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TRIMERIZATION OF NITRILES OF PERFLUOROOXAALKYLCARBOXYLIC ACIDS

G. M. Tolmacheva, V. M. Zhulin,
S. P. Krukovskii, and V. A. Ponomarenko

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The simplest method for the synthesis of tris(fluoroalkyl)triazines is the trimerization of fluoroalkylnitriles. In the absence of a catalyst this reaction proceeds slowly (30-120 h), under drastic conditions (300-350°C and a pressure of 150 kg/cm^2), and with a low yield of the triazine (8-30%) [1]. However, it can be accelerated by the addition of either acid or basic catalysts. In the case of acid catalysis the reaction proceeds as the result of cyclic electron transfer, and in the case of basic catalysis via the formation of the charge-transfer complex [2]. The trimerization of perfluoroalkylnitriles in the presence of various catalysts has been described in considerable detail in the patent literature [3].

In the present paper we studied the trimerization of perfluoro-2-methyl-3-oxahexanenitrile (I) and perfluoro-2,5-dimethyl-3,6-dioxanonanenitrile (II) under high-pressure conditions in the presence of various catalysts.

The effect of various catalysts on the trimerization of perfluoronitriles to triazines is given in Table 1. H_2SO_4 does not cause nitrile (I) to trimerize, but NaOH and $(C_2H_5)_3N$ lead to the formation of the triazine. The yield of the triazine reaches only 10-12% when anhydrous Et_3N is used. The addition of 5% water to the amine as the cocatalyst, with the other conditions kept constant, increases the yield of the triazine by 3-4 times. The optimum amount of the Et_3N-H_2O catalyst is 0.5-2%. Increasing the catalyst concentration in the system to 4-5% leads to a sharp decrease in the yield of the triazine. Based on the IR spectral data, compounds with a system of conjugated C=N bonds (absorption bands at 1480, 1580, 1660, 1680 cm^{-1}) are formed along with the triazine in this case. Increasing the triethylamine concentration up to 10% causes a complete conversion of the nitrile to compounds of this type. A study was also made of the effect of pressure in the

TABLE 1. Effect of Catalysts on Trimerization of $R_f(C\equiv N)$ 14,000 kg/cm^2, 5 h

R_f	Catalyst, wt.% of nitrile	T., °C	Yield of triazine, %
$CF_3CF_2CF_2OCF$ | CF_3	H_2SO_4 0,5	50	—
	NaOH, 0,5	50	30
	$(C_2H_5)_3N$, 0,5	50	10
	$(C_2H_5)_3N$, 0,5	70	12
	$(C_2H_5)_3N-H_2O$, 0,5	80	54
$CF_3CF_2CF_2OCF(CF_3)CF_2OCF$ | CF_3	" 0,5	80	41
	» 1	—	50,5
$CF_3CF_2CF_2OCF$ | CF_3	» 2,2	—	52
	» 3,5	—	17
	» 4,6	—	13
	» 10	—	—

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1424-1426, June, 1976. Original article submitted December 16, 1975.

TABLE 2. Effect of Pressure on Trimerization of $R_f(C\equiv N)$ in Presence of Et_3N-H_2O. 80°, 5 h

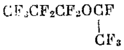
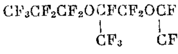
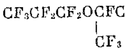
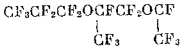
R_f	p, kg/cm^2	Yield of triazine, %
 $CF_3CF_2CF_2O\underset{CF_3}{C}F$	1	8
	10 000	40
	14 000	54
 $CF_3CF_2CF_2O\underset{CF_3}{C}FCF_2O\underset{CF_3}{C}F$	1	4
	1 000	15
	2 000	18
	5 000	20
	10 000	31
	14 000	41

TABLE 3. Effect of Temperature on Trimerization of $R_f(C\equiv N)$ in Presence of Et_3N-H_2O. 10,000 kg/cm^2, 5 h

R_f	T., °C	Yield of triazine, %
 $CF_3CF_2CF_2O\underset{CF_3}{C}FCF_3$	100	58
	150	75
	200	69 *
 $CF_3CF_2CF_2O\underset{CF_3}{C}FCF_2O\underset{CF_3}{C}F$	50	12
	70	20
	88	31
	150	55

*Without a catalyst.

in the range from 500 to 14,000 kg/cm^2 on the trimerization of the perfluoronitriles in the presence of Et_3N-H_2O (Table 2). As can be seen from Table 2, the pressure has an important effect on the trimerization of the nitriles: at atmospheric pressure the yield of the triazine in 5 h is 4-8%, which increases by 2 to 3 times at a pressure of 1000 kg/cm^2, and is over 50% at 14,000 kg/cm^2. The formation of secondary products was not observed here.

The rate of forming the triazine decreases substantially as the process progresses. The conversion of nitrile (I) in 5 h at atmospheric pressure and 80° is 5%, which increases to 8% in 100 h, and to 18% in 400 h. At 14,000 kg/cm^2 the amount of triazine formed in the first 15 min is 40%, and ~60% in 10 h. Increasing the pressure up to 14,000 kg/cm^2, followed by its rapid removal, gives a 24% yield of the triazine. These results make it possible to assume that the values of the triazine yields (18% at atmospheric pressure and 60% at 14,000 kg/cm^2) approach the equilibrium values. The effect of pressure in the trimerization of the discussed nitriles is associated with a shift of the equilibrium toward the formation of the triazines.

The structure of the starting nitrile also has an effect on the yield of the triazine: when nitrile (I) is used the yield of the corresponding triazine is 10-15% higher than in the case of nitrile (II). A similar observation was also made in [1].

In Table 3 it is shown that increasing the temperature from 50 up to 150° at a pressure of 10,000 kg/cm^2 increases the yield of the triazine from 12 up to 55%, while at 200° the trimerization of nitrile (I) at the same pressure proceeds even without a catalyst.

EXPERIMENTAL METHOD

Triethylamine was purified by distillation over NaOH. By collecting the fraction with bp 89-90° we obtained a chromatographically pure product, to which 5% water was added. The experiments under pressure were run in either 2-ml lead or teflon ampuls. The lead ampul was filled in vacuo, after which the ampul outlet was pinched together tightly and soldered. The teflon ampul was filled in a nitrogen atmosphere. The experimental procedure at a pressure of 14,000 kg/cm^2 and a diagram of the apparatus are described in [4].

The conversion of the nitrile and the yield of the triazine were determined via IR spectroscopy and GLC. The IR spectra were taken on a UR-20 instrument. The chromatographic analysis was run on an LKh-8MD chromatograph (column packed with 10% SKTP deposited on Chromatone).

Perfluoro-2-methyl-3-oxahexanenitrile (I) was obtained by the dehydration of perfluoro-2-methyl-3-oxahexanecarboxamide with P_2O_5 in 77% yield, mp 49°. Infrared spectrum (ν, cm^{-1}): 1100-1400 (CF), 2270 ($-C\equiv N$). Found: C 23, 12; F 67.10; N 4.75%. $C_6F_{11}ON$. Calculated: C 23.15; F 67.20; N 4.50%.

Perfluoro-2,5-dimethyl-3,6-dioxanonanenitrile (II) was obtained the same as (I), bp 114°. Infrared spectrum (ν, cm^{-1}): 1100-1400 (CF), 2270 ($C\equiv N$), Found: C 22.45; F 67.58; N 2.96%. $C_9F_{17}O_2N$. Calculated: C 22.60; F 67.61; N 2.94%.

2,4,6-Tris(perfluoro-2-methyl-3-oxahexyl)-1,3,5-triazine. Into a teflon ampul in a N_2 atmosphere were charged 0.14 g of Et_3N-H_2O and 2.3 g of (I); the ampul was placed in the channel of a high-pressure equipment (10,000 kg/cm^2) and kept at 80° for 5 h. After distilling off the unreacted nitrile we obtained 0.92 g (40%) of colorless liquid, bp 81° (8 mm). Infrared spectrum (ν, cm^{-1}): 1100-1400 (CF), 1560 (C (C_3N_3). Found: C 23.30; F 67.28: N 4.45%. $C_{18}F_{33}N_3O_3$. Calculated: C 23.15: F 67.20; N 4.50%.

2,4,6-Tris(perfluoro-2,5-dimethyl-3,6-dioxanonyl)-1,3,5-triazine, bp 86° (1 mm). Infrared spectrum (ν, cm^{-1}); 1100-1400 (CF), 1560 (C_3N_3). Found: C 22.70; F 68.00; N 2.92%. $C_{27}F_{51}N_3O_6$. Calculated: C 22.64; F 67.71; N 2.94%.

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CONCLUSIONS

The trimerization of perfluorooxaalkylnitriles is accelerated by basic catalysts. Sulfuric acid does not catalyze this process.

2. When the nitriles are trimerized in the presence of the Et_3N-H_2O system the yield of the triazines increases with increase in the pressure and temperature.

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SYNTHESIS OF 20,22-EPOXYBISNOR-Δ^5-CHOLEN-3β-OL

Zh. S. Sydykov and G. M. Segal'

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In the course of synthesizing ecdysonelike compounds we encountered the need of obtaining 20,22-epoxybisnor-Δ^5-cholen-3β-ol (I), the presence of whose OH group makes it possible to build both the Δ^7-6-keto and the 2β,3β-glycol grouping [1]. Pregnenolone acetate when reacted with dimsylsodium in DMSO gives acetate (II) in up to 90% yield. However, the latter could not be converted to (I) either by hydrolysis or by treatment with complex metal hydrides under mild conditions. Complex and difficultly separable mixtures of products are formed in both cases. The direct preparation of oxirane (I) from pregnenolone by the Cory–Chaikovskii method also could not lead to the desired result, since the 3β-methylthiomethyl ethers are usually formed in this case [2].

Ester groupings can be removed by treatment with Grignard reagents, with which the oxirane ring reacts quite sluggishly [3], although rearrangements are possible in a number of cases [4]. We attempted to obtain compound (I) by this route. We selected isoamyl-magnesium bromide as the reagent, since the products could be identified without great difficulty even in the case of secondary reaction at the epoxide ring. In the case of opening the $-O-C_{22}$ linkage the 20-hydroxycholesterol (III) would be obtained in addition, which plays an important role in the biosynthesis of steroid hormones [5]. The reaction of (II) with isoamylmagnesium bromide in THF gave a mixture of oxirane (I), a small amount of dimer (IV), and also compound (V), which was assigned the structure of 20-methyl-24-nor-cholestene-3β,21-diol. The yield of (I) was 89%, and its structure was proved by acetylation to the starting acetate (II).

Glycol (V) in its melting point and NMR spectrum differs from the isomeric (20R)- and (20S)-Δ^5-cholestene-3β,20-diols [5]. The structure assigned to it is in good agreement with the physicochemical data. For this reason it may be assumed that (V) is formed by the cleavage of the epoxide ring at the O–C-20 bond.

The increase in the yield of glycol (V) is slight (up to 10-12%) even when the reaction with the Grignard reagent is run under drastic conditions (refluxing in p-xylene for 16 h); up to 20% of weakly polar dehydration

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M. M. Shemyakin Institute of Bioorganic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1426-1428, June, 1976. Original article submitted December 18, 1975.