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PHOTOINDUCED IRREVERSIBLE HYDROGEN TRANSFER IN CHLORINATED TETRAHYDROMETHANOINDANES

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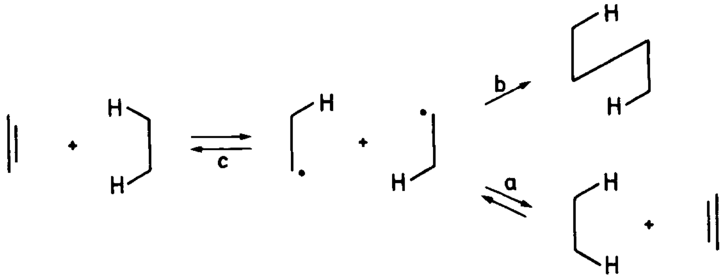
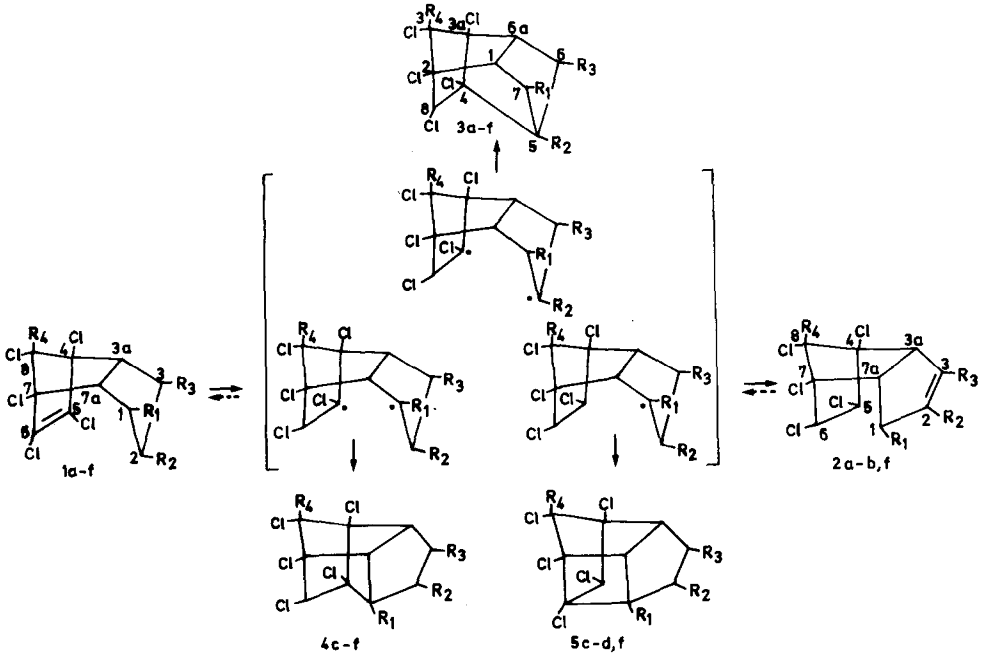
Displacements of two hydrogen atoms from alkanes to alkenes are seldomly observed in non-concerted processes (path a) because the biradicals formed in the first step of the reaction recombine preferentially (path b). Quite fundamentally, the thusly formed new alkene-alkane pair may also be expected to undergo a back-reaction to the starting compounds (path c)[1].



We have shown in an earlier communication that 4,5,6,7,8,8-hexachloro-2,3,3a,4,7,7a-hexahydro-4,7-methano-1H-indene-1,3-dicarboxylic acid dimethylester (1f) at -70° C [69.2 kcal/mole $< E_T <$ 76.3 kcal/mole] reacts exclusively to dimethyl 4,5,6,7,8,8-hexachloro-3a,4,5,6,7,7a-hexahydro-4,7-methano-1H-indene-1,3-dicarboxylate (2f) on UV-irradiation[1,2]. This compound, which is denoted as the hydrogen transfer product, isomerises photochemically above -30° C back to the starting compound (1f). Measurements of the quantum yield ($\Phi_{1\rightarrow2} = 1.983 \cdot 10^{-2}$; $\Phi_{2\rightarrow1} = 0.0438 \cdot 10^{-2}$) indicate that the equilibrium ($1f \rightleftharpoons 2f$) is displaced in favour of compound 2f.

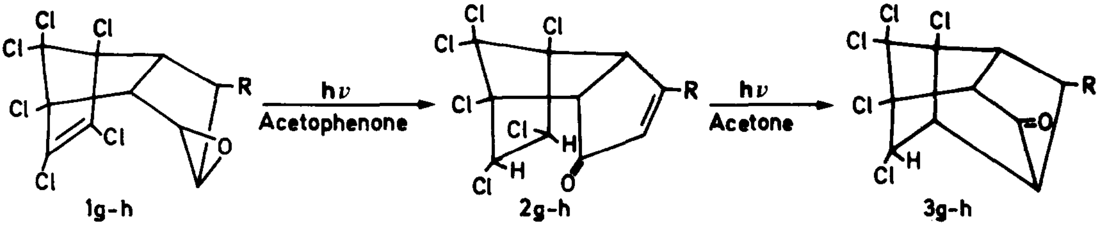
Our new investigations show that the double hydrogen transfers can also proceed in other chlorinated tetrahydromethanoindanes. Thus, on sensitised UV-irradiation compounds 1a and 1b form the hydrogen transfer products in good yield, but unlike compound 2f, they



Compound	R_1	R_2	R_3	R_4
1a-2a-3a	H	H	H	H
1b-2b-3b	H	H	H	Cl
1c-3c-4c-5c	H	H	Cl	Cl
1d-3d-4d-5d	Cl	Cl	H	Cl
1e-3e-4e	Cl	Cl	Cl	Cl
1f-2f-3f-4f-5f	CO_2CH_3	H	CO_2CH_3	Cl

do not rearrange back to the starting products. The reason for this can be seen in the triplet energy transfer which cannot be brought about in the case of compounds 2a-b. The (πσ→2σ) reaction[4,5], which ensues as the main reaction on UV-irradiation of compounds 1c-e, is observed as a concurrent step. It may be formulated as an intramolecular abstraction of one of the endo hydrogen atoms from the excited chlorinated double bond and subsequent C-C bond formation. Product analyses carried out by means of combined gas chromatography and mass spectrometry indicate that the last-named compounds do not react to the expected hydrogen transfer products but react directly to the bridged photoisomers (3a-e, 4c-e and 5c-d).

For the epoxides 1g-h the double hydrogen transfer takes place under epoxide-keton rearrangement. In this way, the reaction step (1⇄2) becomes irreversible. The bridged compounds 3g-h are obtained via (πσ→2σ) reaction of 2g-h. As we were able to show, the lowest triplet states of the α,β-unsaturated ketones (2g-h) lie at above 80 kcal.



Compound	R
1g-2g-3g	H
1h-2h-3h	Cl

Thus, with acetophenone as sensitiser only the chlorinated double bond in 1g-h can be excited, which leads exclusively to the formation of the hydrogen transfer products 2g-h. The acetone-sensitised photoreactions, however, also yield the compounds 3g-h.

Formation of both the hydrogen transfer products (2a-b and 2f-h) and of the photoisomers (3a-h, 4c-e and 5c-d) is strictly intramolecular. UV-irradiation of compounds 1b, 1c, 1f and 1g in D_6-acetone shows that no deuterium was incorporated in the respective products. Furthermore, in the case of compound 1b deuterium labelling of the 2-endo hydrogen atom confirmed the intramolecularity of the reaction. The compounds 2b and 3b isolated after this irradiation contain deuterium atoms in the expected positions (~44% on the C_5 and C_6 of compound 2b and ~99% on the C_8 of compound 3b). The structure proposals for the photoproducts are based on spectroscopic data (see Table 1). Thus, the cis-endo position of protons H_5 and H_6 was confirmed by the M-coupling (J = 1.2 Hz) with proton H_8.

A borosilicate glass apparatus (170 ml) was used for the irradiations; a Philips HPK 125 W high pressure mercury lamp served as the light source. Isolation of the photoproducts proceeded by means of column chromatography (Merck 0.2 - 0.06 silica gel).5:1 n-hexane-acetone was used as the developer for separating 2h, 3h and 2g, 3g and n-hexane was used for the other compounds.

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Table 1. Physical and Spectroscopic Data

Comp.	Mp (C°)	Irra. time (h)	Yield (%)	m/e (rel.Int.%) (Cl=35)	IR (KBr)cm^{-1}	^{1}H-NMR (CDCl$_3$) (ppm)
2a	145	16	33	$M^{+\cdot}$, 304 (6) M-Cl $^{+\cdot}$,269 (100)	3030, 1460	2H(5.7-5.9,m);1H(4.6,d); 1H(4.3,dd);1H(4.5,d);2H (2.8,m);2H(1.8-2.4o,m)
2b	101	16	35	$M^{+\cdot}$, 338 (10) M-Cl $^{+\cdot}$,333(100)	3030, 1455	1H(4.5,d);1H(4.3,d); 2H(2.7,m);2H(1.75-2.40,m)
2g	80	6	78	M^{+},352 (3) M-Cl-HCl $^{+}$, 281 (100)	3050 1705	1H(7.7,dd);1H(6.4,dd); 2H(4.3,s);1H(4.0,m); 1H(3.4,d)
2h	250	14	30	M^{+},386 (20) M-Cl $^{+}$,351 (100)	3030, 1710	1H(6.3,d);2H(4.4,s); 1H(4.07,dd);1H(3.6,d)
3a	174	16	30	M^{+},304 (70) M-Cl $^{+}$,269 (100)	2970 1495	1H(4.6,dd);1H(4.35,dd); 3H(2.7,m);4H(1.7-2.4,m)
3b	130	16	24	M^{+},338 (20) M-Cl $^{+}$,333 (100)	2990 1450	1H(4.4,s);3H(2.8,m); 4H(1.6-2.4,m)
3c	151	8	70	M^{+},372 (19) M-Cl $^{+}$,337 (100)	2990 1450	1H(4.8,s);1H(4.3,dd) 3H(3.5,m);2H(2.6-1.5,m)
3d	-	8	53	M^{+},406 (16) M-Cl $^{+}$, 371 (100)	2990, 1445	1H(4.9,s);1H(4.7,d); 2H(3.4-3.0,m);1H(2.9,dd) 1H(2.30,dd)
3e	73	36	41	M^{+},440 (18) M-Cl $^{+}$,405 (100)	2990	1H(4.9,s);1H(4.6,d); 1H(4.3,m);2H(3.4-3.0,m)
3g	78	6	15	M-Cl $^{+}$,371(100) M-Cl-C=0 $^{+}$, 289 (30)	1760, 1450	1H(4.7,s);1H(3.4,m); 2H(3.1,m);1H(2.5,dd); 1H(1.7,dd)
3h	225	14	12	M-Cl $^{+}$,351(100) M-Cl-C=0 $^{+}$, 323 (40)	1770	1H(4.6,s);1H(3.6,m) 3H(3.2-3.0,m)
4c	-	8	10	M^{+},372 (20) M-Cl $^{+}$,337 (100)	2885	1H(4.6,s);1H(4.1,m); 3H(3.7,m)
4d	138	8	10	M^{+},406 (12) M-Cl^{+} ,371 (100)	2980	1H(2.3,ddd);1H(2.8,ddd); 1H(3.4,d);1H(3.9,ddd); 1H(4.5,dd);1H(6.4,s)
4e	120	36	5	M^{+},440 (10) M-Cl $^{+}$,405 (100)	2990	1H(4.9,s);1H(4.5,d); 1H(4.3,d);1H(3.7,d); 1H(3.3,dd)
5c	113	8	7	M^{+},372 (30) M-Cl $^{+}$,337 (100)	2995	1H(4.8,s);1H(3.9,m); 3H(3.8-3.3,m),2H(2.5-1.6,m)
5d	-	8	1	M^{+}, 406 (15) M-Cl $^{+}$,371 (100)	2985 1445	---