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Regeneration of Carbonyl Compounds from Their Nitrogeneous Derivatives: Chemical Transformation of the Dicarbonyl Compounds

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Regeneration methods of oximes, hydrazones, and N,N-dimethylhydrazones to the related carbonyl compounds were effected using various dicarbonyl compounds which are activated with electron withdrawing substituents such as trifluoromethylated β-diketones, β-acylpyruvates, and α-diketones *via* an equilibrium exchange reaction. The chemical transformations of the dicarbonyl compounds in the exchange reaction were investigated by various spectroscopic methods.

Introduction

Regeneration methods of oximes and hydrazones have received much attention to organic chemists.[1] These nitrogeneous derivatives could be converted to its original carbonyl compounds by a variety of oxidative and reductive methods.[2] And, hydrolytic cleavage method by equilibrium exchange with other carbonyl compounds under acidic conditions are still useful.[3] The latter method includes the use of formaldehyde, acetone, pyruvic acid, and levulinic acid.[4] Excess use of formaldehyde or acetone shift the equlibrium forward,[4a−b] and for pyruvic acid, decomposition of the initially formed pyruvic acid oxime to acetonitrile, water, and carbon dioxide is the driving force in the equilibrium exchange reaction.[5] In the case of levulinic acid the equilibrium is shifted forward in favor of the levulinic acid oxime by internal hydrogen bonding.[4d]

Recently, we have reported that 1,1,1-trifluoro-2,4-pentanedione (TPD or TFAA) proved to be effected in the regeneration of carbonyl compounds from their nitrogeneous derivatives (eq. 1).[6] We also reported that some dicarbonyl compou-
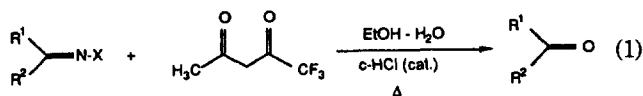
$$X = OH, NH_2, NMe_2, NHSO_2C_7H_7 \qquad (1)$$

nds which are activated with electron withdrawing substituent such as trifluoromethylated β-diketones, β-acylpyruvates, and α-diketones were useful in the deoximation reaction of cyclohexanone oxime to cyclohexanone (eq. 2).[7]

$$\qquad (2)$$
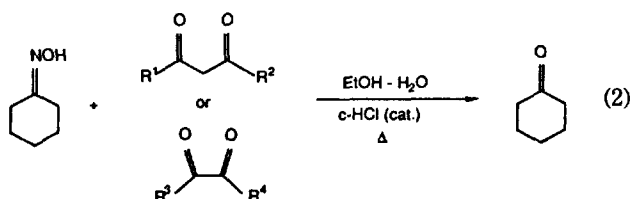
In continuation of our studies on the regeneration of carbonyl compounds, we report herein the chemical transformation of the dicarbonyl compounds in the exchange reaction to pursue the reason for why the equilibrium reaction goes completely by using only moderate excess (1.5-2.0 equiv) of the dicarbonyl compounds.

Results and Discussion

We have examined regeneration of cyclopentanone from its various nitrogeneous derivatives with some selected dicarbonyl compounds 1 as reagents (eq. 3). The yield of cyclo-

$$X = OH, NH_2, NMe_2 \qquad (3)$$
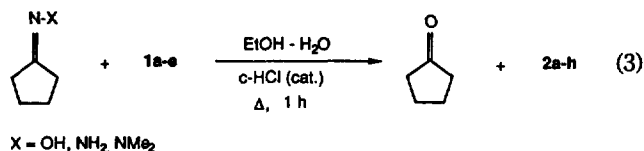
pentanone was quantitative in all cases as described in our reports,[6,7] and concomitantly the dicarbonyl compounds 1a-e were found to be converted to 2a-h. The structures of 1a-e and 2a-h are illustrated in Table 1. The equilibrium exchange reaction shifted toward completion due to the formation of stable heterocyclic molecules (2c, 2e, and 2f) or stabilized nitrogeneous derivatives by intramolecular hydrogen bonding (2a, 2b, 2d, 2g, and 2h). The structures of 2a-h were confirmed by comparison with the authentic samples prepared as described in the Experimental Section. The structures of 2c-f are easily discernible, however, the exact structures of the other compounds (2a, 2b, 2g, and 2h) were not easy to determine. Based on the data obtained from ^{1}H-NMR, ^{13}C-NMR, and IR spectra, we assumed the structures like below.

In ^{1}H-NMR spectra, the methylene protons of 2a appeared at 3.08 and 3.35 ppm, each integrating for one proton. The methylene protons of 2b appeared at 3.54 and 3.76 ppm, and one of the methylene protons at 3.54 ppm split further by the fluorine atoms ($J=1.1$ Hz). The characteristic AB quartets for 2a and 2b demonstrate that the carbonyl groups remain as keto form A in the solution state. Further evidence was supported by ^{13}C-NMR. The peak appeared at 46 ppm corresponding to the methylene carbon in A (for 2a) demonstrates that the carbon is sp^3 hybridized carbon.[8] However, in IR spectra there are no absorption bands representing the carbonyl groups for 2a and 2b whereas strong absorptions appeared at 3183 cm^{-1} and 3156 cm^{-1} for 2a and 2b, respectively. Consequently, these observations would make

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Table 1. Strcutures of 1a-e and 2a-h

Entry	X	1	2[a]
1	OH	(1a)	(2a)
2	OH	(1b)	(2b)
3	OH	(1c)	(2c)
4	OH	(1d)	(2d)[b]
5	OH	(1e)	(2e)[b]
6	NH_2	1a	(2f)[b]
7	NH_2	1b	(2g)[b]
8	NMe_2	1a	(2h)

[a] These compounds were identical with the authentic samples by GC and TLC. [b] Some other unidentified side products were detected on GC.

the structure A implausible, and strongly suggested that the structure B could represent for **2a** and **2b** in the solid state as proposed by us[6] and others.[9] Thus, the compounds **2a** and **2b** are stabilized *via* strong hydrogen bonding between the oxime proton and the fluorine atom,[10] and further stabilized by hydrogen bonding between the enolic proton and the imino nitrogen atom in the solid state. However, in solution state even in non-polar solvent such as deuterated chloroform, a breakage of the hydrogen bond between the enolic proton and the nitrogen atom would give rise to the keto form A.

A B

2a : R = Me
2b : R = Ph
----- weak hydrogen bond
▪▪▪▪▪▪ strong hydrogen bond

But in the case of compound **2g**, it is interesting to note that the carbonyl group remains in the enol form both in solution and in solid state as depicted below. In ^{1}H-NMR

2g

spectrum, the proton at C2 appeared at 6.84 ppm and the enolic proton at 13.3 ppm. In IR spectrum, a strong absorption band corresponding to the intramolecular hydrogen bonded hydroxyl stretching absorptions appeared at 3171

cm^{-1}, and there was no carbonyl absorption band. The strength of hydrogen bond between the enolic proton and the imino nitrogen atom in **2g** could be stronger than in **2a** or **2b** due to the differences in basicity of the imino nitrogen atom.[11]

The structure of compound **2h** could be assumed as a more stable form B, rather than the form A. This assumption is based on the spectroscopic data. In IR spectrum, the bands

A B

2h

in the range of 2800-3300 cm^{-1} might be due to the intramolecular hydrogen bonded N-H stretching vibration, and the consecutive bands in the range of 1678-1582 cm^{-1} might be corresponded to the C=O stretching, C=C stretching, and N-H bending vibrations in structure B. The imino nitrogen atom in structure A is so basic due to the electron donating N,N-dimethylamino group that the enol proton might be shifted to nitrogen atom.

In conclusion, we found that certain dicarbonyl compounds such as trifluoromethylated β-diketones, β-acylpyruvates, and α-diketones can be used conveniently in the regeneration of carbonyl compounds from their nitrogeneous derivatives. All dicarbonyl compounds were activated with electron withdrawing trifluoromethyl group, another carbonyl group, or ester group. Thus, the hydroxylamine, hydrazine, and N,N-dimethylhydrazine which were liberated from the equilibrium[12] react with the dicarbonyl compounds easily. The side products thus formed from the reaction are stable heterocyclic molecules or stabilized compounds by intramolecular hydrogen bonding, so the equilibrium in the reaction can be shifted toward completion in short time with moderate excess of the dicarbonyl compounds. The structures of side products were also studied in detail.

Experimental

Materials and Instruments. 3,5-Dimethylisoxazole (**2c**), 2,3-butanedione monoxime (**2d**), and other starting materials were purchased from Aldrich and used without further purification. Melting points were measured with a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were obtained on a Shimadzu IR-435 spectrophotometer. ^{1}H and ^{13}C-NMR spectra were recorded with a Bruker AM-300 spectrometer using TMS as the internal standard at 300 and 75 MHz, respectively. Mass spectra were obtained on a Shimadzu GCMS-QP 1000 mass spectrometer.

Regeneration of Cyclopentanone; General Procedure. To a stirred solution of nitrogeneous derivatives of cyclopentanone (1 mmol) and dicarbonyl compounds **1a-e** (1 mmol) in 50% aq. ethanol (3 m*l*), a catalytic amount of conc. HCl (50 μ*l*) was added, and the reaction mixture was heated to reflux for 1 h. The reaction mixture was analyzed by GC. In all cases, the yield of regenerated cyclopentanone is quantitative. The major side products **2a-h** were indentified by compa-

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rison with the authentic samples by GC (retention time) and TLC (R_f value), and the minor side products observed in some cases (entry 4, 5, 6, and 7) were not identified further.

1,1,1-Trifluoro-2,4-pentanedione 2-oxime (2a).[13] To a stirred solution of 1,1,1-trifluoro-2,4-pentanedione (**1a**, 6.0 g, 39 mmol) in ethanol (90 m*l*) was added 0.5 N HCl (100 m*l*) and a solution of hydroxylamine hydrochloride (5.34 g, 76 mmol) in water (20 m*l*). After stirred for 20 h, the solvents were removed by evaporation up to ~100 m*l*. Extraction with EtOAc (2×100 m*l*), washed with water (50 m*l*), dried with MgSO₄, and evaporation of the solvents gave the desired product. Flash column chromatography (CH₂Cl₂) afforded analytically pure white solid, 5.31 g (81%). mp. 89-91℃ (lit.[13] 86-87℃); ¹H-NMR (CDCl₃) δ 2.07 (s, 3H), 3.08 (d, *J*=18.3 Hz, 1H), 3.35 (d, *J*=18.3 Hz, 1H), 4.53 (s, 1H); ¹³C-NMR (CDCl₃/acetone-d₆, 1∶1) δ 12.40, 46.02, 102.71 (q, *J*=34 Hz), 122.03 (q, *J*=284 Hz), 155.81; MS (70 eV) m/e 58 (100), 69 (55), 100 (64), 169 (M⁺, 10); IR (KBr) cm⁻¹ 3183, 1485, 1397, 1207, 1180; Anal. Calcd. for C₅H₆F₃NO₂·1/4 H₂O: C. 34.58; H, 3.75; N, 8.07. Found: C. 34.21; H, 3.40; N, 7.99.

4,4,4-Trifluoro-1-phenyl-1,3-butanedione 3-oxime(2b).[13] To a stirred solution of 4,4,4-trifluoro-1-phenyl-1,3-butane-dione (**1b**, 10.8 g, 50 mmol) and hydroxylamine hydrochloride (7.0 g, 100 mmol) in aqueous methanol (H₂O 30 m*l*, MeOH 100 m*l*) was added dropwise a solution of potassium carbonate (6.9 g, 50 mmol) in water (20 m*l*) at room temperature. After stirred for 20 h, methanol was removed and the aqueous phase was extracted with ethyl acetate (2×100 m*l*). After washing with water (100 m*l*), dried with MgSO₄, and evaporated to dryness. The product was recrystallized from benzene to give white needles, 9.82 g (85%). mp. 144-145℃ (lit.[13] 143-144℃); ¹H-NMR (CDCl₃) δ 3.54 (dd, *J*=18.0 and 1.1 Hz, 1H), 3.76 (d, *J*=18.0 Hz, 1H), 7.16 (s, 1H), 7.41-7.70 (m, 5H); ¹H-NMR (DMSO-d₆) δ 3.57 (dd, *J*=18.6 and 1.1 Hz, 1H), 3.96 (d, *J*=18.6 Hz, 1H), 7.37-7.76 (m, 5H), 8.68 (s, 1H); MS (70 eV) m/e 77 (100), 162 (42), 231 (M⁺, 46); IR (KBr) cm⁻¹ 3156, 1370, 1300, 1281, 1192; Anal. Calcd. for C₁₀H₈F₃NO₂: C, 51.95; H, 3.46; N, 6.06. Found: C, 51.73; H, 3.36; N, 6.08.

Methyl 5-methylisoxazole-3-carboxylate (2e).[14] To a stirred solution of methyl acetopyruvate (**1e**, 1.44 g, 10 mmol) in methanol (20 m*l*) was added hydroxylamine hydrochloride (0.8 g, 11.5 mmol), and stirred at room temperature for 24 h. The reaction mixture was poured into water (100 m*l*), and extracted with ether (2×100 m*l*). The organic layers were washed with water (50 m*l*), dried with MgSO₄, and removal of the solvents gave a white solid, 0.8 g (57%). mp. 93-94℃; MS (70 eV) m/e 43 (41), 59 (100), 82 (28), 110 (25), 141 (M⁺, 14).

3-Trifluoromethyl-5-methylpyrazole (2f). To a stirred solution of 1,1,1-trifluoro-2,4-pentanedione (6.0 g, 39 mmol) in ethanol (100 m*l*) was added dropwise hydrazine hydrate (95%, 2.43 g, 46 mmol) during 30 min in water bath. After stirred at room temperature for 20 h, the solvent was removed by evaporation. Flash column chrormatographic separation (CH₂Cl₂) of the residue afforded pure product as a white solid, 5.21 g (80%). mp. 92-94℃; ¹H-NMR (CDCl₃) δ 2.32 (s, 3H), 5.64 (s, 1H), 13.04 (brs, 1H); ¹³C-NMR (CDCl₃) δ 10.31, 102.89, 121.51 (q, *J*=269 Hz), 141.46, 142.79 (q, *J*=37.5 Hz); MS (70 eV) m/e 81 (44), 101 (47), 131 (56), 149 (69), 150 (M⁺, 95), 151 (M⁺+1, 100); IR (KBr) cm⁻¹ 3198, 3125, 2994,

1505, 1439, 1250, 1134; Anal. Calcd. for C₅H₅F₃N₂: C, 40.00; H, 3.33; N, 18.67. Found: C, 39.71; H, 3.25; N, 18.73.

4,4,4-Trifluro-1-phenyl-1,3-butanedione 3-hydrazone (2g). To a stirred solution of 4,4,4-trifluoro-1-phenyl-1,3-butanedione (10.8 g, 50 mmol) in ethanol (200 m*l*) was added dropwise hydrazine hydrate (95%, 2.90 g, 55 mmol) during 30 min in water bath. After stirred at room temperature for 24 h, the solvent was removed by evaporation. Flash column chromatographic separation (CH₂Cl₂) of the residue afforded pure product as a white solid, 10.6 g (92%). mp. 132-135℃; ¹H-NMR (CDCl₃/acetone-d₆, 1∶1) δ 2.90 (brs, 2H), 6.84 (s, 1H), 7.36-7.76 (m, 5H), 13.3 (brs, 1H); MS (70 eV) m/e 77 (46), 161 (100), 230 (M⁺, 37); IR (KBr) cm⁻¹ 3314, 3171, 1343, 1254, 1192, 1165; Anal. Calcd. for C₁₀H₉F₃N₂O: C, 52.17; H, 3.91; N, 12.17. Found: C, 52.37; H, 3.67; N, 12.34.

1,1,1-Trifluoro-2,4-pentanedione 2-dimethylhydrazone (2h). To a stirred solution of 1,1,1-trifluoro-2,4-pentanedione (6.0 g, 39 mmol) in ethanol (100 m*l*) was added dropwise 1,1-dimethylhydrazine (2.33 g, 39 mmol) during 30 min in water bath. After stirred at room temperature for 20 h, the solvent was removed by evaporation. Flash column chromatographic separation (CH₂Cl₂) of the residue afforded pure product as a pale yellow oil, which was solidified slowly as a pale yellow solid, 7.10 g (94%). mp. 40-42℃; ¹H-NMR (CDCl₃) δ 2.20 (s, 3H), 2.61 (s, 6H), 5.23 (s, 1H), 11.50 (s, 1H); ¹³C-NMR (CDCl₃) δ 18.02, 47.71, 86.92, 117.52 (q, *J*=288 Hz), 169.37, 175.02 (q, *J*=32.7 Hz); MS (70 eV) m/e 44 (100), 59 (32), 84 (52), 196 (M⁺, 32); IR (KBr) cm⁻¹ 2997, 2966, 1678, 1616, 1582, 1277, 1250; Anal. Calcd. for C₇H₁₁F₃N₂O: C, 42.86; H, 5.61; N, 14.29. Found: C, 42.79; H, 5.68; N, 14.36.

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Etching of Al and Cu Solids by SiCl₄ Molecules

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The classical trajectory method, previously applied to the reactions of polyatomic molecules with fcc structured metal solids[S. C. Park, C. H. Cho, and C. H. Rhee, *Bull. Kor. Chem. Soc.*, 11, 1(1990)][1] is extended to the collision energy dependence of the reaction of the Al solid by SiCl₄ molecules. We have calculated etching yields, degrees of anisotropy, kinetic energy distributions, and angular distributions for the reactions of the Al solid and compared with those for the reactions of the Cu solid. Over the range of collision energies we considered, the reactions of the Al solid show higher etching yield and better anisotropy than the reactions of the Cu solid. Details of reaction mechanisms and the relevance of these calculations for the dry etching of CuAl alloy are discussed.

Introduction

The study of plasma assisted chemical reactions on metal and semiconductor solids has received extensive attention in recent years.[1-10] The main reason for this is that reactive sputter etching is a widely used process in the micro-fabrication of VLSI (very-large-scale-integrated circuits) and ULSI (ultra-large-scale-integrated circuits). As the dimensions of the VLSI and ULSI chips are reduced, and the number of components per chip increased, the degree of control over the manufacturing processes must necessarily be improved.[11-14] This may only be achieved by a detailed understanding of the mechanisms involved in each of the many steps, such as ion implantation, diffusion, oxidation, film deposition, lithography, etching, *etc.* required to make VLSI and ULSI chips. This micro-world, the potential of which can hardly be fully appreciated even today, has a direct appeal to all those of scientific inclination. However, the role of chemistry in the creation of this world becomes clear only on closer examination of the manufacturing processes. Chemistry plays a key role not only in the understanding of fundamental reactions for the processes, but also in the mass production of semiconductors containing integrated components.

Plasma reactions on metal solids are an important class of reactions in the industrial manufacture of VLSI chips.[11-14] Extensive theoretical and experimental studies of plasma reactions on copper solid have been reported[15-24] and have proposed detailed sputtering mechanisms.[23,24] Key reactions on metal etching in the complementary metaloxide semiconductor (CMOS) micro-fabrication are the reactions of Cu, Al and Cu-Al alloys with polyatomic gas plasmas such as SiCl₄, CCl₄, BCl₃ and mixtures of these gases with Cl₂.[12,25] One of the most difficult problems in CMOS micro-fabrica-tion is the etch of Cu and Al solids which is essential in the CMOS fabrications. Although extensive research and development have been pursued for the reactions in manufacturing point of view, one has not yet found efficient and proper ways of the etching of Cu and Al solids and Al-Cu alloy. It does require the fundamental understanding for the reactions. In spite of the importance for these reactions, not only in industrial interests but also in the fundamental interest of basic science, very little detailed experimental investigation of the reaction on Al solids and Cu-Al alloys has been done, and the mechanisms involved are unknown. Hence there is a need for theoretical investigation of these systems.

This is the second paper in the series of a classical trajectory study of etch reactions on metal surfaces. In the first paper[1], the classical trajectory method for an application to reactions of polyatomic molecule with a fcc metal solid has been employed and has tested to a model Al + SiCl₄ reaction at collision energy 600 eV. In this paper, we present the collision energy dependence of the etch reactions of the aluminum solid by SiCl₄ molecules and compare with the reactions of the copper solid by SiCl₄ molecules previously reported by Park *et al.*[3] A model SiCl₄ + Al(001) system is employed to calculate etching yields, the nature of products of the reactions, and the energy and angular distributions of the products.

A brief review of the theory, and a discussion of the interaction potential and calculation details are given in the next section. The results and discussion are presented in Sec. III. Conclusion and remarks are contained in Sec. IV.

Theory and Calculations

The approach used here to treat the reactions of the Al