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ISOMERIZATION IN THE YLID PREPARATION OF β-SUBSTITUTED PERFLUOROOLEFINS(1)

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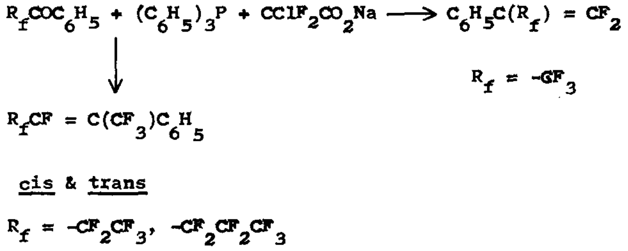
The facile preparation of terminal polyfluorinated olefins *via* a Wittig-type reaction has recently been reported by us.(2) Further examination of the scope and generality of this reaction has demonstrated that, under similar reaction conditions which yielded terminal olefins in the propene series, isomerized products are obtained when the perfluoroalkyl group is other than trifluoromethyl.



$$R_fCOC_6H_5 + (C_6H_5)_3P + CClF_2CO_2Na \longrightarrow C_6H_5C(R_f) = CF_2 \quad R_f = -CF_3$$

$$\downarrow$$

$$R_fCF = C(CF_3)C_6H_5$$

cis & trans

$R_f = -CF_2CF_3,\ -CF_2CF_2CF_3$

Fluoride ion catalyzed rearrangement reactions of terminal perfluoroolefins are well documented,(3) and the rearranged olefins are most likely produced by a fluoride ion catalyzed rearrangement of the initially formed terminal olefin. Support for this hypothesis was found

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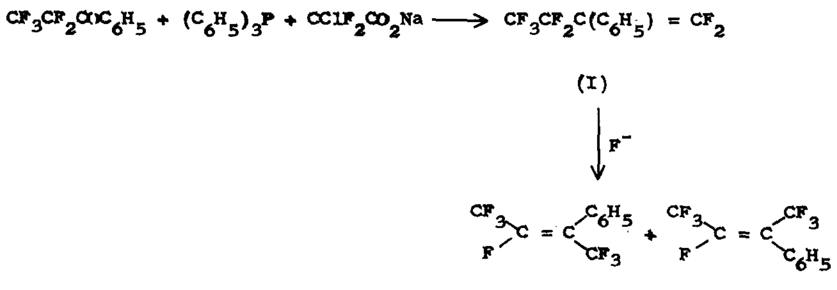


$$CF_3CF_2COC_6H_5 + (C_6H_5)_3P + CClF_2CO_2Na \longrightarrow CF_3CF_2C(C_6H_5) = CF_2$$

(I)

(III) (II)

when the reaction was quenched after six hours (cf. Table I) and 95% of the olefinic product was found to consist of the terminal olefin. A similar reaction carried out for 20 hours yielded only 30% terminal olefin and 70% rearrangement in accordance with initial formation of the terminal olefin and subsequent slow isomerization (in the case of the sodium salt) to the internal olefin.

The addition of other inorganic fluorides (KF, CsF) to the reaction mixture was found to accelerate the decarboxylation of the sodium chlorodifluoroacetate and to yield only rearranged products (see Table I). This was the expected behavior for a fluoride ion catalyzed isomerization of perfluoroolefins--namely, the order of catalytic reactivity being CsF > KF > NaF.

The variance of the cis-trans isomer ratio deserves some additional comment. In earlier investigations of the allylic isomerization of terminal perfluoroolefins by fluoride ion, simple propene systems were utilized. These systems provided excellent models for demonstrating the allylic nature of the rearrangement reaction and for demonstrating the carbanion nature of the intermediate.(3) However, they provided no

Table I

$C_6H_5COC_2F_5$ mMoles	$(C_6H_5)_3P$ mMoles	$CClF_2CO_2Na$ mMoles	Time Hr.	Net Olefin %	I %	II %	III %	$\frac{\text{trans}}{\text{cis}}$
50	50	50	20	60.0	10.6	30.9	58.6	1.9
50	100	100	20	65.0	9.7	33.7	56.6	1.7
50	50	50	6.5	44.3	94.7	2.4	2.8	1.2
50	100	100[a]	20	57.9	0.00	31.4	68.7	2.2
50	50	50[b]	1.0	35.2	0.00	15.6	84.4	5.4
50	50	50[b]	20	47.6	0.00	12.5	87.5	7.0
50	50	50[c]	49.5	25.2	100	0.00	0.00	--
50	50	100[d]	0.5	56.5	91.1	3.1	5.8	1.9

a. 200 mMoles of anhydrous KF added to the reaction mixture.

b. 100 mMoles of dry CsF added to the reaction mixture.

c. $CClF_2CO_2Li$ used in place of $CClF_2CO_2Na$.

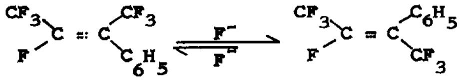
d. $CClF_2CO_2Li$ in N-methylpyrrolidone at 90°C used in place of $CClF_2CO_2Na$ in diglyme.

structural features for stabilization of the intermediate carbanion and were of limited utility for investigating the stability of polyfluorinated carbanions. The previously described ylid reaction(2) has provided a facile method for preparing terminal olefins in which the structural features can be varied widely and, hence, provide attractive systems for measuring stabilities of polyfluorinated carbanions. Such experiments are under active investigation in our laboratory and will be reported in due course.

The variation of the *cis*-*trans* isomer ratio with the addition of the inorganic fluoride salts suggested that two equilibria were probably involved in the isomerization reaction--isomerization to the internal olefin and subsequent equilibration between *cis* and *trans* isomers. In the case of sodium chlorodifluoroacetate and sodium chlorodifluoroacetate with added KF, the isomer distribution appeared to be that derived from the kinetically controlled product rather than the equilibrium controlled product. In the case of the added CsF, if the reaction were quenched rapidly (after one hour), more *cis* isomer was present than if the reaction were allowed to continue for a longer time. This behavior suggested rather slow equilibration by NaF and KF and rapid equilibration by CsF. Preliminary studies with NaF, KF, and CsF utilizing pure *cis* and *trans* olefins has

$$CF_3CF_2C(C_6H_5) = CF_2 \xrightarrow{F^-} CF_3CF = C(CF_3)C_6H_5$$

cis & *trans*



(II) (III)

confirmed these observations.

The preparation of the terminal olefin with little or no isomerization has been found possible by employing lithium chlorodifluoroacetate in the reaction. The rate of decarboxylation of the lithium salt is very slow (49.5 hours for complete decarboxylation) under conditions used for the sodium chlorodifluoroacetate (diglyme at 100°) but can be conveniently carried out in N-methylpyrollidone at 90°. The terminal olefin was formed almost exclusively, the product mixture being > 90% terminal olefin under these conditions (cf. Table I).

Elemental analysis, infrared, ultraviolet, and n.m.r. spectra were in agreement with the assigned structures. Although this report deals in detail only with the 1-phenylpentafluoropropanone, similar results have also been obtained with 1-phenylheptafluorobutanone.

In summary, the utility of this ylid reaction has been extended to encompass the one-step synthesis of both the terminal and internal-substituted perfluoroolefins. The product of the ylid reaction can be determined by the choice of reagents. Lithium chlorodifluoroacetate can be used for the preparation of the terminal olefins, sodium chlorodifluoroacetate for the internal olefin enriched in the cis-isomer, and sodium chlorodifluoroacetate with added cesium fluoride for the equilibrium mixture (enriched in the trans-isomer).

Additional work in this area is in progress.

Acknowledgment: This work was supported in part by a grant from the Public Health Service (GM 11809-02).

1. Although no detailed study of the mechanism of this reaction has been made, it seems reasonable from the products observed that an intermediate ylid is involved.

2. D. J. Burton and F. B. Herkes, Tetrahedron Letters, **23**, 1883 (1965).

3. W. T. Miller, Jr., J. H. Fried, and H. Goldwhite, J. Am. Chem. Soc., **82**, 3091 (1960); W. T. Miller, Jr., W. Frass, and P. R. Resnick, ibid., 83, 1767 (1961) and references cited therein.