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PROPELLANES—LXXIV

BIS-ALKYLATION AT NITROGEN OF A [4.3.3] PROPELLENE-*BIS*-IMIDE*

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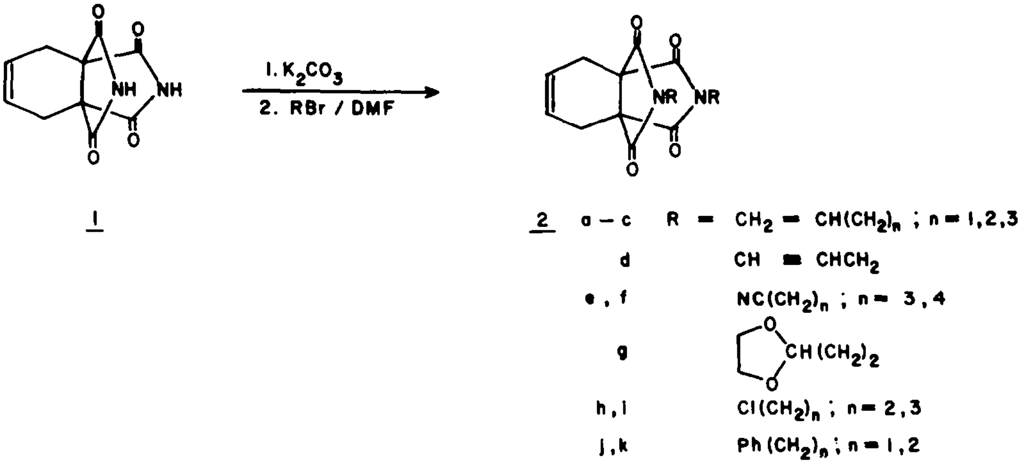
Abstract—Various halides were used to alkylate at both nitrogen atoms of [4.3.3] propell-3-ene-*bis*-imide.

We have studied conditions for alkylating the imide N atoms of the *bis*-imide **1**, in order to obtain intermediates for further synthetic elaboration.



1

2 a – c R = $CH_2=CH(CH_2)_n$; n = 1,2,3
d $CH\equiv CCH_2$
e , f $NC(CH_2)_n$; n = 3 , 4
g
h , i $Cl(CH_2)_n$; n = 2 , 3
j , k $Ph(CH_2)_n$; n = 1 , 2

The imide nitrogens are sufficiently acidic to afford a dipotassium salt when treated with potassium carbonate.[1] Treatment of the latter with the bromides shown above causes *bis*-alkylation in the yields recorded in the experimental section. Compound **2h** was accompanied by the corresponding dibromide and bromide–chloride.

EXPERIMENTAL

IR spectra were measured on a Perkin-Elmer model 257 grating spectrophotometer. NMR spectra were measured on a Varian T-60 spectrometer. Mass spectra were measured on a Varian 711 spectrometer using the heated inlet system at 200°. The electron energy was maintained at 100 eV. Only the major fragments are listed. All m.ps are uncorrected.

General procedure for alkylation

The *bis*-imide **1** (440 mg) and a soln of K_2CO_3 (550 mg) in a minimal volume of water were mixed. The water was removed in a vacuum and replaced by dimethylformamide (20 ml) and the organic bromide added (wt given below). The whole was stirred magnetically at room temp for 5 days. The solvent was removed and the residue was extracted with EtOAc, followed by crystallization of the product.

Compound **2a**. 2.03 g allyl bromide (53% yield); m.p. 118–119° ($CHCl_3$–hexane). (Found: N, 9.12; M.W. 300.1142. $C_{16}H_{16}N_2O_4$ Requires: N, 9.33%; M.W. 300.1110). IR($CHCl_3$): 1770, 1730, 1380, 1340 cm^{-1}. NMR($CDCl_3$): δ 5.95 (t, 2H, ring C–C$\underline{H}$=); 5.95–5.50 (m, 2H, =C$\underline{H}$); 5.20–5.00 (m, C$\underline{H}_2$=C); 4.10 (d, 4H, =CHC$\underline{H}_2$CN); 2.75 (d, 4H, ring C$\underline{H}_2$CH=). MS(*m/e*): 300(100); 285(4); 217(11); 188(77); 162(15).

Compound **2b**. 1.795 g 4-bromo-but-1-ene (43%), m.p. 97–98° (hexane). (Found: N, 8.65; M.W. 328.1433. $C_{18}H_{20}N_2O_4$ Requires: N, 8.58%; M.W. 328.1423). IR($CHCl_3$): 1770, 1730, 1380, 1350, 1100 cm^{-1}. NMR($CDCl_3$): 5.90 (m, 2H, ring, C$\underline{H}$=CH); 5.90–5.30 (m, 2H, C$\underline{H}$=CH$_2$); 5.20–4.70 (m, CH=C$\underline{H}_2$); 3.60 (t, 4H, C$\underline{H}_2$N); 2.70 (d, 4H, ring CH=CHC$\underline{H}_2$); 2.55–2.10 (m, 4H, C$\underline{H}_2$–CH=). MS(*m/e*): 328(100); 287(21); 274(13); 232(5); 216(16); 162(55).

Compound **2c**. 1.82 g 5-bromo-pent-1-ene (34%), oil. (Found: N, 8.05; M.W. 356.1712. $C_{20}H_{24}N_2O_4$ Requires: N, 7.86%; M.W. 356.1735). IR($CHCl_3$): 1770, 1730, 1340 cm^{-1} NMR($CDCl_3$): 5.95 (t, 2H, ring C$\underline{H}$=CH): 5.85–5.35 (m, 2H, 2C$\underline{H}$–CH$_2$); 5.20–4.75 (m, 4H, CH=C$\underline{H}_2$); 3.50 (t, 4H, C$\underline{H}_2$N); 2.70 (d, 4H, ring C$\underline{H}_2$–CH=); 2.20–1.50 (m, 8H, C$\underline{H}_2$). MS(*m/e*): 356(43); 289(100); 247(8); 218(50); 162(97).

Compound **2d**. 1.905 g propargyl bromide (67%), m.p. 177–178° (CH_2Cl_2–hexane). (Found: N, 9.54; M.W. 296.0781. $C_{16}H_{12}N_2O_4$ Requires: N, 9.46%; M.W. 296.0797). IR($CHCl_3$): 1780, 1750, 1370, 1330, 1120, 970 cm^{-1}. NMR($CDCl_3$): 5.90 (m, 2H, ring C$\underline{H}$=), 4.20 (d, 4H, C$\underline{H}_2$N); 2.75 (d, 4H, CH=CH–C$\underline{H}_2$); 2.20 (m, 2H, C≡C$\underline{H}$). MS(*m/e*): 296(100), 257(3); 186(68).

Compound **2e**. 2.38 g γ-bromobutyronitrile (73%), m.p. 125–126° ($CHCl_3$–hexane). (Found: N, 15.45; M.W.

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*Part LXXIII, Previous paper in this issue.

354.1322. $C_{18}H_{18}N_4O_4$ Requires: N, 15.81%; M.W. 354.1327). IR($CHCl_3$): 2240, 1770, 1730, 1340 cm^{-1}. NMR($CDCl_3$): 6.00 (m, 2H, $C\underline{H}$=); 3.70 (t, 4H, $C\underline{H}_2N$); 2.85 (d, 4H, $C\underline{H}_2$–CH=); 2.60–2.30 (m, 4H, $C\underline{H}_2CN$); 2.30–1.80 (m, 4H, $C\underline{H}_2$). MS(m/e): 354(100); 314(8); 288(7); 216(47).

Compound **2f**. 2.14 g γ-bromovaleronitrile (53%), oil. (Found: M.W. 382.1651. $C_{20}H_{22}N_4O_4$ Requires: M.W. 382.1641). IR($CHCl_3$): 2260, 1780, 1740, 1350 cm^{-1}. NMR($CDCl_3$): 6.00 (t, 2H, $C\underline{H}$=); 3.60 (m, 4H, $C\underline{H}_2N$); 2.80 (d, 4H, $C\underline{H}_2$–CH=); 2.45 (t, 4H, $C\underline{H}_2CN$); 2.00–1.50 (m, 8H, $C\underline{H}_2$). MS(m/e): 382(30); 342(49); 231(100); 162(50).

Compound **2g**. 0.94 ml of the ethylene glycol acetal of β-bromopropionaldehyde (80%), oil. (Found: N, 6.73; M.W. 420.1553. $C_{20}H_{24}N_2O_8$ Requires: 6.60%; M.W. 420.1532). IR($CHCl_3$): 1770, 1740, 1380, 1360, 1340, 1130 cm^{-1}. NMR($CDCl_3$): 6,80 (t, 2H, $C\underline{H}$=); 4.90 (t, 2H, $C\underline{H}<{}^{O}_{O}$); 4.10–3.60 (m, 4H, $C\underline{H}_2N$ + 8H, $C\underline{H}_2O$); 2.80 (d, 4H, $C\underline{H}_2CH$=); 2.20–1.80 (m, 4H, $C\underline{H}_2$). MS(m/e): 490(10); 377(100); 376(10); 375(47); 332(4); 277(133); 221(28); 176(15); 162(21); 142(12).

Compound **2h**. 2.54 g 3-bromo-1-chloropropane (20%), m.p. 123–124° (CH_2Cl_2–EtOAc) purified on prep SiO_2 plate with CH_2Cl_2:EtOAc (85:15) as eluent. The major product was **2i** but MS showed that some chloride-bromide was present. (Found: N, 7.19. $C_{14}H_{14}N_2O_4Cl_2$ Requires: N, 7.54%). IR($CHCl_3$): 1770, 1740, 1350, 1110 cm^{-1}. NMR($CDCl_3$): 5.95 (t, 2H, $C\underline{H}$=); 3.80 (m, 8H, $C\underline{H}_2N$ + $C\underline{H}_2Cl$); 2.80 (d, 4H, $C\underline{H}_2CH$=). MS(m/e): 389(2); 387(2); 348(1.5); 346(7.5); 344(15); 215(28); 214(11); 213(100).

Compound **2i**. 2.7 g 1-chloro-2-bromoethane (10%), oil, purified on prep SiO_2 plate with $CHCl_2$:EtOAc as eluent. (Found M.W. peaks corresponding to $C_{16}H_{18}N_2O_4Br_2$, $C_{16}H_{18}N_2O_4BrCl$ and $C_{18}H_{18}N_2O_4Cl_2$). IR($CHCl_3$): 1770, 1740, 1350, 1110 cm^{-1}. NMR($CDCl_3$): 5.90 (t, 2H, $C\underline{H}$=); 3.90–3.20 (m, 4H, CH_2N + 4H, $C\underline{H}_2Cl$); 2.75 (d, 4H, $C\underline{H}_2CH$=); 2.10 (q, 4H, $C\underline{H}_2$). MS(m/e): 463(14); 461(22); 459(13); 418(90); 416(69); 383(29); 376(12); 374(74); 372(100); 310(32); 270(11); 268(11); 227(13); 226(23); 224(39).

Compound **2j**. 2.92 g benzyl bromide (96%), m.p. 192–193° ($CHCl_3$–hexane). (Found: M.W. 400.1401. $C_{24}H_{20}N_2O_4$ Requires: M.W. 400.1422). IR($CHCl_3$): 1770, 1740, 1670, 1330 cm^{-1}. NMR($CDCl_3$): 7.20 (s, 10 arom H); 5.85 (m, 2H, $C\underline{H}$=); 4.60 (s, 4H, $NC\underline{H}_2Ph$); 2.70 (d, 4H, $C\underline{H}_2$–CH=). MS(m/e): 400(100); 372(8.4); 309(12.5); 240(17.9); 162(63.6).

Compound **2k**. 3.2 β-phenethylbromide (74%), m.p. 136–137° ($CHCl_3$–hexane). (Found: N, 6.53; M.W. 428.1721. $C_{26}H_{24}N_2O_4$ Requires: 6.54%; M.W. 428.1736). IR($CHCl_3$): 1770, 1740, 1370, 1340, 1110 cm^{-1}. NMR($CDCl_3$): 7.15 (m, 10 arom H); 5.70 (m, 2H, $C\underline{H}$=); 3.70 (t, 4H, $C\underline{H}_2N$); 2.85 (t, 4H, $C\underline{H}_2Ph$); 2.40 (d, 4H, $C\underline{H}_2CH$=). MS(m/e): 428(100); 337(17); 162(29).

2-Choroethanol gave an 18% yield of impure product but bromobenzene, β-bromopropionic acid, β-bromoethylamine hydrobromide and β-bromopropionitrile did not react with the dipotassium salt of 1 under the above conditions.

REFERENCE

[1] P. Ashkenazi, D. Tatarsky and D. Ginsburg, *Tetrahedron* previous paper.