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A New Synthesis of Allyl Nitrates from Allylmetal (Group IVb) Compounds and Thallium (III) Nitrate

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A new general method for the synthesis of allyl nitrates is described. Allylmetal (group IVb) compounds, on treatment with thallium (III) nitrate in dioxane, gave the corresponding allyl nitrates in good yields.

Keywords——allyl nitrate; thallium (III) nitrate; allylsilane; allylgermane; allylstannane; umpolung

Allyl nitrates have been shown to be useful synthetic intermediates for organic synthesis.[1)] The nitrate group is smoothly replaced by a variety of nucleophiles,[2,3)] for instance, iodide, cyanide, thiocyanate, and alkoxide anions. The cleavage of the nitrogen–oxygen (attached to carbon) bond of allyl nitrates affords the corresponding allyl alcohols under reductive reaction conditions[3,4)] and unsaturated carbonyl compounds are provided by reaction with sterically hindered bases.[3)] Thermal allylic rearrangement of allyl nitrates was also observed.[3)]

Methods for the synthesis of this important class of compounds, however, have been little studied; the usual method involves the metathetical reaction of allyl halides with silver nitrate, mercurous and mercuric nitrates, or sodium nitrate.[2,4,5)] The direct esterification of allyl alcohols producing the corresponding nitrates[6)] is used only for simple compounds. Allylic oxidation of some olefins with thallium (III) nitrate (TTN) or ceric ammonium nitrate giving allyl nitrates has been reported.[3,7)]

In a series of studies on the reaction of organometal (group IVb) compounds, we have reported the allylation reactions of aromatic compounds,[8)] alcohols,[9,10)] carboxylic acids,[10)] and nitriles.[11)] In the reaction, allylmetal compounds A were converted into highly reactive allyl cationic species B, allylthallium (III) or allyliodine (III) compounds, *via* the reaction with thallium (III) trifluoroacetate, thallium (III) acetate, or iodosylbenzene activated with boron trifluoride etherate. We now wish to report a new general method for the synthesis of allyl nitrates by the reaction of allylmetal compounds A with TTN (Chart 1).

(2-Methyl-2-propenyl)trimethylsilane (**2a**) on treatment with TTN in pentane or hexane at room temperature afforded the corresponding allyl nitrate **2b** in 35—43% yield. The presence of the nitrate group was deduced from the characteristic absorption bands which appeared at 1635 and 1280 cm^{-1} in its infrared (IR) spectrum. The structure was determined by comparison with an authentic sample prepared according to the reported procedure.[2)] Much better yields of **2b** were obtained by using dipolar aprotic solvents such as dioxane or 1,2-dimethoxyethane (DME). The results are summarized in Table I. As can be seen in the table, a variety of allyltrimethylsilanes were smoothly converted into allyl nitrates by reaction with TTN in dioxane under nitrogen, and the products were usually isolated by preparative thin layer chromatography (TLC). Cyclohexene-3-nitrate (**7b**) was found to be unstable under

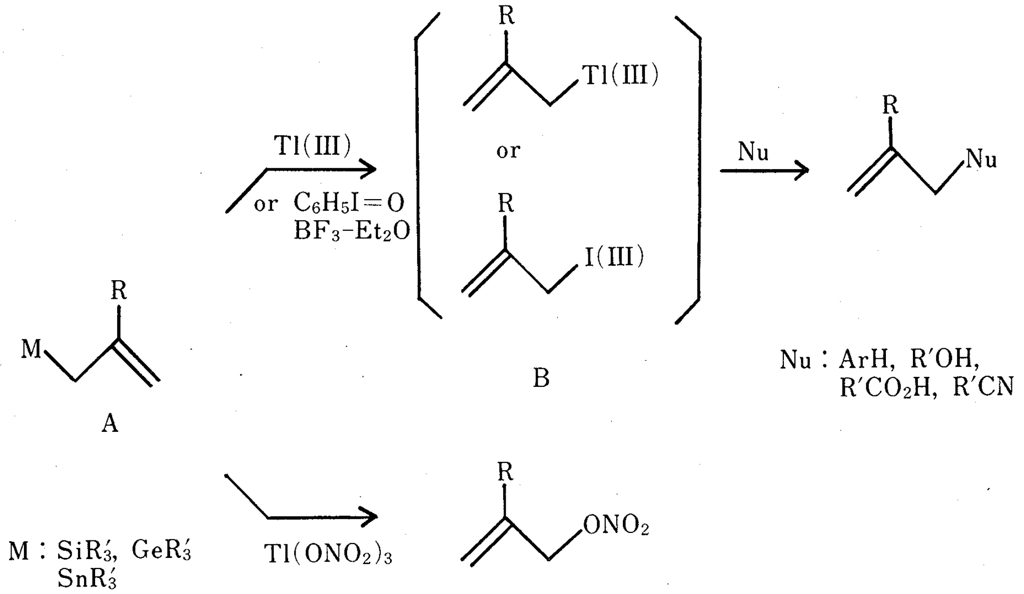
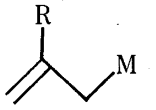
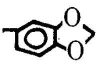


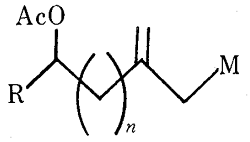
Chart 1

the conditions of chromatographic separation, and easy hydrolysis yielding 2-cyclohexene-1-ol was observed. The product obtained from the reaction of cinnamyltrimethylsilane (**8a**) with TTN was found to be a single nitrate **8b**; no regio- and stereoisomers were observed. The interesting dinitrate **9b** was obtained from 1,1-bis(trimethylsilylmethyl)ethylene **9a** in 85% yield (run 13).

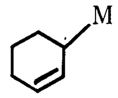


1a,b : R=H
2a,b : R=Me
3a,b : R=CH$_2$CH$_2$-

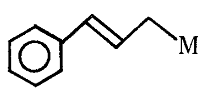




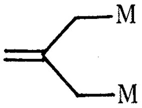
4a,b : n=1, R=H
5a,b : n=1, R=(CH$_2$)$_2$C$_6$H$_5$
6a,b : n=2, R=(CH$_2$)$_5$Me



7a,b



8a,b

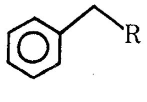


9a,b

a : M=SiMe$_3$
b : M=ONO$_2$

Allyltrimethylgermane (**10**) and allyltributylstannane (**11**), like allyltrimethylsilane (**1a**), were shown to be useful compounds for the synthesis of allyl nitrate **1b** (runs 14—15). Benzyltrimethylsilane (**12**) did not react with TTN at room temperature, but on heating at 90 °C gave benzyl nitrate (**14**) in 72% yield. Reaction of benzyltributylstannane (**13**) proceeded at room temperature and gave a good yield of nitrate **14**.

10 : R=GeMe$_3$
11 : R=SnBu$_3$



12 : R=SiMe$_3$
13 : R=SnBu$_3$
14 : R=ONO$_2$

TABLE I. Synthesis of Allyl Nitrate Esters

Run	Allylmetal compound	Solvent	Reaction conditions	Product	Yield[a] (%)
1	**1a**	Dioxane	RT (15 min)	**1b**	(81)
2	**2a**	Pentane	RT (30 min)	**2b**	(35)
3	**2a**	Hexane	RT (30 min)	**2b**	(43)
4	**2a**	DME	RT (10 min)	**2b**	(92)
5	**2a**	Dioxane	RT (10 min)	**2b**	71 (100)
6	**3a**	DME	0 °C (10 min)	**3b**	58
7	**4a**	Dioxane	RT (10 min)	**4b**	85
8	**5a**	Dioxane	RT (15 min)	**5b**	79
9	**6a**	Hexane	0 °C (30 min) then RT (30 min)	**6b**	52
10	**6a**	Dioxane	RT (15 min)	**6b**	75
11	**7a**	Dioxane	RT (10 min)	**7b**	(91)
12	**8a**	Dioxane	RT (20 min)	**8b**	74[b] (75)[c]
13	**9a**	Dioxane	RT (15 min)	**9b**	85
14	**10**	Dioxane	RT (10 min)	**1b**	(64)
15	**11**	Dioxane	RT (10 min)	**1b**	(71)

a) Isolated yield (GLC yield).
b) The product was contaminated with a small amount of impurity.
c) NMR yield.
RT; room temperature.

Thus we developed a new general method for the synthesis of allyl nitrates.

Experimental

IR spectra were recorded with a JASCO IR-A-1 spectrophotometer. Nuclear magnetic resonance (NMR) spectra were obtained with a JEOL JNM-FX 100 or Hitachi R 40 spectrometer. Chemical shifts are reported relative to internal tetramethylsilane. Mass spectra (MS) were determined on a Hitachi RMU-7L spectrometer. Analytical gas-liquid chromatography (GLC) was performed on a Shimadzu GC-4CM gas chromatograph with 20% Silicone GE SE-30 or 20% Polyethylene glycol 20M on Chromosorb W. Preparative thin layer chromatography (TLC) was carried out on precoated plates of silica gel (Merck, Silica gel F-254).

Materials——Allyltrimethylsilane (**1a**) is commercially available (Shin-Etsu Silicon Chem.). Allylmetal compounds **2a**, **4a**, **7a**, **8a**, **9a**, **10**, and **11** were prepared by the methods described previously.[8b,12)] Synthesis of allylsilanes **3a**, **5a**, and **6a** will be reported in detail elsewhere. Benzylmetal compounds **12** and **13** were prepared by the reaction of benzylmagnesium bromide with trimethylchlorosilane and tributyltin chloride, respectively. Thallium (III) nitrate was used in the form of the trihydrate.

General Procedure for Synthesis of Allyl Nitrates——A solution of allylmetal compound (1 mmol) in dioxane (*ca.* 5 ml) was added dropwise to a stirred suspension of thallium (III) nitrate (1—1.2 mmol) in dioxane (*ca.* 10 ml) under nitrogen. The reaction is slightly exothermic. The mixture was stirred under the conditions described in Table I. The reaction mixture was poured into water and extracted with pentane. The extract was washed with water several times and with brine. After being dried, the pure products were isolated by distillation or preparative TLC. The yields are given in Table I. After the addition of appropriate internal standards, the yields were determined by analytical GLC or from the NMR spectrum in some experiments.

2-Propenyl Nitrate (1b)[2)]——IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1635, 1280, 850. NMR ($CDCl_3$) δ: 4.91 (2H, d, $J=6$ Hz), 5.3—5.6 (2H, m), 5.7—6.2 (1H, m).

2-Methyl-2-propenyl Nitrate (2b)[13)]——bp 78—82 °C (200 Torr): IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1635, 1375, 1280, 1165, 975. NMR ($CDCl_3$) δ: 1.82 (3H, br s), 4.84 (2H, s), 5.09 (2H, br s).

2-[2-(3,4-Methylenedioxyphenethyl)]-2-propenyl Nitrate (3b)——IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1630, 1505, 1490, 1435, 1270, 1240, 1040, 850. MS *m/e*: 251 (M^+), 189, 147, 135 (base peak), 79, 77. High resolution MS: Found 251.0792. Calcd for $C_{12}H_{13}NO_5$ (M^+) 251.0792. NMR ($CDCl_3$) δ: 2.2—2.5 (2H, m), 2.5—2.9 (2H, m), 4.84 (2H, s), 5.08, 5.17 (each 1H, s), 5.90 (2H, s), 6.5—6.8 (3H, m).

2-(2-Acetoxyethyl)-2-propenyl Nitrate (4b)——IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1740, 1635, 1365, 1275, 1035, 970, 915. MS *m/e*: 190, 189 (M^+), 143, 129, 127, 113, 85, 84, 83. High resolution MS: Found 189.0623. Calcd for $C_7H_{11}NO_5$ (M^+) 189.0635. NMR ($CDCl_3$) δ: 2.03 (3H, s), 2.44 (2H, t, $J=6.5$ Hz), 4.20 (2H, t, $J=6.5$ Hz), 4.90 (2H, s), 5.16, 5.25 (each

1H, s).

2-(2-Acetoxy-4-phenylbutyl)-2-propenyl Nitrate (5b)——IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1740, 1640, 1375, 1280, 1020. MS *m/e*: 294, 293 (M$^+$), 233, 187, 169, 143, 129, 117, 91 (base peak), 83. High resolution MS: Found 293.1225. Calcd for $C_{15}H_{19}NO_5$ (M$^+$) 293.1261. NMR (CDCl$_3$) δ: 1.7—2.1 (2H, m), 2.00 (3H, s), 2.37 (2H, d, $J=6$ Hz), 2.5—2.8 (2H, m), 4.88 (2H, s), 5.06 (1H), 5.12, 5.22 (each 1H, s), 7.0—7.4 (5H, m).

2-(2-Acetoxynonyl)-2-propenyl Nitrate (6b)——IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1735, 1640, 1450, 1375, 1280, 850. MS *m/e*: 288, 241, 227, 181, 163, 151, 137, 121, 111, 109, 107, 97, 96. High resolution MS: Found 241.1836. Calcd for $C_{14}H_{25}O_3$ [(M$-$NO$_2$)$^+$] 241.1803. NMR (CDCl$_3$) δ: 0.8—1.0 (3H), 2.0—2.3 (2H, m), 2.04 (3H, s), 4.75—5.05 (1H, m), 4.88 (2H, s), 5.10, 5.18 (each 1H, s).

2-Cyclohexenyl Nitrate (7b)[7b]——IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1620, 1275, 1000, 860. NMR (CDCl$_3$) δ: 1.5—2.3 (6H, m), 5.3—5.55 (1H, m), 5.77 (1H, ddt, $J=10.5$, 3.5, 2 Hz), 6.15 (1H, dt, $J=10.5$, 3.5 Hz).

3-Phenyl-2-propenyl Nitrate (8b)[5a]——IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1645, 1280. NMR (CDCl$_3$) δ: 5.06 (2H, d, $J=7$ Hz), 6.22 (1H, dt, $J=16$, 7 Hz), 6.79 (1H, d, $J=16$ Hz), 7.2—7.5 (5H, m).

2-Hydroxymethyl-2-propen-1-ol Dinitrate (9b)——IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1650, 1285, 840. MS *m/e*: 116, 85, 76, 69, 56. High resolution MS: Found 116.0340. Calcd for $C_4H_6NO_3$ [(M$-$NO$_3$)$^+$] 116.0346. NMR (CDCl$_3$) δ: 4.98 (4H, s), 5.60 (2H, s).

Reaction of Benzyltrimethylsilane (12) with TTN——A solution of benzyltrimethylsilane (**12**) (99 mg, 0.6 mmol) in dioxane (2 ml) was added to a suspension of TTN (400 mg, 0.9 mmol) in dioxane (6 ml), and the mixture was heated at 90 °C for 2 h under nitrogen. After the addition of water, the mixture was extracted with pentane. The extract was washed with water and brine, and dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure to give an oil, which was purified by preparative TLC [hexane–ethyl acetate (10 : 1)] to give benzyl nitrate **14**[14] (66 mg, 72%). IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1630, 1500, 1455, 1275, 970, 905. MS *m/e*: 153 (M$^+$), 107, 105, 91, 79, 77 (base peak). NMR (CDCl$_3$) δ: 5.40 (2H, s), 7.37 (5H, s).

Reaction of Benzyltributylstannane (13) with TTN——Benzyltributylstannane (**13**) (130 mg, 0.34 mmol), on treatment with TTN (182 mg, 0.41 mmol) in dioxane (5 ml) at room temperature for 30 min, afforded benzyl nitrate (**14**) (39.5 mg, 76%).

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