Unusual Product Distributions in the Dehydrobrominations of Dibromomethylcyclohexanes

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Summary Dehydrobromination of either 1,2-dibromo-1-methylcyclohexane or 1,2-dibromo-4-methylcyclohexane, in a bis-(2-methoxyethyl) ether–sodium methoxide mixture, produces products unusually rich in the exocyclic isomer 3-methylenecyclohexene.

RECENTLY we investigated various base-catalysed elimination reactions as possible routes to alkylcyclohexa-1,3-dienes. A particularly attractive pathway would be the double dehydrohalogenation of an alkyldibromocyclohexane, if the direction of elimination could be controlled. Dehydrobromination of dibromomethylcyclohexanes in the usual alcohol–alkoxide media yields alkoxycyclohexenes;[1,2] however, Schaefer and Endres have shown that alkoxides in aprotic solvents can effect the double dehydrobromination of 1,2-dibromocyclohexane to cyclohexa-1,3-diene in good yield. This latter method has the additional advantage that volatile dienes can be flash distilled under reduced pressure from the hot reaction media as they are formed, thus reducing the base-catalysed isomerization of the product diene.

r-1,*c*-2-Dibromo-*t*-4-methylcyclohexane (A) and *r*-1,*c*-2-dibromo-*t*-1-methylcyclohexane (B) were dehydrobrominated essentially by the method of Schaefer and Endres[3] by addition of the dibromide to a bis-(2-methoxyethyl) ether or 1,2-bis-(2-methoxyethoxy)ethane solution of sodium methoxide at 110—115° and 20 mmHg. The diene product was trapped in a Dry Ice–acetone bath as it was flash distilled and was immediately analysed by g.l.c. and u.v. and n.m.r. spectroscopy. The results are shown in Table 1.

TABLE 1

Dehydrobromination products

		% of total product				
Compound	Yield (%)	(1)	(2)	(3)	(4)	(5)
(A)	81	15·8	1·8	1·6	78·7	2·1
(B)	70	0·0	15·7	2·5	77·1	4·7

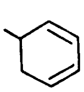
The predominance of 3-methylenecyclohexene in both product mixtures was quite unexpected, since previous studies of base-catalysed isomerizations in the methylcyclohexene system indicate that endocyclic configurations are preferred (>98%).[4,5] However, Bank *et al.*[6] have more recently shown that exocyclic products may result from base-catalysed reactions and in some cases predominate Thus they obtained a 40% yield of ethylidenecyclohexene from 4-vinylcyclohexene by reaction with potassium t-butoxide in DMSO. If we were indeed observing the end result of a base-catalysed isomerization of our initially formed methylcyclohexa-1,3-dienes, then the same reaction should be observable for any mixture of methylcyclohexa-1,3-dienes independent of source. We therefore submitted a mixture of known composition to a variety of conditions, approximating both our reaction conditions and also those of strong base catalysis. These results are shown in Table 2.

TABLE 2

Base-catalysed isomerization of methylcyclohexa-1,3-*dienes*

Reaction conditions	% of total product (1)	(2)	(3)	(4)
Initial mixture	14·8	25·0	45·0	15·2
NaOMe; 110—115°;[a] 20 mmHg; distilled ..	14·4	22·7	40·4	22·5
NaOMe–MeOH;[b] reflux 3 h ..	10·8	25·8	44·7	18·7
NaOMe–MeOH;[b] reflux 6 h ..	6·8	19·6	32·6	41·0

[a] Reaction conditions and solvent identical to those employed for dehydrobromination. [b] Diene mixture (2 g) MeOH, (10 ml) NaOMe (1 g).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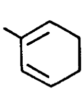
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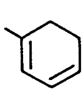
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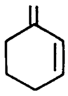
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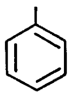
(5)

These results clearly show that, while base-catalysed isomerization to 3-methylenecyclohexene occurs, the relative rate of this process cannot immediately account for the large preponderance of the exocyclic isomer. We interpret this result as being indicative of more than one reaction pathway leading to the exocyclic diene.

One possible alternative to base-catalysed isomerization of the intermediate endocyclic dienes, proceeding through a set of equilibrating carbanions, arises from the observation that alkoxycyclohexenes are obtained from alkoxide–alcohol media. Bromocyclohexenes are probably intermediates in a stepwise dehydrobromination sequence. Under the Schaefer–Endres conditions, ionization and carbonium ion rearrangement *via* intramolecular hydride shifts, followed by proton abstraction by alkoxide ion may occur; however, it is more likely that base-catalysed isomerization of the intermediate bromocyclohexenes is responsible for the rapidity of the reaction. Bates and his co-workers[7] have shown that such pathways are operative in the *p*-menthadiene system, and further, that carbonium ion and carbanion pathways will yield similar product distributions.

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