USE OF DILITHIUM COMPOUNDS FOR THE SYNTHESIS OF FLUORINATED UNSATURATED COMPOUNDS

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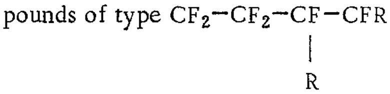
Dilithium compounds of type $Li(CH_2)_nLi$ were first prepared in 1953 by West and Rochow [1] from α, ω-dibromoalkanes $Br(CH_2)_nBr$ and lithium powder in an ether medium. The yields of dilithium compounds with n = 4, 5, 6, and 10 ranged from 63 to 70% (judging from the yield of the product of condensation with chlorotrimethylsilane); for n = 2 and 3 dilithium compounds are not formed under these conditions. The dilithium compound obtained from methylene dibromide CH_2Br_2 is extremely unstable (yield 6%). According to the patent [2], by the use of the α, ω-dichloroalkanes $Cl(CH_2)_nCl$ dilithium compounds can be obtained with n ranging from 3 to 8. An aliphatic or aromatic hydrocarbon is used as a reaction medium, and lithium containing a little (0.3-1 %) sodium is used as a fine dispersion. Admixture of sodium or other alkali metal, alloyed with the lithium, greatly speeds up the reaction. The reaction is conducted under argon with vigorous agitation in steel reactors of the ball-mill type [2]. Yields of dilithium compounds are about 65%. The compounds obtained are used for the polymerization of diolefins [2]. There are only a small number of examples in the literature of the use of aliphatic dilithium compounds in synthesis. We have brought dilithium compounds into condensation with tetrafluoroethylene in order to obtain fluorinated unsaturated compounds of the type $CF_2 = CF(CH_2)_nCH = CF_2$ (n = 4, 5, and 10). The dilithium compounds were prepared from the corresponding dibromo compounds in ether. Lithium was used in the form of "lithium sand". The yields of the dilithium compounds attained 80%, and the yields of the condensation products 45-60%. In this way we prepared 1,1,2,7,8,8-hexafluoro-1,7-octadiene, 1,1,2,8,9,9-hexafluoro-1,8-nonadiene, and 1,1,2,13,14,14-hexafluoro-1,13-tetradecadiene. The latter was obtained in admixture with 20% of hydrocarbon, from which we were unable to free it.

Starting from monolithium compounds we obtained 1,1,2-trifluoro-1-hexene, 1,1,2-trifluoro-1-octene, and 1,1,2-trifluoro-1-decene. By the condensation of tetramethylenedilithium with 1,1,1-trifluoroacetone we obtained a 50% yield of 1,1,1,8,8,8-hexafluoro-2,7-dimethyl-2,7-octanediol, and with N,N-diethyl-2,2-difluoroacetamide we obtained a 35% yield of the corresponding fluorinated diketone. The unsaturated fluorinated olefins $R{-}CF = CF_2$, in which R is an aliphatic group containing 1-18 carbon atoms, are capable of cyclization and formation of compounds of type $CF_2{-}CF_2{-}\underset{\substack{|\\ R}}{CF}{-}CFR$, which are highly thermally stable liquids with good dielectric properties [3].



When an attempt was made to bring about a similar condensation with fluorinated dienes, for example $CF_2 = CF(CH_2)_4CF = CF_2$, in a sealed tube at 300° for a period of 18-20 h, reaction again occurred with formation of dark-colored resinous condensation products.

When heating was for 25-30 h at the same temperature, the resin formed solidified to give a compact glassy mass, insoluble in the usual organic solvents.

EXPERIMENTAL SECTION

Preparation of 1,1,2,7,8,8-Hexafluoro-1,7-octadiene $CF_2 = CF(CH_2)_4CF = CF_2$. 100 ml of dodecane and 5 g of lithium were introduced into a 250-ml flask fitted with a reflux air condenser, and the mixture was heated until the dodecane boiled and the lithium melted. Heating was stopped, a few drops of oleic acid was added, and the flask was closed and shaken vigorously. The lithium broke up into small spheres, 0.5-1 mm in diameter. When cool, the suspension of lithium powder was transferred through a glass connecting tube into a separating funnel, dodecane was poured off, the lithium was washed with two 50-ml portions of ether, a further 100 ml of dry ether was added, and the suspension of lithium was transferred directly though a connecting tube with ground-joints into a reaction flask filled with argon. It was cooled to 0°, and 3 ml of an ethereal solution of 1,4-dibromobutane (21.6 g in 100 ml of dry ether) was added dropwise. As soon as the reaction began the mixture was cooled to −10° and the rest of the solution was added in the course of 40 min. Stirring was for one hour at between −10 and 0° and for 1.5 h at between −10 and + 10°. The mixture was filtered under nitrogen through a dry folded filter into a receiver or into a low-temperature condensation apparatus. We obtained 200 ml of a 0.40 N solution of the dilithium compound (80%). The ethereal solution of tetramethylenedilithium was cooled to −70°, and in the course of 1.5-2 h a fivefold excess of tetrafluoroethylene (about 80 g) was passed in. Reaction went without appreciable evolution of heat. After passage of the gas Gilman's test [1] was positive. The reaction mixture was left at −75° until Gilman's test was negative (the next day). The product was decomposed by pouring the mixture into cold water acidified with hydrochloric acid; it was extracted with ether, and the extract was washed, dried, and distilled. We obtained 8 g (45%) of 1,1,2,7,8,8-hexafluoro-1,7-octadiene; b. p. 72-72.5° (100 mm); n_D^{20} 1.3610; d_4^{20} 1.2458. Found: C 43.94; 43.09; H 3.94; 4.01; F 51.73; 53.08%; MR 38.71. $C_8H_8F_6$. Calculated: C 44.03; H 3.67; F 52.29%; MR 39.070.

Preparation of 1,1,2,8,9,9-Hexafluoro-1,8-nonadiene $CF_2 = CF(CH_2)_5CF = CF_2$. 200 ml of a 0.425 N ethereal solution of pentamethylenedilithium (6.39 g) was introduced into a low-temperature condensation apparatus filled with nitrogen. It was cooled to −70°, and excess of tetrafluoroethylene (about 80 g) was passed in. It was left at −75° until Gilman's test [1] was negative. The further treatment was as described above. We obtained 11.5 g (60%) of 1,1,2,8,9,9-hexafluoro-1,8-nonadiene; b. p. 92° (100 mm); n_D^{20} 1.3681; d_4^{20} 1.2100. Found: C 45.51; 46.56; H 4.18; 4.40; F 48.90; 48.78%; MR 43.14. $C_9H_{10}F_6$. Calculated: C 46.55; H 4.31; F 49.14%; MR 43.708.

Preparation of 1,1,2-Trifluoro-1-octene. 300 ml of 1.16 N ethereal hexyllithium (32 g) was introduced into a low-temperature condensation apparatus, 200 ml of dry ether was added, the mixture was cooled to −75°, and excess of tetrafluoroethylene (about 50 g) was passed in. After this, Gilman's test was negative. The usual treatment was given. We obtained 36.7 g (95%) of 1,1,2-trifluoro-1-octene; b. p. 120.5°; n_D^{20} 1.3770; d_4^{20} 0.977; Found: C 56.96; 57.98; H 7.96; 8.01; F 33.96; 33.79%; MR 39.08. $C_8F_{13}F_3$. Calculated: C 57.75; H 7.84; F 34.40%; MR 39.20.

Preparation of 1,1,2-Trifluoro-1-decene. This was prepared by the above-described method in 81% yield: b. p. 91° (90 mm); n_D^{20} 1.3928. Found: C 62.92; 63.09; H 8.01; 7.96; F 28.87; 28.97%. $C_{10}H_{17}F_3$. Calculated: C 61.86; H 8.76; F 29.38%.

Preparation of 1,1,1,8,8,8-Hexafluoro-2,7-dimethyl-2,7-octanediol $CH_3CF_3C(OH)(CH_2)_4C(OH)CF_3CH_3$. 100 ml of dry ether was added to 200 ml of 0.34 N ethereal tetramethylenedilithium (4.18 g) in an apparatus for work at low temperatures, and the mixture was cooled to −40°. In the course of one hour 13.44 g of 1,1,1-trifluoroacetone in 50 ml of dry ether was added with vigorous stirring; no liberation of heat was observed. At the end of the addition the whole solution was stirred further for 20 min. Gilman's test was negative. After the usual treatment we obtained 8.5 g (50%) of crystalline 1,1,1,8,8,8-hexafluoro-2,7-dimethyl-2,7-octanediol, which was purified by sublimation, m. p. 80°. Found: C 41.74; 43.10; H 6.00; 5.95; F 40.31; 40.00; O 12.95; 10.95%. $C_{10}H_{16}F_6O_2$. Calculated: C 42.55; H 5.67; F 40.42; O 11.35%.

Preparation of 1,1,8,8-Tetrafluoro-2,7-octanedione. 200 ml of 0.4 N ethereal tetramethylenedilithium (5.5 g) was introduced into an apparatus for work at low temperature. It was cooled to −70°, and with vigorous stirring a solution of 24.16 g of N,N-diethyl-2,2-difluoroacetamide in 50 ml of ether was added dropwise in the course of 20-30 min. Stirring was continued further at −75° until Gilman's test was negative (two hours). The solution was treated in the usual way. We obtained 6.2 g (35%) of 1,1,8,8-tetrafluoro-2,7-octanedione; b. p. 95° (20 mm); n_D^{20} 1.4140; d_4^{20} 1.348. Found: C 44.82; H 4.67; F 35.66%; MR 45.90. $C_8H_{10}F_4O_2$. Calculated: C 44.86; H 4.67; F 35.51%; MR 46.20.

CONCLUSIONS

1. The application of aliphatic dilithium compounds in the synthesis of the fluorinated dienes $CF_2 = CF(CH_2)_nCF = CF_2$.

2. 1,1,8,8,8-Hexafluoro-2,7-dimethyl-2,7-octanediol and 1,1,8,8-tetrafluoro-2,7-octanedione was prepared for the first time.

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