Table I. Reaction of Dibenzoyldiimide with Alkoxides

entry	OR^-/solvent	products (mmol/mmol of dibenzoyldiimide) PhCONHNHCOPh	PhCHO	PhCOOH	$PhCOOCH_3$	other	reaction time
1	OMe^-/MeOH	0.408	0.036	0.251[d]	0.571		immediate
2	OMe^-/MeOH[a]	0.356	0.024	0.061[d]	0.851	0.138 cyclohexane	immediate
3	OMe^-/THF	0	0.137	0.219[d]	0.124	see text	4–7 days
4	OMe^-/THF[b]	0	0.131	0.315[d]	0.077	see text	6–10 days
5	OMe^-/THF[c]	0	0.043	0.253[d]	0.163	c	
6	O-*t*-Bu^-/*t*-BuOH	0.134	0.320	1.13	0	e	immediate
7	O-*t*-Bu^-/THF	0.038	0.152	1.09	0	e	immediate

[a] Cyclohexene added. [b] 0.5 equiv of OMe^-. [c] Three equivalents of *tert*-butyl benzoate included; 98% recovered. [d] Benzoic acid is formed from methyl benzoate and methoxide: Bunnett, J. F.; Robison, M. M.; Pennington, F. C. *J. Am. Chem. Soc.* **1950**, *72*, 2378. [e] Trace *tert*-butyl benzoate observed; isobutene also formed.

remaining benzoic acid, methyl benzoate, benzaldehyde, and other minor products were determined by NMR and GC analysis (see Table I).

Reaction of Dibenzoyldiimide with Sodium Methoxide in the Presence of Cyclohexene. To 2.38 g (10.0 mmol) of dibenzoyldiimide and 8.0 g (97.6 mmol) of cyclohexene in 50 mL of dried methanol under N_2 was added 0.54 g (10.0 mmol) of sodium methoxide. The color immediately changed to light yellow as heat and gas were evolved. After 2 h, hexane was used to precipitate dibenzoylhydrazine (0.86 g, 3.56 mmol). The solution was analyzed by GC (see Table I).

Reaction of Dibenzoyldiimide with Sodium Methoxide in THF. To 2.20 g (9.24 mmol) of dibenzoyldiimide in 50 mL of THF, was added 0.50 g (9.26 mmol) of sodium methoxide under N_2. The reaction mixture was allowed to stir 4–7 days until the red color disappeared. The mixture was filtered and the solid washed with hexane and with dilute acid, resulting in isolation of 0.07 g of benzoic acid. On cooling of the hexane filtrate, 1.36 g of solid settled from the solution. Recrystallization and TLC were used to separate tribenzoylhydrazine (1.58 mmol) and compound III (2.63 mmol); the amount of each was determined by NMR. The isolated tribenzoylhydrazine had mp 200–203 °C (lit.[12] mg 206 °C). Compound III: ^1H NMR ($CDCl_3$) δ 1.94 (m, 2 H), 2.18 (m, 2 H), 3.76 (m, 1 H), 4.04 (m, 1 H), 6.00 (t, 1 H), 7.38 (m, 6 H), 7.66 (m, 4 H), 8.50 (s, 1 H); IR (nujol) 3277, 1695, 1680 cm^{-1}; $^{13}C(CDCl_3)$ 171.98, 167.37, 134.428, 132.219, 130.660, 128.648, 128.190 127.671, 127.281, 89.001, 69.001, 28.783, 25.404; mass spectrum $(m/e)^+$ 310, 251, 240, 188, 147, 121; mp 185–187 °C. Anal. Calcd for $C_{18}H_{18}N_2O_3$; C, 69.66; H, 5.84; N, 9.03. Found: C 69.65; H, 5.85; N, 9.00. The solvent volume was reduced, and the remaining residue was analyzed by GC. Benzoic acid, benzaldehyde, methyl benzoate, and benzil (0.17 mmol) were detected (see Table I).

In a separate experiment, 2.20 g (9.24 mmol) of dibenzoyldiimide and 0.25 g (4.63 mmol) of sodium methoxide in 50 mL of THF required 6–10 days for the color to dissipate. The rate of the decomposition also appears to be dependent on stirring. From the reaction mixture tribenzoylhydrazine (0.334 mmol), compound III (4.435 mmol), and benzil (0.157 mmol) were obtained in addition to the compounds listed in Table I. Dibenzoyldiimide (0.9 g) in THF (30 mL) in the absence of base decomposes after 13 days, as noted by the disappearance of red color.

Reaction of Dibenzoyldiimide with Sodium Methoxide in THF with Added *tert*-Butyl Benzoate. To 2.30 g (9.66 mmol) of dibenzoyldiimide in 50 mL of THF under N_2 were added 0.52 g (9.63 mmol) of sodium methoxide and 5.30 g (29.8 mmol) of *tert*-butyl benzoate. After 6 days the solution was decolorized and the hydrazines were precipitated by addition of hexane, giving tribenzoylhydrazine (0.94 mmol) and compound III (2.93 mmol). GC analysis revealed the presence of benzil, methyl benzoate, benzoic acid, benzaldehyde, and recovered *tert*-butyl benzoate as recorded in Table I.

Reaction of Dibenzoyldiimide with Potassium *tert*-Butoxide in THF. To 2.38 g (10.0 mmol) of dibenzoyldiimide in 50 mL THF under N_2 was added 1.12 g (10.0 mmol) of potassium *tert*-butoxide. The solution turned light yellow as heat and gas were evolved. After 1.5 h the light yellow salt was removed by filtration, washed with hexane, and treated with dilute acid. Ether was used to separate the dibenzoylhydrazine, 0.09 g (0.37 mmol), and benzoic acid, 0.31 g.

GC analysis of the remaining solution indicated the presence of benzaldehyde, more benzoic acid, some unidentified compounds, and a trace amount of *tert*-butyl benzoate as shown in Table I.

During the reaction the gases produced were bubbled through a 5% Br_2 in CCl_4 solution which was decolorized.

Reaction of Dibenzoyldiimide with Potassium *tert*-Butoxide in *tert*-Butyl Alcohol. To 1.19 g (5.00 mmol) of dibenzoyldiimide in 50 mL of dried *tert*-butyl alcohol was added 0.56 g (5.00 mmol) of potassium *tert*-butoxide. The solution became light yellow as heat evolved and gas formed. After 2 h, the salt was separated, dried, and treated with dilute acid. Ether was used to separate dibenzoylhydrazine (0.67 mmol) and benzoic acid (0.67 g). The solution volume was decreased before GC analysis, which indicated the presence of benzaldehyde, benzoic acid, and only a trace of *tert*-butyl benzoate, as shown in Table I.

Registry No. III, 85849-97-4; THF, 109-99-9; dibenzoyldiimide, 959-31-9; dibenzoylhydrazine, 787-84-8; sodium methoxide, 124-41-4; potassium *tert*-butoxide, 865-47-7; benzoyl anion, 78944-74-8.

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Unusual Consecutive Rearrangements in the Demjanow Ring-Expansion Reaction of 2-(Aminomethyl)-D_{2d}-dinoradamantane and 9-(Aminomethyl)noradamantane

Masao Nakazaki,* Koichiro Naemura, and Masaki Hashimoto

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan

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Introduction of carbonyl group into D_{2d}-dinoradamantane (1) degenerates its D_{2d} symmetry to give rise to D_{2d}-dinoradamantan-2-one (2) ($C_8H_{10}O$) of chiral C_2 symmetry, which is conspicuous in having four asymmetric carbon atoms interwoven in the molecular framework of eight carbon atoms (Scheme I).

Our continuing interests in high-symmetry chiral cage-shaped molecules prompted us to prepare the (−) enantiomer (2)[1] of this interesting compound, and we have suggested the 1*R*, 3*R*, 5*R*, 7*R* configuration to it by comparing its (−)-Cotton effect around 290 nm with that of (+)-4-isopropyltricyclo[3.3.0.$0^{3,7}$]octan-2-one (3) prepared from (−)-*endo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid of known absolute configuration.[2]

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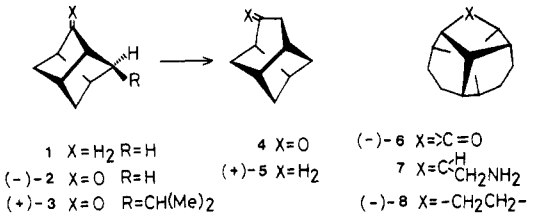
0022-3263/83/1948-2289$01.50/0

Scheme I

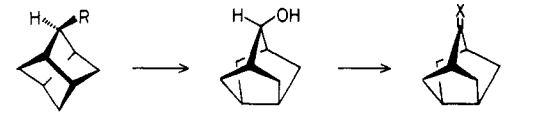


1 X=H$_2$ R=H
(-)-2 X=O R=H
(+)-3 X=O R=CH(Me)$_2$

4 X=O
(+)-5 X=H$_2$

(-)-6 X=>C=O
7 X=C<H/CH$_2$NH$_2$
(-)-8 X=-CH$_2$CH$_2$-

Scheme II

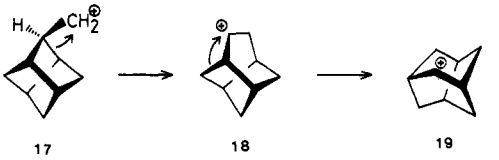


(+)-9 R=CO$_2$H
(+)-10 R=CONH$_2$
11 R=CH$_2$NH$_2$

12

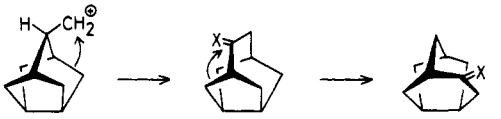
13 X=O
14 X=H$_2$
15 X=<H/CN
16 X=<H/CH$_2$NH$_2$

Scheme III



17 18 19

Scheme IV



20

21 X=H,⊕
22 X=H$_2$

23 X=H,⊕
24 X=<H/OH
25 X=O
26 X=H$_2$

In an effort to secure another direct stereochemical correlation, diazomethane ring expansion of (-)-**2** under various conditions was carried out with the intention of converting (-)-**2** to optically active 4-twist-brendanone (**4**), which could be transformed into (+)-twist-brendane (**5**)[3] of established configuration. However, our observation of a peculiar reluctance of (-)-**2** toward this diazomethane ring-expansion reaction diverted our attention from this approach to the Demjanow ring-expansion reaction, which had been proved successful in the conversion of (-)-4-C_2-methanoditwistanone (**6**) into (-)-D_3-tritwistane (**8**)[4] via the aminomethyl derivative **7**.

Although the Demjanow reaction of 2-(aminomethyl)-D_{2d}-dinoradamantane (**11**) proceeded smoothly (Scheme II), the isolated product was found to possess the noradamantane structure instead of the expected twist-brendane molecular framework.

In this paper, we report this unusual Demjanow rearrangement of **11**, together with the related rearrangement of 9-(aminomethyl)noradamantane (**16**).

Results and Discussion

$LiAlH_4$ reduction of the (+) amide **10** prepared from (+)-2-D_{2d}-dinoradamantanecarboxylic acid (**9**), $[\alpha]_D$ +10.8° (34% optical purity),[1] afforded the required 2-aminomethyl derivative **11** as an oil that was dissolved in 5% acetic acid and refluxed with sodium nitrite. The routine workup of the reaction mixture provided an alcohol (61% yield from **10**) whose identity with 9-noradamantanol (**12**)[5] was indicated by its melting point (243–245 °C) and its optical inactivity.

Although a confirmation of this structure assignment was provided by its Jones oxidation to 9-noradamantanone (**13**)[5] whose ^{13}C NMR spectrum exhibited four signals supporting the C_{2v} symmetry, a more conclusive evidence for its identity was secured from its Wolff–Kishner reduction to give noradamantane (**14**), mp 198–199 °C, whose spectral data were found indistinguishable from those of an authentic specimen.

This unexpected Demjanow rearrangement of **11** can be explained by assuming a reaction pathway (Scheme III) that involves the consecutive skeletal rearrangement of the original cation **17** to twist-brendanyl cation **18** and its further transformation to the noradamantanyl cation **19**.

Our assumption that this migration aptitude of **18** toward **19** should reflect the relative stability[6] between their parent molecules, twist-brendane (**5**) and noradamantane (**14**), led us to examine the related Demjanow ring-expansion reaction of 9-(aminomethyl)noradamantane (**16**) to see if the similar type of consecutive rearrangement can be observed also in this case. Reaction of 9-noradamantanone (**13**) with tosylmethyl isocyanide and potassium *tert*-butoxide gave the nitrile **15**, whose $LiAlH_4$ reduction provided the requisite aminomethyl derivative **16**, as an oil. The Demjanow ring expansion of **16** was carried out by the method similar to that described for **11**, and examination of the reaction product by means of GLC revealed that 5-protoadamantanol (**24**) of unknown configuration at the hydroxyl site was the sole product. Jones oxidation of **24** gave 5-protoadamantanone (**25**), mp 218–220 °C, whose Wolff–Kishner reduction furnished protoadamantane (**26**),[7] mp 214–215 °C, exhibiting IR and NMR spectra identical with an authentic specimen.

Scheme IV illustrates a possible pathway of this ring-expansion reaction involving the intermediate cation **21**, which should rearrange further to protoadamantyl cation **23**. In this case, again, relative stability[6] of the parent hydrocarbon, 9-homonoradamantane (**22**), and protoadamantane (**26**) seems to govern the reaction pathway.

Experimental Section

Melting points are uncorrected. Infrared spectral data were obtained from a Hitachi Model 260-10 spectrophotometer. ^1H NMR and ^{13}C NMR spectra were obtained on JNM-C-60 and JNM-FX-100 spectrometers. Chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane. GLC analyses were performed on a JGC-20K chromatograph equipped with a FID and using a 2 m × 3 mm i.d. column of 10% PEG 20M on UniportHP. Elemental analyses were performed on a Yanagimoto CHN-Corder type II.

(+)-2-D_{2d}-Dinoradamantanecarboxamide (10). To a solution of (+)-D_{2d}-dinoradamantane-2-carboxylic acid (**9**),[1] $[\alpha]_D$ +10.8° (2.00 g, 13.2 mmol), in dry benzene (20 mL) was added thionyl chloride (2.6 g, 21.8 mmol), and the mixture was stirred for 60 h at room temperature. After removal of the excess thionyl chloride in vacuo, the residue was added dropwise to 25% aqueous

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ammonia with ice-cooling, and the mixture was stirred for 1 h at this temperature. A deposited solid was collected and washed with water. Sublimation of the solid at 120–130 °C (5 mm) furnished 1.41 g of the (+)-amide **10** (71% yield): mp 237–239 °C; $[\alpha]^{27}_D$ +15.6° (*c* 0.205, acetone); IR (KBr) 1660, 1620, 1420 cm^{-1}.

Anal. Calcd for $C_9H_{13}ON$: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.35; H, 8.60; N, 9.22.

Formation of 9-Noradamantanol (12) on the Demjanow Rearrangement of 2-(Aminomethyl)-D_{2d}-dinoradamantane (11). A solution of the (+)-amide **10** (1.20 g, 7.95 mmol) in dry THF (60 mL) was added to a stirred suspension of $LiAlH_4$ (500 mg, 13.2 mmol) in dry THF (20 mL), and the mixture was gently refluxed for 4 h. After cooling, saturated aqueous NH_4Cl (5 mL) was added to the mixture, and deposited solid was removed by filtration. Removal of the solvent gave crude 2-(aminomethyl)-D_{2d}-dinoradamantane (**11**) as an oil (1.08 g), which was dissolved in 5% aqueous acetic acid (18 mL). After addition of a solution of sodium nitrite (0.95 g) in water (7.5 mL), the mixture was heated at 100–110 °C for 2 h. Dilution with water was followed by extraction with ether, and the extract was washed with aqueous $NaHCO_3$ and water and dried ($MgSO_4$). The solvent was removed to afford a solid that was chromatographed over alumina. Elution with pentane–ether (1:1, v/v) gave 670 mg of 9-noradamantanol (**12**) (61% overall yield from **10**). An analytical sample was further purified by sublimation at 90 °C (20 mm): mp 243–245 °C (in a sealed tube) (lit.[5a] mp 244–247 °C); $[\alpha]^{27}_D$ 0° (*c* 0.458, EtOH); IR (KBr) 3320, 1015 cm^{-1}.

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.96; H, 10.18.

9-Noradamantanone (13). An excess of Jones reagent (2 mL)[8] was added dropwise to a stirred and chilled (0 °C) solution of 9-noradamantanol (**12**) (340 mg, 2.46 mmol) in acetone (6 mL). After stirring for 2 h with ice cooling, sodium bisulfite was added until the brown color was gone. The mixture was diluted with water and extracted with ether. The extract was washed with aqueous $NaHCO_3$ and water and dried ($MgSO_4$). Concentration left a semisolid (270 mg) that was chromatographed over alumina, and elution with pentane provided 9-noradamantanone (**13**) (225 mg, 67% yield). An analytical sample was prepared by sublimation at 80 °C (20 mm): mp 191–192 °C (in a sealed tube) (lit.[5a] mp 193–195 °C); IR (KBr) 1720, 1460, 1220, 1045, 970 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 36.3, 44.1, 52.0, 213.7.

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.31; H, 8.87.

Noradamantane (14). 9-Noradamantanone (**13**) (120 mg, 0.882 mmol) was mixed with 100% hydrazine hydrate (0.1 mL), KOH (52 mg), and triethylene glycol (1.5 mL). The mixture was heated for 1 h at 110–120 °C and for an additional 4 h at 190–200 °C. During this period, a white solid was observed to condense on the inner wall of the condenser. After cooling, the solid was dissolved in ether and the reaction mixture was diluted with water and extracted with ether. The ether extracts were combined, washed with water, dried ($MgSO_4$), and concentrated to give a solid that was sublimed at 80 °C (20 mm) to provide noradamantane (**14**) (65 mg, 60% yield): mp 198–199 °C (in a sealed tube) (lit.[5a] mp 203 °C). Spectral comparison with an authentic specimen confirmed its identity.

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.35; H, 11.52.

9-Noradamantanecarbonitrile (15). 9-Noradamantanone (**13**) (455 mg, 3.34 mmol) and TosMIC[9] (850 mg, 4.36 mmol) were dissolved in a mixture of absolute ethanol (0.33 mL) and dimethoxyethane (11.7 mL), and the mixture was cooled in an ice bath. After potassium *tert*-butoxide (938 mg, 8.36 mmol) was added to the stirred mixture at such a rate to keep the reaction temperature below 5 °C, the mixture was stirred at room temperature for 1 h and then at 35–40 °C for an additional 1 h. A deposited solid was collected by filtration and washed with ether. The washings were combined with the filtrate, and removal of the solvent left a residue that was chromatographed over alumina. Elution with pentane afforded 9-noradamantanecarbonitrile (**15**) (332 mg, 68% yield), which was further purified by sublimation in vacuo (80 °C (20 mm)): mp 110–113 °C; IR (KBr) 2230, 1460, 1320, 1100 cm^{-1}.

Anal. Calcd for $C_{10}H_{13}N$: C, 81.85; H, 8.90; N, 9.52. Found: C, 81.39; H, 8.88; N, 9.49.

Formation of 5-Protoadamantanol (24) on the Demjanow Rearrangement of 9-(Aminomethyl)noradamantane (16). A solution of the nitrile (**15**) (325 mg, 2.21 mmol) in dry ether (10 mL) was added to a chilled (0 °C) and stirred suspension of $LiAlH_4$ (127 mg, 3.36 mmol) in dry ether (20 mL), and the stirring at this temperature was continued for an additional 1 h. After 20% aqueous NaOH (0.2 mL) and water (0.5 mL) were successively added to the chilled mixture, a deposited solid was collected by filtration and washed with ether. The washings were combined with the filtrate, washed with water, and dried (Na_2SO_4). Removal of the solvent gave crude 9-(aminomethyl)noradamantane (**16**) as an oil, which was dissolved in 5% aqueous acetic acid (4.5 mL). After a solution of sodium nitrite (0.3 g) in water (2.5 mL) was added, the mixture was heated at 100–110 °C for 1 h. The procedure described for the preparation of 9-noradamantanol (**12**) furnished 5-protoadamantanol (**24**) as a semisolid (275 mg), which was oxidized with excess Jones reagent. The routine workup followed by alumina chromatography (pentane elution) and sublimation in vacuo (60 °C (5 mm)) gave 5-protoadamantanone (**25**) (175 mg, 53% overall yield from **15**): mp 218–220 °C (in a sealed tube) (lit.[10] mp 222–225 °C); IR (KBr) 1720, 1450 cm^{-1}.

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.96; H, 9.37.

Protoadamantane (26). The Wolff–Kishner reduction of 5-protoadamantanone (**25**) (125 mg, 0.833 mmol) with 100% hydrazine hydrate (0.11 mL), KOH (60 mg), and triethylene glycol (1.5 mL) was carried out as described for the preparation of noradamantane (**14**). Sublimation (50 °C (20 mm)) of the product furnished protoadamantane (**26**) (70 mg, 62% yield): mp 214–215 °C (in a sealed tube) (lit.[7] mp 215–216 °C). Spectral comparison with an authentic specimen confirmed its identity.

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.10; H, 11.89.

Registry No. (+)-**9**, 64753-43-1; (+)-**9** acid chloride, 85798-29-4; (+)-**10**, 85736-27-2; **11**, 85736-28-3; **12**, 23691-64-7; **13**, 23691-62-5; **14**, 7075-86-7; **15**, 85736-29-4; **16**, 28224-46-6; **17**, 85736-30-7; **18**, 85736-31-8; **19**, 85736-32-9; **20**, 85736-33-0; **21**, 85736-34-1; **23**, 85736-35-2; **24**, 85798-30-7; **25**, 31517-40-5; **26**, 19026-94-9; TosMIC, 36635-61-7.

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Absolute Configuration of Vitamin K Epoxide[1]

Peter C. Preusch and John W. Suttie*

Department of Biochemistry, College of Agricultural and Life Sciences, University of Wisconsin—Madison, Madison, Wisconsin 53706

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A hepatic microsomal enzyme forms vitamin K 2,3-epoxide from reduced vitamin K and molecular oxygen[2-4] in a reaction that appears to be coupled to a vitamin K de-

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