OXYGEN-INITIATED FREE-RADICAL CYANOETHYLATION OF TETRAHYDROFURAN

G. G. Galust'yan and V. G. Glukhovtsev

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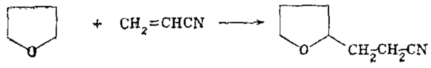
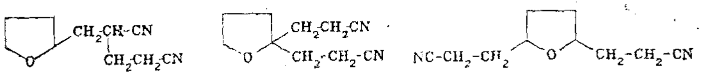
Oxygen has been used as an initiator of the free-radical cyanoethylation of tetrahydrofuran by acrylonitrile. It has been shown that the initiation takes place mainly through the decomposition of tetrahydrofuran hydroperoxide, which is formed in an autooxidation of tetrahydrofuran. The initiating activity of tetrahydrofuran hydroperoxide at various temperatures has been studied. Initation at 130°C is the most effective. The initiating activities of tetrahydrofuran hydroperoxide and of tert-butyl hydroperoxide have been compared.

The cyanoethylation of tetrahydrofuran by acrylonitrile initiated by tert-butyl peroxide or thermally at 200-300°C has been reported previously [1, 2]. The main product of the reaction is 2-(β-cyanoethyl)tetrahydrofuran (I):



I

Adducts of the 1:2 type have also been isolated:



their amount depending on the THF:acrylonitrile ratio.

We have established that in the presence of oxygen, together with compound (I) a very small amount of oxidation products of THF is also formed. In order to elucidate the role of oxygen in this process we have studied the cyanoethylation of THF in an atmosphere of helium and oxygen in the temperature interval of 66-300°C.

The results, which are given in Table 1, show that at 300°C the presence of oxygen had practically no effect on the yield of compound (I): A small amount (0.02-0.2 mole % on the THF) of THF oxidation products — 2-hydroxytetrahydrofuran (II) and γ-butyrolactone (III) — was formed; in the presence of oxygen, the amount of residue was twice as great as in the presence of helium. A different pattern was observed at 130°C: In the helium atmosphere cyanoethylation scarcely took place, but when the helium was replaced by oxygen (0.25 liter per 1 liter of THF), the yield of compound (I) amounted to 45% (expts. 3 and 4). Lowering the temperature to 100°C led to a marked decrease in the yield of the nitrile (I), and in the reaction mixture peroxide compounds were detected (iodometrically) in addition to compounds (II) and (III).

The results obtained permit the following conclusion: At 300°C initiation obviously takes place through the thermolysis of the α-C—H bond of THF; at 130°C, thermolysis of the bond is excluded and initiation is connected with the presence of oxygen in the reaction mixture.

The primary product of the oxidation of THF is its hydroperoxide (IV) [3, 4]. The decomposition of the peroxide (IV) takes place through intermediate tetrahydrofuryloxy, tetrahydro-

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Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 21-24, January, 1984. Original article submitted February 10, 1983.

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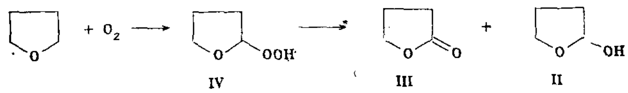
TABLE 1. Cyanoethylation of Tetrahydrofuran

No.	Initiator			Temperature, ℃	Time, h	Yield of compound (I), %		Yield of 1:2 adduct, % on the acrylonitrile	Residue, g
	name	moles per 1 mole				on the acrylonitrile	on the peroxide		
		THF	acrylonitrile						
1	—	—	—	300	0,5	50		9	1,4
2	O_2	$9\cdot10^{-4}$	0,18	300	0,5	48		9	2,9
3	—	—	—	130	4	3		—	—
4	O_2	$9\cdot10^{-4}$	0,18	130	4	45		6	3,5
5	O_2	$9\cdot10^{-4}$	0,18	100	6	7		—	1,8
6	IV	$5\cdot10^{-4}$	0,1	130	4	49	550	8,5	3,5
7	IV	$2{,}5\cdot10^{-4}$	0,05	130	4	40	700	10	2,8
8	IV	$5\cdot10^{-4}$	0,1	100	6	10	90	3	2,6
9	IV	$5\cdot10^{-4}$	0,1	66	9	4	13	Traces	1,4
10	tert-Butyl peroxide	$5\cdot10^{-4}$	0,1	130	4	30	200	5	4

Notes. 1. In all the experiments the THF:acrylonitrile ratio was 200:1, the amount of acrylonitrile being 0.15 mole; its conversion was complete. 2. All the experiments with the exception of 2, 4, and 5, were carried out under conditions excluding autooxidation. 3. The amounts of tetrahydrofuran oxidation products formed were 0.06 on the THF in expt. 4, 0.17% in expt. 5, and traces in expt. 2.

furylperoxy, tetrahydrofuryl, and other radicals [5]; the final products of the oxidation of THF are, depending on the conditions, compound (II) or (III) or mixtures of them:



IV III II

It is known that the rate of generation of a chain in the oxidation of organic compounds by the reaction RH + O_2 in the absence of initiators is small, and the main source of radicals in this process consists of the hydroperoxide formed [4]. On this basis, we have assumed that the initiation of the addition of THF to acrylonitrile by oxygen takes place mainly through the homolytic decomposition of the peroxide (IV) formed in the autooxidation of THF.

To confirm this hypothesis, the peroxide (IV) was synthesized from 2,3-dihydrofuran and hydrogen peroxide as described previously [6]. The cyanoethylation of THF in the presence of this peroxide was studied at 66°C (in an open system and in an autoclave), and at 100 and 130°C under conditions excluding autooxidation. As can be seen from Table 1, at 66 and 100°C the yield of the nitrile (I) amounted to 4-10%; iodometric titration showed that the peroxide (IV) decomposed incompletely under these conditions (expts. 8 and 9). To accelerate the decomposition of the peroxide (IV) we used additions of salts of metals of variable valence (Co^{2+}, Fe^{3+}) and their complexes with 2,2'-bipyridyl and o-phenanthroline. The use of the additives led to the complete decomposition of the peroxide (IV) but the yield of nitrile (I) under these conditions did not increase, and the acrylonitrile polymerized completely. When the temperature was raised to 130°C, the peroxide (IV) initiated the addition of THF to acrylonitrile in a concentration of 0.02-0.04 mole per 1 liter of THF (or 5-10% on the acrylonitrile); compound (I) was then formed with a yield of 40-49%, close to the yield in the experiments initiated by oxygen (expts. 4, 6, and 7).

A comparison of the initiating activities of the peroxide (IV) and of tert-butyl peroxide (expts. 6, 7, and 10) showed that the latter was less effective: The yield of the nitrile (I) under such conditions amounted to 200% on the tert-butyl peroxide and 700% on the peroxide (IV).

The capacity of the peroxide (IV) for initiating the cyanoethylation of THF under conditions excluding autooxidation confirmed our hypothesis that the main contribution to the process of initiation by oxygen is made by the homolytic decomposition of the hydroperoxide (IV) formed.

Thus, oxygen has been used for the first time as an initiator of the free-radical addition of a cyclic ether to an unsaturated compound. This broadens the sphere of application of oxygen as an initiator of radical addition reactions; it has previously been recommended for the initiation of the homolytic addition of aldehydes and ketones to unsaturated compounds [7].

EXPERIMENTAL

The THF was dried over calcium chloride, boiled with caustic potash, and, immediately before an experiment, redistilled over sodium in an inert gas atmosphere. The acrylonitrile was dried over calcium chloride and was redistilled in an inert gas atmosphere before an experiment. The tert-butyl hydroperoxide was synthesized from tert-butanol and hydrogen peroxide in the presence of sulfuric acid [8]. The peroxide (IV) was synthesized from 2,3-dihydrofuran and hydrogen peroxide [6]; bp 38°C (0.8 mm), n_D^{26} 1.4475.

The experiments were performed in a three-liter autoclave by the following method: The air was pumped out from the autoclave to a residual pressure of 1-2 mm Hg and the autoclave was purged with inert gas 2-3 times, the gas being pumped out after each purging. Then the reaction mixture was charged into the autoclave and the residual volume was filled with the corresponding gas to atmospheric pressure. The loading factor of the autoclave was 0.8.

Working up of the reaction mixture: The bulk of the THF was distilled off in a rotary evaporator, and the residue – the concentrated reaction mixture – was analyzed by the GLC method using an internal standard (acetophenone, diethyl phthalate) and was redistilled. The GLC analysis was performed on a Varian chromatograph with a flame-ionization detector. Stationary phase: 10% of FFAP on Chromosorb W; column temperature 150-245°C (programmed at the rate of 3°C/min), inlet 250°C, detector 250°C.

Following, we give a typical experiment as an example. Experiment 6. A mixture of 2430 ml (30 mole) of THF, 7.95 g (0.15 mole) of acrylonitrile, and 1.56 g (0.015 mole) of the peroxide (IV) was heated in an atmosphere of helium at 130°C for 4 h. Distillation of the concentrated reaction mixture in vacuum (10 mm Hg) yielded two fractions: 1) bp 96-98°C (9.9 g); and 2) bp 145-190°C (1.7 g); the residue amounted to 3.5 g. According to GLC, fraction 1 contained 93% of the nitrile (I), 1% of compound (II), and 6% of substance (III); fraction 2 contains 23% of the nitrile (I), and 67% of the 1:2 adduct. The characteristics of the nitrile (I) have been given previously [1]. The 1:2 adduct was isolated from the second fraction by chromatography on a column of alumina; elution was performed successively with petroleum ether, mixtures of petroleum ether with benzene (with a gradual increase in the proportion of benzene), and with benzene. The 1:2 adduct, a viscous oily liquid with bp 175-183°C (10 mm), consisted of a mixture of three isomers: their ratio was 1.2:12:1 as determined from the integral intensities of the 6-6.4 and 5.7-6 ppm signals in their PMR spectra. Their IR spectrum had bands at 2250 cm^{-1} (C≡N) and 1080 cm^{-1} (C—O—C).

Mass spectra and elementary analysis confirmed the structures given for the 1:2 adducts. Compound (II) was detected from an intense band at 1735 cm^{-1} (C=O) in the IR spectrum of the hydroxy aldehyde form of (II), which was identified in the form of the 2,4-dinitrophenylhydrazone [9], mp 116-117°C. The lactone (III) was detected from its intense band at 1730 cm^{-1} and was identified by a comparison of its retention temperatures with those of standard γ-butyrolactone.

LITERATURE CITED

1. G. G. Galust'yan and Ch. Sh. Kadyrov, Khim. Geterosikl. Soedin., No. 2, 376 (1967).
2. Ch. Sh. Kadyrov, G. G. Galust'yan, and L. M. Yun, USSR Inventor's Certificate No. 201370; Byull. Izobret., No. 18, 28 (1967).
3. A. Robertson, Nature (London), 162, 153 (1948).
4. E. T. Denisov, N. I. Mitskevich, and V. E. Agabekov, The Mechanism of the Liquid Phase Oxidation of Oxygen-Containing Compounds [in Russian], Nauka i Tekhnika, Minsk (1975), p. 164.
5. N. Y. Stenburg, Ch. T. Wong, and N. Kulevsky, J. Org. Chem., 35, 1774 (1970).
6. G. I. Nikishin, V. G. Glukhovtsev, and M. A. Nadtochii, Izd. Akad. Nauk SSSR, Ser. Khim., No. 10, p. 2281 (1973).
7. M. G. Vinogradov, R. V. Kereselidze, G. G. Gachechiladze, and G. I. Nikishin, Izd. Akad. Nauk SSSR, Ser. Khim., No. 2, 322 (1969).
8. N. A. Milas and D. I. Surgenor, J. Am. Chem. Soc., 68, 205 (1946).
9. Beilst., 1, E III, 3202 (1953).