REACTION OF UNSYMMETRICAL FLUORINATED β-DIKETONES WITH DIHALOPHOSPHORANES: THE SYNTHESIS OF α,β-YNONES

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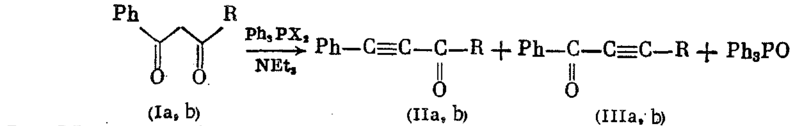
UDC 542.91:547.446.6'161:547.558.1'121

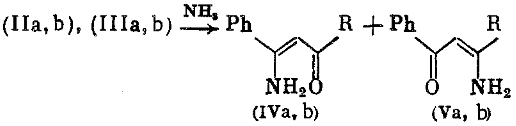
Phenylethynyl phenyl ketone has been obtained by the reaction of dibenzoylmethane with triphenylphosphine dibromide [1].

We have shown that the reaction of unsymmetrical fluorinated β-diketones (I) with dihalophosphoranes proceeds with the formation of a 3:1 mixture of α,β-ynones (II) and (III) in 80-95% overall yield.



R = CF_3 (a), C_3F_7 (b); X = Br, Cl.

The formation of a mixture of isomers (II) and (III) was confirmed spectrally and chemically: their treatment with ammonia gives a mixture of regioisometric β-aminovinyl ketones (IV) and (V), which were compared with authentic samples.



The reaction time was extended from 2 to 8-9 h upon using triphenylphosphine dichloride instead of triphenylphosphine dibromide and the yield of (II) and (III) was reduced by 3-10%. Triphenylphosphine oxide separated in the reaction may be converted to triphenylphosphine dichloride [2] and, thus, reused for the synthesis of α,β-ynones.

EXPERIMENTAL

The β-diketones were obtained according to our previous procedure [3], while β-aminovinyl ketones (IV) and (V) were obtained according to our earlier methods [4]. Triphenylphosphine dibromide obtained according to Armstrong et al. [5] was used *in situ*.

The elemental analysis data for the mixtures of isomers (II) and (III) were in accord with the calculated values. The IR, ^{19}F NMR, and ^{1}H NMR spectral indices for the compounds were presented by Shen et al. [6]. The isomer ratio was determined relative to the ratio of the integral intensities of the CF_3 signals in the ^{19}F NMR spectra.

Reaction of 1-Phenyl-4,4,4-trifluoro-1,3-butanedione (Ia) with Triphenylphosphine Dibromide. A sample of 3.68 g (23 mmoles) Br_2 was added dropwise with stirring to a solution of 6 g (23 mmoles) triphenylphosphine in 50 ml CH_2Cl_2 at 0°C and stirred until the reaction was decolorized. Then the temperature was brought to 20°C. A solution of 4 g (18.5 mmoles) β-diketone (Ia) in 20 ml CH_2Cl_2 was added and 4.6 g (46 mmoles) NEt_3 was added dropwise. At the end of the reaction as indicated by the disappearance of β-diketone by thin-layer chromatography (about 2 h), the mixture was washed with 100 ml dilute hydrochloric acid and 100 ml water. The organic layer was dried over $MgSO_4$. Dichloromethane was removed in vacuum. A sample of 100 ml hexane was added to the residue and the residue of triphenylphosphine oxide was filtered off. Hexane was removed in vacuum and the residue was fractionated in

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Institute of Chemistry, Urals Branch, Academy of Sciences of the USSR, Sverdlovsk. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 203-204, January, 1989. Original article submitted May 17, 1988.

vacuum to give 3.2 g (38%) of a 3:1 mixture of 1-phenyl-4,4,4-trifluoro-2-butyn-1-one (IIa) and 1-phenyl-4,4,4-trifluoro-1-butyn-3-one (IIIa), bp 35°C (1 mm).

Reaction of 1-Phenyl-4,4,5,5,6,6,6-heptafluoro-1,3-hexanedione (Ib) with Triphenylphosphine Dibromide. Analogously, 4 g (12.7 mmoles) β-diketone (Ib) gave 3.7 g (94%) of a 3:1 mixture of α,β-ynones (IIb) and (IIIb), bp 47°C (1 mm).

Reaction of 1-Phenyl-4,4,4-trifluoro-1,3-butanedione (Ia) with Triphenylphosphine Dichloride. A solution of 4 g (18.5 mmoles) β-diketone (Ia) in 20 ml CH_2Cl_2 was added to a solution of 15.2 g triphenylphosphine dichloride containing 45% reagent (23 mmoles) in 100 ml CH_2Cl_2 and 4.6 g (46 mmoles) NEt_3 was added dropwise. The reaction time was 8 h. The product was isolated as indicated above to give 3.1 g (85%) of a 3:1 mixture of α,β-ynones (IIb) and (IIIb), bp 35°C (1 mm).

Reaction of 1-Phenyl-4,4,5,5,6,6,6-heptafluoro-1,3-hexanedione (Ib) with Triphenylphosphine Dichloride. Analogously, 4 g (12.7 mmoles) β-diketone (Ib) gave 3.3 g (84%) of a mixture of α,β-ynones (IIb) and (IIIb), bp 47°C (1 mm). The reaction time was 9 h.

CONCLUSIONS

Unsymmetrical polyfluorinated β-diketones react with dihalophosphoranes to form mixtures of regioisomeric fluorinated α,β-ynones.

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O-PERFLUOROALKENYLOXIMES IN THE CLAISEN REACTION

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UDC 542.944.6:542.952.1:547.288.4'161

The products of the addition of O-nucleophiles to perfluoroisobutylene with the general formula $(CF_3)_2CHCF_2OR$ upon the reaction of base are readily dehydrofluorinated to give $(CF_3)_2C{=}CFOR$ [1]. However, the adduct of acetone oxime to perfluoroisobutylene (I) upon dehydrofluorination gives substituted pyrrolinone (II).

Unstable O-perfluoroisobutylene oxime (III) undergoes prototropic transformation to "enamine" form (IV) and then Claisen-type rearrangement, while iminoacid fluoride (V) cyclizes to give pyrrolinone (II). The analogous transformation of O-alkenyl oximes of alkyl ketones to give substituted pyrroles was described by Sheradsky [2] and Korostova et al. [3].

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 204-205, January, 1989. Original article submitted June 8, 1988.

0568-5230/89/3801-0190$12.50