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REDUCTION OF AROMATIC KETONES BY SOME RARE EARTH METALS IN ETHER. REVERSIBILITY OF THE REDUCTION STEPS.

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ABSTRACT : *The reaction of aromatic ketones with rare earth metals in 1,2-dimethoxyethane produces, by hydrolysis, the corresponding alcohols, pinacols and hydrocarbons depending on the metal, the ketone and the molar ratio of the reactants. The formation of the various reduced products is reversible.*

We recently reported that samarium and ytterbium, in a similar way to e.g. magnesium react in ethers with unsaturated hydrocarbons such as anthracene, producing dianionic species [1]. Now it has been found that organic compounds with higher electron affinities react not only with samarium but also with other rare earth metals such as cerium, gadolinium and neodymium. The reactivity of aromatic ketones is all the more interesting in that, similar to the alkali metals, one or two reduction products can form [2].

The reduction state depends not only on the metal:ketone molar ratio as demonstrated by Fujiwara for ytterbium [3], but also on the reaction time, the nature of the ketone and the metal. In fact, a reversible equilibrium exists between the ketone, its radical-anion, its dianion and a higher reduced species.

In this present work the reduced species were characterized after hydrolysis, the anion-radical producing the pinacol, the dianon the alcohol.

RESULTS AND DISCUSSION.

The results we obtained with benzophenone are given in table I.

In the presence of an excess of samarium and neodymium (runs 1,5) benzhydrol practicaly forms quantitatively. However as observed at shorter reaction times, the kinetic product is the radical-anion.

For ytterbium, cerium and gadolinium in our conditions the reaction attains a lower conversion (runs 7, 9, 10).

In the presence of an excess of ketone (runs 2, 6, 8), all three species were present.

In experiments 3 and 4, samarium and benzophenone were first reacted in the given molar ratio for one day. After this initial reaction period a sufficient amount of one of the two reactants was added so as to obtain the reverse molar ratio. The results prove that the electronic transfer step (step "a" ; scheme I) is reversible.

In order to demonstrate the reversibility of the coupling reaction (step "b" ; scheme I), we tried to prepare the Sm^{II} benzopinacolate directly. We first synthesized the soluble 1,8-dihexylanthracene-samarium by reacting an excess of powdered metal with the aromatic hydrocarbon. Then the excess metal was filtered out and the blue solution was reacted with a stoicheometric amount of benzopinacol. The coloration immediately turned brown. After a one day reaction time at room temperature hydrolysis provided the expected products for the reversible reaction (benzhydrol, benzophenone) and some 9,10-dihydro 1,8-dihexylanthracene. However the absence of any pinacol and the presence of 1,8-dihexylanthracene proved that, besides the expected alcoholysis of the anthracene-samarium adduct, an electron transfer probably produces benzhydrol directly. A similar electron transfer was observed by B. Bogdanovic[4] and C.L. Raston[5] by reacting magnesium anthracene with, e.g. some halogenated compounds.

Fluorenone reacts in a similar way (Table 2). In the presence of an an excess of samarium and ytterbium (runs 13,16), not only fluorenol formed, but also fluorene, the product of reductive deoxygenation. In these reactions the anion-radical forms first, then the dianion and lastly the tetranegative species (run 11).

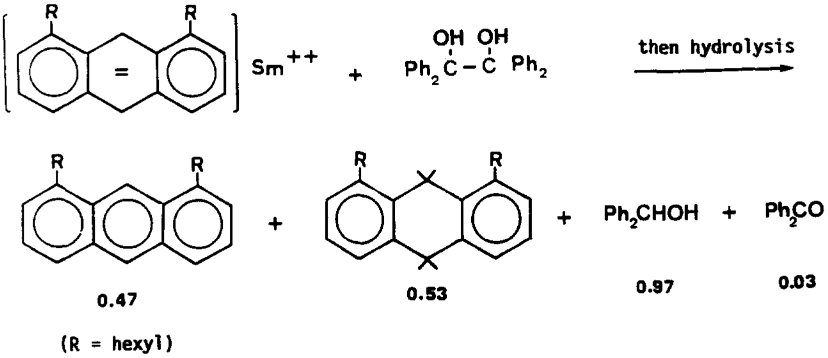
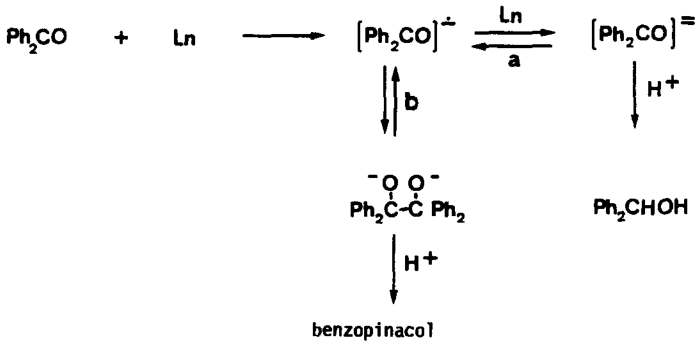


Table 1. Reaction of benzophenone with some rare earth metals (2 mmol; 40 mesh powder). Solvent = dimethoxyethane (5 ml) ; 2 hr activation by 0.1 mmol ICH_2CH_2I. Room temperature. HPLC analysis.

Run	Metal:ketone molar ratio	Reaction time	Benzophenone	Benzopinacol	Benzhydrol
				weight %	
	Sm:ketone				
1	2:1	2h	1	44	55
		1 day			100[a]
2	1:3	3 days	25	66	8
3	1:2	1 day	3	78	19
	then				
	4:1	1 day	1		99
4	2:1	1 day			100
	then				
	1:2	1 day	traces	86	14
	Nd:ketone				
5	2:1	2h	5	85	10
		1 day			100
6	1:3	1 day	46	49	5
	Yb:ketone				
7	2:1	1 day	1	15	84
8	1:2	1 day	4	80	10
	Ce:ketone				
9	4:1	1 day	1	17	82
	Gd:ketone				
10	3:1	1 day	1	83	16

a- trace amounts of diphenylmethane.



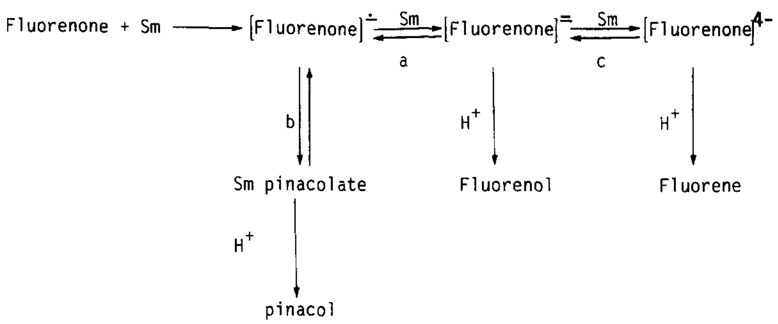
Scheme I

Table 2. Reaction of fluorenone with some rare earth metals (2 mmol, ~ 40 mesh powder). Concentration of fluorenone in dimethoxyethane : 0.1 mole L^{-1} (except a : 2 mmol metal, 5 mL of ether).2 hr activation by 5% molar ICH_2CH_2I. Room temperature. Analysis by HPLC.

Run	Metal:ketone molar ratio	Reaction time	Fluorenone	Pinacol	Fluorenol	Fluorene
				weight %		
	Sm:Ketone					
11	$2:1^{a)}$	4hr	1	18	76	5
12	1:2	1 day	5	70	25	
13	4:1	1 day	traces		62	38
	then					
	1:2	1 day	5	75	20	traces
	Nd:ketone					
14	$4:1^{a)}$	1 day		79	21	
15	$1:2^{a)}$	1 day	3	84	13	
	Yb:ketone					
16	4:1	1 day	traces		62	38

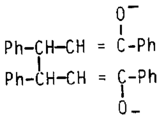
In Experiment 13, samarium and fluorenone were first reacted in a 4:1 molar ratio. Then a sufficient amount of fluorenone was added to obtain a 1:2 molar ratio . After hydrolysis the same distribution of products as observed in run 12 was measured. Thus, not only step "a" and unexpectedly step "c" (scheme II) were reversible. At the present time the structure of the organometallic species responsible for the formation of fluorene can be only speculative.

In our conditions, neodymium does not form fluorene (runs 14, 15).



Scheme II

Other ketones such as chalcone and benzil gave complex mixtures of saturated aromatic ketones, alcohols, keto-alcohols and hydrocarbons. Thus, reacting chalcone with an excess of neodymium (4:1) gave, among other unidentified products,cis 1,3,4-triphenyl 2-benzoyl 1-hydroxy-cyclopentane (isolated yield : 36 %), which was previously obtained by electrochemical reduction[6] and which might be formed via cyclization of the 1,4-coupling product of the radical anion, i.e.



$$\begin{array}{l} \qquad\qquad\quad O^- \\ \text{Ph-CH-CH} = \text{C-Ph} \\ \text{Ph-CH-CH} = \text{C-Ph} \\ \qquad\qquad\quad O^- \end{array}$$

An excess samarium or ytterbium gave dihydro chalcone, the product of a two-electron reduction.

On the other hand, reacting benzil with samarium, ytterbium or neodymium in excess yielded, besides other compounds, the product of monodeoxygenation, i.e. phenylacetophenone and several products of dideoxygenation such as stilbene (cis and trans), 1,2- diphenylethane and, more unexpectedly, 9,10-dihydrophenanthrene.

The monodeoxygenation of ketones by organolanthanides has previously been described by I.P. Beletskaya[7] and Y. Fujiwara[8].

REMARK : As observed previously[3] and as in all our experiments, an activation step by an alkyl-iodide is essential for the reaction. However, a quite similar effect is observed by using a catalytic amount of a divalent lanthanide iodide such as Sm I_2, suggesting the intermediacy of an RLnI adduct.

EXPERIMENTAL.

All the experiments were carried out in argon either in a glove-box or in Schlenk tubes. Lanthanide powders were commercially available (Aldrich ; 40 mesh). If necessary the packaging oil was washed out several times with pentane. All organic compounds used were commercial grade. 1,2-dimethoxyethane (DME) was distilled from sodium-benzophenone ketyl before use. Isolated reaction products were characterized by NMR. Mixtures were quantitatively analyzed by HPLC equipped with a UV detector (colunn ZORBAX ODS from du Pont ; 1 = 20 cm ; mobile phase 30:70 water:acetonitrile.

Typical procedure.

Sm metal (2 mmol) was transfered from a glove box into a Schlenk flask containing a magnetic stirring bar. The flask was charged with 1mL of a solution of 1,2-diiodoethane (0.1 mmol) in DME. After activation for 2 hr at room temperature, the flask was cooled to -20 °C and 5 mL of a solution of benzophenone (2 mmol) in DME was added. The medium immediatly turned violet, then brown and then blue.

After a one hour reaction time a brown suspension formed. The mixture was then warmed to room temperature and stirred overnight. The products were treated by 1 ml methanol and solvent evaporated, and the product was extracted by methylene dichloride after treatment with diluted sulfuric acid.

Synthesis of 1,8-dihexylanthracene

According to a general alkylation procedure[9], to a solution of 15g (60,7mmol) of 1,8 dichloroantracene and 0.24g (0.45 mmol) of $NiCl_2$ bisdiphenylphosphinopropane in 250 mL of ethyl ether was added dropwise at 0° 68 mL of a solution of n-hexyl Mg Br (136.6 mmol) in ethyl ether. The suspension was stirred overnight at room temperature. Then the mixture was quenched with H Cl 2N and the organic part extracted with ethyl ether, washed with aqueous saturated sodium bicarbonate, then dried and concentrated. Yellow needles (15g). ^1H NMR($CDCl_3$) : δ (ppm) 8.75 (1H,s, aryl group), 8.40 (1H,s, aryl group), 7.81 (2H,d, aryl group), 7.2-7.4 (4H,m, aryl group), 3.2 (4H,t, benzylic group), 1.8-1.9 (4H,m), 1.2-1.5 (16H,m), 0.9 (6H,t).

Synthesis of 1,8-dihexylanthracene-samarium.

At -20 °C, 4 mL of a solution of 1,8-dihexylanthracene (0.5 mmol) in DME was added to samarium powder (2 mmol) activated as described above. After one hour of stirring, a blue solution formed, then the flask was warmed to room temperature and stirred overnight. The excess metal was filtered out, and part of the solution was hydrolyzed for analysis [10]. The organic product was identified as pure 9,10-dihydro-1,8-dihexylanthracene (DHDHA). Samarium was determined by titration with disodium ethylene diaminetetracetate using xylenol orange as indicator. The molar ratio of samarium to DHDHA was found to be 1,0 + 0,05. DHDHA : ^1H NMR ($CDCl_3$) : 7.0 (6H,m, aryl groups), 3.9 (4H,d, CH_2 between the two aryl groups), 2.7 (4H,t, benzylic group), 1.2-1.6 (16H,m), 0.9 (6H,t).

REFERENCES :

1. Saussine, L.; Olivier, H.; Commereuc, D.; Chauvin, Y. New J. Chem. 1988,12.
2. For pinacol formation by some rare earth metal derivatives see : a) Deacon, G.B.; Tuong, T.D. J. Organomet. Chem. 1981, 205, C4. b) Imamoto, T.; Kusumoto, T.; Hatanaka, Y.; Yokoyama, M. Tetrahedron Lett. 1982, 23, 1353. c) Namy, J.L.; Souppe, J.; Kagan, H.B. Tetrahedron Lett. 1983, 24, 765.
3. Hou, Z.; Takamine, K.; Fujiwara, Y.; Taniguchi, H. Chem. Lett. 1987, 2061
4. Bogdanovic, B., unpublished results.
5. Harvey, S.; Junk, P.C.; Raston, C.L.; Salem, G.; J. Org. Chem. 1988, 53, 3134.
6. Fournier, F.; Berthelot, J.; Basselier, J.J. Tetrahedron, 1985, 41, 5667
7. Beletskaya, I.P.; Sigalov, A.B.; Rybakova L.F; Petrov, E.S. Dokl. Akad. Nauk SSSR, 1984, 274 1385.
8. Hou, Z.; Mine, N.; Fujiwara, Y.; Taniguchi, H.; J.Chem. Soc., Chem. Commun. 1985, 1700.
9. Kumada, M.; Tamao, K.; Sumitani, K. Organic Syntheses 1978, 58, 127.
10. Deacon, G.B.; Raverty, W.D.; Vince, D.G. J. Organomet. Chem. , 1977, 135, 103.