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A NOVEL DOUBLE ELIMINATION OF ARSONIUM SALTS. ONE-POT SYNTHESIS OF 4-TRIFLUOROMETHYL-2,4-DIENYL CARBOXYLATES

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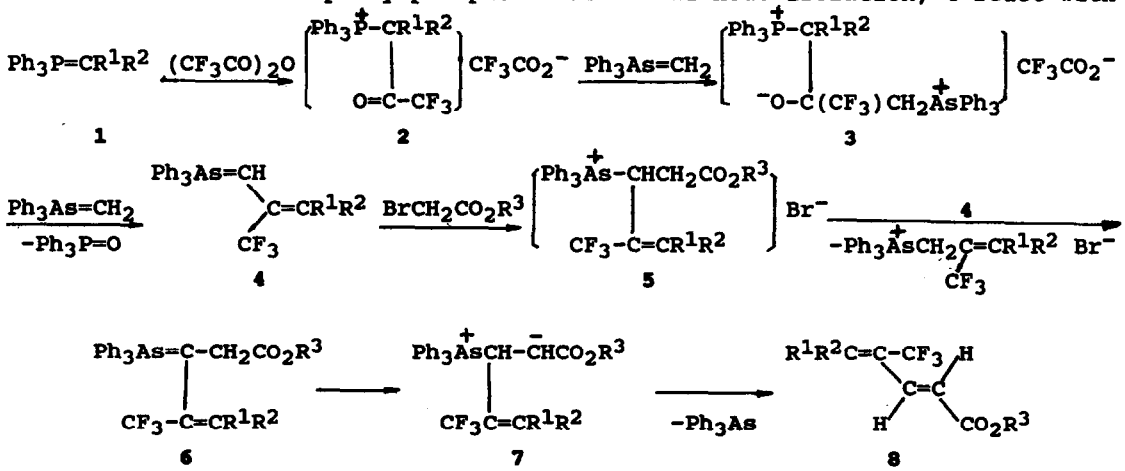
Summary. A novel double elimination of arsonium salts and its application to the synthesis of 4-trifluoromethyl-2,4-dienyl carboxylates are described.

2,4-Dienyl carboxylates are useful intermediates in organic synthesis, particularly in the synthesis of various natural products.[1] Tsuji et al. reported a palladium-catalyzed carbonylation of propargylic carbonates for the preparation of 2,4-dienyl carboxylates.[2] A four-steps process for their synthesis in an overall yield of 35% has been reported by Byrne et al.[3] Several other synthetic methods have also appeared in the literature.[4] However, the methods for the preparation of the trifluoromethyl analogues which is a key intermediate of trifluoromethylated polyene possessing biological activity[5] are still limited. The synthesis of 3-trifluoromethyl analogues starting from the corresponding allenic compounds was reported by Kobayashi et al.[5] We now wish to report a novel double elimination of arsonium salts and its application to the synthesis of 4-trifluoromethyl-2,4-dienyl carboxylates.

Trifluoromethylated arsoranes (4) were prepared by perfluoroacylation of 1,nucleophilic addition of methylenetriphenylarsorane to 2,deprotonation of 3 and elimination of triphenylphosphine oxide.[6] Without isolation, 4 react with



bromoacetic esters to give arsonium salts (5) in which a double elimination occurs affording 4-trifluoro-methyl-2,4-dienyl carboxylaters (8) in 43-69% yields (3 steps).

The first elimination of HBr takes place when 5 reacts with another molecule of 4 to give 6 which converts to 7 via hydrogen transfer, followed by second elimination of triphenylarsine to afford the products 8. The key steps are the conversion of 6 to 7 and subsequent elimination of triphenylarsine. It may be rationalized that 7 is more stable than 6 due to the negative charge can be stabilized by CO_2R^3 group.

The results are shown in Table 1. All compounds are new and characterized by microanalyses and IR, NMR and mass spectroscopies.

Table 1. Preparation of 4-Trifluoromethyl-2,4-dienyl Carboxylates

Compound	R^1	R^2	R^3	b.p.(°C/mm)	Yield(%)
8a	CH_3	CH_3	CH_3	66/10	45
8b	CH_3	CH_3	C_2H_5	72/10	43
8c	CH_3	CH_3	n-C_4H_9	82/10	65
8d	CH_3	CH_3	sec-C_4H_9	88/10	59
8e	-$(CH_2)_4$-		CH_3	52/2	62
8f	-$(CH_2)_4$-		C_2H_5	62/2	68
8g	-$(CH_2)_4$-		n-C_4H_9	76/2	69
8h	-$(CH_2)_4$-		sec-C_4H_9	74/2	69

In a typical procedure phenyllithium (4 mmol in 20 ml Et_2O) is added dropwise with stirring to a suspension of isopropyltriphenylphosphonium iodide (1.73g, 4 mmol) in absolute THF (30 ml) at -20°C under nitrogen. The reaction mixture is stirred for 30 min at -20°C, trifluoroacetic anhydride (0.63g, 3 mmol) is slowly added at -70°C until the characteristic ylidic colour disappeared.After stirring at -70°C for 15 min, a solution of methylenetriphenylarsorane [generted from methyltriphenylarsonium iodide (6 mmol) and phenyllithium (6 mmol) in diethyl ether (40 ml)] is slowly added over 0.5h and then methyl bromoacetate (0.23g, 1.5 mmol) is added and the mixture is stirred at 20°C for 1 h. The product is isolated by column chromatography (0.14g,45%).

This one-pot synthesis of trifluoromethyl 2,4-dienyl carboxylates is quite convenient with high stereoselectivity under mild conditions giving 2,E-isomer exclusively as judged on the basis of NMR spectroscopy and should be useful in the synthesis of biologically active compounds.

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