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SYNTHESIS OF α, α'-ASYMMETRIC NITROXIDE RADICALS BY *C*OR *O*-ACYLATION OF RADICAL-ENOLATE INTERMEDIATES GENERATED BY REDUCTION OF HOMOALLYLIC NITRO ENONES WITH SAMARIUM(II) IODIDE

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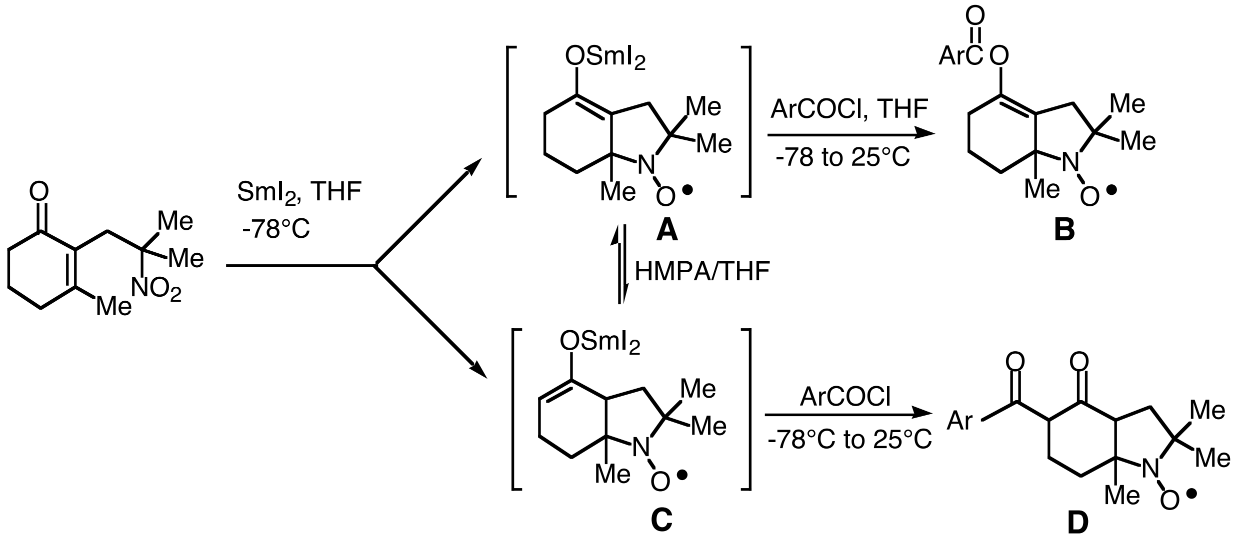
Abstract- A new synthetic method to form two structurally different α, α'-asymmetric bicyclic nitroxides from the same substrate is described. Reduction of certain homoallylic nitro enones bearing a long alkyl chain with 3.0 equiv of SmI_2 in THF at -78°C gave a nitroxide radical-anion species of type **A**, while the same reduction followed by addition of HMPA at -78°C resulted in the isomerization of the double bond to afford a different nitroxide radical anion species of type **C**. The former radical-anion undergoes *O*-acylation by the reaction with acyl chlorides to give α, α'-asymmetric bicyclic ester-nitroxides of type **B**, while the latter one does *C*-acylation to produce α, α'-asymmetric bicyclic β-diketonitroxides of type **D**.

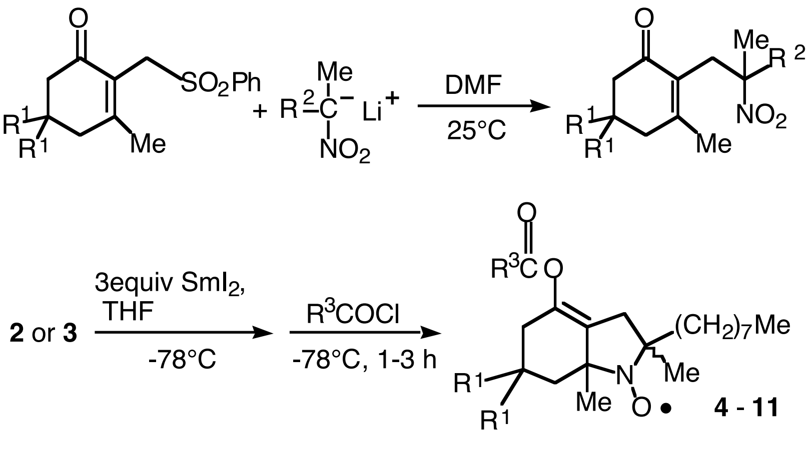
Recently we reported a direct synthetic method of α-asymmetric bicyclic nitroxide radicals of type **B** by three-electron reduction of homoallylic nitroenones with SmI_2 followed by *O*-acylation of the resulting nitroxide radical-enolate intermediate of type **A** with acyl chlorides (Scheme 1).[1-3] In order to utilizethis synthetic procedure for the preparation of purely organic paramagnetic liquid crystals containing a chiral nitroxide radical moiety as a paramagnetic center in the core portion, (1) we have investigated the synthetic generality for introduction of long alkyl chains necessary to induce the liquid crystal property into the nitroxide radicals and (2) we have attempted the isomerization of the less reactive nitroxide radical-enolate of type **A** into the more reactive one of type **C** that can afford a new nitroxide radical structure of type **D** after *C*-acylation. In this paper, we report the experimental results on *C*- and *O*-acylation of the two different radical-enolate intermediates of types **A** and **C**, respectively, derived from the same substrate with a long alkyl chain.

Dedidated to Professor Shô Itô on the occasion of his 77th birthday.



Scheme 1

As the substrate with a long alkyl chain, racemic homoallylic nitro enones (**2**) and (**3**) were prepared by the $S_{RN}1$ reaction of the corresponding homoallylic sulfonyl enone with the lithium salt of 2-nitrooctane in a similar way to the synthesis of **1** (Scheme 2).[2,5,6] First, *O*-acylation of the radical-enolate intermediates of type **A**, which were generated by the reduction of the substrates with 3.0 equiv of SmI_2 at -78°C, with acyl chlorides such as 3,5-bis(trifluoromethyl)benzoyl chloride, octanoyl chloride, 4-octyloxybenzoyl chloride and 4-(4-octyloxyphenyl)benzoyl chloride has been examined. Both the reduction with SmI_2 and *O*-acylation with acyl chlorides occurred as expected (Scheme 2 and Table 1). The yields of the products with the benzoyl chloride having an electron-withdrawing group or the alkanoyl chloride were 52 - 54% (runs 1 - 4 in Table 1), while the use of benzoyl chlorides substituted by an electron-donating group led to 20 to 27% yields due to the low reactivity of the samarium enolate intermeditate (runs 5 - 8).[7] The IR, EPR and MS spectroscopies, and elemental analyses of these products were consistent with the molecular structures of **4** - **11**.[8]



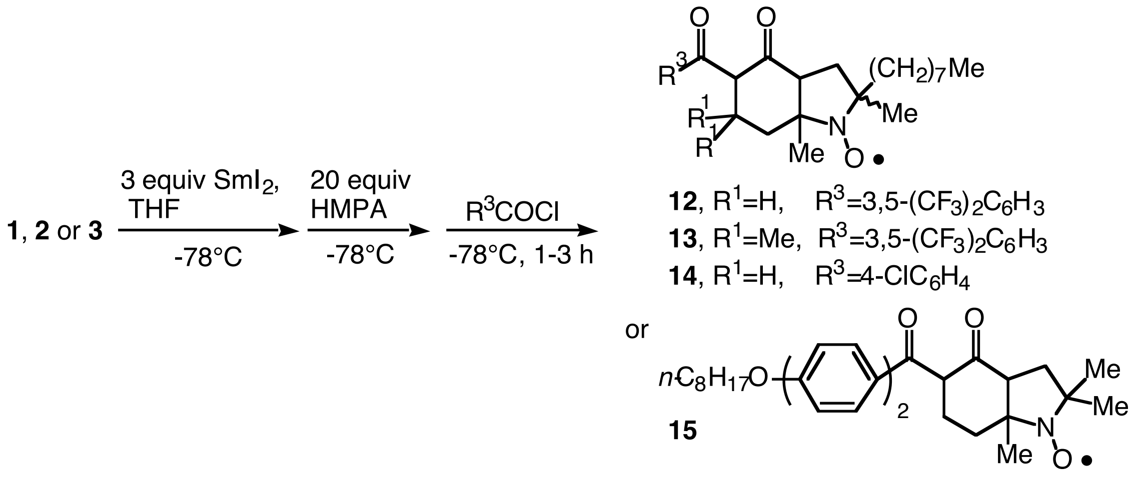
1, R^1=H, R^2=Me
2, R^1=H, R^2=$Me(CH_2)_7$
3, R^1=Me, R^2=$Me(CH_2)_7$

4, R^1=H, R^3=3,5-$(CF_3)_2C_6H_3$
5, R^1=Me, R^3=3,5-$(CF_3)_2C_6H_3$
6, R^1=H, R^3=$Me(CH_2)_6$
7, R^1=Me, R^3=$Me(CH_2)_6$
8, R^1=H, R^3=4-*n*-$C_8H_{17}OC_6H_4$
9, R^1=Me, R^3=4-*n*-$C_8H_{17}OC_6H_4$
10, R^1=H, R^3=4-(4-*n*-$C_8H_{17}OC_6H_4)C_6H_4$
11, R^1=Me, R^3=4-(4-*n*-$C_8H_{17}OC_6H_4)C_6H_4$

Table 1. Preparation of α, α'-Asymmetric and α-Asymmetric Nitroxide Radicals (Schemes 2 and 3)

					EPR data[a]	
run	nitroenone	R^3COCl	Product	yield %	*g*	a_N (mT)
1	**2**	$3,5\text{-}(CF_3)_2C_6H_3COCl$	**4**	55	2.0062	1.42
2	**3**	$3,5\text{-}(CF_3)_2C_6H_3COCl$	**5**	52	2.0063	1.47
3	**2**	$Me(CH_2)_6COCl$	**6**	54	2.0062	1.43
4	**3**	$Me(CH_2)_6COCl$	**7**	53	2.0062	1.46
5	**2**	$4\text{-}C_8H_{17}OC_6H_4COCl$	**8**	26	2.0061	1.47
6	**3**	$4\text{-}C_8H_{17}OC_6H_4COCl$	**9**	27	2.0061	1.42
7	**2**	$4\text{-}(4\text{-}C_8H_{17}OC_6H_4)C_6H_4COCl$	**10**	27	2.0062	1.41
8	**3**	$4\text{-}(4\text{-}C_8H_{17}OC_6H_4)C_6H_4COCl$	**11**	20	2.0062	1.45
9	**2**	$3,5\text{-}(CF_3)_2C_6H_3COCl$	**12**	68	2.0062	1.41
10	**3**	$3,5\text{-}(CF_3)_2C_6H_3COCl$	**13**	14	2.0062	1.41
11	**2**	$4\text{-}ClC_6H_4COCl$	**14**	65	2.0063	1.40
12	**2**	$Me(CH_2)_6COCl$	—[b]	—	—	—
13	**2**	$4\text{-}C_8H_{17}OC_6H_4COCl$	—[b]	—	—	—
14	**1**	$4\text{-}(4\text{-}C_8H_{17}OC_6H_4)C_6H_4COCl$	**15**	52	2.0061	1.40

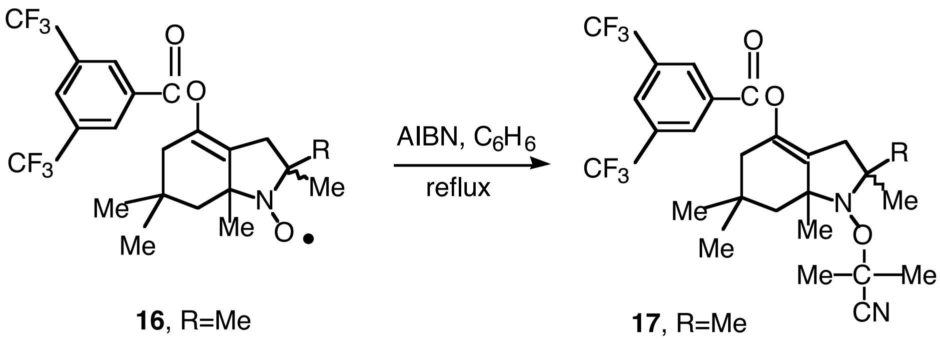
[a] In THF at 25°C. [b] Unable to be isolated.



Scheme 3

Next, with the aim of isomerizing the nitroxide radical-enolate of type **A** into the different one of type **C** and enhancing the reactivity of the resulting enolate portion, a THF solution of 20 equiv of HMPA was added to the reaction mixture at -78°C immediately after the reduction of the substrate with SmI_2, and the electrophile was subsequently added at the same temperature (Scheme 3).[9] As expected, the product was not an *O*-acylated compound but a *C*-acylated one of type **D** (runs 9 -11 and 14 in Table 1). Since the obtained *C*-acylated products are all liquid, their characterization has been carried out by IR, EPR and MS spectroscopies, and elemental analyses. Unequivocally the *C*-acylated products contain both β-diketo and nitroxide structures. The low yield (14%) of **13** (R^1=Me) can be rationalized in terms of the steric yield (runs 9 and 10). Comparison of the yields between radical products (**4**) and (**12**) (runs 1 and 9) indicates that the nitroxide radical-enolate of type **C** may be more reactive than the corresponding one of type **A**. Although the *C*-acylated products expected from the reaction of **2** with octanoyl chloride, 4-octyloxybenzoyl chloride and 4-(4-octyloxyphenyl)benzoyl chloride were surely formed, they were unable to be isolated by flash column chromatography on silica gel to give a mixture of decomposed products during purification (runs 12 and 13) .

The purities of both the *C*- and *O*-acylated products (**4**) - (**15**) determined by HPLC analysis were more than 95% after usual flash column chromatography on silica gel. Analytically pure compounds were obtained by HPLC purification using a silica gel stationary-phase column. The HPLC elution time of the *C*-acylated product was apparently longer than that of the corresponding *O*-acylated one, owing to the more polar nature of the β-diketone structure. Since *O*-acyloxy nitroxide (**16**) could be converted into the corresponding *O*-alkylated derivative (**17**) by reaction with AIBN in refluxing benzene, the diastereomeric ratio of product (**5**), which must be the same with respect to products (**4**) and (**6**) - (**14**), was determined to be approximately 1:1 by the HPLC analysis of its *O*-cyanopropylated derivative (**18**) obtained similarly (eq. 1). No peak separation was observed by the direct HPLC analysis of **4** - **14**.



(1)

16, R=Me
5, R=Me(CH$_2$)$_7$

17, R=Me
18, R=Me(CH$_2$)$_7$

Since molecular orbital calculations using the PM3 method[10] showed that the metal-free molecule of the radical-enolate of type **A** is more stable than the corresponding *cis* isomer of type **C** by 9.1 kcal/mol (Scheme 1), it is easily deduced that the activation energy of the isomerization of the double bond is lessened by the action of HMPA[11] and there exists an equilibrium between two radical-enolates of types **A** and **C**. Therefore, the radical-enolate of type **C** must be more reactive than the corresponding type **A**, because only product obtained in the presence of HMPA was type **D**.

We have described a new synthetic method for new α, α'-asymmetric bicyclic β-diketo-nitroxide radicals of type **D** as well as α, α'-asymmetric bicyclic ester-nitroxide radicals of type **B** starting from the same substrate with a long alkyl chain.

EXPERIMENTAL

IR spectra were recorded as liquid films on NaCl plates. ^{1}H NMR spectra were recorded at 400 MHz, and ^{13}C NMR were recorded at 100 MHz; $CDCl_3$ was used as the solvent. EPR spectra were recorded at 25°C. HPLC analysis and purification were carried out by using silica gel stationary-phase columns (0.46 x 30 cm and 2.0 x 25 cm), UV-Vis spectrophotometer (254 nm) and RI refractometer as the detector, and a mixture of hexane and and ethyl acetate (9:1 and 4:1) as the eluent, respectively. All solvents were distilled before use. All reactions were run under Ar.

Homoallylic nitro enone (**1**) was prepared according to a published procedure.[2] The analogous compounds (**2**) and (**3**) were prepared similarly; the yields of **2** and **3** in the final $S_{RN}1$ reaction (Scheme 2) were 86 and 66%, respectively.

2: IR (neat) 1659, 1618, 1534, 1456, 1427, 1379, 1350 cm^{-1}; ^{1}H NMR δ 3.01 (d, 1H, J=14.6 Hz), 2.95 (d, 1H, J=14.6 Hz), 2.47-2.25 (m, 4H), 2.15-2.03 (m, 1H), 1.90-1.81 (m, 2H), 1.83 (s, 3H), 1.73-1.60 (m, 1H), 1.37 (s, 3H), 1.26-1.14 (m, 12H), 0.86 (t, 3H, J=6.8 Hz); ^{13}C NMR δ 199.0, 161.3, 130.9, 92.3, 40.6, 38.2, 36.0, 34.0, 32.4, 32.2, 30.3, 29.9, 29.8, 24.6, 23.3, 22.4, 21.8, 14.7. Anal. Calcd for $C_{18}H_{31}NO_3$: C, 69.87; H, 10.10; N, 4.53. Found: C, 69,71; H, 10.11; N, 4.74.

3: IR (neat) 1666, 1617, 1552, 1535, 1460, 1375 cm^{-1}; ^{1}H NMR δ 3.02 (d, 1H, J=14.6 Hz), 2.97 (d, 1H, J=14.6 Hz), 2.35-2.20 (m, 4H), 2.18-2.06 (m, 1H), 1.81 (s, 3H), 1.76-1.65 (m, 1H), 1.41 (s, 3H), 1.40-1.20 (m, 12H), 1.03 (s, 3H), 1.02 (s, 3H), 0.88 (t, 3H, J=6.8 Hz); ^{13}C NMR δ 198.5, 158.2, 129.1, 91.7, 51.0, 47.3, 39.9, 35.6, 32.0, 31.8, 29.6, 29.2, 29.1, 28.4, 27.9, 24.0, 22.6, 21.8, 21.4, 14.1. Anal. Calcd for $C_{20}H_{35}NO_3$: C, 71.18; H 10.45 ; N 4.15. Found: C, 70.99; H, 10.63; N, 4.49.

General Procedure for Preparation of α, α'-Asymmetric Nitroxide Radicals (4) - (11) of Type B. To a solution of the homoallylic nitroenone (**2**) or (**3**) (1.00 mmol) in THF (20 mL) was added dropwise a freshly prepared THF solution of SmI_2 (0.1 mol/L, 30 mL, 3.0 mmol) at -78°C under argon atmosphere, followed by the dropwise addition of a solution of the acyl chloride (1.10 mmol) in THF (2 mL) at the same temperature. The resulting red solution was stirred at -78°C for 1-3 h and then slowly allowed to warm to rt over 1 h. After removal of the yellowish brown precipitate by filtration in the air, the filtrate was concentarated to give viscous red material. From this residue, the crude organic product was extracted with ether (3 x 10 mL) with vigorously stirring. The ethereal solution was separated from the resulting yellowish brown precipitate by filtration and concentrated to give red oily material, which was dissolved in a small amount of $CHCl_3$ and subjected to flash column chromatography on silica gel (9:1 hexane/EtOAc) to give the radical product with around 95% purity as judged by HPLC analysis. Analytically pure nitroxide radical was obtained by preparative HPLC purification of the product.

4: orange oil; IR (neat) 1747, 1457, 1385, 1280, 1238, 1179 cm^{-1}; HRMS (FD) calcd for $C_{27}H_{34}NO_3F_6$ 534.2444, found 534.2447. Anal. Calcd for $C_{27}H_{34}NO_3F_6$: C, 60.67; H, 6.41; N, 2.62. Found: C, 60.99; H, 6.30; N, 2.77.

5: orange oil; IR (neat) 1746, 1456, 1384, 1280, 1240, 1183 cm^{-1}; HRMS (FD) calcd for $C_{29}H_{38}NO_3F_6$ 562.2757, found 562.2742. Anal. Calcd for $C_{29}H_{38}NO_3F_6$: C, 61.91; H, 6.81; N, 2.49. Found: C, 61.76; H, 7.05; N, 2.33.

6: amber oil; IR (neat) 1735, 1457, 1380, 1260, 1165 cm^{-1}; HRMS (FD) calcd for $C_{26}H_{46}NO_3$ 420.3480, found 420.3444. Anal. Calcd for $C_{26}H_{46}NO_3$: C, 74.24; H, 11.02; N, 3.33. Found: C, 74.01; H, 11.33; N, 3.05.

7: amber oil; IR (neat) 1734, 1663, 1475, 1375, 1227, 1166 cm^{-1}; HRMS (FD) calcd for $C_{28}H_{50}NO_3$ 448.3793, found 448.3777. Anal. Calcd for $C_{28}H_{50}NO_3$: C, 74.95; H, 11.23; N, 3.12. Found: C, 75.22; H, 11.40; N, 2.99.

8: deep red oil; IR (neat) 1718, 1606, 1509, 1466, 1380, 1255, 1166 cm^{-1}; HRMS (FD) calcd for $C_{33}H_{52}NO_4$ 526.3899, found 526.3865. Anal. Calcd for $C_{33}H_{52}NO_4$: C, 75.24; H, 9.95; N, 2.66. Found: C, 75.55; H, 10.31; N, 2.59.

9: amber oil; IR (neat) 1722, 1606, 1510, 1466, 1370, 1255, 1166 cm^{-1}; HRMS (FD) calcd for $C_{35}H_{56}NO_4$ 554.4212, found 554.4223. Anal. Calcd for $C_{35}H_{56}NO_4$: C, 75.77; H, 10.17; N, 2.52. Found: C, 75.89; H, 10.33; N, 2.69.

10: deep red oil; IR (neat) 1718, 1653, 1605, 1522, 1465, 1377, 1275 1196 cm^{-1}; HRMS (FD) calcd for $C_{39}H_{56}NO_4$ 602.4212, found 602.4227. Anal. Calcd for $C_{39}H_{56}NO_4$: C, 77.70; H, 9.36; N, 2.32. Found: C, 77.81; H, 9.70; N, 1.99.

11: deep red oil; IR (neat) 1718, 1653, 1605, 1522, 1465, 1386, 1262, 1198 cm^{-1}; HRMS (FD) calcd for $C_{41}H_{60}NO_4$ 630.4525, found 630.4505. Anal. Calcd for $C_{41}H_{60}NO_4$: C, 78.05; H, 9.58; N, 2.22. Found: C, 77.80; H, 9.88; N, 2.51.

General Procedure for Preparation of Nitroxide Radicals (12) - (15) of Type D.

To a solution of the homoallylic nitroenone (**1**), (**2**) or (**3**) (1.00 mmol) in THF (20 mL) was added dropwise a freshly prepared THF solution of SmI_2 (0.1 mol/L, 30 mL, 3.0 mmol) at -78°C under argon atmosphere, followed by the dropwise addition of a solution of HMPA (3.5 mL, 20 mmol) in THF (3 mL) at the same temperature. A solution of the acyl chloride (1.10 mmol) in THF (2 mL) was added to the yellowish brown solution at -78°C. The resulting red solution was stirred at -78°C for 1-3 h and then slowly allowed to warm to rt over 1 h. After removal of the yellowish brown precipitate by filtration in the air, the filtrate was concentarated. From this residue, the crude organic product including HMPA was extracted with ether (3 x 10 mL) with vigorously stirring. The ethereal solution was separated from the resulting yellowish brown precipitate by filtration and concentrated to give liquid material, which was dissolved in a small amount of $CHCl_3$ and subjected to flash column chromatography on silica gel (9:1 hexane/ethyl acetate) to give the radical product with around 95% purity as judged by HPLC analysis. Analytically pure nitroxide radical was obtained by preparative HPLC purification of the product.

12: green oil; IR (neat) 1664, 1510, 1381, 1278, 1237, 1139 cm^{-1}; HRMS (FD) calcd for $C_{27}H_{34}NO_3F_6$ 534.2444, found 534.2465. Anal. Calcd for $C_{27}H_{34}NO_3F_6$: C, 60.67; H, 6.41; N, 2.62. Found: C, 60.98; H, 6.69; N, 2.28.

13: green oil; IR (neat) 1668, 1537, 1465, 1378, 1279, 1243, 1181 cm^{-1}; HRMS (FD) calcd for $C_{29}H_{38}NO_3F_6$ 562.2757, found 562.2735. Anal. Calcd for $C_{29}H_{38}NO_3F_6$: C, 61.91; H, 6.81; N, 2.49. Found: C, 62.22; H, 7.09; N, 2.33.

14: green oil; IR (neat) 1667, 1554, 1457, 1378, 1269, 1091 cm^{-1}; HRMS (FD) calcd for $C_{25}H_{35}NO_3Cl$ 432.2308, found 432.2322. Anal. Calcd for $C_{25}H_{35}NO_3Cl$: C, 69.35; H, 8.15; N, 3.23. Found: C, 69.00; H, 8.52; N, 2.98.

15: brown oil; IR (neat) 1710, 1665, 1537, 1458, 1373, 1247, 1185 cm^{-1}; HRMS (FD) calcd for $C_{32}H_{41}NO_4$ 503.3037, found 503.3001. Anal. Calcd for $C_{32}H_{41}NO_4$: C, 76.31; H, 8.20; N, 2.78. Found: C, 75.95; H, 8.56; N, 2.62.

Preparation of O-Cyanopropylated Derivatives (17) and (18) from Nitroxide Radicals (16) and (5)

A mixture of nitroxide radical (**16**) (0.052 g, 0.11 mmol) and AIBN (0.018 g, 0.11 mmol) in benzene (10 mL) was heated under reflux for 2 h. After cooling to rt, the mixture was concentrated and the residue was subjected to preparative TLC (silica gel, 9:1 hexane/ethyl acetate) to give 0.035 g (60%) of **17** as a colorless oil. The ^{1}H NMR spectrum of analytically pure **17** indicated the presence of diastereomers probably due to the generation of atropisomerism between the bicyclic portion and the ester structure, although the presence of the diastereomers can not be confirmed by HPLC analysis. The ^{1}H and ^{13}C NMR spectra shown below are referred to the major isomer.

17: IR (neat) 2260, 1790, 1680, 1560, 1480, 1390 cm^{-1}; ^{1}H NMR δ 8.52 (s, 2H), 8.10 (s, 1H), 2.46-1.92 (m, 4H), 1.75-1.58 (m, 2H),, 1.63 (s, 3H), 1.61 (s, 3H), 1.34 (s, 3H), 1.32 (s, 3H), 1.26 (s, 3H), 1.127 (s, 3H), 1.124 (s, 3H); ^{13}C NMR δ 187.0, 161.8, 140.7, 136.1, 129.9, 125.6, 122.8, 115.2, 112.2, 74.1, 64.6, 57.2, 49.8, 41.0, 39.5, 32.3, 31.1, 30.0, 27.3, 27.2, 26.0, 22.3; MS (FD) *m/z* (%) 532 (100, M$^+$), 464 (35). Anal. Calcd for $C_{26}H_{30}N_2O_3F_6$: C, 58.64; H, 5.68; N, 5.26. Found: C, 58.99; H, 5.95; N, 4.97.

Similarly, **5** (0.096 g, 0.17 mmol) was reacted with AIBN (0.028 g, 0.17 mmol) in refluxing benzene (8 mL). The diastereomeric ratio of the crude product (**18**) was determined to be approximately 1:1 by means of HPLC analysis before purification by preparative TLC giving 0.043 g (40%) of **18** (1:1 mixture of diastereomers) as a colorless oil. However, analytically pure **18** showed a very complex ^{1}H NMR pattern probably because of the generation of atropisomerism between the bicyclic portion and the ester structure, although only two diastereomers were detected by HPLC analysis. The ^{1}H NMR spectrum shown below is referred to one major isomer among possible four diastereomers.

18 (a mixture of diastereomers): IR (neat) 2252, 1793, 1646, 1558, 1471, 1382 cm^{-1}; ^{1}H NMR (a major isomer) δ 8.52 (s, 2H), 8.10 (s, 1H), 2.46-1.95 (m, 4H), 1.78-1.58 (m, 2H), 1.63 (s, 3H), 1.60 (s, 3H), 1.35-1.20 (m, 14H), 1.33 (s, 3H), 1.22 (s, 3H), 1.13 (s, 3H), 1.12 (s, 3H), 0.86 (t, 3H, J=6.8 Hz); MS (FD) *m/z* (%) 630 (26, M$^+$), 562 (100). Anal. Calcd for $C_{33}H_{44}N_2O_3F_6$: C, 62.84; H, 7.03; N, 4.44. Found: C, 62.66; H, 7.35; N, 4.08.

ACKNOWLEDGEMENT

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