T. I. Yurzhenko, M. R. Vilenskaya, V. A. Osetskaya

1965

SovietRxiv

Abstract

Full Text

T. I. Yurzhenko, M. R. Vilenskaya, V. A. Osetskaya

SYNTHESIS OF POLYMERIZABLE PEROXIDE ESTERS OF ACRYLIC AND METHACRYLIC ACIDS

(Presented by Academician B. A. Arbuzov on 25 XI 1964)

Peroxide esters of saturated organic acids have been known since 1901 [1], and by the present time, according to the literature, about 250 of their representatives have been synthesized. The synthesis of peroxide esters of unsaturated acids began to develop in 1946, when Milas [2] first obtained *tert*-butyl percrotonate and *tert*-butyl perundecylenate. Until recently, only 6 representatives of peresters of this type had been synthesized. In the present work, peroxide esters of acrylic and methacrylic acids were synthesized; these readily polymerize by themselves and also copolymerize with nonperoxide vinyl and diene monomers. Thus, the peresters obtained are typical peroxide monomers, which may find application in the chemistry of high-molecular-weight compounds. In the production of polymeric materials and products made from them, peroxide monomers may have a new application, not only as polymerization initiators. By copolymerizing them with nonperoxide monomers, peroxide groups can be introduced into macromolecules; these groups may subsequently serve as grafting centers in the preparation of graft polymers, or as active groups in the structuring of polymers, including in the vulcanization process.

Tert-butyl peracrylate $CH_2{=}CH{-}CO{-}OO{-}C(CH_3)_3$ was synthesized by the reaction of acryloyl chloride and the sodium salt of *tert*-butyl hydroperoxide in the presence of CCl_4 as solvent. The initial acryloyl chloride was prepared by the known procedure [3], and *tert*-butyl hydroperoxide and its sodium salt by the method of Milas [4]. The prepared salt contained: pure product 55-60%, water 25-29%, and an impurity of sodium carbonate. The synthesis was carried out as follows: to 600 ml of solvent was added the salt (1.1 mol, calculated as pure product), and with stirring at a temperature of 0-5° acryloyl chloride (1 mol), dissolved in 100 ml of solvent, was added. After 1.5-2 hours of stirring, the precipitated sodium chloride was filtered off, and the filtrate was washed with water, with a 3% solution of sodium bicarbonate, and dried over anhydrous

---

[1]

[2]

[3]

[4]

magnesium sulfate. The solvent was distilled off in vacuo at room temperature, and the pure perester was distilled in a nitrogen atmosphere at 38°/1.5 mm. *Tert*-butyl peracrylate is a transparent liquid, n_D^{20} 1.4258; d_4^{20} 0.945; MR found 38.65; calculated 38.45; molecular weight (cryoscopically in benzene) 143.2; calculated 144; active oxygen [O_2], found iodometrically 10.9%; calculated 11.11%; decomposition temperature 83° with explosion.

Found, %: C 58.26; H 8.38
$C_7H_{12}O_3$. Calculated, %: C 58.33; H 8.33

The structure was confirmed by decomposition of the perester with sodium methylate (alcoholysis), with isolation of *tert*-butyl hydroperoxide (n_D^{20} 1.4011) and methyl acrylate (b.p. 80°).

In a weak aqueous solution of NaOH, the perester hydrolyzes at 20° with $K =$ 27.3, and at 40° with $K = 65.3\ \mathrm{mol}^{-1} \cdot \mathrm{min}^{-1}$, with an activation energy of 8 kcal/mol. In an aqueous 0.02 N HCl solution the perester is considerably more stable: at 20° over 25 days it hydrolyzed by 10%. In comparison with methyl acrylate, in hydrochloric-acid solution *tert*-butyl peracrylate hydrolyzes somewhat more slowly, and in alkaline solution at the same rate.

tert-Amyl peracrylate $CH_2{=}CH{-}CO{-}OO{-}C(CH_3)_2C_2H_5$ was synthesized by the reaction of acryloyl chloride with the sodium salt of tert-amyl hydroperoxide in the presence of the same solvent, according to the procedure described above. The starting tert-amyl hydroperoxide was obtained according to Milas (^{5}). The perester was purified by vacuum distillation at 22.5-23°/0.2 mm and had the following characteristics: n_D^{20} 1.4338; d_4^{20} 0.950; MR found 43.26; calculated 42.70; molecular weight found 153.8; calculated 158; active oxygen was determined iodometrically as only 70.8% of the theoretical value. Upon hydrolysis in alkaline medium in the presence of acetone for 50 h, the amount of acid found corresponded to the pure perester.

Found %: C 60.83; H 9.30
$C_8H_{14}O_3$. Calculated %: C 60.73; H 8.91

Dimethylethynylmethyl peracrylate $CH_2{=}CH{-}CO{-}OO{-}C(CH_3)_2{-}C{\equiv}CH$. The starting dimethylethynylmethyl hydroperoxide was prepared according to Milas (^{6}). In the experiments a salt containing 50% pure product was used. The pure perester distilled at 29°/1 mm and had the following characteristics: n_D^{20} 1.4485; d_4^{20} 1.002; MR found 41.19; calculated 41.066; molecular weight found 151.8; calculated 154; [O_2] found 10.4%; calculated 10.4%. Decomposition temperature 85° with explosion.

Found %: C 62.39; H 6.48
$C_8H_{10}O_3$. Calculated %: C 62.32; H 6.56

Upon hydrolysis in alkaline medium, the amount of acid found corresponded to the pure perester.

2,5-Bis(acryloylperoxy)-2,5-dimethylhexyne-3

$CH_2{=}CH{-}CO{-}OO{-}C(CH_3)_2{-}C{\equiv}C{-}C(CH_3)_2{-}OO{-}CO{-}CH{=}CH_2$. The starting 2,5-dimethyl-3-hexyne-2,5-dihydroperoxide ([6]) was obtained from 2,5-dimethyl-3-hexyne-2,5-diol synthesized by us by the action of 50% H_2O_2 on it. Purification of the perester was carried out by repeated freezing out from a mixture of petroleum ether and diethyl ether at -40°. The pure perester was a viscous, slightly yellowish liquid with the following characteristics: n_D^{20} 1.4701; d_4^{20} 1.066; MR found 73.81; calculated 72.97; molecular weight found 275; calculated 282; $[O_2]$ found 11.1%; calculated 11.3%.

Found %: C 59.46; H 6.27
$C_{14}H_{18}O_6$. Calculated %: C 59.55; H 6.43

By hydrolysis of the perester in alkaline medium, the amount of acid found corresponded to the pure product.

Cumyl peracrylate $CH_2{=}CH{-}CO{-}OO{-}C(CH_3)_2{-}C_2H_5$ was synthesized in *n*-hexane, and its purification was carried out by freezing out from a hexane solution. The perester obtained was a slightly yellowish liquid with the following characteristics: n_D^{20} 1.5170; d_4^{20} 1.073; MR found 58.15; calculated 58.93; molecular weight found 213; calculated 206; $[O_2]$ found 7.1%; calculated 7.6%.

Found %: C 69.99; H 7.05
$C_{12}H_{14}O_3$. Calculated %: C 69.90; H 6.80

This perester is of low stability; at room temperature over 24 h the active oxygen content decreases from 7.10 to 5%, and in the cold over 10 days to 6.3%. Upon decomposition of the perester, phenol is formed, which was isolated as tribromophenol, and acetone (isolated as the semicarbazone).

Thus, cumyl peracrylate is prone to heterolytic rearrangement into a nonperoxidic compound, which is observed for certain other peresters ([7]), including cumyl peracetate ([8]). Rearrangement-

treatment with subsequent hydrolysis proceeds according to the scheme:

$$CH_2{=}CH{-}CO{-}OO{-}C(CH_3)_2C_6H_5 \rightarrow CH_2{=}CH{-}CO{-}O{-}C(CH_3)_2{-}$$

$$-O{-}C_6H_5 \xrightarrow{H_2O} CH_2{=}CH{-}CO{-}OH + C_6H_5OH + CH_3COCH_3.$$

***p*-Chlorocumyl peracrylate**
$CH_2{=}CH{-}CO{-}OO{-}C(CH_3)_2{-}C_6H_4{-}Cl$ was obtained by the reaction of acryloyl chloride with the sodium salt of *p*-chlorocumyl hydroperoxide in CCl_4. The starting *p*-chlorocumyl hydroperoxide was prepared by autoxidation of *p*-chlorocumene (9), which was synthesized from chlorobenzene and isopropyl bromide in the presence of anhydrous aluminum chloride (10). The perether was

purified by freezing out from petroleum ether and had the following characteristics: n_D^{20} 1.5243; d_4^{20} 1.189; MR found 62.0; calculated 62.75; molecular weight found 226.5; calculated 240.69; $[O_2]$ found 5.18%, calculated 6.64%.

Found, %:	C 59.89; H 5.56; Cl 14.93
$C_{12}H_{13}O_3Cl$. Calculated, %:	C 59.88; H 5.44; Cl 14.73

On storage of the perether in the cold, a decrease in active oxygen from 5.18 to 4.6% was observed over 4 days.

***p*-Bromocumyl peracrylate**
$CH_2{=}CH{-}CO{-}OO{-}C(CH_3)_2{-}C_6H_4{-}Br$. The starting *p*-bromocumyl hydroperoxide was obtained by autoxidation of *p*-bromocumene (9), which was synthesized by bromination of cumene (11). The perether was purified by freezing out from a mixture of petroleum and diethyl ethers and had the following characteristics: n_D^{20} 1.5484; d_4^{20} 1.389; MR found 65.21; calculated 65.54; molecular weight found 268.3; calculated 285.15; $[O_2]$ found 5.21%; calculated 5.61%.

Found, %:	C 50.98; H 4.51; Br 28.0
$C_{12}H_{13}O_3Br$. Calculated, %:	C 50.54; H 4.59; Br 28.02

Over 8 weeks the active-oxygen content decreased by 50%.

***p*-Nitrocumyl peracrylate**
$CH_2{=}CH{-}CO{-}OO{-}C(CH_3)_2{-}C_6H_4{-}NO_2$. The starting *p*-nitrocumyl hydroperoxide was obtained by autoxidation of *p*-nitrocumene (12), which was prepared by nitration of cumene (13). The perether was recrystallized at low temperature from a mixture of petroleum and diethyl ethers and had the following characteristics: m.p. 8-10°; n_D^{20} 1.5394; d_4^{20} 1.230; MR found 63.98; calculated 64.09; molecular weight found 237.1; calculated 251.1; $[O_2]$ found 6.12%; calculated 6.37%.

Found, %:	C 56.90; H 5.34; N 5.96
$C_{12}H_{13}O_5N$. Calculated, %:	C 57.39; H 5.23; N 5.67

The perether is stable: on storage for one year, no loss of active oxygen was observed.

tert-Butyl permethacrylate $CH_2{=}C(CH_3){-}CO{-}OO{-}C(CH_3)_3$ was synthesized by the reaction of methacryloyl chloride with the sodium salt of tert-butyl hydroperoxide in CCl_4. The starting methacryloyl chloride was obtained by two methods (3, 14). Purification of the perether was difficult owing to its great tendency to polymerize—during distillation, approximately 1/3 is converted into a viscous polymer, and in some cases intensive decomposition with explosion is observed. The pure perether was distilled at 45°/2.5 mm and 23.5°/0.07 mm and had the following characteristics: n_D^{20} 1.4298; d_4^{20} 0.941; MR found 43.38; calculated 43.07; molecular weight found 156.2; calculated 158; $[O_2]$ found 10.5%; calculated 10.12%.

Found, %:	C 60.55; H 8.71
$C_8H_{14}O_3$. Calculated, %:	C 60.72; H 8.93

The structure was confirmed by alcoholysis with isolation of tert-butyl hydroperoxide and methyl methacrylate.

Cumyl permethacrylate
$CH_2{=}C(CH_3){-}CO{-}OO{-}C(CH_3)_2{-}C_6H_5$. The perether was synthesized by the reaction of methacryloyl chloride with the sodium salt of cumyl hydroperoxide in *n*-hexane. The perether was isolated by crystallization from the hexane solution at −10°, and then purified

by threefold recrystallization from petroleum ether; characteristics: m.p. 32–33°; molecular weight found 209.2; calculated 220.0; $[O_2]$ found 6.8%; calculated 7.2%.

Found, %:	C 70.80; H 7.45
$C_{13}H_{16}O_3$. Calculated, %:	C 70.84; H 7.33

On hydrolysis in 0.1 N NaOH solution, the amount of acid found corresponded to the pure product. The perester is of low stability—at room temperature over 48 h a decrease in the content of active oxygen to 2.3% is observed, while in the cold over 14 days only from 6.8 to 6.4%. Thus, cumyl permethacrylate also undergoes heterolytic rearrangement into nonperoxide compounds according to the scheme indicated earlier.

p-Chlorocumyl permethacrylate
$CH_2{=}C(CH_3){—}CO{—}OO{—}C(CH_3)_2{—}C_6H_4{—}Cl$ was obtained from the corresponding products in CCl_4, purified by freezing out, and had the following characteristics: n_D^{20} 1.5210; d_4^{20} 1.1470; MR found 67.62; calculated 67.36; molecular weight found 244.9; calculated 254.72; $[O_2]$ found 5.97%; calculated 6.28%.

Found, %:	C 60.98; H 5.93; Cl 13.87
$C_{13}H_{15}O_3Cl$. Calculated, %:	C 61.30; H 5.94; Cl 13.92

On storage in the cold for 24 h, a decrease in the content of active oxygen from 5.97 to 5.37% is observed.

Analogously, *p*-bromo- and *p*-nitrocumyl permethacrylates were obtained.

p-Bromocumyl permethacrylate
$CH_2{=}C(CH_3){—}CO{—}OO{—}C(CH_3)_2{—}C_6H_4{—}Br$. n_D^{20} 1.5406; d_4^{20} 1.348; MR

found 69.69; calculated 70.16; molecular weight found 267.1; calculated 299.18; $[O_2]$ found 4.48; calculated 5.35%.

Found, %:	C 52.01; H 4.92; Br 26.96
$C_{13}H_{15}O_3Br$. Calculated, %:	C 52.17; H 5.05; Br 26.71

On storage in the cold, a decrease in the content of active oxygen is observed.

p-Nitrocumyl permethacrylate
$CH_2{=}C(CH_3){-}CO{-}OO{-}C(CH_3)_2{-}C_6H_4{-}NO_2$. n_D^{20} 1.5343; d_4^{20} 1.174; MR found 69.27; calculated 68.62; molecular weight found 240.0; calculated 265.27; $[O_2]$ found 6.03%; calculated 6.03%. On storage in the cold for 3 weeks, a decrease in active oxygen from 6.03 to 5.0% was observed.

In conclusion it may be noted that, among the synthesized peresters, the peresters of alkyl hydroperoxides are relatively the most stable; moreover, the peracrylates are more stable than the permethacrylates, which are more prone to polymerization. Peresters of aralkyl hydroperoxides–isopropylbenzene and its substituted derivatives–are characterized by low stability owing to the manifestation in them of heterolytic rearrangement into nonperoxide products. Furthermore, the peresters of hydroperoxides of substituted isopropylbenzene are relatively more stable than those of the unsubstituted compound, and their stability increases with increasing electronegativity of the substituent in the order $Br < Cl < NO_2$.

Lviv Polytechnic Institute

Received
22 XI 1964

CITED LITERATURE

1. A. Baeyer, V. Villiger, Ber., **34**, 738 (1901).
2. N. A. Milas, D. M. Surgenor, J. Am. Chem. Soc., **68**, 642 (1946).
3. G. H. Stempel, R. P. Cross, J. Am. Chem. Soc., **72**, 2299 (1950).
4. N. A. Milas, D. M. Surgenor, J. Am. Chem. Soc., **68**, 205 (1946).
5. N. A. Milas, D. M. Surgenor, J. Am. Chem. Soc., **68**, 643 (1946).
6. N. A. Milas, O. Mageli, J. Am. Chem. Soc., **74**, 1471 (1952).
7. R. Criegee, Ber., **77**, 22 (1944).

8. V. A. Shushunov, V. A. Yablokov, N. V. Yablokova, Collection "Chemistry of Peroxide Compounds," Publ. House of the USSR Academy of Sciences, 1963, p. 253.
9. M. A. Dikii, T. I. Yurzhenko, ZhOKh, **33**, 1360 (1963).
10. T. I. Yurzhenko, M. A. Dikii, DAN, **137**, 1137 (1961).
11. O. Jacobsen, Ber., **12**, 430 (1879).
12. P. G. Sergeev, A. M. Gladkov, ZhOKh, **27**, 538 (1957).
13. J. W. Haun, K. A. Kole, Ind. and Eng. Chem., **43**, 2355 (1951).
14. I. A. Arbuzova, L. I. Medvedeva, S. A. Plotkina, ZhOKh, **26**, 1127 (1956).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.