

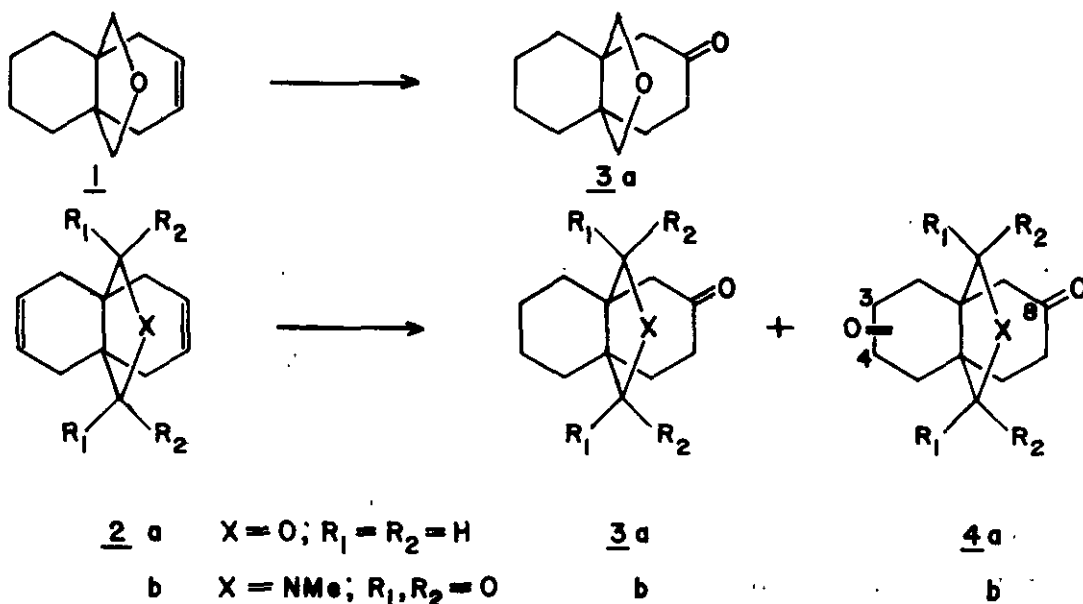
PROPELLANES. LXIV. PREPARATION OF PROPELLANONES FROM PROPELLENES BY
CONSECUTIVE HYDROBORATION AND OXIDATION^{*,†}

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Abstract - Hydroboration and subsequent oxidation of various olefinic propellanes leads to propellanonones. The yields are low for diolefinic substrates.

We wished to prepare propellanonones of types 3 and 4 from olefinic propellanes of types 1 and 2 by hydroboration followed by oxidation.



When only one double bond is present in the substrate, e.g. 1, a high yield of the monoketone 3a was formed (84%). But we were more interested in the diketones which we planned to use as starting materials for forming connections between the two cyclohexanone rings in the corresponding propellanediones 4a and 4b. Symmetry dictates the possible existence of two diones which may be formed from the precursors 2a and 2b, the 3,8-dione and the 4,8-dione.

In the event, it was clear that when one equivalent of NaBH_4 was used per double bond in 2a

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Dedicated to Professor Herbert C. Brown on the occasion of his 70th birthday.

[†]Part 63. I. Sataty, M. Kapon, M. Kaftory and D. Ginsburg, *Heterocycles*, K. Tsuda dedicatory issue.

or 2b hydroboration of only one of these occurred whilst the other was, in the main, reduced.¹ Thus, after oxidation of the intermediate, 2a gave 3a, the same product which was formed from 1, albeit in much lower yield (23%). A minor part also underwent hydroboration but the yield of 4a was only 8%. In the case of 2b the yields of 3b and 4b were 15% and 4%, respectively. Moreover, column chromatography of the product of the pertinent fraction with 2,4-dinitrophenylhydrazine on alumina clearly indicates the presence of both 3,8- and 4,8-diketone in 4a and 4b. We do not know whether 4a and 4b, each isolated as a single product (see below), are the 3,8- or the 4,8-diketone.

General experimental procedure. - A solution of the olefin 1 or 2 (1 mmol) in dry THF (25 ml) was treated with 1.37 mmol NaBH₄ (for 1) or 2.42 mmol (for 2) followed by a solution of 2.9 mmol BF₃·Et₂O (for 1) or 5 mmol (for 2) in dry THF (5 ml), at room temp.² After stirring overnight at room temp, water was added, and THF was removed by evaporation. The residue was extracted with ether (20 ml) and then oxidized in a two phase system with CrO₃ (2 ml for 1 and 6 ml for 2a and 2b) during 2hr.³ Ether extraction and washing the extract with aq NaHCO₃ solution, drying (MgSO₄) and removal of ether afforded a residue which was separated on a prep SiO₂ plate (CHCl₃).

3a: 163 mg from 1 (84%) was an oil which crystallized, m.p. 87-89°. IR(CHCl₃): 1715, 1680, 1450, 1050, 1030, 900 cm⁻¹. NMR(CDCl₃): δ 3.85, 3.70 (4H, CH₂O); 2.60-1.20 (m, 14H, CH₂). M.S. ^m/e: M⁺, 194(6); 179(30); 151(23); 145(100); 123(23); 119(39). (Found: M.W. 194·1314. C₁₂H₁₈O₂ requires 194·1307). 3a was also obtained from 2a, 43 mg (23%), along with 4a.

4a: From aq phase by extraction with ethyl acetate followed by workup with aq NaHCO₃ and removal of solvent, 17 mg (8%), m.p. 160-162° (chloroform-hexane). IR(CHCl₃): 1720, 1710, 1100, 1080, 1050, 930 cm⁻¹. NMR(CDCl₃): δ 3.80, 3.60 (4H, CH₂O); 2.60-1.70 (m, 12H, CH₂). M.S. ^m/e: M⁺, 208(42); 190(19); 150(29); 137(100). (Found: M.W. 208·1099. C₁₂H₁₆O₃ requires 208·1099).

3b: 36 mg from 2b (15%) was an oil. IR(CHCl₃): 1700, 1050 cm⁻¹. NMR(CDCl₃): δ 3.10 (s, 3H, NCH₃); 2.80-1.20 (m, 14H, CH₂). M.S. ^m/e: M⁺, 235(100); 219(9); 207(47); 180(43); 152(50). (Found: M.W. 235·1198. C₁₃H₁₇NO₃ requires 235·1208).

4b: From aq phase, as above, with ethyl acetate, 10 mg (4%), m.p. 171-173° (chloroform-hexane). IR(CHCl₃): 1710 cm⁻¹. NMR(CDCl₃): δ 3.10 (s, 3H, NCH₃); 3.00-1.80 (m, 12H, CH₂). M.S. ^m/e: M⁺, 249(100); 221(15); 194(38); 179(28). (Found: M.W. 249·0929. C₁₃H₁₅NO₄ requires 249·0915).

REFERENCES

1. We are studying the mechanism of this reduction; we believe a transannular intermediate is involved.
2. B.P. Mundy, A.R. DeBernardis and R.D. Otzenberger, *J Org. Chem.*, **36**, 3830 (1971).
3. See H.C. Brown, C.P. Gang and K.T. Liu, *Ibid*, **36**, 387 (1971) for the preparation of this solution.

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