ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 4, pp. 659–662. © Pleiades Publishing, Ltd., 2012.
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# Synthesis of Diesters by Addition of Acids to 5-Alkoxycarbonylnorborn-2-ene and Related 5-Methyl Derivatives

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Received January 25, 2011

**Abstract**—The addition of saturated aliphatic acids $C_1$–$C_5$ to 5-alkoxycarbonylnorborn-2-enes and 5-methyl-5-alkoxycarbonylnorborn-2-enes in the presence of catalyst $BF_3{\cdot}O(C_2H_5)_2$ was studied and new representatives of the norbornane hydroxyacids diesters were synthesized.

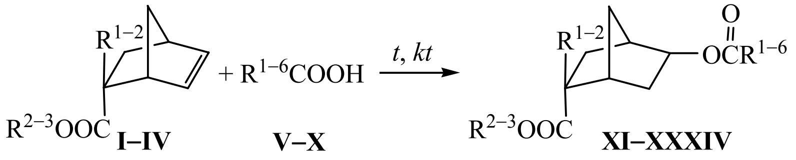
**DOI:** 10.1134/S1070363212040081

Bicyclic diesters of diols and hydroxy acids are practically valuable organic compounds that have been successfully used in various fields as effective solvents [1], plasticizer for polymers [2], synthetic oils [3], and aroma substances [4].

Due to the urgency of obtaining bicyclic diol diesters, we formerly carried out the addition of monocarboxylic saturated acids $C_1$–$C_6$ and unsaturated acrylic and methacrylic acids to the acetoxy- and acetoxymethylnorbornene that resulted in the synthesis of the corresponding diesters, which can be used as fragrance compounds and monomers [5–7].

In this paper we studied a reaction of catalytic addition of saturated monocarboxylic acids to 5-alkoxycarbonylnorborn-2-enes and related 5-methyl derivatives for the synthesis of new classes of bicyclic diesters.

The studies showed that saturated monocarboxylic acids are regioselectively added in the presence of catalyst $BF_3{\cdot}O(C_2H_5)_2$ to alkoxycarbonylnorbornene to form the diesters, 2-acyloxy-5-alkoxycarbonylnorbornanes.



$R^1$ = H, $R^2$ = $CH_3$, $R^3$ = $CH_3CH_2$, $R^4$ = $CH_3CH_2CH_2$, $R^5$ = $(CH_3)_2CH$, $R^6$ = $CH_3CH_2CH_2CH_2$.

To find the optimal conditions for the reaction of the diesters formation, we studied the effect of molar ratio of reacting components in the range 0.5–1.3:1 on the addition of acetic acid to 5-methoxycarbonylnorborn-2-ene as an example, at the temperature 50–90ºC, reaction duration 1.8 h, and amount of catalyst $BF_3{\cdot}O(C_2H_5)_2$ 0.06–0.14 wt % to acetic acid. The results are shown in the figure.

As seen from the data obtained, the optimal conditions of the formation of diester in the reaction of acetic acid with 5-methoxycarbonylnorborn-2-ene in the presence of boron trifluoride etherate are as follows: the molar ratio of 5-methoxycarbonylnorborn-2-ene to acetic acid 1:1.1, the amount of $BF_3{\cdot}O(C_2H_5)_2$ 0.1 wt % to acetic acid, temperature 80ºC, duration 4 h. Under these conditions, the yield of 5-methoxycarbonylnorborn-2-yl acetate is 88.0%.

The found optimum conditions were also implemented to the addition of other saturated monocarpboxylic acids: formic, propionic, butyric, isobutyric, and valeric. The yields of diesters depend on the structure of the monocarboxylic acid and decrease from 92.0 to 61.5% in the series from formic to valeric acid:

| Acid | HCOOH | $CH_3COOH$ | $C_2H_5COOH$ | $C_3H_7COOH$ | *i*-$C_3H_7COOH$ | $C_4H_9COOH$ |
|---|---|---|---|---|---|---|
| Yield, % | 92.0 | 88.0 | 78.5 | 72.9 | 69.0 | 61.5 |

To obtain the diesters, we have also studied the addition of saturated monocarboxylic acids to 5-ethoxycarbonylnorborn-2-ene in the presence of the boron trifluoride etherate. The experiments were carried out at the found optimum conditions. Yields of the diesters ranged from 90.1% (formic acid) to 60.9% (valeric acid). Consequently, in the addition reaction of saturated monocarboxylic acids to 5-ethoxycarbonylnorborn-2-ene the same pattern was observed. The change in the yield is due to a decrease in the degree of dissociation of saturated monobasic acids in the series.

The study of addition of the saturated $C_1$–$C_5$ acids to 5-methyl-5-methoxycarbonylnorborn-2-ene in the presence of the boron trifluoride etherate showed the same regular decrease in the yield of diesters from 87.0 to 69.0%. The presence in the molecule of electron-releasing methyl group and steric factors have a negative effect on the reactivity of the π-double bond of norbornene ring, which leads to a relative decrease in the yield of diesters compared with the case of 5-methoxycarbonylnorborn-2-ene.

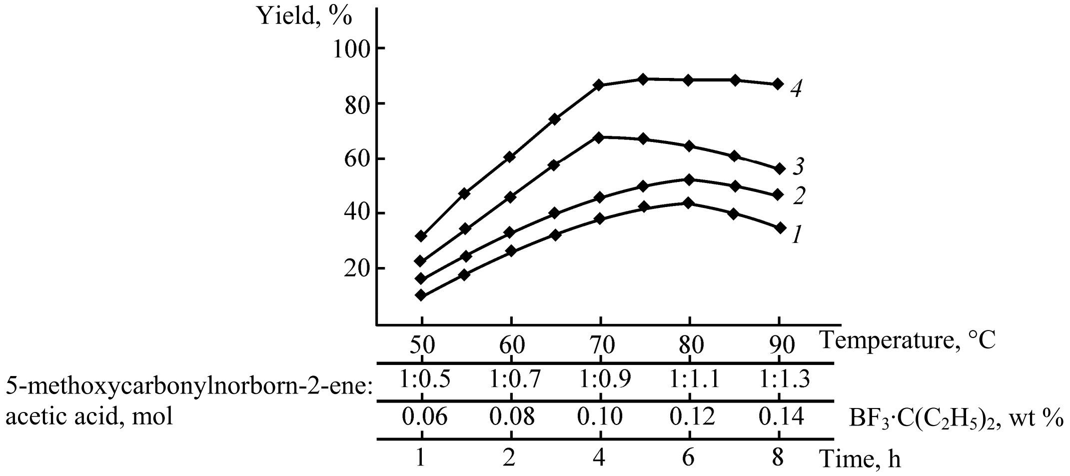
The addition of the saturated monocarboxylic acids to 5-methyl-5-ethoxycarbonylnorborn-2-ene under the found optimal conditions led to similar results.

The chromatographic analysis showed that the synthesized compounds consist of two regioisomers: 2,5- and 2,6-substituted derivatives in the ratio 91.0–95.0% to 5.0–9.0%. Because of the close boiling temperatures of the isomers it was impossible to separate them by vacuum distillation. Therefore the physicochemical properties of mixtures of these isomers were determined, which are listed in Table 1.

Structures of the synthesized diesters of hydroxy acids are confirmed by the data of IR and $^1$H, $^{13}$C NMR spectroscopy. The IR spectra contain strong absorption bands in the regions of 1730–1740 cm$^{-1}$ indicating the presence of carbonyl group, 1200–1190 cm$^{-1}$ corresponding to ester groups, and 1380 cm$^{-1}$ of $CH_3$ groups. The absorption bands in the region of 850–890 cm$^{-1}$ confirm the existence of *exo,exo*-isomer in the molecules of the synthesized diesters.

The signals of the methyl group from the propyl substituent in the $^1$H NMR spectra occur at 2.20 ppm, the protons of *endo*-methylene groups, at 2.5 ppm, and the signals at 4.8, 5.1 ppm show that the diesters are in the *exo*-form. Table 2 lists the chemical shifts of the signals in $^1$H and $^{13}$C NMR spectra of the synthesized diesters.

The diesters are colorless liquids with characteristic odor. Some compounds have a pleasant smell, for example, 5-ethoxycarbonylnorbornyl 2-acetate and its 5-methyl-substituted derivative have a fruity smell and can be used as synthetic aroma chemicals for the preparation of the composition of perfumes and as odorant for detergents.



(*1*) Effect of temperature, (*2*) molar ratio of 5-methoxycarbonylnorborn-2-ene to the acetic acid, (*3*) the amount of catalyst $BF_3 \cdot O(C_2H_5)_2$, and (*4*) the experiment duration on the yield of 5-methoxycarbonylnorbornyl 2-acetate.

**Table 1.** Physicochemical properties, elemental composition, and yield of diesters

| Comp. no. | R | Yield, % | *bp*, °C (3 mm Hg) | $d_4^{20}$ | $n_D^{20}$ | Found, % |  | Formula | Calculated, % |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  | C | H |  | C | H |
| **XI** | $R^1, R^2, R^1$ | 92.0 | 65–66 | 1.1815 | 1.4791 | 60.33 | 7.00 | $C_{10}H_{14}O_4$ | 60.61 | 7.07 |
| **XII** | $R^1, R^2, R^2$ | 88.0 | 70–71 | 1.0912 | 1.4799 | 62.01 | 7.39 | $C_{11}H_{16}O_4$ | 62.24 | 7.59 |
| **XIII** | $R^1, R^2, R^3$ | 78.5 | 110–112 | 1.0819 | 1.4805 | 63.48 | 8.01 | $C_{12}H_{18}O_4$ | 63.65 | 8.02 |
| **XIV** | $R^1, R^2, R^4$ | 72.9 | 120–122 | 1.0797 | 1.4822 | 64.79 | 8.25 | $C_{13}H_{20}O_4$ | 64.98 | 8.39 |
| **XV** | $R^1, R^2, R^5$ | 69.0 | 110–113 | 1.0334 | 1.4706 | 64.88 | 8.28 | $C_{13}H_{20}O_4$ | 64.98 | 8.39 |
| **XVI** | $R^1, R^2, R^6$ | 61.5 | 132–135 | 1.0224 | 1.4851 | 66.04 | 8.49 | $C_{14}H_{22}O_4$ | 66.14 | 8.61 |
| **XVII** | $R^1, R^3, R^1$ | 90.1 | 78–80 | 1.1205 | 1.4892 | 62.11 | 7.49 | $C_{11}H_{16}O_4$ | 62.24 | 7.59 |
| **XVIII** | $R^1, R^3, R^2$ | 85.4 | 89–91 | 1.0781 | 1.4885 | 63.48 | 8.00 | $C_{12}H_{18}O_4$ | 63.65 | 8.02 |
| **XIX** | $R^1, R^3, R^3$ | 76.0 | 114–116 | 1.0614 | 1.4801 | 64.79 | 8.28 | $C_{13}H_{20}O_4$ | 64.98 | 8.39 |
| **XX** | $R^1, R^3, R^4$ | 72.5 | 129–131 | 1.0359 | 1.4809 | 66.03 | 8.41 | $C_{14}H_{22}O_4$ | 66.14 | 8.61 |
| **XXI** | $R^1, R^3, R^5$ | 64.0 | 121–123 | 1.0221 | 1.4712 | 66.02 | 8.52 | $C_{14}H_{22}O_4$ | 66.14 | 8.61 |
| **XXII** | $R^1, R^3, R^6$ | 60,9 | 144–146 | 1.0181 | 1.4938 | 67.04 | 9.00 | $C_{15}H_{24}O_4$ | 67.14 | 9.01 |
| **XXIII** | $R^2, R^2, R^1$ | 87,0 | 76–79 | 1.0711 | 1.4746 | 62.11 | 7.47 | $C_{11}H_{16}O_4$ | 62.24 | 7.59 |
| **XXIV** | $R^2, R^2, R^2$ | 84,5 | 87–90 | 1.0554 | 1.4763 | 63.49 | 8.00 | $C_{12}H_{18}O_4$ | 63.65 | 8.02 |
| **XXV** | $R^2, R^2, R^3$ | 82.0 | 110–114 | 1.0315 | 1.4876 | 64.85 | 8.18 | $C_{13}H_{20}O_4$ | 64.98 | 8.39 |
| **XXVI** | $R^2, R^2, R^4$ | 78.3 | 128–130 | 1.0201 | 1.4881 | 64.03 | 8.51 | $C_{14}H_{22}O_4$ | 66.14 | 8.61 |
| **XXVII** | $R^2, R^2, R^5$ | 72.8 | 118–120 | 1.0012 | 1.4768 | 66.01 | 8.60 | $C_{14}H_{22}O_4$ | 66.14 | 8.61 |
| **XXVIII** | $R^2, R^2, R^6$ | 69.0 | 140–142 | 0.9951 | 1.4915 | 67.05 | 8.99 | $C_{15}H_{24}O_4$ | 67.14 | 9.01 |
| **XXIX** | $R^2, R^3, R^1$ | 82.0 | 84–85 | 1.0401 | 1.4806 | 63.11 | 8.00 | $C_{12}H_{18}O_4$ | 63.69 | 8.08 |
| **XXX** | $R^2, R^3, R^2$ | 78.1 | 97–98 | 1.0211 | 1.4818 | 64.81 | 8.21 | $C_{13}H_{20}O_4$ | 64.97 | 8.39 |
| **XXXI** | $R^2, R^3, R^3$ | 75.4 | 119–120 | 1.0202 | 1.4855 | 66.00 | 8.53 | $C_{14}H_{22}O_4$ | 66.11 | 8.71 |
| **XXXII** | $R^2, R^3, R^4$ | 71.6 | 135–137 | 1.0109 | 1.4867 | 67.03 | 10.52 | $C_{15}H_{24}O_4$ | 67.67 | 9.02 |
| **XXXIII** | $R^2, R^3, R^5$ | 68.0 | 121–122 | 1.0011 | 1.4853 | 67.01 | 10.50 | $C_{15}H_{24}O_4$ | 67.67 | 9.02 |
| **XXXIV** | $R^2, R^3, R^6$ | 61.5 | 149–150 | 0.9906 | 1.4966 | 68.03 | 9.07 | $C_{16}H_{26}O_4$ | 68.57 | 9.28 |

## EXPERIMENTAL

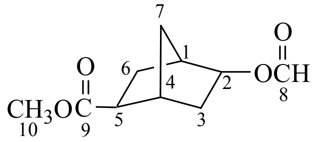
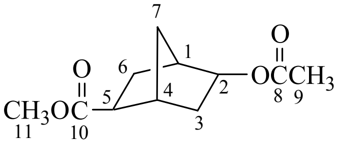
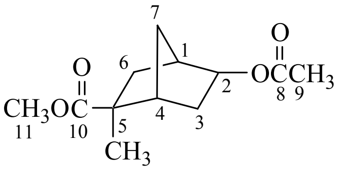
The purity and isomeric composition of the synthesized diesters as well as of the parent components was identified by GLC analysis. The analysis was performed on a LKhM-8MD chromatograph, column length 1.5 m, the stationary phase 10.0 wt % of polyethyleneglycol succinate on spherochrome, carrier gas helium, flow rate 45 ml min$^{-1}$, temperature 120–150°C, the temperature of evaporator 200–250°C, the detector current 100 mA.

The IR spectra were recorded on a UR-20 spectrophotometer, $^1$H and $^{13}$C NMR spectra, on a Bruker 300 MHz spectrometer, internal reference was acetone-$d_6$ solvent.

Physicochemical constants of the used saturated monobasic acids coincided with published data [8].

The starting 5-alkoxycarbonylnorborn-2-enes and their 5-methyl-derivatives were synthesized by condensation of methyl and ethyl acrylates and methacrylates with cyclopentadiene as described in [9]. Their

**Table 2.** $^1$H and $^{13}$C NMR chemical shifts of 5-methoxycarbonylnorborn-2-yl formate, 5-methoxy-2-carbonylnorbonyl acetate, and 5-methyl-5-methoxycarbonylnorborn-2-en-2-yl acetate.

| Diester | Chemical shift, δ, ppm | |
|---|---|---|
| | $^1$H | $^{13}$C |
|  | 8.22 (H$^8$), 4.15 (H$^2$), 5.10 (H$^5$), 2.10 (H$^4$), 1.80 (H$^1$), 2.52 (H$^{10}$), 2.19 (H$^6$), 1.47 (H$^3$), 1.18 (H$^7$) | 158 (C$^8$), 156 (C$^9$), 74 (C$^2$), 84 (C$^5$), 38 (C$^1$), 36 (C$^4$), 32 (C$^6$), 30 (C$^3$), 28 (C$^7$), 19 (C$^{10}$) |
|  | 5.12 (H$^8$), 4.10 (H$^2$), 2.21 (H$^9$), 2.35 (H$^{11}$), 2.40–2.60 (H$^{1,4}$), 1.85–1.90 (H$^{3,6}$), 1.70 (H$^7$) | 128 (C$^{10}$), 126 (C$^8$), 110 (C$^2$), 79 (C$^5$), 48 (C$^1$), 44 (C$^4$), 38 (C$^3$), 35 (C$^6$), 29 (C$^7$), 20 (C$^9$), 18 (C$^{11}$) |
|  | 4.10 (H$^2$), 2.41–2.60 (H$^{1,4}$), 1.90 (H$^3$), 2.00 (H$^6$), 1.85 (H$^7$), 1.71 (H$^9$), 1.74 (H$^{11}$), 1.69 (H$^{12}$) | 128 (C$^{10}$), 126 (C$^8$), 111 (C$^2$), 80 (C$^5$), 48 (C$^1$), 44 (C$^4$), 37 (C$^6$), 34 (C$^6$), 29 (C$^7$), 20 (C$^9$), 19 (C$^{11}$), 18 (C$^{12}$) |

physicochemical constants were as follows: 5-methoxycarbonylnorborn-2-ene, bp 78–79°C (17 mm Hg), $d_4^{20}$ 1.0516, $n_D^{20}$ 1.4761; 5-methyl-5-methoxycarbonylnorborn-2-ene, bp 105–106°C (17 mm Hg), $d_4^{20}$ 1.0309, $n_D^{20}$ 1.4712; 5-ethoxycarbonylnorborn-2-ene, bp 90–91 (17 mm Hg) $d_4^{20}$ 1.0208, $n_D^{20}$ 1.4686; 5-methyl-5-ethoxycarbonylnorborn-2-ene, bp 112–113°C (17 mm Hg), $d_4^{20}$ 1.0361, $n_D^{20}$ 1.4785.

The syntheses of the diesters was carried out in a setup with permanent stirring. After the reaction completion, the catalysate was washed with distilled water, dried over anhydrous $MgSO_4$, and the target diester was isolated by vacuum distillation.

## REFERENCES

1. USA Patent no. 4390717, 1983; *Ref. Zh. Khim.*, 1984, 5N84P.
2. Gasanov, A.G., Azizov, A.G., Alieva, L.I., Mamedov, E.G., Babaeva, R.Z., Rustamov, R.A., and Ayuubov, I.G. *Zh. Prikl. Khim.*, 2008, vol. 81, no. 4, p. 684.
3. Gurbanov, G.N. and Mamed'yarov, M.A., *Azerb. Khim. Zh.*, 2006, no. 1, p. 20.
4. Republik Azerbaidzhan Patent no. 990185, 1999.
5. Mamedov, M.K., *Zh. Org. Khim.*, 1997, vol. 36, no. 2, p. 225.
6. Mamedov, M.K., Piraliev, A.G., and Rasulova, R.A., *Zh. Prikl. Khim.*, 2007, vol. 80, no. 12, p. 2007.
7. Mamedov, M.K., *Zh. Org. Khim.*, 1997, vol. 33, no. 2, p. 197.
8. *Spravochnik khimika* (Chemist's Handbook), Moscow: Khimiya, 1964, vol. II.
9. Mekhtiev, S.D., Mamedov, M.K., and Gashimov, Kh.M., *Azerb. Khim. Zh.,* 1986, no. 2, p. 36.