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CONFIGURATIONAL STABILITY OF CYCLOPROPYL RADICALS IN ELECTRON-TRANSFER REACTIONS WITH NAPHTHALENE RADICAL ANION

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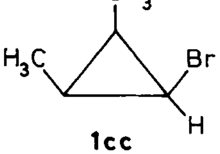
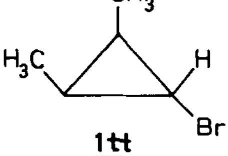
Cyclopropyl radicals normally undergo complete thermodynamic equilibration of configuration before they react, e.g., with bromine in the Hunsdiecker reaction[1]. Incomplete equilibration is normally due to steric or cage effects[2], and to surface effects when cyclopropyl halides are reduced with metals[3,4]. Jacobus and Pensak, however, proposed that an optically active tertiary cyclopropyl radical had been trapped by sodium naphthalene when optically active 1-methyl-2,2-diphenylcyclopropyl bromide was reacted with this one-electron-transfer reagent[5].

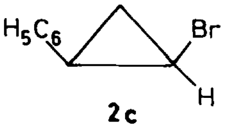
We studied the reaction of other substituted cyclopropyl bromides (1cc, 1tt, 2c and 2t) with lithium naphthalene ($Li^+Naph^{\dot{-}}$)[6] in order to find out whether we could confirm the above mentioned result.



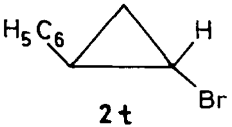
1cc



1tt

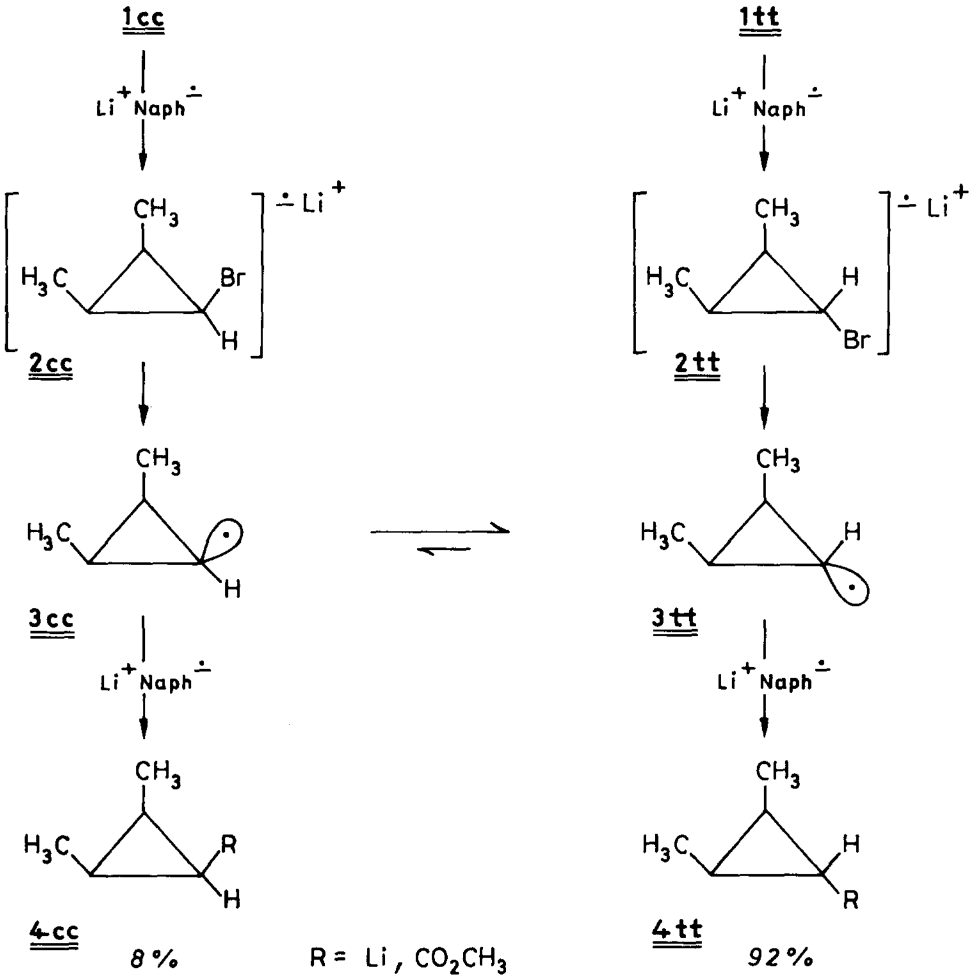


2c



2t

Reaction of $Li^+Naph^{\dot{-}}$ with 1-bromo-cis,cis-2,3-dimethylcyclopropane (1cc) or with the trans,trans-isomer 1tt[7,9] led after carboxylation and methylation to the identical 8:92 mixture of the cis,cis- and trans,trans-carboxymethylates 4cc ($R=CO_2CH_3$) and 4tt ($R=CO_2CH_3$), respectively[10].



A completely analogous result was obtained with *cis*- and *trans*-1-bromo-2-phenyl cyclopropanes (**2c** and **2t**, respectively)[12]: Both isomers yielded the identical 21:79 mixture of *cis*- and *trans*-2-phenylcyclopropyl carboxymethylates[14]. These results have two implications:

(1) There is no indication that bromide containing cyclopropyl radical anions $RX^{\dot{-}}M^{+}$ like **2cc** and **2tt** can be trapped by lithium naphthalene. Either they decompose very rapidly[16] or dissociative electron transfer takes place to give cyclopropyl radicals like **3cc** and **3tt** directly. Garst[17] arrived at the same conclusion for alkyl halide radical anions $RX^{\dot{-}}M^{+}$.

(2) Inversion of secondary cyclopropyl radicals to reach the thermodynamic equilibrium is faster than electron transfer from $Li^{+}Naph^{\dot{-}}$ to give configu-

rationally stable cyclopropyl lithium compounds like 4cc and 4tt (R=Li). This is in contrast to the result of Jacobus and Pensak[5].

Assuming a similar rate constant for the reaction of cyclopropyl radicals like 3cc with $Li^+Naph^{\dot{-}}$ in THF as for the reaction of primary alkyl radicals with $Na^+Naph^{\dot{-}}$ in DME ($k = 1.6 \cdot 10^9$ l/mol·s)[18], the rate constant for the inversion 3cc $\rightleftharpoons$ 3tt is $\geqslant 5 \cdot 10^9\ s^{-1}$, corresponding to $\Delta G^{\ddagger} \leqslant 3.7$ kcal·mole^{-1}. Thus, our results derived from chemical reactions are in good agreement with ESR spectroscopic data both of Fessenden and Schuler[19] who reported in 1963 that inversion of the cyclopropyl radical in cyclopropane at -120°C "occurs at high frequency", and of Kawamura et al.[20] who recently showed that cyclopropyl radicals invert at -99°C with $k > 8 \cdot 10^7\ s^{-1}$. Kawamura et al. also found that 3tt is more stable than 3cc, corresponding to our findings.

In conclusion, cyclopropyl bromide radical anions cannot be trapped with $Li^+Naph^{\dot{-}}$ (0.9 M) in THF at room temperature. Similarly, inversion of secondary cyclopropyl radicals to reach the thermodynamic equilibrium is faster than electron transfer from $Li^+Naph^{\dot{-}}$.

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References and Notes

1. K.Kobayashi and J.B.Lambert, J.Org.Chem. 42, 1254 (1977).
2. H.M.Walborsky and C.-J.Chen, J.Amer.Chem.Soc. 89, 5499 (1967); ibid. 93, 671 (1971); L.J.Altman and B.W.Nelson, J.Amer.Chem.Soc. 91, 5163 (1969); L.J.Altman and T.R.Erdman, Tetrahedron Lett. 1970, 4891.
3. H.M.Walborsky and M.S.Aronoff, J.Organomet.Chem. 51, 31 (1973); ibid. 51, 55 (1973).
4. M.J.S.Dewar and J.M.Harris, J.Amer.Chem.Soc. 91, 3652 (1969). As shown by these authors, the reaction of 1cc (1tt) with lithium yields 54 (31) % 4cc (R=Li) and 46 (69) % 4tt (R=Li). Thus, the reduction with Li is totally different from the reduction with lithium naphthalene reported in

this work.

5. J.Jacobus and D.Pensak, Chem.Commun. 1969, 400.
6. Lithium naphthalene was used because cyclopropyl sodium and cyclopropyl potassium compounds react immediately with the solvent THF to give cyclopropanes.
7. **1cc** and **1tt** were prepared from 1,1-dibromo-*cis*-2,3-dimethylcyclopropane by reduction with tri-n-butyltinhydride, separated by glc, and identified by comparison with authentic samples[8].
8. G.L.Closs and J.J.Coyle, J.Amer.Chem.Soc. 87, 4270 (1965).
9. 1.0 ml of a 0.9 M solution of **1cc** (or of **1tt**) in THF was added to 10 ml of a 0.9 M solution of $Li^+Naph^{\dot{-}}$ in THF at ambient temperature. Inverse addition gave the same results.
10. Ratios of **4cc** and **4tt** ($R=CO_2CH_3$, prepared from the carboxylic acids with CH_3OH/BF_3) were determined by glc; identification was accomplished by comparison with authentic samples[11].
11. D.E.McGreer, P.Morris and G.Carmichael, Can.J.Chem. 41, 726 (1963).
12. **2c** and **2t** were prepared from 1,1-dibromo-2-phenylcyclopropane by reductions with Zn/CH_3COOH and n-butyllithium at -100°C, respectively. In the reductions, 73:27 and 28:72 mixtures of **2c** and **2t** were used; reaction conditions like [9]. Identification was accomplished by comparison with authentic samples[13].
13. J.W.Hausser and M.J.Grubber, J.Org.Chem. 37, 2648 (1972).
14. Ratios of *cis*- and *trans*- carboxymethylates were determined by glc; identification was achieved by comparison with authentic samples[15].
15. G.L.Krueger, F.Kaplan, M.Orchin and W.H.Faul, Tetrahedron Lett. 1965,3979.
16. According to J.F.Garst, R.D.Roberts and J.A.Pacifici, J.Amer.Chem.Soc. 99, 3528 (1977), the rate constant for the decomposition of aliphatic $RX^{\dot{-}}M^+$ is 10^{10} s^{-1}.
17. J.F.Garst, Acc.Chem.Res. 4, 400 (1971).
18. J.F.Garst and F.E.Barton II, J.Amer.Chem.Soc. 96, 523 (1974).
19. R.W.Fessenden and R.H.Schuler, J.Chem.Phys. 39, 2147 (1963).
20. T.Kawamura, M.Tsumura, Y.Yokomichi and T.Yonezawa, J.Amer.Chem.Soc. 99, 8251 (1977).