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A New Alkoxyiodination and Nitratoiodination of Olefins Using Iodine-Cerium(IV) Ammonium Nitrate

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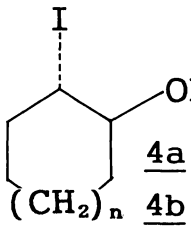
Reactions of cycloolefins with iodine-cerium(IV) ammonium nitrate in alcohols (methanol, ethanol, 1-propanol, and 2-propanol) under reflux gave the corresponding vicinal alkoxyiodocycloalkanes in good yields. In the case of t-butyl alcohol, trans-iodo nitrates were obtained.

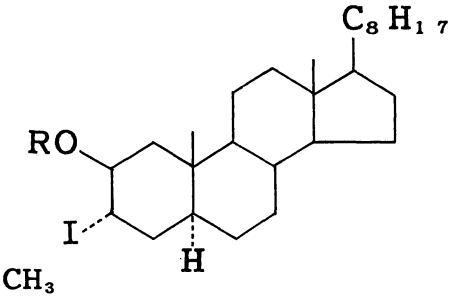
trans-1-Iodo-2-alkoxy and 2-nitrate ester derivatives are important synthetic intermediates. There have been known some procedures for syntheses of trans-alkoxyiodoalkane, namely, trans-addition to olefins using iodine-mercury(II) oxide,[1] iodine-silver(I) perchlorate,[2] iodine-copper(I) chloride,[3] potassium iodide-copper(II) salt,[3] and iodine-copper(II) acetate.[4] On the other hand, it was reported that the reaction of the olefin with iodine monochloride-silver nitrate gave iodoaliphatic nitrate esters.[5]

In a previous paper,[6] we reported a novel α-iodination of ketones using iodine-cerium(IV) ammonium nitrate (CAN) in acetic acid or methanol. Now in this paper, we would like to report that the reactions of olefins with iodine-CAN in alcohol gave the corresponding alkoxyiodo compounds in good yields, while in the case of tert-butyl alcohol the trans-iodoaliphatic nitrate esters were obtained in good yields. A typical procedure is as follows. A mixture of cyclohexene (1) (500 mg), iodine (382 mg), CAN (849 mg), and methanol (50 ml) was stirred at 50 ℃. After 6 h, the reaction mixture turned to pale yellow; and then it was concentrated. The residue was poured into water and extracted with ether. The ethereal solution was washed with water, dried, and evaporated. The residue was purified by distillation; trans-1-iodo-2-methoxycyclohexane (4a) (331 mg), bp 97-98 ℃/11 mmHg (lit,[1] bp 99.5-101 ℃/20 mmHg). A mixture of 1 (300 mg), iodine (465 mg), CAN (1.00 g), and 2-methyl-2-propanol (30 ml) was stirred under reflux for 5.5 h. After the usual work-up, the resulting oil was purified by distillation; trans-2-iodocyclohexanol nitrate (4f) (792 mg), bp 125-127



4a: n=1, R=CH_3
4b: n=1, R=CH_2CH_3
4c: n=1, R=$CH_2CH_2CH_3$
4d: n=1, R=$CH(CH_3)_2$
4e: n=1, R=CH_2CH_2OH
4f: n=1, R=NO_2
4g: n=1, R=$COCH_3$

5a: n=2, R=CH_3
5b: n=2, R=CH_2CH_3
5c: n=2, R=$CH_2CH_2CH_3$
5d: n=2, R=$CH(CH_3)_2$
5f: n=2, R=NO_2
5g: n=2, R=$COCH_3$



6a: R=CH_3
6b: R=CH_2CH_3
6c: R=NO_2

Table 1. Alkoxyiodination and Nitratoiodination of Olefins Using Iodine-Cerium(IV) Ammonium Nitrate

Run	Olefin	Solvent	Temp/℃	Time/h	Product	Yield/%
1	Cyclohexene(1)	MeOH	50	6	4a	92
2	1	EtOH	reflux	8.5	4b	78
3	1	1-PrOH	reflux	6	4c	90
4	1	2-PrOH	reflux	6	4d	76
5	1	EG[a)]/MeCN	reflux	5	4e	100
6	1	t-BuOH	reflux	5.5	4f	80
7	1	AcOH	50	4	4f+4g[b)]	100
8	1	AcOH	reflux	10	4h[c)]	80
9	Cycloheptene(2)	MeOH	50	8	5a	82
10	2	EtOH	50	8	5b	70
11	2	1-PrOH	reflux	8	5c	100
12	2	2-PrOH	reflux	7	5d	77
13	2	t-BuOH	reflux	5	5f	81
14	2	AcOH	50	4	5f+5g[b)]	100
15	2	AcOH	reflux	10	5h[c)]	70
16	5α-Cholest-2-ene(3)	MeOH	50	4	6a	70
17	3	EtOH	50	10	6b	65
18	3	t-BuOH	reflux	10	6c	45
19	3	AcOH	50	4	6c	86

a)EG: Ethylene Glycol. b)The composition of reaction mixtures was determined from the peak area ratio of NMR spectrum (4f:4g=5f:5g=1:1). c)The compound 4h and 5h are cis-diol monoacetate.

℃ /12 mmHg (lit,[2] bp 113 ℃ /1.3 mmHg). These results are summarized in the Table. The NMR spectra of alkoxyiodo compounds showed a multiplet (W/2=26 Hz) at δ ca. 4.1 for 4a-4e and at δ ca. 4.3 for 5a-5d; and a multiplet (W/2=26 Hz) at δ ca. 3.4 for 4a-4e, and at δ ca. 3.6 for 5a-5d. These results suggest that these alkoxyiodo compounds have a trans-diequatorial conformation. Iodo nitrates showed very intense IR absorption at 1636 cm^{-1} due to nitrate ester. The NMR spectra of these compounds showed a multiplet (W/2=24 and 20 Hz) at δ ca. 5.1 for 4f (ca. 5.3 for 5f) and a multiplet (W/2=24 and 20 Hz) at δ ca. 4.1 for 4f (ca. 4.3 for 5f). On the basis of of these spectral data for 4f and 5f, the structures of these iodo nitrates were determined to have a trans-diequatorial conformation. On the other hand, the structures of steroidal alkoxyiodo compounds (6a and 6b) and iodo nitrate (6c) were determined from coupling constants (J=8.6 Hz) to have a trans-diaxial conformation.

As can be seen in the Table 1, the present nitratoiodination appears more efficient than the method described by Diner and Lown.[5] In the case of the reaction of cyclohexene in acetic acid, it seems to proceed by the following reaction pathway:trans-iodo nitrate ———→ trans-iodoacetate ———→ cis-diol monoacetate. It is particularly noteworthy that this reaction may provide us a new synthetic method for trans-1,2-alkoxyiodo and trans-1,2-iodonitrato compound, more convenient than the methods used heretofore.

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Representative spectral data of the products are as follows:
4b: bp 95-96 ℃ (8 mmHg);IR(NaCl):1170 and 1110 cm^{-1};^{1}H-NMR($CDCl_3$): δ 3.32 (m,1H) and 4.10 (m,1H);^{13}C-NMR($CDCl_3$): δ 15.6, 23.7, 27.2, 31.4, 36.1, 37.9, 64.8, and 82.4.
4c: bp 78-80 ℃ (3 mmHg);IR(NaCl):1112 cm^{-1};^{1}H-NMR($CDCl_3$):δ 0.96(t,3H),

3.27-3.35(m,1H), 3.38-3.47(m,1H), 3.52-3.59(m,2H), and 4.02-4.12(m,1H); ^{13}C-NMR($CDCl_3$): δ 10.8, 23.3, 23.7, 27.2, 31.2, 36.0, 38.0, 71.2, and 82.5.

4d: bp 65-66 ℃ (1 mmHg);IR(NaCl):1090 cm^{-1};^{1}H-NMR($CDCl_3$):δ 1.19(dd,6H), 3.35-3.41(m,1H), 3.75-3.81(m,1H), and 3.98-4.08(m,1H);^{13}C-NMR($CDCl_3$): δ 22.6, 23.2, 23.9, 27.3, 33.1, 37.1, 38.3, 71.2, and 80.6.

4e: bp 110-112 ℃ (3 mmHg);IR(NaCl):3420 and 1120 cm^{-1};^{1}H-NMR($CDCl_3$):δ 3.31-3.38(m,1H), 3.45-3.56(m,2H), and 4.01-4.09(m,1H);^{13}C-NMR($CDCl_3$): δ 23.9, 27.7, 31.6, 36.4, 38.5, 61.9, 70.4, and 83.2.

4f: bp 125-127 ℃ (12 mmHg);IR(NaCl):1636 and 1278 cm^{-1};^{1}H-NMR($CDCl_3$):δ 4.13(m,1H) and 5.09 (m,1H);^{13}C-NMR($CDCl_3$):δ 23.0, 25.8, 26.3, 29.4, 36.9, and 84.9.

5a: bp 105-107 ℃ (7 mmHg);IR(NaCl):1106 cm^{-1};^{1}H-NMR($CDCl_3$):δ 3.37(s, 3H), 3.57-3.62(m,1H), 4.28-4.34(m,1H);^{13}C-NMR($CDCl_3$): δ 22.0, 26.7, 27.8, 29.1 36.5, 39.3, 57.1, and 89.1.

5b: bp 76-77 ℃ (1 mmHg);IR(NaCl):1108 cm^{-1};^{1}H-NMR($CDCl_3$):δ 3.46-3.52(m, 1H), 3.56-3.68(m,2H) and 4.28-4.33(m,1H);^{13}C-NMR($CDCl_3$):δ 15.6, 22.2, 26.7 27.8, 30.2, 36.6, 40.2, 64.9, and 87.4.

5c: bp 100-101 ℃ (7 mmHg);IR(NaCl):1106 cm^{-1};^{1}H-NMR($CDCl_3$):δ 0.95(t, 3H), 3.34-3.52(m,2H), 3.64-3.70(m,1H), and 4.30-4.36(m,1H);^{13}C-NMR($CDCl_3$): δ 10.8, 22.2, 23.3, 26.7, 27.8, 30.0, 36.6, 40.1, 71.3, and 87.5.

5d: bp 57-58 ℃ (1 mmHg);IR(NaCl):1124 cm^{-1};^{1}H-NMR($CDCl_3$):δ 1.17(dd,6H), 3.67-3.78(m,2H), and 4.26-4.34(m,1H);^{13}C-NMR($CDCl_3$):δ 22.3, 22.5, 23.1, 26.5, 27.9, 31.5, 36.6, 41.2, 70.6, and 84.9.

5f: bp 125-128 ℃ (13 mmHg);IR(NaCl):1636 and 1289 cm^{-1};^{1}H-NMR($CDCl_3$):δ 4.28-4.36(m,1H) and 5.31-5.40(m,1H);^{13}C-NMR($CDCl_3$): δ 22.0, 26.5, 27.5, 30.0, 30.1, 36.3, and 90.3.

6a: mp 97-99 ℃ ;IR(KBr):1084 cm^{-1};^{1}H-NMR($CDCl_3$): δ 3.30(s,3H), 3.71(m, W/2=8.6 Hz,1H) and 4.69(m,W/2=8.6 Hz,1H).

6b: mp 58-60 ℃ ;IR(KBr):1086 cm^{-1};^{1}H-NMR($CDCl_3$): δ 1.14(t,3H), 3.45(q, 2H), 3.80(m,W/2=8.6 Hz,1H), and 4.67(m,W/2=8.6 Hz,1H).

6c: mp 131-132 ℃ ;IR(KBr):1630 and 1288 cm^{-1};^{1}H-NMR($CDCl_3$):δ 4.65(m,W/2=8.6 Hz,1H) and 5.36(m,W/2=8.6 Hz,1H).

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