PROPELLANES. LXIV. PREPARATION OF PROPELLANONES FROM PROPELLENES BY CONSECUTIVE HYDROBORATION AND OXIDATION[*,†]

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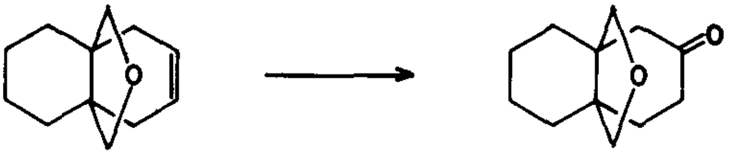
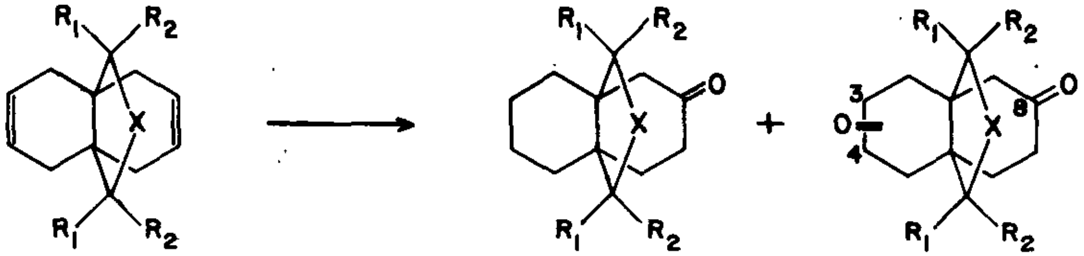
Abstract - Hydroboration and subsequent oxidation of various olefinic propellanes leads to propellanones. The yields are low for diolefinic substrates.

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



1 3a



2 a X = O; $R_1 = R_2 = H$ 3a 4a

b X = NMe; $R_1, R_2 = O$ b b

When only one double bond is present in the substrate, e.g. *1*, a high yield of the monoketone *3*a 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 *4*a and *4*b. Symmetry dictates the possible existence of two diones which may be formed from the percursors *2*a and *2*b, 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 *2*a

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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 $NaBH_4$ (for 1) or 2.42 mmol (for 2) followed by a solution of 2.9 mmol $BF_3 \cdot Et_2O$ (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 CrO_3 (2 ml for 1 and 6 ml for 2a and 2b) during 2hr.[3] Ether extraction and washing the extract with aq $NaHCO_3$ solution, drying ($MgSO_4$) and removal of ether afforded a residue which was separated on a prep SiO_2 plate ($CHCl_3$).

3a: 163 mg from 1 (84%) was an oil which crystallized, m.p. 87-89°. IR($CHCl_3$): 1715, 1680, 1450, 1050, 1030, 900 cm^{-1}. NMR($CDCl_3$): δ 3.85, 3.70 (4H, $C\underline{H}_2O$); 2.60-1.20 (m, 14H, $C\underline{H}_2$). M.S. $^m/e$: M^+, 194(6); 179(30); 151(23); 145(100); 123(23); 119(39). (Found: M.W. 194·1314. $C_{12}H_{18}O_2$ 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 $NaHCO_3$ and removal of solvent, 17 mg (8%), m.p. 160-162° (chloroform-hexane). IR($CHCl_3$): 1720, 1710, 1100, 1080, 1050, 930 cm^{-1}. NMR($CDCl_3$): δ 3.80, 3.60 (4H, $C\underline{H}_2O$);2.60-1.70(m, 12H, $C\underline{H}_2$). M.S. $^m/e$: M^+, 208(42); 190(19); 150(29); 137(100). (Found: M.W. 208·1099. $C_{12}H_{16}O_3$ requires 208·1099).

3b: 36 mg from 2b (15%) was an oil. IR($CHCl_3$): 1700, 1050 cm^{-1}. NMR($CDCl_3$): δ 3.10 (s, 3H, $NC\underline{H}_3$);2.80-1.20(m, 14H, $C\underline{H}_2$). M.S. $^m/e$: M^+, 235(100); 219(9); 207(47); 180(43); 152(50). (Found: M.W. 235·1198. $C_{13}H_{17}NO_3$ requires 235·1208).

4b: From aq phase, as above, with ethyl acetate, 10 mg (4%), m.p. 171-173°(chloroform-hexane). IR($CHCl_3$): 1710 cm^{-1}. NMR($CDCl_3$): δ 3.10 (s, 3H, $NC\underline{H}_3$);3.00-1.80(m, 12H, $C\underline{H}_2$). M.S. $^m/e$: M^+, 249(100); 221(15); 194(38); 179(28). (Found: M.W. 249·0929. $C_{13}H_{15}NO_4$ 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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