

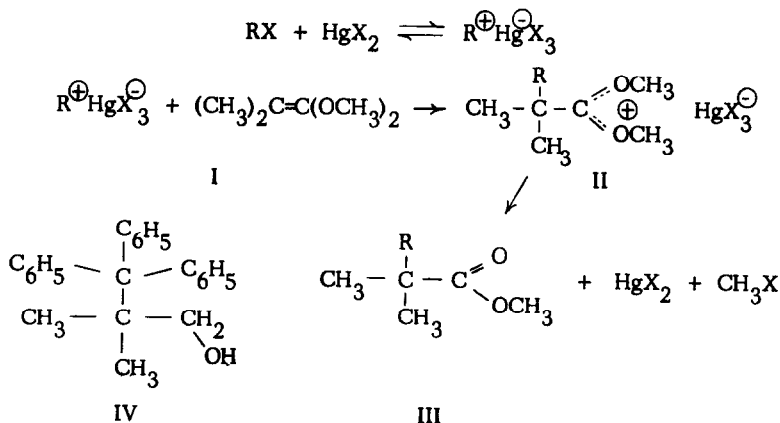
REACTION OF THE TRITYL CATION
 WITH DIMETHYLKETENE DIMETHYLACETAL (I)

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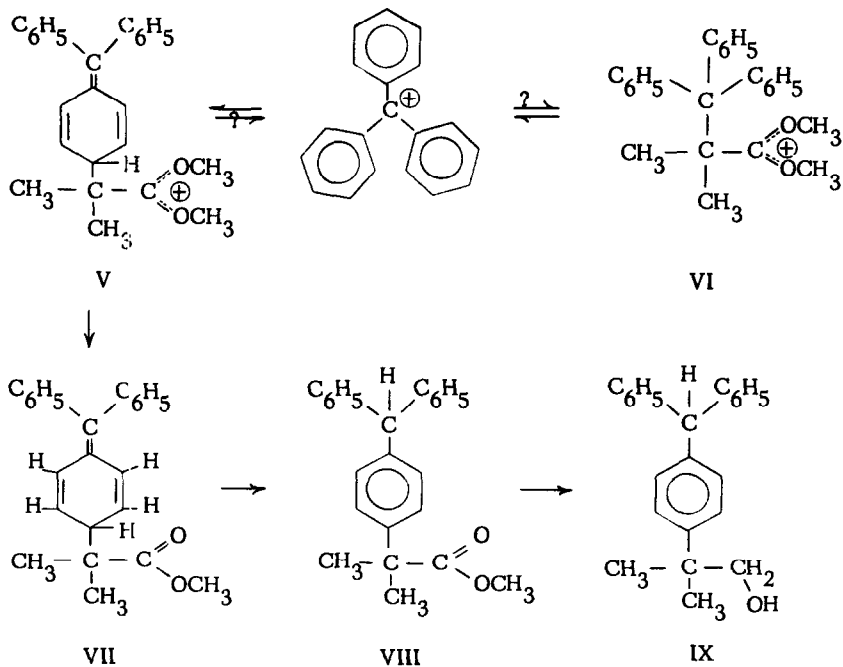
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Recent interest in the behavior of trityl cationic intermediates (2) prompts us to report the interesting behavior of the trityl cation toward dimethylketene dimethylacetal (I) which we noted some years ago (3) while employing McElvain's method (4) of preparing esters of type III from a reactive halide (RX), mercuric chloride and a ketene acetal (I). This synthesis presumably involves attack of a carbonium ion species on the ketene acetal to yield cation II; nucleophilic attack on one of the methoxyl methyl groups then yields III.



Trityl bromide was employed in the synthesis in order to prepare ester III with R = trityl for eventual lithium aluminum hydride reduction to alcohol IV containing a β -trityl group. However, the final alcohol, m. p. 75-76°, with a correct C,H-analysis, proved not to be IV. The behavior of its p-bromobenzenesulfonate derivative, m. p. 125-126° (dec.), in acetolysis did not correspond to the IV structure, and, in fact, the alcohol and its p-bromobenzenesulfonate derivative proved to be identical with p-benzhydrylneophyl alcohol (IX), m. p. 75.5-77°, and its bromobenzenesulfonate, respectively, which we synthesized and have already described elsewhere (5). The identity was confirmed by mixed m. p. and acetolysis rate of the bromobenzenesulfonate at 50° and 75°.



Thus, the reaction of trityl bromide with dimethylketene dimethylacetal (I) does not yield ester III with R = trityl as supposed by McElvain (4) by analogy with the various other syntheses carried out by this general method. The ester obtained, m. p. 105-107°, is instead the quinoidal derivative VII, resulting from reaction of the trityl cation at a para position. The ultraviolet spectrum of this material, with λ_{max} at 310 m μ in isooctane ($\epsilon = 25, 200$), is in accord with structure VII, as is also the n. m. r. spectrum. Taken in CDCl₃, the n. m. r. spectrum of VII shows signals for 10 aromatic protons at τ 2.80, 2 vinyl protons at 3.47, 2 other vinyl protons at 4.33, 3 methoxyl methyl protons at 6.31, 1 bisallylic proton at 6.46 and 6 methyl protons at 8.80 p. p. m.

Treatment of ester VII with methanolic sodium methoxide converts it to the aromatized isomer VIII, $n_D^{25} 1.5853$, with a correct C, H analysis. The isomerization presumably proceeds by formation and re-protonation of a trityl type anion (6). Both the quinoidal and aromatic isomers VII and VIII are converted to the p-benzhydrylneophyl alcohol IX on lithium aluminum hydride reduction.

The formation of the quinoidal ester VII makes it clear that the trityl ion reacts at a para position with dimethylketene acetal as a relatively highly hindered nucleophile to give the quinoidal cation V which then leads to the quinoidal ester VII. Whether the isomeric cation VI is also formed reversibly to any extent during the reaction is not known. In any case, the present results emphasize the possibility of reactions of the trityl cation with nucleophiles at a benzene ring position, giving rise to new final products or possible transient intermediates with the nucleophile at

a ring position instead of the central carbon atom (7).

REFERENCES

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