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Superacidic and HUSY-zeolite activation of 1,3-indandione: reactions with benzene and cyclohexane

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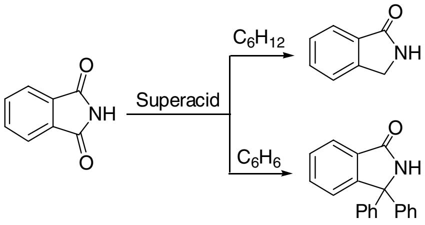
Abstract—1,3-Indandione (**1**) readily condenses with benzene and undergoes selective ionic hydrogenation with cyclohexane when activated by superacids, such as CF_3SO_3H, $AlCl_3$ and $AlBr_3$ to give 3,3-diphenyl-1-indanone (**4**) and 1-indanone (**7**), respectively. Combination of these reactions in 'one-pot' yields 3-phenyl-1-indanone (**5**). In addition, similar reactions have been carried out using the regenerable solid acid, HUSY-zeolite, providing an effective excess of acidic sites. The mechanism of these reactions, with potential involvement of superelectrophilic dicationic intermediates, is discussed.

1. Introduction

A key point of superelectrophilic activation is additional protonation or coordination to a Lewis acid of a low reactive monocationic species to initiate its reactivity towards weak nucleophiles.[1] Thus, 1,2-di- as well as 1,2,3-tricarbonyl compounds demonstrated enhanced reactivity towards benzene when activated in superacids via in situ generation of the corresponding 1,2-*O*,*O*-diprotonated species.[2] Similar dicationic activation of phthalimide via 1,3-*O*,*O*-diprotonation or coordination with aluminum halides was successfully applied to perform synthetically useful reactions with cyclohexane and benzene to obtain phthalimidines (Scheme 1).[3]



Scheme 1.

Recently, the possibility of replacing superacids by regenerable solid acids of moderate proton acidity, such as H-zeolites (Ho ≈ -6) was reported in order to carry out reactions involving the key superelectrophilic intermediates.[4]

In this Letter, both superacid and H-zeolite mediated reactivity of 1,3-indandione (**1**), the carbocyclic analogue of phthalimide, towards benzene and cyclohexane is disclosed. The model reactions discussed are considered as additional and simple synthetic routes to important 1-indanones.[4b,5]

2. Results

Initially, the behaviour of **1** in H_2SO_4 (Ho = -12), CF_3SO_3H (triflic acid, Ho = -14.1) as well as in the presence of a fourfold molar excess of $AlBr_3$ and $AlCl_3$ was studied by means of ^1H and ^{13}C NMR spectroscopies (Table 1). The data obtained revealed that precursor **1** undergoes extensive *O*-protonation (complexation) in superacidic media (Ho < -12), where at the limit, dicationic species **3** are probably formed.[6]

As expected, **1** did not react with benzene or cyclohexane in sulfuric acid. Instead, the self-condensation of **1** to give bis-indanone (bindone) **2** was the only observed reaction beside sulfonation of benzene.[7] However, **1**

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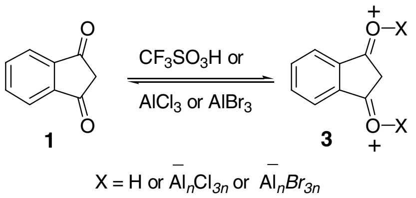
Table 1. NMR data of **1** in $CDCl_3$ (A), H_2SO_4 (B), CF_3SO_3H (C), $AlBr_3$–CH_2Br_2 (D) and $AlCl_3$–CH_2Cl_2 (E) at 25 °C[a]



	^{1}H NMR data, δ, ppm (250 MHz)	^{13}C NMR data, δ, ppm (63 MHz)				
		$C^{1,3}$	C^2	$C^{4,7}$	$C^{5,6}$	$C^{8,9}$
A	3.24 (s, 2H), 7.8–8 (m, 4H)	197.5	45.2	123.3	135.7	143.5
B	3.90 (s, 2H), 8.2 (br s, 4H)[b]	205.9	43.9	126.2	140.1	141.7[b]
C	4.41 (s, 2H), 8.45–8.55 (m, 4H)[b]	209.4	45.3	129.8	144.4	142.7[b]
D[c]	—,[d] 8.61–8.72 (m, 4H)	209.8	46.2	129.7	143.1	139.8
E[c]	4.81 (s, 2H), 8.45–8.65 (m, 4H)[b]	209.5	47.1	130.2	143.9	141.5[b]
F[e]	5.2 (s, 2H), 8.94 (s, 4H)	213.2	43.9	134.5	147.8	138.0

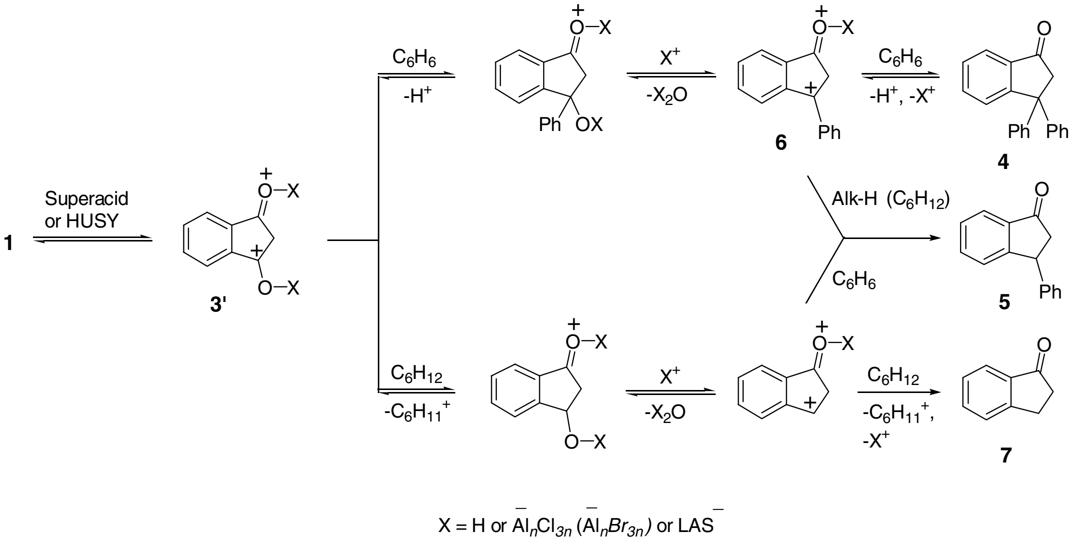
[a] 0.2 M solutions.

[b] Chemical shifts are given with respect to CH_2Cl_2 as internal standard (5.3 and 53.5 ppm, respectively, in the ^{1}H and ^{13}C NMR spectra).

[c] Only solutions (no suspensions) were formed, when a 2–4-fold molar excess of $AlBr_3$ or $AlCl_3$ used.

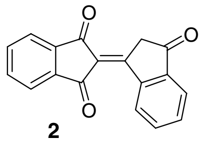
[d] The signal of the CH_2 protons overlapped the CH_2Br_2 signal at 4.8–5.2 ppm.

[e] HSO_3F–SbF_5–SO_2, −70 °C (Ref. 6a).



Scheme 2.

readily reacts with benzene in triflic acid to give, at room temperature over several hours, 3,3-diphenyl-1-indanone (**4**) in quantitative isolated yield (Scheme 2). Similarly **1** reacts with benzene in the presence of a 3.5-fold molar excess of $AlCl_3$, but at elevated temperature (80 °C, 1.5 h) to give, according to GC–MS and NMR data, **4** (73%) along with 3-phenyl-1-indanone (**5**, 27%). The latter product is obviously produced by competing ionic hydrogenation of intermediate **6** with partially saturated hydrocarbons (AlkH) derived from benzene.[8] The analogous side reaction is also known for phthalimide.[3] It is noteworthy, that when **1** is treated with benzene and a 3.5-fold molar excess of $AlBr_3$ (room temperature, 140 h), **5** was obtained as the major product in >90% yield. This is in accord with significant parallel accumulation of AlkH compounds in the reaction mixture (NMR monitoring). In agreement with these observations, the reaction of **1** with benzene/cyclohexane (1:1) mixture and triflic acid gave compound **4** (82%) along with **5** (18%) over 3 h at 25 °C. Continuation of this reaction for 120 h gave **5** as the predominant product in 83% yield. In addition, in a separate experiment, **4** was converted into **5** quantitatively, upon reaction with cyclohexane and triflic acid under similar conditions. The latter results are plausibly explained by the reverse reaction **4**→**6**, followed by irreversible ionic reduction of intermediate **6** as shown in Scheme 2.



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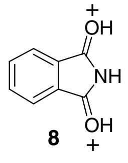
When activated in 15 M excess triflic acid, **1** smoothly reacts with cyclohexane at room temperature to give 1-indanone (**7**) in ~90% yield in 40 h (Scheme 2). While **1** is inert towards cyclohexane in the heterogeneous $AlCl_3$–CH_2Cl_2 system, it reacted with cyclohexane in the homogenous $AlBr_3$–CH_2Br_2 system to give **7** in 84% yield (fourfold molar excess of $AlBr_3$, 25 °C, 30 h). Also, **1** reacted with cyclohexane in the presence of aluminum chloride at 80 °C without solvent to give **7** in ~70% yield in 2 h.

The probable mechanism of these reactions includes involvement of dicationic species **3** (Table 1, Scheme 2), which is more electrophilic than isoelectronic dication **8**, since phthalimide reacted more slowly with benzene and cyclohexane.[3] This however, may be related to a lower stability (concentration in the reaction media) of **8**, generated earlier in the extremely acidic $HF(HSO_3F)$–SbF_5–SO_2ClF systems at −80 °C.[9] The enhanced reactivity of **3** and **8** is in sharp contrast with the poor reactivity of closely-related dication **9** (derived from diprotonation of 1,4-naphthalenediol), which is totally inert towards benzene and cyclohexane.[10] On the other hand, compound **1** (like phthalimide)[3] does not react with *o*-dichlorobenzene, even when using a 100 M excess of triflic acid (25 °C) or a 10-fold molar excess of $AlBr_3$ (120 °C). This indicates the relatively moderate reactivity of **3** in comparison with other dicationic species, which are often reactive towards *o*-dichlorobenzene.[11]



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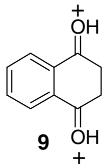

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Furthermore, the analogous reactions of **1** with benzene and cyclohexane have been carried out using HUSY zeolite.[12] In accordance with our previous observations,[4] dicationic activation on this solid requires a large molar excess of acidic sites.[13] Thus, **1** reacted with benzene at 130 °C (pressure tube) to give a mixture of **4, 5** and bindone **2** in a 1:6:2 molar ratio after 6 h, providing ~20 M excess of acidic sites. When less HUSY was used, compound **2** formed predominantly. 1,3-Indandione **1** reacts more selectively with cyclohexane and HUSY. Indeed, under similar conditions (20 M excess of acidic sites, 130 °C, 10 h) **1** underwent ionic reduction to give indanone **7** in 78% yield, while the mass balance was the starting material **1** and traces of **2**.

It seems that the HUSY framework provides sufficient proximity of Lewis acidic sites (LAS) and/or proton acid sites for the formation of dicationic species **3** ($X = LAS^-$ or H), and the lack of acid strength is compensated by a confinement effect[14] and nucleophilic assistance of lattice oxygens in the transition state[15] during the second protonation (complexation). Obviously, intermediates **3** on the solid can not be observed by spectroscopy due to both their short life time and low concentration.[16]

3. Typical procedure

3.1. 3,3-Diphenyl-1-indanone (4)

To a solution of **1** (0.1 g, 0.7 mmol) in CF_3SO_3H (4 g, 26 mmol) was added benzene (1 mL). The resulting mixture was stirred at 25 °C for 4 h followed by quenching with several grams of ice and subsequent extraction with $CHCl_3$.[17] The organic phase was washed with aqueous $NaHCO_3$ and then dried over anhydrous $MgSO_4$. Concentration in vacuo provided pure (according to NMR data) compound **4** (0.187 g, 96%), mp 128–130 °C (benzene), lit.[18] mp 128–130 °C. ^1H NMR ($CDCl_3$): δ 3.51 (s, 2H), 7.15–7.35 (m, 10H), 7.37 (d, $J = 7.7$ Hz, 1H), 7.42 (td, $J = 7.7$, 1.3 Hz, 1H), 7.6 (t, $J = 7.7$ Hz, 1H), 7.82 (d, $J = 7.7$ Hz, 1H).[18] ^{13}C NMR ($CDCl_3$): $\delta = 56.2$, 56.3, 123.8, 126.7, 128.1, 128.2, 128.6, 134.9, 135.9, 146.9, 160.1, 205.1.[18] GC–MS (M^+): 284.

Analytical data of indanones **2**, **5** and **7,** isolated by silica gel column chromatography with benzene-acetone, were analogous with those previously reported.[5,7]

In summary, superacidic as well as HUSY-zeolite activation of **1** leads to superelectrophilic (dicationic) reactivity towards weak nucleophiles, such as benzene and cyclohexane.[19] The reaction procedures using readily available acids are simple and reproducible. When HUSY is used, the necessity for excess of acidic sites is required and, in accord with previous results,[4] can be interpreted in terms of key dicationic intermediates on the solid.

Acknowledgements

Students of Novosibirsk State University: I. Skobelev, Z. Danzanov and K. Akhmetova are gratefully acknowledged for their contribution in the experimental work.

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