

THE CHROMYL CHLORIDE OXIDATION OF NORBORNENES

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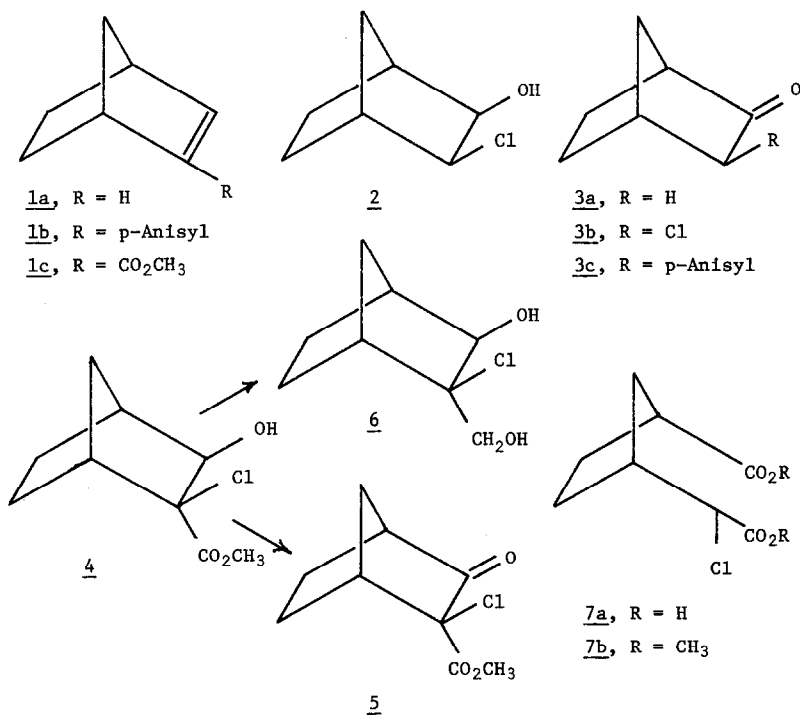
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The oxidation of norbornene (1a) by chromyl chloride has recently been carried out by Freeman et al. as part of a kinetic study of the mechanism of oxidation by this reagent (1). Unfortunately no product analysis was made. We have repeated this reaction and the products which we have isolated and identified refute the mechanism proposed. The products predicted by Freeman's hypothetical intermediates would be those which correspond to a cis-glycol or epoxide rearrangement products. We have found that 74% of the isolated products are accounted for by the initial formation of an exo-cis-chlorohydrin (2). Only about 5% of the isolated products correspond to those predicted by Freeman's mechanism, i.e., norcamphor (3a) and a rearranged unidentified aldehyde.

Our reactions were carried out at -80°C and worked up by treating the complex with 10% aqueous sodium bicarbonate. From the oxidation of norbornene with freshly distilled chromyl chloride we were able to isolate 3-exo-chloro-2-exo-hydroxynorbornene (2) (63%) (2), 3 exo-chloro norcamphor (3b) (11%) (2) norcamphor (3a) (3.1%) and an unidentified aldehyde (1.7%). These components were separated and purified by a combination of fractional distillation and preparative gas chromatography. At higher reaction temperatures more chloronorcamphor is formed at the expense of the chlorohydrin. No trans-chlorohydrin was found in contrast to reactions of chromyl chloride on cyclopentene or cyclohexene (3) which yield both the cis and trans-isomers. These isomers are presumably formed by different mechanisms and our interest centers on that which produces the cis-isomer.

Cis-additions frequently occur with olefins in strained rings, particularly in 1,3-dipolar type reactions. Norbornene is a particularly good example of this type of reaction. Further,

because of steric interactions it tends to add stereospecifically to the exo-position. Many non-concerted additions give mixtures of cis and trans isomers with norbornene but only concerted reactions give exclusively the cis-exo-adducts (4-8). This evidence speaks strongly for a concerted 1,3-addition of oxygen and chlorine from the chromyl chloride but does not distinguish between a dipolar or a free radical mechanism. In view of the recent analysis of 1,3-dipolar additions by Firestone (9) it seems that either would appear equally likely. In order to examine these possibilities further we oxidized 2-p-anisylnorbornene (1b) and 2-carbomethoxynorbornene (1c) with chromyl chloride. If the addition is dipolar and initiated by a positive oxygen as would be predicted by all previous examples the direction of addition should be opposite in the two models. On the other hand, if the reaction is free radical both additions should occur with the same orientation of the oxygen and chlorine.



No chlorine containing products were found when 2-p-anisylbornene (1b) was treated with chromyl chloride. The major product was a dimer which had incorporated an additional atom of oxygen and the structure of this product is presently under investigation. There was also isolated 3-exo-p-anisylbornane (3c). This product could have resulted either from the elimination of hydrogen chloride from a chlorohydrin or by rearrangement of an epoxide. In view of our results on norbornene, we tend to favor the former, which implies the addition of oxygen at the position β - to the aromatic ring attachment and chlorine at the α -position.

The oxidation of 2-carbomethoxynorbornene (1c) with chromyl chloride yielded two major products in the ratio of about 4:1. These were, respectively, a chlorohydrin¹ (4) and a chloroketone (5). The chlorohydrin could be readily converted to the chloroketone by Jones oxidation. Reduction of the chlorohydrin by LiAlH_4 yielded a diol (6) which was resistant to cleavage by aqueous sodium periodate after 9 hours at room temperature. This rules out the possibility of an α -glycol system. Treatment of the chloroketone (5) with methanolic potassium hydroxide results in cleavage via a reverse Claisen reaction to yield the chlorodiacid (7a) which on esterification with diazomethane gives the diester (7b).

This evidence strongly supports the suggestion that the cis-chlorohydrin addition products from chromyl chloride on olefins is a free radical process. The formation of the oxygen containing dimer is also very suggestive that the attack by the oxygen in chromyl chloride may itself be a free radical process. This result compares favorably with a number of 1,3-polar addition reactions which add in what appears to be an orientation contrary to the dipole (5,10). A particularly good example of this is the addition of nitrile oxides to unsaturated esters where the oxygen atom of the nitrile oxide becomes attached to the α -carbon atom of the ester. As pointed out by Firestone (9) these are undoubtedly free radical reactions.

¹ All new compounds were characterized by NMR, IR and mass spectroscopic analysis and were satisfactory for the structures proposed.

REFERENCES

1. F. Freeman and N. J. Yamachika, J. Am. Chem. Soc., 94, 1214 (1972).
2. E. Tobler, D. E. Battin and D. J. Foster, J. Org. Chem., 29, 2834 (1964).
3. R. A. Stairs, D. G. M. Diaper and A. L. Gatzke, Can. J. Chem., 41, 1059 (1963).

4. L. Kaplan, H. Kwart and P. von R. Schleyer, J. Am. Chem. Soc., 82, 2341 (1960).
5. R. Huisgen, Ang. Chem. Int. Ed. Engl., 2, 565 (1963).
6. Erich Tobler, D. E. Battin, D. J. Foster, J. Org. Chem., 29, 2834 (1964).
7. H. Kwart and J. L. Nyce, J. Am. Chem. Soc., 86, 2601 (1964).
8. E. W. Garbisch Jr., S. M. Schildcrout, D. B. Patterson and C. M. Sprecher, J. Am. Chem. Soc., 87, 2932 (1965).
9. R. A. Firestone, J. Org. Chem., 37, 2181 (1972).
10. R. Huisgen and M. Christl, Angew. Chem. Int. Ed. Engl., 6, 456 (1967).