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REARRANGEMENT OF 2-BROMOTROPONE KETALS[1]

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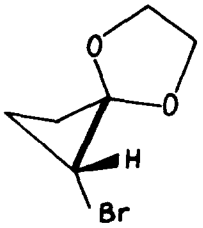
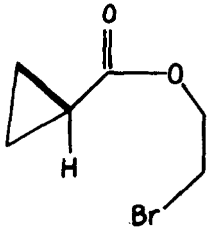
Salaun and Conia (4) have just reported that several 2-bromocyclobutanone ketals rearrange thermally to give cyclopropanecarboxylates and alkyl bromides. The dioxolane I gave 2-bromoethyl cyclopropanecarboxylate (II). The reactions were considered specific for cyclobutyl systems and probably concerted.



I

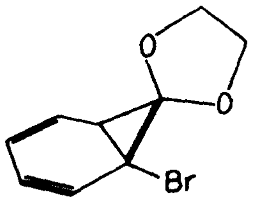


II

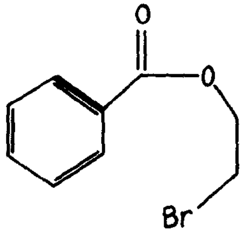
We have observed rearrangements during attempted preparations of 2-bromotropone ketals which are formally analogous.

2-Bromotropone (5), when heated at reflux in benzene containing ethylene glycol or trimethylene glycol and p-toluenesulfonic acid, gave 2-bromoethyl or 3-bromopropyl benzoate, respectively. The rearrangement products were identified through direct spectroscopic comparisons with authentic samples (6,7).

In so far as cyclobutyl systems may be usefully viewed as homocyclopropyl derivatives (8-10), and a norcaradiene valence tautomer (11) of a 2-bromotropone ketal may be considered a likely intermediate for the observed rearrangements (12), the formal analogy is sustained. But can one envisage a concerted valence reorganization giving the conversion III → IV?

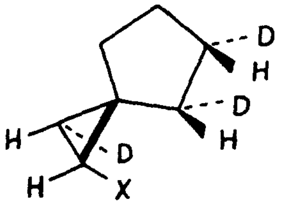


III

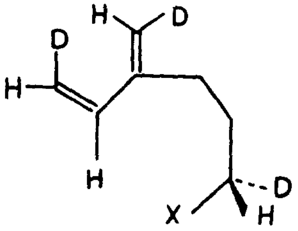


IV

Recent advances in theory relating orbital symmetry with chemical reactivity (13) make it possible to analyze this isomerization and recognize that the geometrical features of the substrate are well suited to accommodate a general but heretofore unproposed 6-electron process, allowed to be concerted with the following stereochemical specificity (V → VI).



V



VI

All ionic mechanisms for the conversion III → IV, including fully intramolecular ion-pair versions, would predict inversion of configuration at the migration terminus. The concerted $(\sigma^2_{\underline{a}} + \sigma^2_{\underline{s}} + \sigma^2_{\underline{a}})$ pathway, however, unambiguously predicts retention at this carbon atom.

Experimental work testing for the intermolecular or intramolecular transfer of halogen, and attempting determination of stereochemistry for such a reaction in appropriate systems, is in progress.

References

1. Supported in part by the National Science Foundation and a DuPont Grant-in-Aid.
2. Alfred P. Sloan Foundation Fellow; address inquiries to the Department of Chemistry, University of Oregon, Eugene, Oregon 97403.

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