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A ONE-STEP SYNTHESIS OF 1,1-DIFLUOROOLEFINS FROM KETONES

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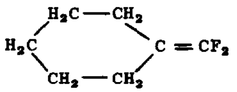
We recently reported a one-step transformation of aldehydes into 1,1-difluoroolefins by heating an aldehyde, triphenylphosphine and sodium chlorodifluoroacetate in monoglyme or diglyme.[1]

Attempts to extend this reaction to ketones, using the same conditions, were not successful. A gas chromatography (G.L.C.) examination of the reaction mixture of cyclohexanone, triphenylphosphine and sodium chlorodifluoroacetate in diglyme showed none of the desired product. Replacement of triphenylphosphine with tributylphosphine or replacement of diglyme with N-methylpyrrolidone resulted in a 1-2% yield (G.L.C.) of difluoromethylenecyclohexane I (b.p. 105-106°, $\lambda_{\max}^{\text{film}}$ 5.70 μ)



I

However, the use of both tributylphosphine and N-methylpyrrolidone gave a 46% yield of I. Other satisfactory polar solvents, used with tributylphosphine, were tetramethylurea, dimethylformamide, dimethylacetamide, and dimethyl sulfoxide. A 41% yield of I (based on sodium chlorodifluoroacetate) was obtained using excess cyclohexanone as solvent.

Similar treatment of acetophenone with tributylphosphine and sodium chlorodifluoroacetate in N-methylpyrrolidone gave a 34.6% yield of

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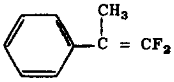
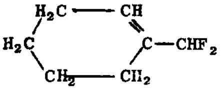
*Deceased

β,β-difluoro-α-methylstyrene II (b.p. 58-59°/21 mm., λ_{max}^{film} 5.80 μ).



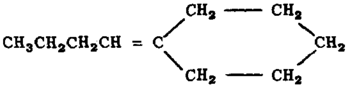
II

In general, the synthesis of 1,1-difluoroolefins from ketones, in comparison with that from aldehydes, gave poorer yields and several side products. Thus, the following products were separated by G.L.C. from the reaction of cyclohexanone with tributylphosphine and sodium chlorodifluoroacetate: 1-difluoromethylcyclohexene-1 III (the endo isomer of I),



III

and butylidenecyclohexane IV.



IV

A typical procedure is as follows. To a stirred, hot (160-180° bath) solution of 0.06 mole of the ketone, 0.066 mole of tributylphosphine in 10 ml. of dry N-methylpyrrolidone in a nitrogen atmosphere, was added dropwise over one hour a warm solution (60°) of 0.12 mole of sodium chlorodifluoroacetate in 50 ml. of dry N-methylpyrrolidone. The products, solvent, and unreacted ketone were flash-distilled at 1 mm. and a bath temperature of 100° into a receiver cooled with dry-ice. This distillate was fractionated through a spinning-band column.

Analytical samples were prepared by gas chromatography. Elemental analysis, infrared, mass, and n.m.r. spectra were consonant with the assigned structures.

Further exploitation of this convenient route to 1,1-difluoroolefins, and mechanistic justification for side reactions will be presented at a later date.

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REFERENCES

(1.) S. A. Fuqua, W. G. Duncan, and R. M. Silverstein, Tetrahedron Letters, 23, 1461 (1964)