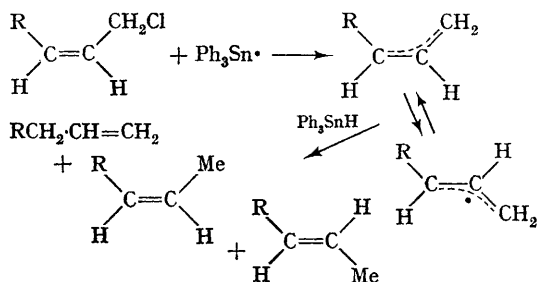# cis–trans-Isomerisation of Allylic Radicals

By DONALD B. DENNEY,* ROBERT M. HOYTE, and PAUL T. MACGREGOR

(*Department of Chemistry, Rutgers, The State University, New Brunswick, New Jersey* 08903)

THE possibility of interconversion of *cis*- and *trans*-allylic radicals has been recognised and several isolated examples of such interconversions have been reported.[1] It has now been found that *cis–trans*-isomerisation of allylic radicals is particularly easy and occurs with many structures. The radicals are generated by reduction of the appropriate allylic chlorides with triphenyltin

hydride, by a well established mechanism.[2] The key steps involve abstraction of halogen by triphenyltin radical to give an allylic radical which further reacts with triphenyltin hydride to give hydrocarbons. By varying the concentration of reactants one can vary the lifetime of the intermediate radicals. The results of such reductions, which were carried out at 80° in hydrocarbon

solvents with AIBN (azobis-isobutyronitrile) as initiator, are collected in the Table 1.



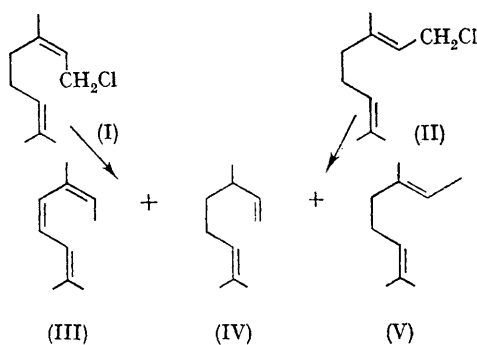The reductions of neryl (I) and geranyl chloride (II) were also conducted under a variety of conditions (see Table 2).

The data clearly show that all of the pairs of allylic chlorides give the same products if the concentrations of starting materials are low enough. At intermediate concentrations incomplete isomerisation has been observed in some cases. Reduction of neryl chloride in the absence of solvent at 20° gave only compounds (III) and (IV).

Unfortunately it is not possible to assign rate constants to these isomerisations; however, it is clear that the barrier to rotation is not large and that the interconversions can compete effectively with the reaction with triphenyltin hydride. The isomerisation of other allylic radicals is currently under investigation and an attempt is being made to obtain rates for these processes.

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TABLE 1

| $RCH=CH-CH_2Cl$ (Conc.)[a] | | | | | $\%$ $RCH_2CH=CH_2$ | $\%$ cis $RCH=CHCH_3$ | $\%$ trans $RCH=CHCH_3$ |
|---|---|---|---|---|---|---|---|
| trans, R=Me (0·27) | .. | .. | .. | .. | 28 | 23 | 49 |
| trans, R=Me (0·027) | .. | .. | .. | .. | 36 | 22 | 42 |
| trans, R=Me (0·0135) | .. | .. | .. | .. | 36 | 23 | 41 |
| cis, R=Me (88%) (0·027) trans, R=Me (12%) | .. | .. | .. | | 34 | 25 | 41 |
| cis, R=Me (88%) (0·0135) trans, R=Me (12%) | .. | .. | .. | | 35 | 24 | 41 |
| trans, R=Et (0·027) | .. | .. | .. | .. | 28 | 17 | 55 |
| trans, R=Et (0·0135) | .. | .. | .. | .. | 30 | 17 | 53 |
| cis, R=Et (0·027) | .. | .. | .. | .. | 33 | 17 | 50 |
| cis, R=Et (0·0135) | .. | .. | .. | .. | 29 | 18 | 53 |
| trans, R=Me₃C (0·27) | .. | .. | .. | .. | ? | 0 | ca. 100 |
| cis, R=Me₃C (0·27) | .. | .. | .. | .. | ? | 0 | ca. 100 |

[a] Concentrations of allylic chloride and triphenyltin hydride were equivalent.

TABLE 2

| Compound (Conc.)[a] | Temp. | (IV) / ((III) + (V)) | (III)/(V) |
|---|---|---|---|
| (I) (0·027) | 80° | 0·15 | 0·51 |
| (I) (0·082) | 80° | 0·15 | 0·56 |
| (I) (0·29) | 80° | 0·16 | 0·73 |
| (II) (0·027) | 80° | 0·14 | 0·48 |
| (II) (0·082) | 80° | 0·15 | 0·45 |
| (II) (0·29) | 80° | 0·16 | 0·38 |
| (II) (0·29) | 18°[b] | 0·12 | 0·09 |
| (II) (0·029) | 18°[b] | 0·15 | 0·33 |

[a] Concentrations of allylic chloride and triphenyltin hydride were the same.
[b] Irradiated with a G.E. sun lamp.

[1] (a) C. Walling and W. Thaler, J. Amer. Chem. Soc., 1961, 83, 3882; (b) W. A. Thaler, A. A. Oswald, and B. E. Hudson, J. Amer. Chem. Soc., 1965, 87, 311; (c) W. P. Neumann, H. J. Albert, and W. Kaiser, Tetrahedron Letters, 1967, 2041.
[2] L. W. Menapace and H. G. Kuivila, J. Amer. Chem. Soc., 1964, 86, 3047.