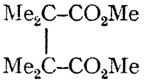
Elucidation of an Electron Transfer Pathway in the Conversion of *vic*-Dibromides to Olefins by Stabilized Carbanions

By DAVID G. KORZAN, FRANCIS CHEN, and C. AINSWORTH*

(*Department of Chemistry, Colorado State University, Fort Collins, Colorado* 80521)

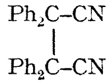
Summary An electron transfer mechanism is indicated, rather than an E_2 pathway, for the formation of olefins from the reaction of *vic*-dibromides and carbanions.

IN recent studies on the alkylation of methyl isobutyrate anion (**1**),† we observed that treatment of (**1**) with 1,2-dibromoethane resulted, not in twofold alkylation, but in the formation of a small amount of the dimer (**2**) and ethylene. The reaction was carried out in refluxing glyme and the major product formed was the self-condensate 3-oxo-2,2,4-trimethylvalerate. The novel formation of (**2**) had an analogy in the work of Kofron and Hauser[1] who reported that more acidic substrates, such as diphenylacetonitrile, could be coupled by various *vic* dihalides in liquid ammonia solutions of potassium amide to give the dimer (**3**). These accounts contain evidence for direct attack of diphenylacetonitrile anion (**4**) at the halogen atom (Scheme 1) with subsequent reaction of (**4**) and (**5**) to form (**3**). A key reaction sequence which these workers[1b] present as evidence for displacement at halogen may, however, be rationalized in terms of an electron-transfer process.



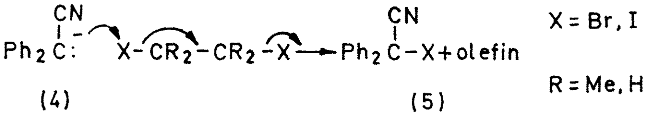
$\mathrm{Me_2C{-}CO_2Me}$ | $\mathrm{Me_2C{-}CO_2Me}$

(2)



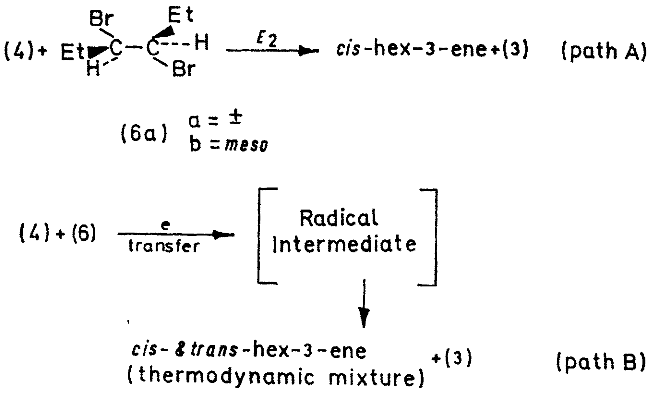
$\mathrm{Ph_2C{-}CN}$ | $\mathrm{Ph_2C{-}CN}$

(3)



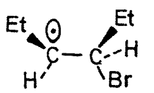
SCHEME 1

Recent literature,[2] however, favours electron transfer pathways in explaining analogous conversions. It was found that the reaction of (**4**) in liquid ammonia with a *vic* dibromide to form (**3**) was entirely quenched by 1 equiv. of *p*-dinitrobenzene, which suggests an electron transfer pathway.[3] Paths A and B (Scheme 2) could be differentiated by the use of (±)-3,4-dibromohexane (**6a**) as the *vic* dihalide.‡ If path A operates as previously assumed,[2] the resulting olefin should be *cis*-hex-3-ene, exclusively.[4] The fact that *cis*- and *trans*-hex-3-ene exhibit markedly different vinylic proton shifts in their n.m.r. spectra permitted the identification of olefin mixtures to within 5%. Addition of (**6a**) to a liquid ammonia solution of (**4**) gave *trans*-hex-3-ene as the *sole* olefinic product. [When (**6b**) was used it also formed exclusively *trans*-olefin. If one assumes no change in mechanism between (**6a**) and (**6b**), *cis*-elimination is ruled out. Also, in a subsequent experiment, *cis*-hex-3-ene was added with (**6a**) to the reaction mixture and found to be stable to the reaction conditions. The alternative possibility that (**6a**) was converted *via* a radical mechanism into (**6b**) seems remote.]

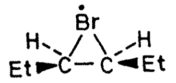


SCHEME 2

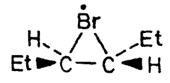
The application of this diagnostic method to the dimerization of (**1**) to form (**2**) gave the same olefin result. Although the absence of *trans*-olefin in these dimerizations would not have precluded path B, the *exclusive* presence of it seems to rule out the stereospecific E_2 mode[4] previously suggested (path A). The exact nature of the electron transfer pathway must explain why the formation of *trans*-olefin should prevail over that of a thermodynamic mixture (*ca.* 60% *trans*-, 40% *cis*-olefin),[5] because inversion–rotation of the planar radical (**7**)§ should compete very effectively with collapse to olefin, or addition of a second electron with concomitant olefin formation.



(7)



(8)



(9)

Skell[6] and others have postulated that α-halogeno radicals exhibit a marked interaction between radicals and halogen atoms which manifests itself in the formation of bridged radicals such as (**8**) and (**9**). We propose that the mixture of (**8**) and (**9**) arising from (**7**) will, in time, equilibrate entirely to the more stable (**9**), such that addition of

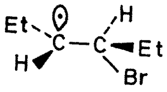
---

† These anions were generated by treating methyl isobutyrate with lithium di-isopropyl amide or trityl sodium.

‡ (±)-3,4-Dibromohexane was prepared by the addition of bromine in carbon tetrachloride to a solution of *cis*-hex-3-ene in carbon tetrachloride.

§ Spin trapping experiments revealed a marked inability for intermediates in these processes to be trapped by nitrosobenzene or nitroso-t-butane (see E. G. Janzen, *Accounts Chem. Res.*, 1971, **4**, 31), nor were CIDNP effects observable (see A. R. Lepley, *J. Amer. Chem. Soc.*, 1968, **90**, 2710).

a second electron will give rise to exclusive formation of *trans*-olefin. (Schubert and his co-workers[4] found that similar reductions of 2,3-dibromobutanes to butenes produce *cis–trans* ratios very similar to ours for hexenes. We found that *cis*-hex-3-ene was not isomerized under the reaction conditions. High dilution experiments involving the reduction of (**6**) with potassium in liquid ammonia have, however, been thwarted by our inability to recover hexenes from large quantities of solvent.) Thus, reagents that are relatively slow to donate a second electron will lead to *trans*-olefin as a sole product. In this connection, we have observed that while sodium or potassium in liquid ammonia reduced (**6**) to a 60:40 *trans*:*cis* thermodynamic mixture of olefins, sodium naphthalenide[8] in diglyme resulted in a 95:5 *trans*:*cis* ratio and the bulky anions (**1**) and (**4**) gave *trans-olefin* exclusively. Thus, *vic* dibromides such as (**6**) may prove to be of utility in the elucidation of sequential electron transfer processes. A referee has suggested that rehybridization of (**7**) forms the more stable (**7a**). The energy difference between (**7**) and (**7a**) would provably be such that a considerable amount of *cis*-isomer would be observed rather than exclusive *trans*. We suggest that the energy difference between (**8**) and (**9**) is of greater order than that of (**7**) and (**7a**), as a result of larger steric interactions in (**8**) compared with (**9**),[8] and that the higher activation energy involving bond-breaking in the interconversion of (**8**) and (**9**) results in a non-mobile equilibrium, in contrast to that between (**7**) and (**7a**).



(7a)

We gratefully acknowledge support of this work by the National Science Foundation. We thank Drs. Larry L. Millerand Frank R. Stermitz for helpful discussions, and Dr. G. E. Gream for an authentic sample of compound (**2**).

(*Received*, *May* 10*th*, 1971; *Com*. 737.)

[1] (a) W. G. Kofron and C. R. Hauser, *J. Org. Chem.*, 1970, **35**, 2085; W. G. Kofron and C. R. Hauser, *J. Amer. Chem. Soc.*, 1968, **90**, 4126; F. H. Rash, S. Boatman, and C. R. Hauser, *J. Org. Chem.*, 1967, **32**, 327; (b) W. G. Kofron and C. R. Hauser, *ibid.*, 1963, **28**,577.

[2] M. J. S. Dewar and J. M. Harris, *J. Amer. Chem. Soc.*, 1969, **91**, 3652; J. Jacobus and D. Pensak, *Chem. Comm.*, 1969, 400; H. M. Walborsky, F. P. Johnson, and J. B. Pierce, *J. Amer. Chem. Soc.*, 1068, **90**, 5222; J. K. Kim and J. F. Bunnett, *ibid.*, 1970, **92**, 7463; N. Kornblum and S. D. Boyd, *ibid.*, 1970, **92**, 5784; J. K. Kochi, *Science*, 1967, **155**, 415; R. N. McDonald and D. G. Frickey, *J. Amer. Chem. Soc.*, 1968, **90**, 5315 found that a *cis*-1,2-dichloride, while inert to most reductive dehalogenation reagents, was converted smoothly into olefin using disodium phenanthrene.

[3] R. C. Kerber, G. W. Urry and N. Kornblum, *J. Amer. Chem. Soc.*, 1965, **87**, 4520.

[4] F. G. Bordwell, *Accounts. Chem. Res.*, 1970, **3**, 281.

[5] W. M. Schubert, B. S. Rabinovitch, N. R. Larson, and V. A. Sims, *J. Amer. Chem. Soc.*, 1952, **74**, 4590.

[6] P. S. Skell and P. D. Readio, *J. Amer. Chem. Soc.*, 1964, **86**, 3334.

[7] The steric repulsion of *cis*-1,2-dimethylcyclopropane compared with *trans*-1,2-dimethylcyclopropane is 1·1 kcal/mol. (M. C. Flowers and H. M. Frey, *Proc Roy. Soc.*, 1960, **A257**, 122.)

[8] J. F. Garst and F. E. Barton, *Tetrahedron Letters*, 1969, 587; G. D. Sargent, J. N. Cron, and S. Bank, *J. Amer. Chem. Soc.* 1966, **88**, 5363.