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Chemistry

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Abstract

Full Text

Chemistry

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Synthesis of $\alpha, \alpha^{'}$-Difluoro-$\alpha, \alpha^{'}$-Dialkylethylenes by Means of Organolithium Compounds

In connection with the study of the reactivity of the double bond in fluorinated compounds, we were interested in the synthesis of α, α'-difluoro-α, α'-dialkylethylenes, RCF=CFR′, with identical and different radicals R and R′.

Compounds with identical radicals were obtained by us through the action of organolithium compounds of the aliphatic and aromatic series on tetrafluoroethylene ([1]-[4]). For the synthesis of unsymmetrical compounds with different radicals, we started from α, β, β-trifluorostyrenes or aliphatic unsaturated compounds with a fluorinated double bond $RCF{=}CF_2$. Aliphatic organolithium compounds in ether at −75° react with tetrafluoroethylene, forming monosubstituted trifluoroolefins in yields of up to 90% ([4]). By this route we obtained $RCF{=}CF_2$, where R = n-C_4H_9, n-C_6H_{13}, and n-C_8H_{17} (yields, respectively, 95, 90, and 85%). When the reaction of aliphatic RLi with these compounds is carried out at 25-30°, the synthesis of the difluoroolefin RCF=CFR′ proceeds in a yield of about 75%. Symmetrical compounds of this series, RCF=CFR, where R is a normal aliphatic radical, are smoothly formed from RLi and tetrafluoroethylene at 25-30° in ether with a yield of about 75%. The reactions in both cases are exothermic and cooling is necessary. For example, the yield of α, α'-difluoro-α, α'-dihexylethylene, synthesized from tetrafluoroethylene and from α, β-trifluorooctene-1, is 72-75%.

It is of interest that aromatic organolithium compounds, usually less reactive than aliphatic ones, are in this case more active than aliphatic RLi.

It is known that at −80° tetrafluoroethylene reacts in ether with phenyllithium, forming a mixture of α, β, β-trifluorostyrene, α, α'-difluorostilbene (predominantly), and a small amount of α-fluoro-α, α', α'-triphenylethylene. When the reaction temperature is raised to 25°, only the last two compounds are formed, in yields of 55-60% and 10-13% ([3]).

By the condensation of RLi with tetrafluoroethylene at 25-30°, we obtained a series of symmetrical α, α'-difluorostilbenes, several α, β, β-trifluorostyrenes ([1], [2]), and the corresponding stilbenes at a reaction temperature of −75°. It is of interest that the possibility of synthesizing α, β, β-trifluorostyrene by this route and the yield of α, α'-difluorostilbene depend on the structure of

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the aromatic radical in the organolithium compound. Thus, under certain conditions, a yield of α,β,β-trifluorostyrene of 15–40% and of its ortho-, meta-, and para-methyl analogs of 55, 46, and 40% ([1]) can be achieved. But α,β,β-trifluoro-1-vinylnaphthalene is formed even in low yield ([2]). From 3,4-dimethylphenyllithium and *p*-ethylphenyllithium, the yields of the corresponding styrenes are extremely small. It was not possible at −75° to obtain even a small amount of styrene from tetrafluoroethylene and mesityllithium, although the starting organolithium compounds can be obtained in yields of no less than 75–85% and the reaction with tetrafluoroethylene apparently proceeds. For example, if the organolithium compound at low temperature is present as a suspension of a crystalline etherate, in the case of mesityllithium or α-naphthyllithium, or as a triple complex with ether and lithium bromide, as phenyllithium or tolyllithium, then, as ···

Table 1

Compound	Yield, %	B.p., °C/mm Hg	Found, % C	Found, % H	Found, % F	Calculated, % C	Calculated, % H	Calculated, % F
n-$C_4H_9CF{=}CF_2$ 1	95	70/atm. press.	52.68 52.92	7.03 6.95	39.84 39.91	52.17	6.52	41.30
n-$C_6H_{13}CF{=}CF_2$ 2	90	120.5/atm. press.	56.96 57.98	7.96 8.01	33.96 33.79	57.75	7.84	34.40
n-$C_8H_{17}CF{=}CF_2$ 3	85	91/90	62.92 63.09	8.90 17.96	28.87 28.97	61.86	8.76	29.38
n-$C_6H_{13}CF{=}CFC_6H_{13}$ 4	75	100–102/4	72.26 72.17	11.16 11.04	16.00 16.14	72.41	11.20	16.38
$C_6H_5CF{=}CFCH_3$	65	95–96/70	69.90 70.62	5.30 5.61	24.51 24.40	70.13	5.20	24.68
$C_6H_5CF{=}CFC_4H_9$-*n* 6	60	95–96/5	73.05 73.10	7.08 7.11	19.46 19.43	73.47	7.14	19.39
$C_6H_5CF{=}CFC_8H_{17}$-*n* 7	60	143–145/2	77.36 77.82	8.69 8.59	13.68 13.61	77.57	8.00	14.45
n-$BrC_6H_4CF{=}CFC_6H_4Br$-*n* 5	25	138	44.90 44.98	1.95 2.09	10.00[9] 9.93	44.92	2.14	10.16
n-$ClC_6H_4CF{=}CFC_6H_4Cl$-*n*	15	133	—	—	—	—	—	—
n-$FC_6H_4CF{=}CFC_6H_4F$-*n*		112–112.5	66.89 66.36	3.29 3.31	30.10 30.02	66.66	3.17	30.16

Compound	Yield, %	B.p., °C/mm Hg	Found, % C	Found, % H	Found, % F	Calculated, % C	Calculated, % H	Calculated, % F
3,4-$(CH_3)_2C_6H_3CF{=}CFC_6H_3(CH_3)_2$	40	126–126/5	79.58 79.98	6.97 7.00	13.34 13.36	79.41	6.62	13.97
2,4,6-$(CH_3)_3C_6H_2CF{=}CFC_6H_2(CH_3)_3$	15	69–70	80.01 80.07	7.99 7.97	12.20 11.98	80.00	7.33	12.66
2,4,6-$(CH_3)_3C_6H_2CF{=}CFC_6H_4(CH_3)$-2	40	130–135/1	79.66 79.87	6.75 16.43	13.35 13.37	79.50	6.60	13.90
2,4,6-$(CH_3)_3C_6H_2CF{=}CFC_6H_5$[8]	40	118–120/1	79.02 79.56	6.53 6.55	13.44 13.63	79.50	6.60	13.90
n-$BrC_6H_4CF{=}CFC_6H_5$	50	109	57.01 56.80	3.51 3.60	12.24[10] 12.42	56.95	3.50	12.81
n-$ClC_6H_4CF{=}CFC_6H_5$	26.5	98.5	66.92 67.10	3.41 3.60	15.50[11] 14.98	67.06	3.59	15.16
α-$C_{10}H_7CF{=}CFC_{10}H_7$-$\alpha$	40	146–147	83.73 83.84	4.76 4.80	11.43 11.38	83.54	4.43	12.02
n-$BrC_6H_4CF{=}CFC_6H_4(CH_3)$-$o$	50	180–182/2	57.94 57.98	4.00 3.98	11.77[12] 12.05	57.14	2.72	12.92
n-$C_6H_5C_6H_4CF{=}CFC_6H_4C_6H_5$-$n$	40	280	84.91 84.84	4.75 4.82	10.34 10.34	84.78	4.89	10.32
n-$C_6H_5CF{=}CFC_6H_4CF{=}CFC_6H_5$	50	176	70.88 71.11	3.86 4.00	21.16 21.01	74.50	3.94	21.46

[1] n_D^{20} 1.3481.
[2] n_D^{20} 1.3770; d_4^{20} 0.977; MR_{found} 39.08; MR_{calc} 39.20, mol. wt.: found 164.55, calculated 166.
[3] n_D^{20} 1.3928.
[4] n_D^{20} 1.4233; d_4^{20} 0.886; MR_{found} 66.77; MR_{calc} 65.90, mol. wt.: found 234.35, calculated 232.
[5] n_D^{20} 1.5121, d_4^{20} 1.1133; MR_{found} 41.72; MR_{calc} 41.50.
[6] n_D^{20} 1.5017; d_4^{20} 1.0361, MR_{found} 56.104; MR_{calc} 55.80.
[7] n_D^{20} 1.5008.
[8] n_D^{20} 1.5700; d_4^{20} 1.1094.
[9] Br found, %: 42.76; 42.54; calculated 42.78.
[10] Br found, %: 27.28; 27.56; calculated 27.11.
[11] Cl found, %: 14.10; 14.20; calculated 14.16.
[12] Br found, %: 25.80; 26.05; calculated 27.21.

After tetrafluoroethylene has been passed through, the precipitate usually al-

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most completely goes into solution. Precipitation of lithium fluoride, which is poorly soluble in ether, is often not observed.

The yield of α, α'-difluorostilbene also depends to some extent on the radical RLi. Symmetrical stilbenes, RCF=CFR, are formed in 40–50% yield at 25° from tetrafluoroethylene and phenyllithium, *o*-tolyllithium, *m*-tolyllithium, *n*-tolyllithium, 4-lithiodiphenyl, and α-naphthyllithium. The same yield (40%) of 4,4′-α, α'-tetrafluorostilbene is obtained from *n*-fluorophenyllithium at −50°. The formation of α, α'-difluoro-4,4′-dibromostilbene proceeds in lower yield at 15–20° from *n*-bromophenyllithium (25%), and of α, α'-difluoro-4,4′-dichlorostilbene (12–15%) from *n*-chlorophenyllithium at 25°. Starting from *n*-dilithiobenzene and α, β, β-trifluorostyrene, a compound of structure $C_6H_5CF{=}CFC_6H_4CF{=}CFC_6H_5$ is obtained in 50% yield. This same compound is formed as a side product in the reaction of tetrafluoroethylene with *n*-bromophenyllithium, along with stilbene. When aromatic organolithium compounds act on α, β, β-trifluoroolefins, α, β-difluoro-β-alkylstyrenes are obtained in 70–75% yield. The reaction proceeds at the boiling point of ether over 15–16 hours.

In the reverse action of aliphatic RLi on α, β, β-trifluorostyrenes, the reaction proceeds very rapidly and exothermically, with formation of α, β-difluoro-

β-alkylstyrenes in yields of the same order. The compounds obtained are given in Table 1. The constants we give refer to a mixture of the cis and trans forms. It is not possible to isolate the pure forms by recrystallization.

Experimental Part

The starting organolithium compounds are prepared by the usual methods in an atmosphere of pure nitrogen and filtered under argon through a dry fluted filter. Low-temperature condensations are carried out in a cylindrical reactor under nitrogen, with cooling by solid carbon dioxide + alcohol. Examples of individual syntheses are given below.

Preparation of α,α'-difluoro-bis-(hexyl)-ethylene. In 50 ml of dry ether, 13.3 g of α,β,β-trifluorooctene-1 (0.08 mole) is dissolved and, under nitrogen, dropwise, with ice cooling, 79 ml of an ethereal solution of *n*-hexyllithium (1.02 *N*, 0.08 mole) is added. The temperature is maintained at about 20°. After the addition is complete, the mixture is stirred for 20 min. The test with Michler' s ketone is negative. After work-up, 14 g of α,α'-difluorobis-(hexyl)-ethylene is obtained (75%), b.p. 100–102°/4 mm, n_D^{20} 1.4233, d^{20} 0.886; MR: found 66.77, calculated 66.90. Molecular weight found 234.35, calculated 232.

Reaction of tetrafluoroethylene with *n*-hexyllithium. When an excess of tetrafluoroethylene is passed at 25° under nitrogen into 250 ml of a 1.02 *N* solution of *n*-hexyllithium with cooling, a vigorous reaction takes place. The gas is passed through for 1.5 h, until a negative test for RLi. After work-up, 20 g of α,α'-difluoro-bis-(hexyl)-ethylene is obtained (72%).

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Preparation of α,β-difluoro-β-*n*-octyl-*p*-methylstyrene. With vigorous stirring, to 55 ml of a 1.3 *N* solution of *n*-tolyllithium (0.059 mole) and 150 ml of dry ether, with cooling, 10 g of α,β,β-trifluorodecene-1 (0.059 mole) in 20 ml of ether is added. The mixture is then heated to boiling and refluxed for 16 h (until a negative test for RLi). After work-up, 10.3 g (70%) of α,β-difluoro-β-*n*-octyl-*p*-methylstyrene is obtained, b.p. 143–145°/2 mm, n_D^{20} 1.5008.

Reaction of α,β,β-trifluoro-*p*-methylstyrene with *n*-octyllithium. To 0.05 mole of an ethereal solution of *n*-octyllithium (5.4 g), with cooling, 7.5 g of α,β,β-trifluoro-*p*-methylstyrene (0.05 mole) in 10 ml of ether is added. After the addition is complete, the test for RLi is negative. The yield of α,β-difluoro-β-*n*-octyl-*p*-methylstyrene is 60%, b.p. 143–145°/2 mm, n_D^{20} 1.5008.

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