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# SYNTHESES OF FLUORINE-CONTAINING INDANES AND INDENES : A NOVEL RADICAL CYCLOADDITION OF ALKYLBENZENES WITH HEXAFLUOROPROPENE

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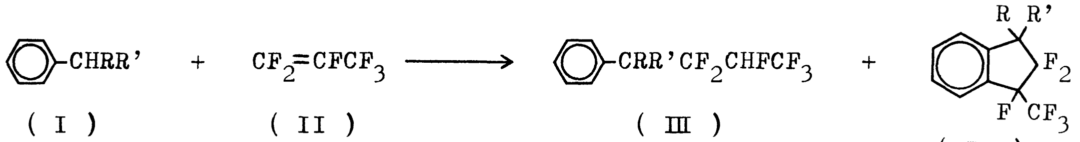
Four 1-trifluoromethyl-1,2,2-trifluoroindanes(IV) were synthesized in one step from alkylbenzenes(I) and hexafluoropropene(II) in the presence of di-*t*-butyl peroxide. The dehydrofluorination of IV gave the corresponding 1-trifluoromethyl-1,2-difluoroindenes(V).

As part of the study on radical addition reactions of fluoroolefins, we investigated[1)] the addition reaction of alkylbenzenes(I) to hexafluoropropene(II). Besides normal addition products(III), a small amount ( 1∼3% ) of 1-trifluoromethyl-1,2,2-trifluoroindanes(IV) were obtained as by-products. These products(IV) might be formed by a novel type of radical cycloaddition reaction of I with II. Formation

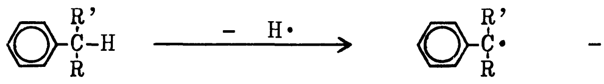


( I ) ( II ) ( III ) ( IV )

(Ia), (IIIa), (IVa) : R = R' = H ; (Ib), (IIIb), (IVb) : R = H, R' = $CH_3$ ;
(Ic), (IIIc), (IVc) : R = R' = $CH_3$

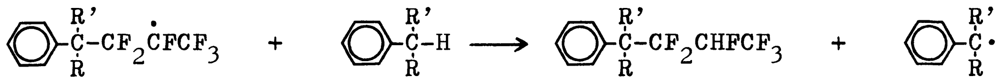
of the similar five-membered rings fused to aromatic ring in a radical reaction was reported in several papers,[2)] but their yields were poor as for the preparative purpose. Therefore, in this communication we reported an attempt to find the optimum reaction condition for synthesis of the indanes(IV).

The products, III and IV, are presumably formed by the following mechanism ;

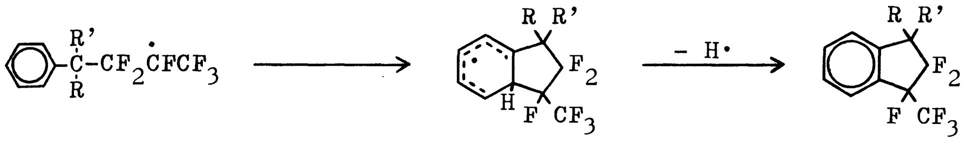


$$C_6H_5CRR'H \xrightarrow{-\ H\cdot} C_6H_5CRR'\cdot \qquad (1)$$

- - - - - - - - - ( 2 )



- - ( 3 )



- - - - ( 4 )

Accordingly, the ratio of III to IV should be determined by the competition between the intermolecular hydrogen abstraction ( eq. 3 ) and the intramolecular cycloaddition followed by loss of a hydrogen radical ( eq. 4 ). The following reaction conditions were adopted to get higher yields of IV : ( method **A** ) decrease in the molar ratio of I, increase in the amount of the initiator, and higher reaction temperature ; ( method B ) use of an inert solvent such as 1,1,2-trichloro-1,2,2-trifluoroethane in addition to the conditions used for method **A**.

The typical procedures employed are shown in an example of the addition reaction of toluene(Ia) ;

method **A** : A mixture of Ia ( 37g, 0.40 mol ), II ( 96g, 0.64 mol ) and DTBP ( 60g, 0.41 mol ) was heated in a 300ml stainless steel autoclave at temperature gradually rising from 130°C to 160°C for about 6 hours. After cooling, the reaction mixture was washed twice with 10% sodium hydrogen carbonate, and dried over magnesium sulfate. By vacuum distillation, unchanged Ia ( 4g, 0.043 mol, 11% ), IIIa ( 19g, 0.079 mol, 22% ), IVa ( 13g, 0.054 mol, 15% ) and high boiling residue ( 49g ) were obtained.

method B : A mixture of Ia ( 37g, 0.40 mol ), II ( 93g, 0.62 mol ) and DTBP ( 60g, 0.41 mol ) in 1,1,2-trichloro-1,2,2-trifluoroethane ( 187g, 1.00 mol ) was heated in a 500ml stainless steel autoclave, under the same reaction conditions as used for the method **A**. Distillation of the products gave the unchanged Ia ( 4g, 0.043 mol, 11% ), IIIa ( 13g, 0.054 mol, 16 % ), IVa ( 9g, 0.038 mol, 11% ) and high boiling residue ( 50g ).

In a similar procedure, methyl-substituted indanes ( IVb and IVc ) were prepared from ethylbenzene(Ib) and isopropylbenzene(Ic) respectively. In the case of **Ib**, equal amount of two stereoisomers ( IVb-1 and IVb-2 ) were obtained, and the isomers were separated using a preparative GLC. Their reaction conditions and product's yield were summarized in Table 1.

Table 1 The Radical Reactions of Alkylbenzenes with Hexafluoropropene

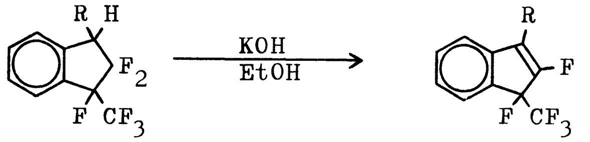
| Alkylbenzene ( mol ) | | HFP ( mol ) | DTBP ( mol ) | Method | III / IV * | Yield | | Higher boiling products ( g ) |
|---|---|---|---|---|---|---|---|---|
| | | | | | | III ( % ) | IV ( % ) | |
| (Ia) | 0.40 | 0.64 | 0.41 | A | 2.00 | 22.2 | 15.2 | 49 |
| (Ia) | 0.40 | 0.62 | 0.41 | B | 1.22 | 15.8 | 11.1 | 50 |
| (Ib) | 0.40 | 0.63 | 0.41 | A | 0.35 | 3.0 | 13.8 | 55 |
| (Ib) | 0.40 | 0.62 | 0.41 | B | 0.17 | 2.0 | 11.4 | 51 |
| (Ic) | 0.40 | 0.64 | 0.41 | A | 0 | – | 6.4 | 48 |
| (Ic) | 0.40 | 0.60 | 0.41 | B | 0 | – | 6.8 | 56 |

*) determined by the peak areas of GLC

From the Table 1, a large variation is observed in the ratios of III to IV. While the yields of III decreased markedly with increase in the number of the methyl group of the substrates due to steric hindrance, those of IV decreased only slightly.

Between two methods, A and B, method B is better than A in obtaining higher ratio of IV / III, but smaller in total conversion. Eventually the yield of IV was not much different in both methods.

The corresponding indenes(V) were prepared by dehydrofluorination of IV.



( IV ) ( V )

( IVa, Va : R = H ;
IVb, Vb : R = $CH_3$ )

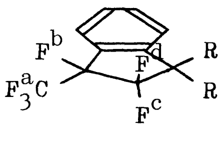
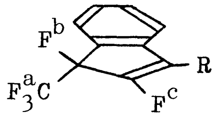
A typical procedure was the following : A solution of potassium hydroxide ( 2g, 36 mmol ) in 10 ml of absolute ethanol was stirred at room-temperature while IVa ( 2g, 8.3 mmol ) was added dropwise during 5 minutes. The reaction was slightly exothermic, and the color of the solution changed from pale yellow to dark reddish brown. After the solution was left standing for 5 hours, it was poured into dilute hydrochloric acid, extracted with 20 ml of dichloromethane, and dried over magnesium sulfate. Vaccum distillation gave 1.6g ( yield 88% ) of crude 1-trifluoromethyl-1,2-difluoroindene(Va) together with a small amount of 1-trifluoromethyl-1-fluoro-2-ethoxyindene.

In the case of IVb,3) Vb was obtained in 75% yields together with 7% of the unchanged indane, which was found to be only the low-boiling isomer(IVb-1).

The structures of the products were established by means of their elemental analyses and spectral data. The configuration of the two isomers, IVb-1 and IVb-2, was estimated by long-range couplings and chemical shifts of their fluorine NMR spectra and dehydrofluorination rate. In competitive dehydrofluorination,[4)] the high-boiling isomer(IVb-2) reacted four times faster than the low-boiling isomer (IVb-1). This may be partly due to the steric hindrance of a trifluoromethyl group of IVb-1 to the attack of the ethoxide anion and partly due to the steric repulsion between the leaving fluorine and the vicinal methyl or trifluoromethyl group of IVb-2 ( steric acceleration ).

Physical properties and spectral data were shown in Table 2.

Table 2 Physical Properties and Spectral Data of the Fluorinated Indanes and Indenes

| Compound | | R | R' | B.p. (°C) | $n_D^{20}$ | $d_4^{20}$ | $^{19}F$ NMR chemical shifts* $\delta_{F^a}$ | $\delta_{F^b}$ | $\delta_{F^c}$ | $\delta_{F^d}$ |
|---|---|---|---|---|---|---|---|---|---|---|
|  | ( IVa ) | H | H | 184 | 1.4272 | 1.422 | -1.1 | 92.3 | 36.4 | 33.3 |
| | (IVb-1) | H | Me | 195 | 1.4342 | 1.366 | -0.4 | 94.4 | 39.3 | 46.0 |
| | (IVb-2) | Me | H | 198 | ( M.p. 28°C ) | | -3.9 | 83.7 | 50.3 | 38.5 |
| | ( IVc ) | Me | Me | 200 | ( M.p. 37°C ) | | -4.0 | 76.8 | 43.0 | 46.0 |
|  | ( Va ) | H | | 172 | 1.4529 | 1.376 | 0.9 | 114.4 | 56.1 | 1656** |
| | ( Vb ) | Me | | 193 | 1.4549 | 1.346 | 0.4 | 112.3 | 66.7 | 1698** |

*) neat, $CF_3COOH$ as an external standard, ( ppm )

**) $\nu_{c=c}$ ( $cm^{-1}$ )

## References

1) H.Kimoto, H.Muramatsu, and K.Inukai, Nippon Kagaku Kaishi, in press.

2) a) E.L.Zaitseva, T.V.Rozantseva, I.I.Chicherina, and A.Ya.Yakubovich, J.Org. Chem.USSR.,7,2647(1971) ; b) V.C.R.McLoughlin and J.Thrower, Tetrahedron, 25,5921(1969) ; c) K.Fujita, K.Yamamoto, and T.Shono, Nippon Kagaku Kaishi, 1933(1973).

3) IVb consisted of equal amount of two stereoisomers, IVb-1 and IVb-2.

4) Monitored by fluorine NMR.

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