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CATALYSIS OF THE CYCLOHEXADIENONE-PHENOL REARRANGEMENT BY A LEWIS-ACIDIC CLAY SYSTEM

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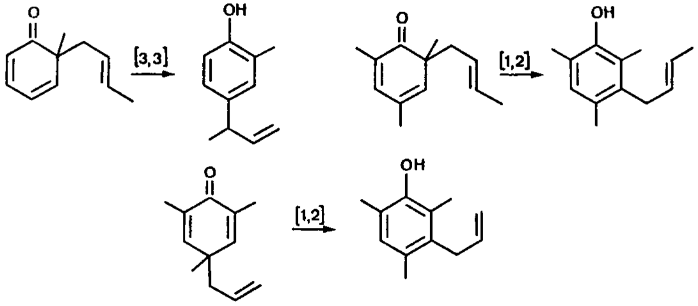
Abstract : The Fe^{3+}-doped acidic K10 clay accelerates greatly, by factors of 10^5-10^6, the title reaction. These rearrangements thus occur in a few minutes at room temperature, according to [1,2] and [3,3] pathways.



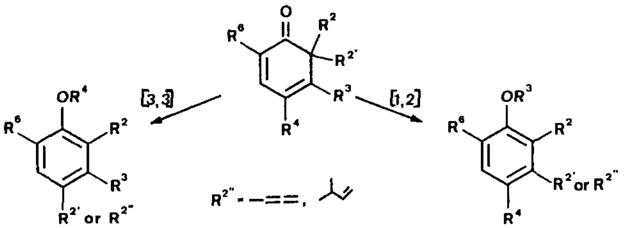
FACILE symmetry-allowed pericyclic reactions -- such as Diels-Alder cycloadditions, Claisen and Cope rearrangements -- nevertheless require quite high reaction temperatures and/or pressures[1-3]. In that, they are representative; organic reactions are not particularly easy, in an operational sense [2]. Hence, we have set upon a general program, viz. to refurbish reactions to make them yet more important to organic chemistry. We hold that rational design can set optimal reaction conditions The reactions will have high yields, they will be selective and easily worked-up, they will run at ambient temperatures and pressures, and still they will need only low-cost reagents and catalysts. We have thus devised solid acidic [4-5] and basic [6-7] catalysts for a number of organic reactions [2]. For instance, we have issued a three-part report on catalysis of the Diels-Alder reaction by clays and modified clays, acting as cation radical [8], as Brønsted acidic [2], as Lewis acidic [9], or as water reservoir [10] catalysts.

Cyclohexadienones are very prone to rearrange [11]. They follow multiple paths, depending on the migrating group (allyl, benzyl, propargyl, etc.) and on the reaction conditions, thermal or acidic [12]. The cyclohexadienone-phenol rearrangement is thus an excellent candidate for catalysis. The two main objectives are to cut down drastically the (i) number of pathways, in order to boost product selectivity; and (ii) reaction temperature : three hours of heating above 100 ° C can be considered as the norm till now [12-13].

Our rationale here is firstly to build upon the previous observations of acidic catalysis [12], and to improve markedly upon the Thiele conditions -- i.e. acetic anhydride co-mixed with a little sulfuric acid, as solvent -- with a solid acid catalyst. Secondly, introduction of ferric ions, we thought, might open new catalyzed routes. These would result from the Lewis acidity, and from singl electron transfer pathways due to oxidation of the organic substrate by the transition metal, in like manner to what was observed with the isoelectronic Diels-Alder reaction [8-9]. An oxygen-containing system would be all the more liable to Lewis acid catalysis. As for promotion of radical or radical cationic paths, these could reasonably be expected given the magnitudes of the first ionization potentials in the cyclohexadienone-phenol system.

Standard Procedure : To a solution of the dienone (500 mg) in n-hexane as solvent (10 ml), 1 g of catalyst [5,8-10] is added. The mixture is stirred for the time stated in the Tables. The reaction mixture is filtered, and the solid catalyst is washed with methylene chloride (50 ml) and methanol (50 ml). All these operations are conducted at room temperature. After solvent evaporation, the crude product may be purified by (I) recrystallization; or (II) column chromatography : silicagel with 9:1 n-pentane/ diethyl ether as eluent; or (III) distillation.

We are pleased to report that the iron(III)- doped montmorillonite K10 clay fulfills these objectives with spectacular success (Tables 1 and 2) :



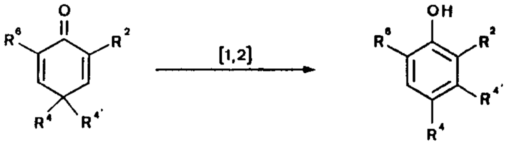
R^2	$R^{2'}$	R^3	R^4	R^6	reaction time (min)	product	isolated yield (%)	purif.
CH_3	allyl	H	CH_3	CH_3	20	[1,2]	98	I
CH_3	benzyl	H	CH_3	CH_3	60	[1,2]	98	I
CH_3	propargyl	H	CH_3	CH_3	60[a]	[1,2][b]	87	II
CH_3	crotyl	H	CH_3	CH_3	10	[1,2]	95	I

CH_3	crotyl	H	H	H	15	[3,3]	80	II
CH_3	allyl	H	H	CH_3	20	[3,3]	75	II
CH_3	allyl	CH_3	H	H	6	[3,3]	80	II
CH_3	allyl	H	H	H	15	[3,3]	95	III
CH_3	allyl	H	CH_3	H	12	[1,2]^c	80	II

(a) : acetic anhydride as solvent; (b) : mixture of phenol acetates, having a propargyl group (40 %) or an allene substituent (60 %) at C-3; (c) : most plausible pathway; it is followed by competing [1,2] and [3,3] shifts, leading to products with the allyl group at C-5 (30 %) and at C-6 (70 %).

Table 1 - Rearrangements of o-Cyclohexadienones Catalyzed by K10-Fe^{3+} in n-Hexane .

The exceptional ease of these reactions is striking, they are quantitative, in a jiffy, at room temperature. Take the first entry in Table 1 : it is accelerated, with respect to the earlier standard ($k = 10^{-5}\ s^{-1}$ at 75 °C [13]), by between five and six orders of magnitude ! Of note also are modifications brought by the catalyst to the product distributions. Allyl groups migrate principally by [3,3] shifts in the solution acid-catalyzed rearrangement of o-cyclohexadienones [12,15-16]. We see here the same for C-4 unsubstituted compounds. By contrast, C-4, C-6 substituted allyl-cyclohexadienones rearrange exclusively by [1,2] shifts under our conditions. C-4 substituted, C-6 unsubstituted dienones give here a mix of [1,2] and [3,3] shifts. Whereas benzyl groups undergo [1,5] shifts under acidic catalysis, here they undergo [1,2] migrations instead. As for the propargyl group, we find a coexistence of [3s,4s] and [1s,2s] processes, as did Schmid et al. [17].



R^2	R^4	$R^{4'}$	R^6	reaction time (min)	product	isolated yield (%)	purif.
CH_3	CH_3	allyl	CH_3	15	[1,2]	98	I
CH_3	CH_3	benzyl	CH_3	20	[1,2]	98	I
CH_3	CH_3	propargyl	CH_3	15^a	[1,2]	93	I

Table 2 - Rearrangements of p-Cyclohexadienones Catalyzed by K10-Fe^{3+} in n-Hexane.

Allyl-substituted p-cyclohexadienones undergo normally a predominant [3,3] shift and a small percentage of [1,2] shift : with our procedure the latter becomes the exclusive route.

In summary, catalysis by a modified acidic clay of the cyclohexadienone-phenol rearrangement, while privileging carbocationic modes of reaction, has turned this transposition into an efficient smooth, and better controlled reaction.

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References

1. R.P. Lutz, Chem.Rev., 84, 205 (1984).
2. P. Laszlo, Accounts Chem. Res., in press.
3. W.G. Dauben and H.O. Krabbenhoft, J.Am.Chem.Soc., 98, 1992 (1976).
4. S. Chalais, A. Cornelis, A. Gerstmans, W. Kołodziejski, P. Laszlo, A. Mathy, and P. Metra, Helv.Chim.Acta, 68, 1196 (1985).
5. A. Cornelis and P. Laszlo, Synthesis, 909 (1985).
6. S. Chalais, P. Laszlo, and A. Mathy, Tetrahedron Lett., 26, 4453 (1985).
7. P. Laszlo and P. Pennetreau, Tetrahedron Lett., 26, 2645 (1985).
8. P. Laszlo and J. Lucchetti, Tetrahedron Lett., 25, 1567 (1984).
9. P. Laszlo and J. Lucchetti, Tetrahedron Lett., 25, 4387 (1984).
10. P. Laszlo and J. Lucchetti, Tetrahedron Lett., 25, 2147 (1984).
11. G.R. Clemo, R.D. Haworth, and E. Walton, J.Chem.Soc., 1110 (1930).
12. B. Miller, Accounts Chem. Res., 8, 245 (1975).
13. D.Y. Curtin and R.J. Crawford, J.Am.Chem.Soc., 79, 3156 (1957).
14. H.J. Shine, in D.H. Fey, FRS and H. Zollinger, eds., MTP International Review of Science, Organic Chemistry, Series 1, vol.3, Butterworths, London, 1973, 65-103.
15. P. Fahrni, A. Habich, and H. Schmid, Helv.Chim.Acta, 43, 448 (1960).
16. J. Leitich, Monatsh.Chem., 92, 1167 (1961).
17. U. Widmer, H-J. Hansen, and H. Schmid, Helv.Chim.Acta, 56, 1895 (1973).

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