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THE STEREOSELECTIVE SYNTHESIS OF TRISUBSTITUTED OLEFINS. CONCERTED RING-OPENING OF CYCLOPROPYLOXIRANES

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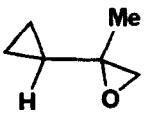
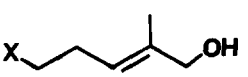
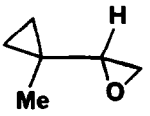
Of the many reactions available for stereoselective synthesis of trisubstituted olefins,[1] the Julia-Johnson rearrangement of cyclopropylcarbinols[2,3] offers the advantages of widespread applicability and fairly high stereoselectivity to a unique degree. Unfortunately, however, a structural consequence of the sequence is the formation of a terminally functionalized homoallylic system; therefore, it is generally unsuited for the synthesis of 2- or 3-methyl-2-alken-1-ols (the chain terminal unit of an isoprene).[4] Herein we disclose a novel adaptation of the Julia-Johnson olefin synthesis, which has afforded both allylic alcohols of the type 2 and 4 in good yields and with exceedingly high stereoselectivity.



1



2a: X = Br
2b: X = I



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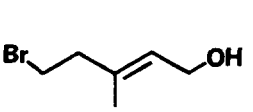

4

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The oxirane 1,[5,6] on treatment with 48% hydrobromic acid at 0° for 1 hr,[2] was converted into the acid sensitive[3] (E)-5-bromo-2-methyl-2-penten-1-ol (2a), with >96% stereoselectivity in 90% crude yield (81% after tlc purification). The nmr spectrum[7] at 100 MHz was consistent with this structure,[8] showing in particular a one proton triplet at 5.37 (olefinic), a two proton singlet at 3.91 ($=C-CH_2O$), a three proton singlet at 1.64 ($=C-CH_3$), and only minor absorptions (<4%) at 4.02 and 1.78 ppm each corresponding to the geometrically isomeric olefin of (Z) stereochemistry.[4] The structure of 2a was further confirmed by oxidation with manganese dioxide to the corresponding aldehyde whose nmr exhibited the absorption at 9.29 ppm characteristic for (E)-2-methyl-2-alkenal; lit:[8a,8c] (E) 9.3; (Z) 9.9 ppm. Alternatively, and even more efficiently, the oxirane 1 was transformed into the (E) iodide 2b[9] by the action of sodium iodide in acetic acid-propionic acid-sodium acetate[10] at -18° for 30 min

and 25° for 1 hr.

The similar treatment of the isomeric oxirane 3[10] with 48% hydrobromic acid or sodium iodide in acetic acid buffer produced none of the desired product. However, the synthesis of (E)-5-bromo-3-methyl-2-penten-1-ol (4)[12] from 3 was effected on treatment with anhydrous zinc bromide in ether at 0° for 2 hr[3] (73% yield after tlc purification). The stereochemistry of 4 is clearly indicated by analysis[13] of the 100 MHz nmr spectrum[7] which reveals peaks at 5.42 (t, 1H), 4.05 (d, 2H), and 1.69 (s, 3H) accompanied with very small peak at 1.79 ppm (<3%: (Z) isomer).

The rigorous stereoselectivity of this novel reaction[14] can be rationalized on the basis of a concerted process via the transition state 5.[15] The scope and stereochemistry of the reaction will be detailed in a separate paper.

NOTES AND REFERENCES

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2) M. Julia, S. Julia, and R. Guégan, Bull. Soc. Chim. France, 1072 (1962).
3) S. F. Brady, M. A. Ilton, and W. S. Johnson, J. Amer. Chem. Soc., 90, 2882 (1968).
4) Methods for stereospecific syntheses of trisubstituted chain terminal units: E. J. Corey and H. Yamamoto, ibid., 92, 226 (1970), and references cited therein.
5) All new compounds have been characterized spectrometrically and analytically.
6) Prepared from cyclopropyl methyl ketone and dimethylsulfonium methylide in DMSO at -5° for 20 min and 25° for 1 hr, bp 107°.
7) Chemical shifts are expressed as ppm downfield from TMS in CCl_4.
8) (a) K. C. Chan, R. A. Jewell, W. H. Nutting, and H. Rapoport, J. Org. Chem., 33, 3382 (1968); (b) R. G. Lewis, D. H. Gustafson, and W. F. Erman, Tetrahedron Lett., 401 (1967); (c) V. T. Bhalerao and H. Rapoport, J. Amer. Chem. Soc., 93, 4835 (1971).
9) Stereoselectivity: >95% (glpc assay); crude yield: 75%.
10) J. W. Cornforth, R. H. Cornforth, and K. K. Mathew, J. Chem. Soc., 112 (1959).
11) Prepared from 1-methyl-1-vinylcyclopropane [R. J. Ellis and H. M. Frey, ibid., 959 (1964)] and m-chloroperbenzoic acid in pentane, bp 106°.
12) Non-stereoselective route: E. J. Corey and E. Hamanaka, J. Amer. Chem. Soc., 89, 2758 (1967).
13) Identical in all respects with authentic spectra. We are indebted to Prof. E. J. Corey for providing spectral data.
14) The cyclopropyloxirane rearrangement in formic acid to produce the (E)-disubstituted olefin in ca. 3% yield was reported: G. Just, C. Simonovitch, F. H. Lincoln, W. P. Schneider, U. Azen, G. B. Spero, and J. E. Pike, ibid., 91, 5364 (1969).
15) Although the relative stability of the conformer 5 could be explained by essentially the same arguments used to rationalized the Julia-Johnson rearrangements,[3] other factor might also play an important role for the stabilization of 5, including a p_π-p_π interaction through the σ-bond between epoxide and cyclopropane rings. Thus, in contrast to the high stereoselectivity of this reaction, only ca. 75% selectivity was reported in the reaction of butylcyclopropylmethylcarbinol in HBr.[3]