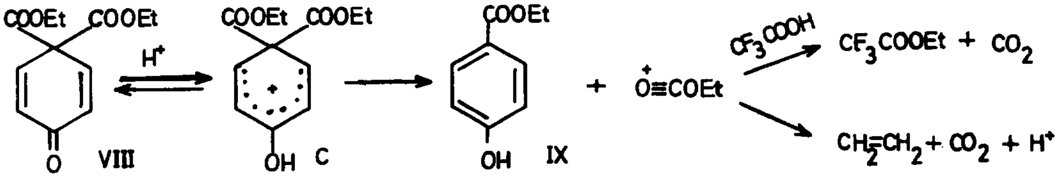


We now report an attempt to force the dienone-phenol rearrangement to follow path b, in order to quantitatively evaluate by rate measurements, just how destabilized ion B is. Our approach is to study the rearrangement of a dienone I containing two electronegative substituents. We have chosen the dienone of type I where R = X = COOEt (Compound VIII). The prediction can be made that if migration occurs, the rearrangement should be several orders of magnitude slower than in the dienone I, where R = CH_3, X = COOEt and path a is followed.[1]

Synthesis of 4,4-dicarbethoxycyclohexadienone (VIII) was accomplished, utilizing Danishefsky's cyclohexenone synthesis.[3] Thus methylene diethylmalonate (V)[4,5] was allowed to react under N_2 in refluxing benzene for 24 hours with 1-methoxy-3-trimethylsiloxy-1,3-butadiene (IV), to give the adduct VI. As expected,[3] none of the product of the alternative mode of Diels-Alder addition could be detected. The adduct VI was hydrolyzed directly with excess 0.1 N HCl in THF for one hour at 25° to give the cyclohexenone VII (64%); nmr: $\delta(CCl_4)$; 1.27, 6H, t, J = 7; 2.48, 4H, s; 4.22, 4H, q, J = 7; 6.00, 1H, d, J = 10; 7.02, 1H, d, J = 10. IR: ν_{CHCl_3} 1700-1730 (br); 1630 cm^{-1}; semicarbazone, mp 203-204°. Oxidation of VII with SeO_2 in t-BuOH-HOAC gave the dienone VII (78%); $bp_{0.2}$ 116-122°; nmr: $\delta(CCl_4)$; 1.29, 6H, t, J = 7; 4.32, 4H, q, J = 7; 6.31 2H, d, J = 10; 7.09, 2H, d, J = 10; IR: ν_{CHCl_3} 1690-1725 (br), 1630 cm^{-1}; M^+, m/e 238. Other approaches to the dienone were unsuccessful.[6]



The dienone VII reacted rapidly with anhydrous trifluoroacetic acid with gas evolution. At 25°, the half-life was ca. 2 minutes. The products were 4-carbethoxyphenol, mp 111-112°; carbon dioxide; ethylene identified by trapping as ethylene dibromide; and ethyl trifluoroacetate.



The observed products are consistent with the above mechanism, as are the following facts: (i) The carbethoxy group is normally stable for days in anhydrous trifluoroacetic acid; (ii) malonic esters are also normally stable in CF_3COOH, even in the cyclohexeneone VII; (iii) mechanisms involving ester hydrolysis were ruled out by use of anhydrous conditions; (iv) the ion C can be detected by nmr by the downfield shift of the vinyl protons (α protons shifted 0.39 ppm and β protons shifted 0.49 ppm), as is found for other dienones in this medium;[1] (v) the fragmentation was found to proceed, although much slower (half-life ca. 8 hrs. at 25°) in anhydrous formic acid, and both ethylene and ethyl formate were formed; (vi) generation of the ethoxyacylium ion by other means, e.g., $AgBF_4$ on ethyl chloroformate,[11] gives rapid fragmentation analogous to that observed in this work.

The rapid fragmentation reaction observed with 4,4-dicarbethoxycyclohexadienone unfortunately does not give any direct evidence on the dienone-phenol rearrangement. However, it does give supportive evidence that path b of Scheme I is a high energy pathway since the compound follows a fragmentation pathway instead.

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5. Methylene diethylmalonate, nmr: $\delta(CCl_4)$; 1.31, 6H, t, J = 7; 4.24, 4H, q, J = 7; 6.42, 2H, s, as prepared by reference 4, was contaminated with some unidentified saturated products, presumably dimers, which could not be easily removed by distillation. Since the desired product repolymerizes easily and the contaminants were inert in the Diels-Alder reaction, the crude material was used.
6. Addition of diethylmalonate to divinylketone[7] or vinyl β-chloroethylketone[8] gave only low yields of 4,4-dicarbethoxycyclohexanone. The compound has been made by another route.[9] Attempted condensation of diethyl malonate with bis-β-chlorovinyl ketone[10] gave none of the desired cyclohexadienone VIII.
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