Tetrahedron Letters No. 35, pp 3211 - 3214.
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0040-4039/78/0822-3211$02.00/0

CHROMYL CHLORIDE OXIDATION OF NORBORNADIENE

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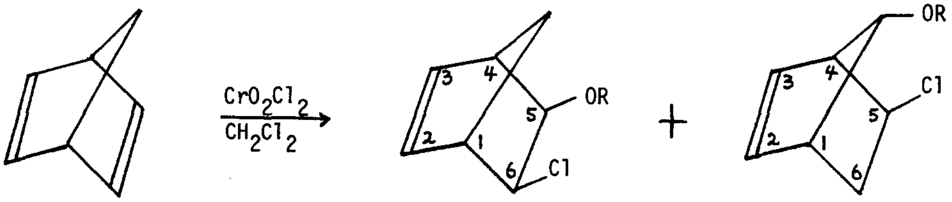
In the recent years, the nature of the active oxygen species in the biological monooxygenase reactions has been a subject of considerable interest and speculation.[1] Among other possible "oxenoid" (electron-deficient oxygen) reagents, certain oxotransition metal compounds of chromium and manganese were noted to show chemical features similar to those of monooxygenase-catalyzed reaction. For example, chromyl reagents hydroxylate hydrocarbons with partial retention of stereochemistry, epoxidize olefins with retention of the olefin geometry and also hydroxylate aromatic compounds with concomitant "NIH Shift".[2]

The detailed mechanism for the chromyl chloride oxidation of olefins is not well understood. The initial proposals involve an electrophilic attack of $[O_2CrCl]^+$ on the olefin to generate a three-centered oxonium or a ring-opened carbonium ion intermediate, which is then attacked by chloride ion.[3-5] More recently, however, Sharpless[6] and Bachelor[7] have argued against significant cationic charge development in the intermediate wherein the carbon-chlorine bond is formed, based on their experimental observations with (E)-tert-butylmethylethylene and norbornene, respectively.

One of the difficulties in studying the chromyl chloride oxidation of olefins is the production of complex mixtures of products. It was recently established that when the oxidation was conducted at low temperature only three primary products are produced -- epoxide, chlorohydrin, and in some cases vicinal dichloride.[6] The norbornadiene system is known to be very sensitive to the cationic charge development and has been extensively employed as a probe in the mechanistic studies of solvolyses and electrophilic addition reactions.[8] Therefore, it seemed of interest to study chromyl chloride oxidation of norbornadiene at low temperature.

Norbornadiene was oxidized with fresh chromyl chloride (1.5 molar equiv., -78°, CH_2Cl_2, dark, 2 hr) according to a literature procedure.[6] An extractive work-up (CH_2Cl_2) from an ice-cold aqueous $NaHSO_3$ solution yielded a product mixture. The vpc analysis (5 ft x 0.25 in column packed with 10% FFAP on Anakrom-CD, 60-70 mesh) indicated the presence of two major products, 1a (in 50% yield) and 2a (37%) among no less than 10 products. The product mixture was acetylated (Ac_2O in pyridine) and the two major products 1b (50%) and 2b (37%) were separated by a preparative vpc. The structures are assigned based on their spectroscopic data (ir, nmr and mass spectra). Nmr peak assignments are consistent with the complete systematic decoupling experiments.



1a. R = H

1b. R = Ac

2a. R = H

2b. R = Ac

1b: nmr ($CDCl_3$) δ 6.16 (t, J = 1.6 hz, 2H, H_2 and H_3), 4.72 (d, d, J = 6, 1.6 hz, 1H, H_5), 4.01 (d, d, J = 6, 1.7 hz, 1H, H_6), 2.95 (br. m, 1H, H_1), 2.83 (br. m, 1H, H_4), 2.12 (S, 3H, acetate), 2.08 (m, 1H, H_7-syn), 1.78 (t d, J = 10, 2, 1H, H_7-anti); ir ($CHCl_3$) 2890, 2870, 1735, 1490, 1445, 1375 cm^{-1}; ms (m/e) (15 ev) 188 (M^+, ^{37}Cl), 186 (M^+, ^{35}Cl), 151 (M^+ -Cl), 129, 127 (M^+ -OAc), 109 (base peak), 91 (C_7H_7), 79, 66.

2b: nmr ($CDCl_3$) δ 6.10 and 6.08 (each t, J = 2 hz, 1H, H_2 and H_3), 4.54 (br. S, 1H, H_7-anti), 3.80 (d, d, d, J = 8, 4.3 & 1.3, 1H, H_5-endo), 3.18 (m, 1H, H_1), 2.88 (m, 1H, H_4), 2.07 (m, 2H, H_6), 2.05 (S, 3H, acetate); ir ($CHCl_3$) 2980, 2870, 1735, 1490, 1445, 1382 cm^{-1}; ms (m/e) (15 ev) 188 (M^+, ^{37}Cl), 186 (M^+, ^{35}Cl), 151 (M^+ -Cl), 129, 127 (M^+ -OAc), 109 (base peak), 91, 79, 66.

The present observation, when compared with the product distribution of other electrophilic additions to norbornadiene (Table 1), is quite informative on the extent of cation charge development in the intermediate wherein the carbon-chloride bond formation takes place. The 1,2-addition product is clearly the result of a concerted addition, and the ratios of Wagner-Meerwein products over the nortricyclyl products reflect the extent of the cationic charge development and the ion pair association. Chromyl chloride oxidation of norbornadiene generates only a partial carbonium ion character sufficient to cause the Wagner-Meerwein rearrangement, while strong electrophiles (e.g. TsOH in HOAc, and Br_2) generate more fully developed carbonium ion intermediates leading predominantly to the nortricyclyl products. These results are consistent with a study of the electron demand reflected in the reaction constant (ρ^+) on the reaction of styrenes with Br_2 (-4.30), CrO_2Cl_2 (-1.99) and epoxidation (-1.3).[5]

Table 1. Summary of results of addition reactions.

Reagent	Solvent	Temp., °C	% 1,2-addition	% Wagner-Meerwein Rearrangement	% Nortricyclene
[a]$Hg(OAc)_2$	HOAc	Kinetic Control	100	---	---
[a]$Tl(OAc)_3$	$CHCl_3$	Kinetic Control	100	---	---
[b]CrO_2Cl_2	CH_2Cl_2	-78	50	37	(trace)
[c]DOAc	---	100	22	11	67
[d]TsOH/HOAc	---	---	---	15	85
[d]Br_2	CCl_4	-20	---	17	83

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b. this work

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ACKNOWLEDGMENT: I am grateful to Research Corporation and Texas A&M University (Organized Research Fund) for their financial assistance, and to Dr. Paul Fagerness for the nmr decoupling experiments.

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(Received in USA 13 June 1978; received in UK for publication 4 July 1978)