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Cyclization of 1-phenyl-2-propen-1-ones into 1-indanones using H-zeolite and other solid acids. The role of mono- and dicationic intermediates

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Abstract—Cyclization of aryl vinyl ketones into 1-indanones was previously known to proceed only in drastic acidic or superacidic conditions due to the necessity of dicationic, superelectrophilic activation of starting compounds. In this paper, we disclose that available solid acids such as HUSY–zeolite, sulfated zirconia or heteropolyacid, $H_3PW_{12}O_{40}$ can be successfully applied instead of superacids to perform these and related reactions. The cases, when the effective excess of acidic sites of the solid is required to carry out the reaction, are interpreted in terms of key dicationic (superelectrophilic) intermediates on the solid.

An active area of research involving dicationic intermediates (superelectrophiles)[1] ranges from enzymatic reactions[2] to industrial applications.[3] A key point of superelectrophilic activation is an additional protonation or coordination to a Lewis acid of a low reactive monocationic species to initiate its reactivity toward weak nucleophiles: benzene, deactivated arenes, H_2 and alkanes. Generally, it requires excess of Brønsted or Lewis superacid and for this reason has often eluded synthetic interest. However, recently we have found that superelectrophilic activation can be carried out successfully by replacing superacids with solid acids such as zeolites, sulfated zirconia and, less efficiently, Nafion.[4] Noteworthy, an effective excess of acidic sites of the solids appeared to be an essential condition to provide these results.

In this contribution, we give a remarkable example in which phenyl vinyl ketones are cyclized into practically important 1-indanones,[5] a reaction up to now claimed to proceed only in drastic acidic or superacidic conditions and involving key dicationic intermediates for which, based on theoretical studies, the authors have shown that the energy barrier for cyclization was considerably lower than for monocationic intermediates.[5a] Initially, two isomeric starting compounds, 1,2-diphenyl-2-propenone (**1a**) and chalcone (**1b**) were tested to be thus cyclized using H-zeolite, HUSY (Si/Al 2.5), sulfated zirconia and heteropolyacid, $H_3PW_{12}O_{40}$.[6] All reactions were carried out in pressure tubes as described previously[4] using benzene, *o*-dichlorobenzene or CCl_4 as solvent. Both starting compounds appeared to be reactive at 130 °C to give expected 2-phenyl-1-indanone (**2a**) and 3-phenyl-1-indanone (**2b**), respectively. However, whereas **1a** reacted even in the presence of catalytic amounts of HUSY, **1b** notably reacted only in the presence of HUSY and sulfated zirconia when >2.5 molar excess of Brønsted acid sites[7] was used (Table 1). This remarkable difference is also in accord with the better reactivity of **1a** in homogeneous phase. Thus, cyclization **1a** into **2a** occurs in triflic acid (CF_3SO_3H) as well as in less acidic CF_3SO_3H–CF_3CO_2H mixtures ($-14.1 < Ho < -9$) at room temperature.[5a] In contrast, **1b** is inert in triflic acid at 80 °C,[5a] but reacts however in stronger[8] acid, $AlCl_3$–NaCl melt or polyphosphoric acid at 130–200 °C to give **2b**.[9]

The mechanistic pathways suggested earlier for a variety of (super)acid induced reactions of α,β-unsaturated ketones proposed the intermediacy of mono- and dicationic species, analogous to **3–5** (Scheme 1).[1,5a,10] For example, the key intermediacy of O,O-diprotonated

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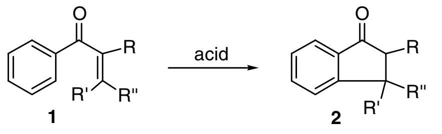
Table 1. Solid acid mediated cyclizations of enones **1a–e** into indanones **2a–e** and their dependence on the amount of catalyst[a]



	R	R'	R''
a	Ph	H	H
b	H	H	Ph
c	Me	H	H
d	H	H	p-C_6H_4OMe
e	H	Me	Me

Enone	Acid	Weight ratio of acid/enone	Molar ratio of the acidic sites/enone	Solvent	Time (h)	Indanone (yield, %)[b]
1a	HUSY	1.7	1.5	C_6H_6	15	**2a** (>95)
1a	HUSY	1.1	1	C_6H_6	15	**2a** (84)
1a	HUSY	0.55	0.5	C_6H_6	15	**2a** (60)[c]
1b	HUSY	5.5	5	$C_6H_4Cl_2$	60	**2b** (81)[d]
1b	HUSY	2.8	2.5	$C_6H_4Cl_2$	120	**2b** (80)[d]
1b	HUSY	2.25	2	$C_6H_4Cl_2$	60	**2b** (14)[c]
1b	HUSY	2.25	2	$C_6H_4Cl_2$	90	**2b** (14)[c]
1b	HUSY	2.25	2	$C_6H_4Cl_2$	140	**2b** (14)[c]
1b	HUSY	2.25	2	CCl_4	60	**2b** (7)[c]
1b	HUSY	1.25	1.1	$C_6H_4Cl_2$	60	**2b** (6)[c]
1b	ZrO_2/SO_4^{2-}	23	3	CCl_4	15	**2b** (75)
1b	ZrO_2/SO_4^{2-}	7	1	CCl_4	15	**2b** (14)[c]
1b	$H_3PW_{12}O_{40}$	45	10	CCl_4	15	**2b** (20)[c]
1c	HUSY	2.3	1.5	C_6H_6	15	**2c** (53)[c]
1c	HUSY	1.5	1	C_6H_6	200	**2c** (46)[c]
1c	HUSY	0.8	0.5	C_6H_6	80	**2c** (17)[c]
1d	HUSY	9.1	10	CCl_4	40	**2d** (63)[e]
1d	HUSY	4.7	5	CCl_4	40	**2d** (13)[c]
1d	HUSY	1.9	2	CCl_4	40	**2d** (6)[c]
1e	HUSY	6.7	5	CCl_4	10	**2e** (95)
1e	HUSY	2.7	2	CCl_4	30	**2e** (24)[c]

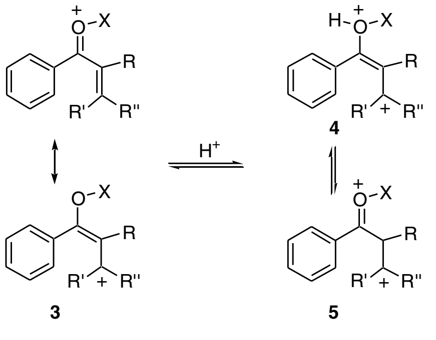
[a] Typically, mixture of acid (0.2–1 g), enone (0.1–0.4 g) and solvent (4 mL) was magnetically stirred at 130 °C in 15 mL pressure tube. After cooling, water (5 mL) was introduced to the mixture followed by continuous solid–liquid extractions with ether. The organic phase was dried (Na_2SO_4) and concentrated to provide the residue analyzed by NMR.

[b] Based on ^1H NMR data. Analytical data of isolated indanones were convincing with those previously reported (Ref. 5a,d).

[c] Significant recovery of starting material was observed.

[d] The mixture contains 2–7% of **6**.

[e] The overall yield of **2d** and its demethylation product.



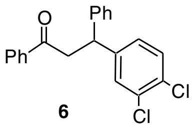
X = H or LA$^-$ (LA = Lewis acid or Lewis acid site)

Scheme 1.

dications **4a** rather than ions **3a** was suggested for reaction **1a**→**2a** due to acceleration of this reaction with increase of acidity in the region of Ho < −9 where the substrate is already extensively protonated.[5a] However, the second O-protonation with acid of moderate strength seems unlikely and, in general, has still not been directly observed in superacids.[11] In contrast, energetically favorable O,α-C-diprotonated dications, analogous to **5**, have been detected as long-living species when some α,β-unsaturated ketones were dissolved in superacids.[10c] Moreover, similar dications were also produced from 2-napthols,[12] α,β-unsaturated acids[5c,8a] and amides.[8,13]

The formation of monocationic species analogous to **3** in H-zeolites has been confirmed by NMR studies.[14] Generation of **4**, which requires double protonation (coordination) of the same atom seems improbable on zeolites and other solid acids because of discrete distribution of acidic sites. On the other hand, the framework of zeolites and sulfated zirconia may provide sufficient proximity of Lewis and Brønsted acidic sites for the formation of dicationic species **5**, whereas the lack of proton acidity may be compensated by a confinement effect[15] (for zeolites) and effective nucleophilic assistance of lattice oxygens in transition state[14] resulting in the increase of the protonation rate. However, a heteropolyacid, being comparatively strong but purely protonic, with relatively dispersed acidic sites, should not be expected to be efficient in dicationic activation.

Taking into account the catalytic character of reaction **1a**→**2a**, we think that this reaction, proceeding as well on solid as in liquid acid, involves monocations **3a** as the key reactive intermediates. In contrast, reaction **1b**→**2b**, which is not catalytic, probably involves the intermediacy of **5b**. That is also in accord with found competition of this reaction with intermolecular alkylation of benzene, when used as solvent to give mostly 1,3,3-triphenyl-1-propanone.[16] Even the use of *o*-dichlorobenzene, normally inert toward monocationic C-electrophiles,[17] but often reactive with dicationic species,[3,4,5c,8] offers about 5% of impurity of **6**,[18] thus supporting the idea of generation of highly activated dicationic[19] species **5b** upon the reaction conditions. The strong dependence of reactivity of **1b** and, in less extent of **1a**, on the ratio of acidic sites/enone can be related to the influence of adsorption on the acidity of catalyst.[15,20] This influence, of course, will play a critical role when the second protonation (or protonation of enone→LA complex) is required to initiate cyclization.



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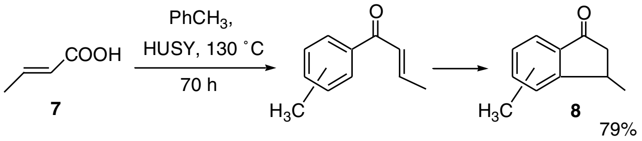
Unfortunately, intermediates **5** cannot be observed on the solid spectroscopically due to both their short lifetime and low concentration. The analogous dications, as was mentioned above, have been generated as long-living species by only using extremely acidic $HF(HSO_3F)–SbF_5–SOClF$ systems at −80 to −40 °C. An alternate possibility could be the Nazarov electrocyclization suggested by Shudo.[5a] However, deuterium labeling of the acid catalyst would not enable us to distinguish between Nazarov and Friedel–Crafts mechanisms as H/D exchange between catalyst and substrate is known to be very fast under our conditions on the aromatic ring[21] as well as on the α-carbon due to the keto-enolic tautomerization of **3**.[22]

The difference found in reactivity of **1a** and **1b** as model substrates motivated us to investigate the reaction of analogous ketones **1c–e** (Table 1). As expected, 1-phenyl-2-methyl-2-propenone (**1c**) reacts in the same way as **1a**, in the presence of moderate amounts of acid. In contrast, enones **1d–e** due to electrodonating nature of substituents R″(R′) react similar to **1b**, generally requiring 5–10 molar excess of acidic sites. These results could be also interpreted in terms of mono- and dicationic activation, respectively. In the series of experiments, we have used CCl_4 as solvent due to its low boiling point facilitating separation from products. However, when using this solvent we should be aware that it is not totally inert toward zeolites.[23]

In addition, we reinvestigated the related reaction of crotonic acid (**7**) with toluene, previously carried out in the presence of catalytic amount of heteropolyacids and large-pore zeolites to obtain indanones **8** in negligible yield, whereas similar reaction with isomeric xylenes gave better results.[24] As expected, the use of HUSY (Si/Al 2.5), providing ~10 molar excess of acidic sites, gave **8** in good yield (Scheme 2). Moreover, **7** also reacts with benzene in similar conditions to give 3-methyl-1-indanone in 66% yield.[16] These results can be rationalized as it was done for **1b**,**d**,**e**, by involvement of key dicationic intermediacy in the cyclization step. On the contrary, the catalytic reaction of **7** with sufficiently activated xylenes should involve monocationic intermediates.



Scheme 2.

In summary, the successful cyclization of phenyl vinyl ketones into indanones using HUSY and other available solid acids seems promising for practical applications. We think that the necessity of the excess of acidic sites to accomplish cyclization of **1b**,**d**,**e** into **2b**,**d**,**e** as well as the conversion of **7** into **8** is not occasional and, in accord with our previous results,[4] can be interpreted in terms of key dicationic intermediates. We also suggest to take into account this argument, which may clarify the involvement of mono- or dicationic intermediates in mechanistic considerations.

Acknowledgements

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References and notes

1. (a) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 767–788; (b) Nenajdenko, V. G.; Shevchenko, N. E.; Balenkova, E. S.; Alabugin, I. V. *Chem. Rev.* **2003**, *103*, 229–282; (c) Olah, G. A.; Klumpp, D. A. *Acc. Chem. Res.* **2004**, *37*, 211–220.
2. Berkessel, A.; Thauer, R. K. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2247–2250.
3. (a) Vukics, K.; Fodor, T.; Fischer, J.; Fellegvary, I.; Levai, S. *Org. Process Res. Dev.* **2002**, *6*, 82; (b) Repinskaya, I. B.; Koltunov, K. Yu.; Shakirov, M. M.; Shchegoleva, L. N.; Koptyug, V. A. *Russ. J. Org. Chem.* **1993**, *29*, 803–812; (c) Repinskaya, I. B.; Koltunov, K. Yu. *Sib. Khim. Zh.* **1993**, *3*, 73–76.
4. (a) Koltunov, K. Yu.; Walspurger, S.; Sommer, J. *Chem. Commun.* **2004**, *15*, 1754–1755(b) Koltunov, K. Yu.; Walspurger, S.; Sommer, J. *J. Mol. Catal. A*, accepted for publication.
5. For general synthetic routs to 1-indanones and their practical applications see, for example: (a) Suzuki, T.; Ohwada, T.; Shudo, K. *J. Am. Chem. Soc.* **1997**, *119*, 6774–6780; (b) Prakash, G. K. S.; Yan, P.; Torok, B.; Olah, G. A. *Catal. Lett.* **2003**, *87*, 109–112; (c) Rendy, R.; Zhang, Y.; McElrea, A.; Gomez, A.; Klumpp, D. A. *J. Org. Chem.* **2004**, *69*, 2340–2347; (d) Gagnier, S. V.; Larock, R. C. *J. Am. Chem. Soc.* **2003**, *125*, 4804–4807; (e) Cui, D.-M.; Zhang, C.; Kawamura, M.; Shimada, S. *Tetrahedron Lett.* **2004**, *45*, 1741–1745, and references cited therein.

6. Zeolite USY (Si/Al = 2.5, CBV500, Zeolyst International) in NH_4^+ form was activated at 550 °C under air. The heteropolyacid was activated at 300 °C under nitrogen. Sulfated zirconia promoted with alumina was synthesized as described previously, then calcined at 650 °C and activated at 450 °C before using. See: Hua, W.; Goeppert, A.; Sommer, J. *J. Catal.* **2001**, *197*, 406–413.
7. On solid acids Brønsted acid sites are generally protons attached on oxygen atoms of the lattice. The acidity depends on the polarity of this bond. For quantitative estimation, see: Louis, B.; Walspurger, S.; Sommer, J. *Catal. Lett.* **2004**, *93*, 81–84.
8. For consideration of an excess of aluminum chloride as a source of protonic superacidity see, for example: (a) Koltunov, K. Yu.; Walspurger, S.; Sommer, J. *Eur. J. Org. Chem.* **2004**, *19*, 4039–4047; (b) Koltunov, K. Yu.; Walspurger, S.; Sommer, J. *Tetrahedron Lett.* **2004**, *45*, 3547–3549; (c) Smith, G. P.; Dworkin, A. S.; Pagni, R. M.; Zingg, S. P. *J. Am. Chem. Soc.* **1989**, *111*, 5075–5077, and references cited therein.
9. (a) Bruce, D. B.; Sorrie, A. J. S.; Thomson, R. H. *J. Chem. Soc.* **1953**, 2403–2406; (b) Allen, J. M.; Johnson, K. M.; Jones, J. F.; Shotter, R. G. *Tetrahedron* **1977**, *33*, 2083–2087.
10. (a) Hogeveen, H. *Rec. Trav. Chim. Pays-Bas* **1968**, *87*, 1295; (b) Coustard, J. M.; Douteau, M. H.; Jacquesy, J. C.; Jacquesy, R. *Tetrahedron Lett.* **1975**, *25*, 2029–2030; (c) Koltunov, K. Yu.; Repinskaya, I. B. *Russ. J. Org. Chem.* **1994**, *30*, 97–100; (d) Koltunov, K. Yu.; Repinskaya, I. B.; Borodkin, G. I. *Russ. J. Org. Chem.* **2001**, *37*, 1534–1541; (e) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; Wiley: New York, 1985.
11. It should be noted that the preliminary O,O-diprotonation of a carbonyl group in this and analogous reactions repeatedly cited in the literature (Ref. 1) is not needed to explain the dependence of the reaction rates on acidity. See, for relevant examples: (a) Olah, G. A.; Germain, A.; Lin, H. C.; Forsyth, D. A. *J. Am. Chem. Soc.* **1975**, *97*, 2928–2929; (b) Koltunov, K. Yu.; Walspurger, S.; Sommer, J. *Catal. Lett.* **2004**, *98*, 89–94.
12. Repinskaya, I. B.; Koltunov, K. Yu.; Shakirov, M. M.; Koptyug, V. A. *J. Org. Chem. USSR* **1992**, *28*, 785–793.
13. Koltunov, K. Yu.; Prakash, G. K. S.; Rasul, G.; Olah, G. A. *Heterocycles* **2004**, *62*, 757–772.
14. Haw, J. F. *Phys. Chem. Chem. Phys.* **2002**, *4*, 5431–5441, and references sited therein.
15. Corma, A. *J. Catal.* **2003**, *216*, 298–312.
16. The HUSY-mediated intermolecular reactions of α,β-unsaturated ketones, acids and amides with aromatic compounds will be reported elsewhere. For preliminary results, see Ref. 4a.
17. Taylor, R. *Electrophilic Aromatic Substitution*; Wiley: New York, 1990, Chapter 2.
18. For comparison, treatment of **1b** with 6 molar excess of $AlCl_3$ in *o*-dichlorobenzene during 10 h at 25 °C gave **6** as major product in 67% isolated yield, whereas **1a** gave only **2a** (~50%) under similar conditions. Selected data for **6**: ^{1}H NMR ($CDCl_3$) δ 3.72 (d, 2H), 4.81 (t, 1H), 7.1–7.6 (m, 6H), 7.93 (d, 2H). ^{13}C NMR ($CDCl_3$) δ 44.4 (α-CH_2), 45.1 (β-CH), 126–145 (14 signals), 197.3 (C=O). $C_{21}H_{16}Cl_2O$ (355.3): calcld C 71, H 4.5; found: C 70.7, H 4.6.
19. Intermediates **5** on the solid should not be considered as free dications or protonated complexes, but as transient species strongly solvated by the oxygen lone pairs at the surface. For the nature of the binding of cations to the zeolite structure, see: Tuma, C.; Sauer, J. *Angew. Chem., Int. Ed.* **2005**, *44*, 4769–4771.
20. Derouane, E. G. *J. Mol. Catal. A* **1998**, *134*, 29–45.
21. Beck, L. W.; Xu, T.; Nicholas, J. B.; Haw, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 11594–11595.
22. Xu, M.; Wang, W.; Hunger, M. *Chem. Commun.* **2003**, 722–723.
23. Howe, R. F. *Appl. Catal. A* **2004**, *271*, 3–11.
24. De Castro, C.; Primo, J.; Corma, A. *J. Mol. Catal. A* **1998**, *134*, 215–222.