$\overrightarrow{E}C\overleftarrow{E}$-Catalysed Isomerisation of Quadricyclanes

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Quadricyclane (**1a**) as well as its 3-substituted derivatives were rapidly isomerized to norbornadiene (**2a**) and the corresponding derivatives by the action of catalytic amounts of tris-(*p*-bromophenyl)ammoniumyl salts (**5**).

The catalysed isomerisation of quadricyclane (**1**) to norbornadiene (**2**) has found recent attention in connection with the storage of solar energy.[1] A wide variety of catalysts, be it Lewis acids[2] or transition metal compounds,[3] have been shown to be effective. Even if the nature of the catalysis is not fully understood, it is obvious that the catalyst has to interact with the strained σ-bonds of (**1**). Hence it is not surprising that those quadricyclanes which carried substituents capable of donor interactions with Lewis acids or transition metals, *e.g.* (**1c**, **e**, **f**), turned out to be refractory in such isomerisations. This became clear to us in a study devoted to the synthesis of 7-substituted norbornadienes; it was apparent that a different type of catalysis was required. We report here that $\overrightarrow{E}C\overleftarrow{E}$-catalysis[4] by tris-(*p*-bromophenyl)ammoniumyl salts is effective in some such cases.

The radical cation (**3**) of (**1**) is known to isomerise spontaneously to the radical cation (**4**) of (**2**).[5] This isomerisation has

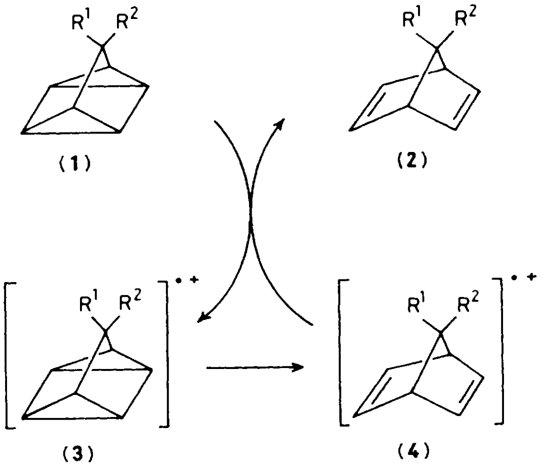

Table 1. Catalytic conversion of the quadricyclanes (**1**)[12] into the norbornadienes (**2**).

(**1**)	R^1	R^2	Equiv. of catalysts	Reaction time at 25 °C	% Conversion into (**2**) (by n.m.r.)
a	H	H	0.01, (**5a**)	10 min	100
			0.10, (**5b**)	10 min	70
			0.01, (**6a**)	1 h	94
			0.10, (**6b**)	2 days	0
b	H	OBu^t	0.01, (**5a**)	20 h	100
			0.01, (**6a**)	5 days	88
c	$-S-CH_2-CH_2-S-$		0.022, (**5a**)	24 h	100
			0.05, (**6a**)	5 days	98
d	H	CN	0.10, (**6a**)	10 days	100
e	NMe_2	CN	0.10, (**6a**)	7 days	37
f	N=CHPh	CN	0.10, (**6a**)	6 days	32

been observed during the quenching of excited acceptor molecules by quadricyclane.[6] The known oxidation potentials of (**1a**) (+0.91 V, *vs.* saturated calomel electrode, S.C.E.) and (**2a**) (+1.56 V, *vs.* S.C.E.)[7] suggested that this isomerisation could be catalysed in an $\overrightarrow{\mathrm{E}}\mathrm{C}\overleftarrow{\mathrm{E}}$-process by an oxidant of intermediate oxidation potential.[8]

$(p\text{-}BrC_6H_4)_3N^{\cdot +}\ X^-$ (**5**)

$Ph_3\overset{+}{P}Me\ X^-$ (**6**)

a; X = $SbCl_6$
b; X = $GaCl_4$

This was put to practice by the interaction of (**1a**) (0.6 M solution in CH_2Cl_2) with 0.01 equiv. of (**5a**) (+1.05 V, *vs.* S.C.E.)[9] resulting in an exothermic conversion into (**2a**). Further examples are in Table 1. This reaction could easily be extended to (**1c**) without interference from the dithiolan group.[10] The catalytic activity is not solely connected with the cationic portion of (**5**), but also with the hexachloroantimonate[11] anion; the phosphonium salt (**6a**) was also active, but to a smaller extent, in a number of cases, *cf.* Table 1. In consequence the tetrachlorogallate (**5b**) turned out to be less active than (**5a**), whereas (**6b**) was inactive as expected. Although not proven by our experiments, these isomerisations are most readily accounted for in terms of an $\overrightarrow{\mathrm{E}}\mathrm{C}\overleftarrow{\mathrm{E}}$-reaction[4] *via* (**3**) and (**4**).

This study was supported by the Fonds der Chemischen Industrie and by a fellowship to W.B. by the Friedrich-Ebert-Stiftung. We also thank the Deutsche Shell Chemie GmbH for generous gifts of chemicals.

Received, 13th January 1983; Com. 066

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