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EVIDENCE FOR SINGLE ELECTRON TRANSFER IN THE REACTION OF ALKOXIDES WITH ALKYL HALIDES

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Abstract: Evidence for a radical process in the reaction of lithium alkoxides with alkyl iodides was obtained by the observation of cyclization of appropriate radical probes, by the trapping of radicals, and by EPR spectroscopic observations relating to the one electron donor properties of alkoxides.

In recent years the occurence of a single electron transfer (SET) mechanism has been demonstrated in a variety of organic reactions involving main group organometallic and metal hydride compounds.[1] Although metal alkoxides are very common reagents, such species have not been studied in much detail with regard to the possible occurrence of SET pathways[2]. Since the substitution reaction involving an alkyl halide and a metal alkoxide is one of the most classic examples of an S_N2 process, we decided to study this reaction in detail in order to determine if SET is involved. Herein we now present the results of studies which indicate that a lithium alkoxide can react with a 1° alkyl iodide by a SET pathway.

We, and others, have shown previously that perylene,[3] p-dinitrobenzene[4] and benzophenone[5] are excellent spectroscopic probes for the detection of SET. When $LiOPr^i$ was allowed to react with the above substrates in THF-10% HMPA, well defined EPR spectra were observed in each case which were consistent with the known spectra of the corresponding substrate radical anions (eq. 1). Thus, these EPR observations provide strong indications that $LiOPr^i$ can serve as a one electron donor toward organic substrates.

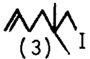
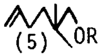
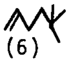
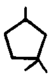
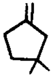
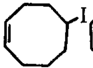
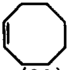
$$LiOPr^i + \text{Perylene} \xrightarrow{\text{THF-10\%/HMPA}} [\text{Perylene}]^{\dot{-}} + [LiOPr^i]^{\dot{+}} \quad (1)$$

Having established that alkoxides can function as one electron donors toward various organic substrates, we decided to react alkoxides with alkyl halides and look for evidence of electron transfer. Since alkyl halides which contain a 5-hexenyl group have been found previously to be good probes for SET by exhibiting characteristic radical cyclization[6], the reactions of $LiOPr^i$ (1) and $LiOBu^t$ (2) with such alkyl iodide radical probes were examined and the results are given in Table I.

The reaction of $LiOPr^i$ with the radical probe compound 2,2-dimethyl-1-iodo-5-hexene[7] (3) was studied in detail, since this probe has the extra added feature of not being able to undergo elimination. The results of exp. 1 show that 1 reacts slowly with 3 in HMPA solvent

Table I

Reaction of 1^o and 2^o Alkyl Iodide Radical Probes with Lithium Alkoxides in HMPA and THF

Exp.	Substrate	LiOR (mol. equiv.)	Additive (mol. equiv.)	Solvent	Time	Products (%)^a  (3)	 (5)	 (6)	 (7)	 (8)
1	, (3)	$3LiOPr^i$, (1)	0.0	HMPA	23 days	30	28	0.0	13	17
2	3	3 1	1 DCPH	HMPA	1 hr.	1.0	0.0	2.0	91	2.0
3	3	3 1	1 DCPD	HMPA	1 hr.	0.0	0.0	1.0	92.7 (74%-d_1)	5.4
4	3	0.1 1	10 DCPH	HMPA	48 hrs.	84	0.0	0.0	9.0	0.0
5	3	3 1	1.5 DCPH 0.17 9	HMPA	2 hrs.	40.3	0.0	0.6	48.8	1.0
6	3	3 1	0.0	THF	48 hrs.	99	0.0	0.0	0.0	0.0
7	3	3 1	1 DCPH	THF	27 hrs.	73	0.0	0.0	22	0.0
8	3	$3LiOBu^t$, (2)	0.0	HMPA	14 days	65	0	trace	11.2	14.0
9	3	3 2	1.1 DCPH	HMPA	1 hr.	0.0	0.0	6.4	78.5	1.0
10	3	3 2	1.5 DCPD	HMPA	1 hr.	0.0	0.0	1.5 100%-d_1	87.5 97%-d_1	trace
						 (4)	 (10)	 (11)	Cyclooctadienes (12)	
11	, (4)	3 1	0.0	THF-10%HMPA	2 days	1.0	4.2	0.0	88.8	
12	4	3 1	1.3 DCPH	THF-10%HMPA	2 hrs.	0.0	85.6	trace	7.0	
13	4	3 1	1.5 DCPD	THF-10%HMPA	2 hrs.	0.0	55.8 (25%-d_1)	1.0	33.6	
14	4	3 2	0.0	THF-10%HMPA	2 days	14.8	3.9	0.0	78.3	
15	4	3 2	5 DCPH	THF-10%HMPA	2 hrs.	0.0	55.2	trace	34.2	
16	4	3 2	1.5 DCPD	THF-10%HMPA	2 hrs.	5.6	27.6 (69%-d_1)	1.0	60.1	
17	4	3 1	5 DCPH	THF	2 days	46.7	38.9	2.3	7.4	

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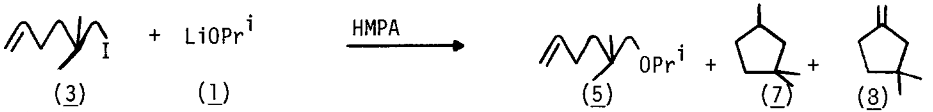
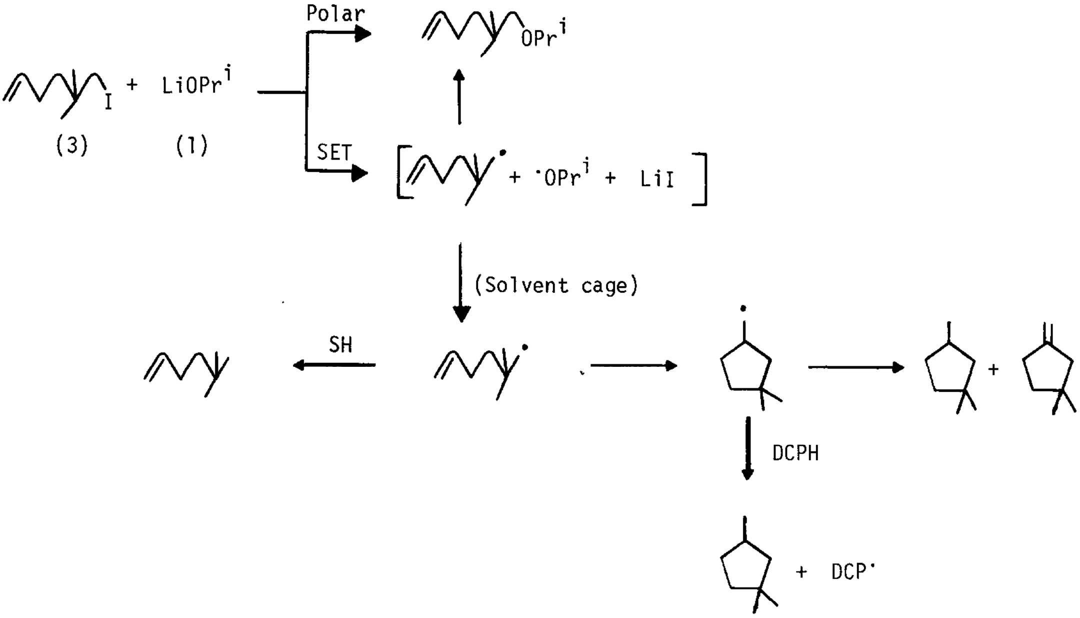
a) Yields were determined by GLC using internal standards. Alkoxides were prepared from n-BuLi and an excess of the corresponding alcohols in hexane, followed by removal of hexane and alcohols under vacuum. All new compounds gave satisfactory analyses.

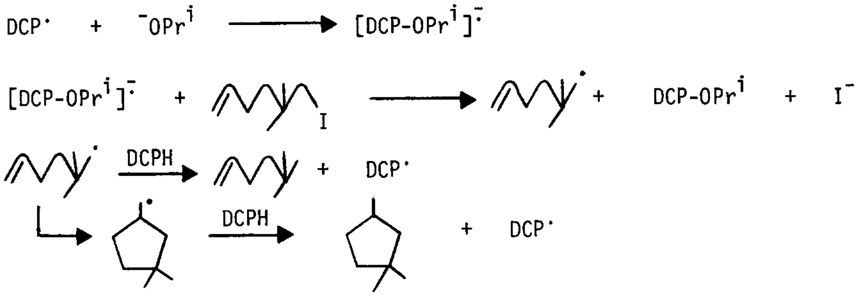
to form 2,2-dimethyl-5-hexenylisopropyl ether (5), 1,1,3-trimethylcyclopentane (7) and methylene-3,3-dimethylcyclopentane (8) (eq. 2). The formation of the cyclic hydrocarbons (7 and 8) is highly suggestive of a radical intermediate which undergoes disproportionation. The observation of a high yield of (7) (91%) when 1 was allowed to react with 3 in the presence of the radical trap dicyclohexylphosphine[8-9] (DCPH) (exp. 2) provides convincing evidence that DCPH is trapping the radical intermediate even before it can form the normal substitution product (5). It is very interesting that DCPH does not just simply act as a hydrogen atom donor, but also speeds up the reaction rate dramatically. We have found that a significant amount of the by-product, identified as $(C_6H_{11})_2P\text{-}OPr^i$, was formed in the reaction of 1 with 3 in the presence of DCPH and the rate of this reaction was retarded by the presence of the radical anion scavenger[10] [p-dinitrobenzene (9)] (exp. 5). Thus, it appears that a radical intermediate is formed in the reaction of 1 with 3 and an additional $S_{RN}1$ chain process is induced by the presence of DCPH (Scheme I). In addition, several control experiments were carried out to rule out other possibilities.



(2)

Scheme I





In order to increase the scope of these studies, the reactions of 2 with 3 were also examined (exps. 8-10). We found that a total of 25% of 7 and 8, but no substitution product (5), was formed in the absence of additive (exp. 8). The lack of substitution products is probably due to the increased steric hinderance of the alkoxide. Next, we focused on the reactions of 5-iodo-1-cyclooctene (4) with 1 and 2 (exps. 11-17). In both cases, varying amounts of hydrocarbon products were formed on addition of the alkoxide alone or on addition of alkoxide and additive. Again, these results show that the reaction of alkoxides (1 and 2) with alkyl iodide involves the formation of a radical intermediate which leads to the formation of hydrocarbons 10 and 11.

Thus, in addition to the well known S_N2 pathway for reactions of alkoxides with alkyl halides these studies suggest the involvement of radical intermediates in reactions involving 1° alkyl iodides and in this particular case, a sterically hindered 1° alkyl iodide in which a competing S_N2 pathway is discouraged. We are now pursuing further studies concerning the steric effect in the reactions of alkoxides with a wide variety of alkyl halides.[11]

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