A New and Mild Heterogeneous Catalytic Decomposition of α-Diazo Carbonyl Compounds Using Montmorillonite or Zeolite

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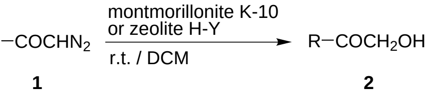
Abstract: A very mild method of decomposition of various α-diazo carbonyl compounds **1** in the presence of environmentally attractive solid acids such as montmorillonite K-10 or zeolite H-Y in a heterogeneous manner to furnish α-hydroxy/alkoxy ketones in very good yield is reported. Interestingly, novel bicycloalkane-1,3-diones and 3-furanones were obtained as unusual products in the case of aliphatic/alicyclic α-diazo carbonyl compounds.

Key words: diazo ketones, heterogeneous catalysts, hydroxy ketones, O-H insertion, montmorillonite, zeolite

The ready availability, relative stability and facile decomposition, under thermal, photochemical, acid, base and transition-metal catalyzed conditions of α-diazo carbonyl compounds make them useful intermediates in organic synthesis. The utility of α-diazo carbonyl compounds in modern organic synthesis and their participation in a variety of transformations such as ylide formation, cyclopropanation and insertion reactions is well documented.[1,2] The formation of inter- and intramolecular ether linkages from diazo ketones and alcohols in the presence of rhodium(II) acetate is well studied.[3] The decomposition of α-diazo carbonyl compounds dominantly with protic/aprotic and Lewis acids has been well studied[1,4] and also applied[2] to the synthesis of important natural products. The use of solid acidic catalysts such as ion-exchange resins,[5–7] clays[8–12] and zeolites[13,14] has received substantial attention in different areas of organic synthesis because of their environmental compatibility, greater selectivity, experimental simplicity, low cost, high efficiency and ease of isolation of the products. In particular, clay and zeolite catalysts make reaction processes expedient; cost effective, environmentally benign, and act as both Brønsted and Lewis acids in their natural or ion-exchanged forms, enabling them to function as efficient catalysts for various organic transformations. Very recently, we have reported[15] that a solid ionic matrix (such as Amberlyst-15®) mediated decomposition of α-diazo ketones to afford α-hydroxy ketones. Albeit reactions of α-diazo carbonyl compounds in classic/Lewis acidic medium have been studied, such procedures require careful handling and an aqueous work-up.[4]

In continuation of our interest in α-diazo ketones[15–17] and the discovery of new and effective catalysts for their decomposition, we herein report the mild heterogeneous catalytic decomposition of α-diazo carbonyl compounds with montmorillonite clay K-10 or zeolite H-Y as applied to the synthesis of α-hydroxy/alkoxy ketones, bicycloalkane-1,3-diones, 3-furanone ring systems.

To the best of our knowledge, there is no report, which deals with the reaction of α-diazo carbonyl compounds with solid acids such as clays or zeolites. Montmorillonite clay K-10[8–12] and zeolites[13,14] have many applications in modern organic synthesis such as catalysts for Michael addition reactions, Friedel–Crafts reactions, methoxymethylation of alcohols and deprotection of acetal/silyl groups.



$$\underset{\mathbf{1}}{\mathrm{R{-}COCHN_2}} \xrightarrow[\text{r.t. / DCM}]{\text{montmorillonite K-10 or zeolite H-Y}} \underset{\mathbf{2}}{\mathrm{R{-}COCH_2OH}}$$

Scheme 1

α-Diazo ketones **1**, **3** and **5**–**7** involved in this work were prepared according to literature precedents.[1,16] To a solution of α-diazo ketone **1a** (100 mg) in 4 mL of commercial grade dichloromethane was added montmorillonite clay K-10 (175 mg) and decomposition started with slow evolution of nitrogen gas. The reaction mixture was allowed to stir at room temperature for 5 hours and followed by TLC until the disappearance of starting material. The reaction mixture was filtered, concentrated under reduced pressure and the crude reaction mixture was purified using silica gel column chromatography to furnish α-hydroxy ketone[15] **2a** in 90% yield (Scheme 1).

This reaction stimulated us to study further the decomposition of other α-diazo ketones **1b**–**h** with montmorillonite to afford the corresponding α-hydroxy ketones **2b**–**h** in very good yield (Table 1). We have studied this reaction with both aromatic/aliphatic diazo compounds **1** which afforded the respective α-hydroxy ketones **2** as a result of O-H insertion.[3] It is significant that α-hydroxy ketones are very useful intermediates in organic synthesis[18] and their chemistry is being exploited intensively in asymmetric Aldol reactions.[19] In some representative cases we have carried out the decomposition of diazo ketones **1a**,**b** in the presence of clay K-10 under ultrasonication to furnish products **2a**,**b** in 1.5 hours and 2.5 hours, respectively.

Similarly, we carried out the reaction of α-diazo ketones **1a**–**h** in commercial dichloromethane in the presence of

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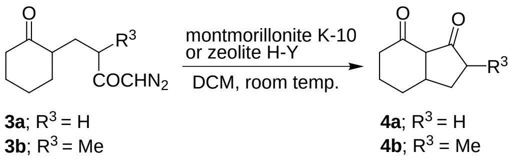
zeolite H-Y as described above. The decomposition of α-diazo ketones **1a**–**h** takes place to afford the corresponding α-hydroxy ketones **2a**–**h** (Scheme 1). It may be noted that the yield of α-hydroxy ketones in both montmorillonite clay K-10 as well as zeolite H-Y mediated reactions of α-diazo ketones were found to be the same (see Table 1).



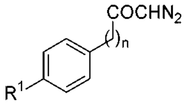
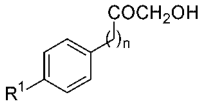
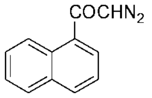
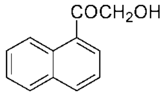
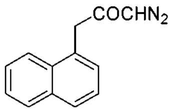
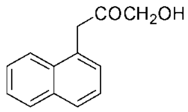
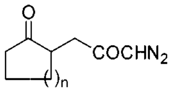
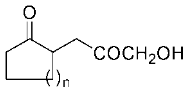
Scheme 2

We have shown that diazo compounds **3a**,**b** having a three-carbon chain tethered to a cyclohexanone ring system, react with Amberlyst-15[15] or Lewis acid[20] to furnish the rearranged 1,3-diones **4a**,**b** instead of the corresponding α-hydroxy ketones. We were keen to study the effect of montmorillonite K-10 or zeolite H-Y with diazo ketones **3a**,**b**. To a solution of diazo ketone **3a** (100 mg) in dichloromethane was added montmorillonite K-10 (125 mg) and the reaction was followed by TLC until the disappearance of starting material. Filtration, followed by concentration of the filtrate under reduced pressure, gave a residue which was subjected to silica gel column chromatography to afford product[15,20] **4a** (68%) in a regioselective manner (Scheme 2). The reaction was repeated with zeolite H-Y and also afforded product **4a**. Under similar conditions, the product **4b** was obtained from **3b** using clay K-10 as well as zeolite H-Y.

We further extended the solid acid mediated reactions of α-diazo compounds **5**–**7**. In the case of **5**, purification on neutral alumina column afforded the novel 3-furanone derivative **8** in 85% yield (Table 2). The presence of characteristic singlet at $\delta = 2.72$ ppm for OH proton and two doublets at $\delta = 4.14$ and 4.06 ppm having coupling constant $J = 16.6$ Hz for the OCH_2 protons in ^1H NMR spectrum; the presence of three sp^3 carbons, one sp^2 carbon, three quaternary carbons in ^{13}C/DEPT-135 analyses revealed the structure of **8**. Moreover, FT-IR spectrum and the deutrium exchange experiment in NMR confirmed the presence of hydroxy group in **8**. A plausible mechanism for the formation of isomeric furanone skeleton **8** instead of the corresponding alcohol **8a** from **5** involves intramolecular cyclization of the initially formed O-H insertion product **8a** (Scheme 3). It is noteworthy that the formation of furan ring has also been observed from γ-keto alcohols of type **8a**.[21] Diazo ketones **6**,**7** under similar reaction conditions afforded the corresponding furanones **9**, **10** in very good yield. The same results were observed using zeolite H-Y instead of clay K-10.

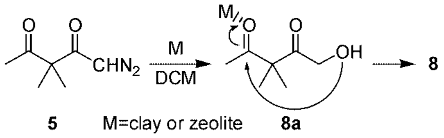
Finally, we were eager to study the O-H insertion reactions of α-diazo carbonyl compounds **1a**,**b** with alcohols in the presence of clay or zeolite to obtain α-alkoxy ketones **11**. Thus, diazo ketone **1a** (50 mg) in absolute meth-

Table 1 α-Hydroxy Ketones Produced via Scheme 1

α-Diazo Ketones **1**	α-Hydroxy Ketones **2**	Time[a] (h) r.t.	Clay Method Yield[b] (%)	Zeolite Method Yield[b] (%)
 **1a**; n = 0, R^1 = H **1b**; n = 0, R^1 = OMe **1c**; n = 1, R^1 = H **1d**; n = 2, R^1 = H	 **2a**; n = 0, R^1 = H **2b**; n = 0, R^1 = OMe **2c**; n = 1, R^1 = H **2d**; n = 2, R^1 = H	5/4 9/8 4/4 3.5/4	**2a**; 90 **2b**; 80 **2c**; 83 **2d**; 86	**2a**; 92 **2b**; 84 **2c**; 87 **2d**; 86
 **1e**	 **2e**	6/5	82	85
 **1f**	 **2f**	7/5	79	82
 **1g**; n = 1 **1h**; n = 2	 **2g**; n = 1 **2h**; n = 2	3/2.5 4/2.5	**2g**; 73 **2h**; 76	**2g**; 79 **2h**; 82

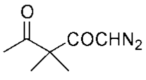
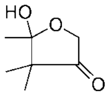
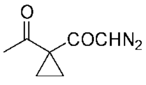
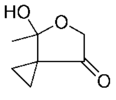
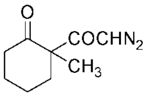
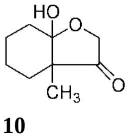
[a] The reaction time for clay/zeolite method.

[b] Yields (unoptimized) refer to chromatographically isolated and pure compounds **2**.



Scheme 3

Table 2 3-Furanones prepared by the Decomposition of α-Diazo Ketones in the Presence of Montmorillonite Clay K-10 or Zeolite H-Y

α-Diazo Ketones	3-Furanones	Reaction Time[a] (min)	Montmorillonite Clay Method Yield[b] (%)	Zeolite Method Yield[b] (%)
 **5**	 **8**	15/12	85	89
 **6**	 **9**	20/15	72	81
 **7**	 **10**	18/11	87	89

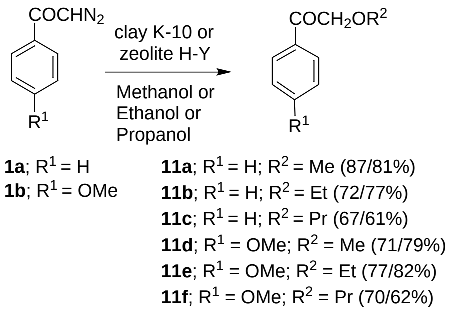
[a] The reaction time for clay/zeolite method.

[b] Yields (unoptimized) refer to chromatographically isolated and pure compounds.

anol in the presence of clay (100 mg) afforded α-methoxy ketone **11a** (87%). The use of zeolite H-Y under similar experimental conditions produced compound **11a** in 81% yield (Scheme 4). We have performed the above reaction of compounds **1a**,**b** using clay in absolute ethanol and propanol to furnish products **11b**–**f**. A similar trend was observed using zeolite H-Y in the above reactions. All new compounds gave satisfactory spectral data consistent with their structures.[22]

Yields of products in all reactions were comparable whether the reaction was carried out using clay or zeolite. There is no formation of other products due to C-H insertion. Significantly in all these reactions the use of the solid acid catalysts clay or zeolite produced high yield of products involving filtration of catalyst without any aqueous work-up.

In summary, we have discovered and explored that the decomposition of various α-diazo carbonyl compounds using new and environmentally acceptable solid acid catalysts such as montmorilonite K-10 or zeolite H-Y under mild heterogeneous conditions furnished α-hydroxy/alkoxy ketones, bicycloalkane-1,3-diones and 3-furanones. This solid acid method is in particularly attractive since it does not need any aqueous work up; mere filtration of the catalyst offering high yields of product.



Scheme 4

Acknowledgement

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References

(1) Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds. From Cyclopropanes to Ylides*; Wiley-Interscience: New York, **1998**.
(2) (a) Padwa, A. *Top. Curr. Chem.* **1997**, *189*, 121. (b) Padwa, A.; Hornbuckle, S. A. *Chem. Rev.* **1991**, *91*, 263. (c) Ye, T.; McKervey, M. A. *Chem. Rev.* **1994**, *94*, 1091. (d) Padwa, A.; Weingarten, M. D. *Chem. Rev.* **1996**, *96*, 223.
(3) (a) Miller, D. J.; Moody, C. J. *Tetrahedron* **1995**, *51*, 10811. (b) Bulugahapitiya, P.; Landais, Y.; Parra-Rapado, L.; Planchenault, D.; Weber, V. *J. Org. Chem.* **1997**, *62*, 1630. (c) Benati, L.; Nanni, D.; Spagnolo, P. *J. Chem. Soc., Perkin Trans. 1* **1997**, 457.
(4) Regitz, M.; Mass, G. *Diazo Compounds-Properties and Synthesis*; Academic Press: New York, **1986**, 90.
(5) Coppola, G. M. *Synthesis* **1984**, 1021.
(6) Perni, R. B. *Synth. Commun.* **1989**, *19*, 2383.
(7) (a) Patwardhan, S. A.; Dev, S. *Synthesis* **1974**, 348. (b) Gupta, S. K. *J. Org. Chem.* **1976**, *41*, 2642. (c) Dann, A. E.; Davis, J. B.; Nagler, J. *J. Chem. Soc., Perkin Trans. 1* **1979**, 158. (d) Ballini, R.; Marziali, P.; Mozzicafreddo, A. *J. Org. Chem.* **1996**, *61*, 3209.
(8) (a) Balogh, M.; Laszlo, P. *Organic Chemistry using Clay*; Spinger-Verlag: New York, **1993**. (b) Ponde, D. E.; Despande, V. H.; Bulbule, V. J.; Sudalai, A.; Gajare, A. S. *J. Org. Chem.* **1998**, *63*, 1058.
(9) Ponde, D. E.; Borate, H. B.; Sudalai, A.; Ravindranathan, T.; Deshpande, V. H. *Tetrahedron Lett.* **1996**, *37*, 4605.
(10) Upadhya, T. T.; Daniel, T.; Sudalai, A.; Ravindranathan, T.; Sabu, K. R. *Synth. Commun.* **1996**, *26*, 4539.
(11) Asakura, J.-I.; Robins, M. J.; Asaka, Y.; Kim, T. H. *J. Org. Chem.* **1996**, *61*, 9026.
(12) Lakshmi Kantham, M.; Lakshmi Shanthi, P. *Indian J. Chem. B.* **1990**, *35B*, 260.
(13) Sreekumar, R.; Rugmini, P.; Padmakumar, R. *Tetrahedron Lett.* **1997**, *38*, 6557; and references cited therein.
(14) Van Herwijnen, H. W. G.; Brinker, U. H. *J. Org. Chem.* **2001**, *66*, 2874.
(15) Muthusamy, S.; Babu, S. A.; Gunanathan, C.; Jasra, R. V. *Tetrahedron Lett.* **2001**, *42*, 5113.

(16) Muthusamy, S.; Babu, S. A.; Gunanathan, C.; Suresh, E.; Dastidar, P.; Jasra, R. V. *Tetrahedron* **2000**, *56*, 6307.

(17) (a) Muthusamy, S.; Babu, S. A.; Gunanathan, C. *Tetrahedron Lett.* **2000**, *41*, 8839. (b) Muthusamy, S.; Gunanathan, C.; Babu, S. A. *Tetrahedron Lett.* **2001**, *42*, 523. (c) Muthusamy, S.; Babu, S. A.; Gunanathan, C.; Suresh, E.; Dastidar, P. *Synlett* **2001**, 1407. (d) Muthusamy, S.; Babu, S. A.; Gunanathan, C.; Suresh, E.; Dastidar, P.; Jasra, R. V. *Tetrahedron* **2001**, *57*, 7009.

(18) Whitsell, J. K.; Buchanan, C. M. *J. Org. Chem.* **1986**, *51*, 5443.

(19) (a) Trost, B. M.; Ito, H.; Silcoff, E. R. *J. Am. Chem. Soc.* **2001**, *123*, 3367. (b) Hoffmann, T.; Zhong, T.; List, B.; Shabat, D.; Anderson, J.; Gramatikova, S.; Lerner, R. A.; Barbas, C. F. III. *J. Am. Chem. Soc.* **1998**, *120*, 2768.

(20) Muthusamy, S.; Babu, S. A.; Gunanathan, C. *Synth. Commun.* **2001**, *31*, 1205.

(21) Elander, M.; Leander, K.; Rosenblom, J.; Ruusa, E. *Acta Chem. Scand.* **1973**, *27*, 1907.

(22) **Typical Experimental Procedure**: The clay/zeolite catalysts used in this work were activated at 200 °C for 3 h. To a solution containing α-diazo ketone **1a** (100 mg) in commercial grade dichloromethane was added zeolite H-Y (175 mg) or montmorillonite clay K-10 (175 mg) and the mixture stirred at r.t. or ultrasonicated. Slow nitrogen evolution took place and the reaction mixture was followed by TLC until disappearance of starting material. The reaction mixture was then filtered, concentrated under reduced pressure and purified by silica gel column chromatography to afford product **2a**. All novel compounds gave satisfactory spectral data consistent with their structures. Selected spectral data of **5-Hydroxy-4,4,5-trimethyldihydrofuran-3-one** (**8**): colourless solid, mp 63–65 ºC; IR (KBr): 3372, 2998, 2978, 2913, 2934, 1744, 1704, 1471, 1453, 1396, 1121, 1039, 932, 851 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.14, (d, 1 H, J = 16.6 Hz, OCH_2), 4.06 (d, 1 H, J = 16.6 Hz, OCH_2), 2.72 (s, 1 H, OH), 1.50 (s, 3 H, CH_3), 1.09 (s, 3 H, CH_3), 1.05 (s, 3 H, CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 16.5 (CH_3), 22.0 (CH_3), 22.3 (CH_3), 51.1 (quat-C), 67.9 (OCH_2), 107.4 (quat-C), 218.6 (C=O); MS: m/z = 144 [M$^+$]; Anal. Calcd for $C_7H_{12}O_3$: C, 58.31; H, 8.39. Found: C, 58.40; H, 8.44. **2-Methoxy-1-(4-methoxyphenyl)ethanone** (**11d**): colourless thick liquid; IR(neat): 3059, 2934, 2842, 1776, 1691, 1602, 1576, 1512, 1462, 1422, 1312, 1259, 1175, 1128, 1026 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.93 (d, 2 H, J = 8.6 Hz, Arom-H), 6.93 (d, 2 H, J = 8.6 Hz, Arom-H), 4.65 (s, 2 H, OCH_2), 3.87 (s, 3 H, OCH_3), 3.50 (s, 3 H, OCH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 55.9 (OCH_3), 59.8 (OCH_3), 75.5 (OCH_2), 114.0 (=CH), 130.6 (=CH), 133.2 (quat-C), 164.2 (quat-C), 195.1 (C=O); MS: m/z = 180 [M$^+$]; Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.72; H, 6.65.