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Photochemical Cleavage of Ethers and Alkylation of Benzylic Alcohols with Trialkylaluminium Compounds

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Summary Upon irradiation in the presence of trialkylaluminiums, various ethers are cleaved and the hydroxy-group of benzylic alcohols can be replaced by alkyl groups.

ETHERS are known to form thermally stable 1 : 1 complexes with organoaluminium compounds.[1] We have found that irradiation of the complexes between ethers and trialkylaluminiums in benzene or cyclohexane causes cleavage of the ether linkage at room temperature according to equation (1).

$$\underset{\downarrow \, AlR^2_3}{R^1\text{–}O\text{–}R^1} \xrightarrow[C_6H_6 \text{ or } C_6H_{12}]{h\nu} R^1\text{–}H + R^1\text{–}R^2 + R^1\text{–}OH \quad (1)$$

$$(R^1 = \text{alkyl or aryl, } R^2 = \text{alkyl})$$

Irradiation was carried out under nitrogen using a 300 W high-pressure mercury lamp with a quartz housing. Both aliphatic and aromatic ethers were cleaved by Et_3Al (Table 1). Di-*p*-tolyl ether reacted twice as fast as bis-2-phenylethyl ether in a competitive experiment.[2] The rates of the reaction in cyclohexane were comparable to those in benzene.

The case of alkyl aryl ethers (Table 2) is interesting. While benzyl phenyl ether was cleaved by Et_3Al exclusively at the benzylic carbon–oxygen bond, aryl-oxygen bond fission was observed with 2-phenylethyl *p*-tolyl ether at least to an equal extent as alkyl-oxygen bond scission. Moreover, anisoles were cleaved predominantly at the aryl–oxygen bond. Thermal cleavage of simple alkyl aryl ethers with organometallic compounds has hitherto occurred exclusively or almost exclusively at the alkyl–oxygen linkage.[2,3] The present reaction thus constitutes a particularly simple example of preferential displacement on benzene ring carbon atoms in 'unactivated' alkyl aryl ethers. It was not expected that reduction products (ArH) would be obtained together with the normal methylated products (ArMe), from the reaction of substituted anisoles (ArOMe) with Me_3Al.

TABLE 1

Photo-cleavage of diaryl and dialkyl ethers by Et_3Al[a]

		Products (mol %)[b]		
R in R_2O	Solvent	RH	REt	ROH
Ph ..	.. C_6H_6	—	13	91
p-Tolyl ..	.. C_6H_6	54	19	88
p-Tolyl ..	.. C_6H_{12}	54	19	80
$PhCH_2CH_2$	.. C_6H_6	19	22	50
$PhCH_2CH_2$	.. C_6H_{12}	17	31	65
n-Octyl ..	.. C_6H_6	26	39	69
n-Octyl ..	.. C_6H_{12}	33	49	95

[a] A solution of the ether (2·2—3·0 mmol) and Et_3Al (1·0—1·2 mol. equiv.) in 20 ml of solvent was irradiated for 48—73 h. The ethers were consumed almost completely. [b] Yields are based on the consumed ether.

The ethers could also be cleaved photochemically by Et_2AlCl or $EtAlCl_2$ but the reaction was shown to be rather

TABLE 2

Photo-cleavage of alkyl aryl ethers (R^1OAr) by trialkylaluminiums (R^2_3Al) in benzene[a]

Ether	R^2 in R^2_3Al	Products from R^1–O bond fission (%)[b]			Products from Ar–O bond fission (%)[b]		
		R^1H	R^1R^2	ArOH	ArH	ArR^2	R^1OH
$PhCH_2OPh$	Et	6	37	65	—	0	0
2-Phenylethyl *p*-tolyl ether	Et	12	8	13	22	15	21
2-Phenylethyl *p*-tolyl ether[c]	Et	9	11	21	16	21	36
p-Methylanisole	Et	N.D.[d]	N.D.	2	33	25	N.D.
p-Methylanisole	Me	N.D.	N.D.	5	17	32	N.D.
1,2,4-Trimethylanisole	Et	N.D.	N.D.	7	21	33	N.D.

[a] Irradiation was carried out similarly to that of the symmetric ethers. [b] Yields are based on the consumed ether. [c] In cyclohexane. [d] Not determined.

complicated. The reported photorearrangements[4] of some of the aromatic ethers used were slow in solution and the formation of the rearranged products was in any case negligible in the presence of the trialkylaluminiums.

TABLE 3

Photodecomposition of benzyl alcohols with trialkylaluminiums[a]

$$R^1OH + R^2_3Al \longrightarrow R^1OAlR^2_2 \xrightarrow{h\nu} R^1R^2 + R^1H$$

R^1OH	R^2_3Al	Products (%)[b] R^1R^2	R^1H
Benzyl alcohol	Me_3Al[c]	65	—
Benzyl alcohol	Et_3Al	60	19
Benzyl alcohol	Bu^i_3Al	83	11
2-Phenylethyl alcohol	Et_3Al	65	18
Diphenylmethanol	Me_3Al[d]	67	—
Diphenylmethanol	Et_3Al	60	15
Diphenylmethanol[e]	Bu^i_3Al	59	7·9

[a] An equimolar mixture of the benzyl alcohol and the trialkylaluminium in dry benzene (0·10M) was irradiated for *ca.* 30 h. Starting alcohols were almost completely consumed unless otherwise stated. [b] Yields are based on the consumed alcohol. [c] Irradiated for 55 h (37% conversion). [d] Irradiated for 54 h (20% conversion). [e] Thermal reaction at 150° gave R^1R^2 (32%) and R^1H (36%).

Photocleavage of dibenzyl ether by Et_3Al yielded > 1 mol. equiv. of n-propylbenzene per mol. equiv. of the ether consumed while benzyl alcohol was not found. It was assumed that benzyl alcohol (as its aluminium alcoholate) decomposes further under the reaction conditions to give n-propylbenzene and toluene also. In fact, benzene solutions of dialkylaluminium alcoholates prepared *in situ* from benzyl alcohols and trialkylaluminiums were shown to be unstable photochemically and the expected alkylation and reduction products were obtained (Table 3).

This anomalous deoxyalkylation is similar to the analogous thermal alkylation of alcohols by trialkylaluminiums,[5] but there are some differences. Firstly, photochemical alkylation can be applied only to benzylic alcohols, although tertiary alcohols as well as benzylic alcohols have been reported to be alkylated thermally. Secondly, use of 2 mol. equiv. of Me_3Al per mol. equiv. of alcohol with an acid catalyst has been recommended for the thermal alkylation, while addition of 1 mol. equiv. of aluminium components without catalyst is satisfactory for photoalkylation. Thirdly, the order of reactivity of the aluminium compounds in the photochemical reaction (Bu^i_3Al, $Et_3Al > Me_3Al$; Table 3) is reversed in the thermal reaction ($Me_3Al > Et_3Al > Bu^i_3Al$).

It has been suggested that thermal fission of the alkyl–oxygen bonds of the aluminium alcoholates is ionic in nature.[5] In our reactions, homolytic scission of the benzylic carbon–oxygen bonds may occur since products of coupling of the benzyl radicals (1,2-diphenylethanes) were always obtained in low yield as side-products in place of the products of Friedel–Crafts alkylation of benzene solvent.[6]

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