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THE ABSOLUTE CONFIGURATION OF (+)-3-METHYL-3-t-BUTYL-1-CHLOROALLENE

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SINCE the absolute configuration of (+)-tartaric acid was established by Bijvoet et al.,[1] the configuration of any other compound containing one or more asymmetric carbons may, in principle, be established by correlation with (+)- or (-)-tartaric acid. One of the remaining general problems of static stereochemistry is the assignment of configuration to optically active compounds not containing asymmetric atoms. For the case of dissymmetric biphenyls, this problem has been solved elegantly by Mislow and by Berson and their coworkers.[2] The correlation with centroasymmetric compounds they obtained necessarily rests on mechanistic arguments. We wish now to present a similar argument which suggests the (R)-configuration[3] for (+)-3-methyl-3-t-butyl-1-chloroallene (I, Fig. 2),[4] a representative of the class of dissymmetric allenes.

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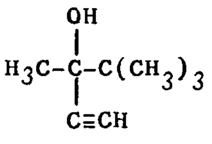
[1] J.M. Bijvoet, A.F. Peerdeman and A.J. van Bommel, Nature, Lond. **168**, 271 (1951); see also W.W. Wood, W. Pickett and J.G. Kirkwood, J. Chem. Phys. **20**, 561 (1952).

[2] cf. K. Mislow, Angew. Chem. **70**, 683 (1958).

[3] cf. R.S. Cahn, C.K. Ingold and V. Prelog, Experientia **12**, 81 (1956).

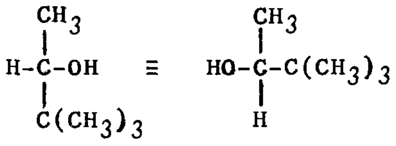
[4] S.R. Landor and R. Taylor-Smith, Proc. Chem. Soc. 154 (1959).

(+)-I was synthesized by Landor and Taylor-Smith[4] from (+)-methylethynyl-t-butyl carbinol (II) and thionyl chloride. To deduce from this the configuration of (+)-I, one must first assign configuration to (+)-II. This could be done on the basis of arguments presented by Brewster[5] if one knew the polarizability sequence of the groups ethynyl, methyl, t-butyl and hydroxyl. Of these groups, ethynyl undoubtedly has the highest polarizability.[5] The polarizability order of the remaining three groups may be deduced from the fact[6] that (+)-pinacolyl alcohol (III) (in which the hydrogen is the substituent of lowest polarizability) has the D- or (S)-configuration as shown in Fig. 1. In its simplest form, the argument is that since the ethynyl group in II is the group of highest polarizability whereas the hydrogen in III is the group of lowest polarizability, the other three substituents in II and III being the same, therefore (+)-II and (+)-III must have the opposite arrangement of groups (ethynyl taking the place of hydrogen).



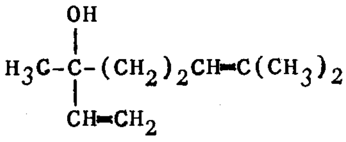
$H_3C-\overset{OH}{\underset{C\equiv CH}{C}}-C(CH_3)_3$

(S)-(+)-II



$H-\overset{CH_3}{\underset{C(CH_3)_3}{C}}-OH \equiv HO-\overset{CH_3}{\underset{H}{C}}-C(CH_3)_3$

(S)-(+)-III



$H_3C-\overset{OH}{\underset{CH=CH_2}{C}}-(CH_2)_2CH=C(CH_3)_2$

(R)-(+)-IV

FIG. 1.

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[5] J.H. Brewster, J. Amer. Chem. Soc. 81, 5475 (1959).

[6] H.S. Mosher and E. La Combe, J. Amer. Chem. Soc. 72, 3994 (1950); cf. J.A. Mills and W. Klyne in Progress in Stereochemistry Vol. 1, p. 201 (Edited by W. Klyne). Butterworths, London (1954).

[That the configurational symbol for (+)-II and (+)III is the same - (S) - is a consequence of the nomenclature sequence rule[3] and is immaterial to the argument.] It may be worth mentioning that the configuration of (+)-II so assigned corresponds to the known[7] configuration of (+)-linalool (IV), isohexenyl taking the place of t-butyl.

Landor and Taylor-Smith[4] associated an S_Ni' mechanism[8] with the stereospecific conversion of (+)-II to (+)-I. If this is accepted, the configuration of (+)-I is (R), as shown in Fig. 2 (right-hand side), because as cyclic transition state (or its ion pair equivalent) is involved in the S_Ni' mechanism.[9] A plausible alternative to the S_Ni' path would seem to be an S_N2' mechanism[8] (Fig. 2, left-hand side). Fortunately, this should also give rise to (R)-3-methyl-3-t-butyl-1-chloroallene, since the S_N2' mechanism has been shown[10] to involve a double inversion.

The assumptions involved in the assignment of the (R)-configuration to (+)-I are as follows: (I) (+)-II has the (S)-configuration (Fig. 1). (2) The conversion of (+)-II to (+)-I proceeds by either an S_Ni' or an S_N2' mechanism. (3) The stereochemistry of the S_N2' mechanism is as shown (Fig. 2).

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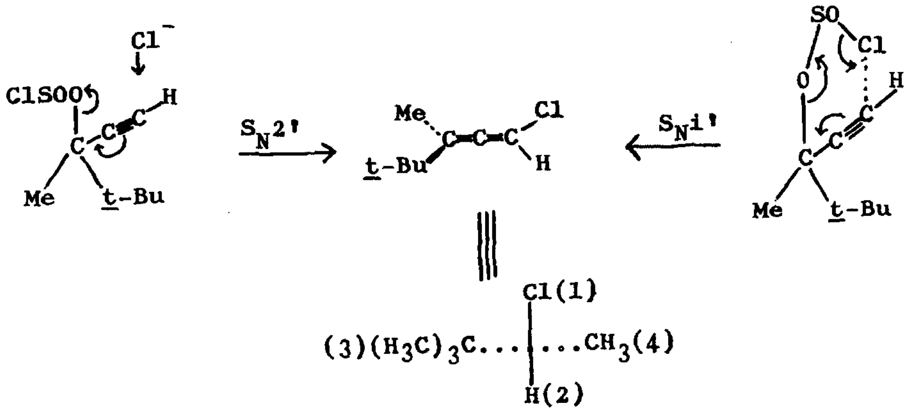
[7] V. Prelog and W. Eiji, Liebigs Ann. **603**, 1 (1957). Actually it was shown that (-)-linalool has the (S)-configuration.

[8] cf. R.H. DeWolfe and W.G. Young, Chem. Rev. **56**, 814,769 (1956).

[9] H.L. Goering, T.D. Nevitt and E.F. Silversmith, J. Amer. Chem. Soc. **77**, 4042 (1955); F.D. Caserio, G.E. Dennis, R.H. DeWolfe and W.G. Young, Ibid. **77**, 4182 (1955).

[10] G. Stork and W.N. White, J. Amer. Chem. Soc. **78**, 4609 (1956).



(R)-(+)-I

FIG. 2.

We believe these assumptions are reasonable and likely to be correct. If they are not, the argument presented is obviously no longer cogent even though it may fortuitously give the right answer.