

Regeneration of Carbonyl Compounds from Their Nitrogenous Derivatives: Chemical Transformation of the Dicarboxyl Compounds

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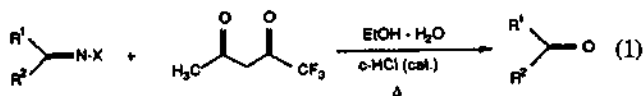
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Taedeog-Tanji, Taejon 305-606. Received December 13, 1991

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

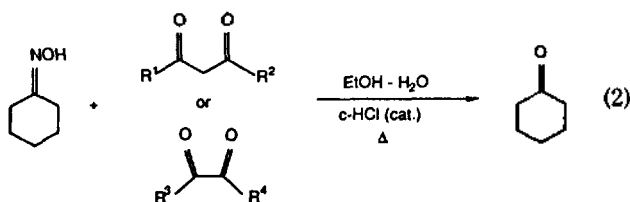
Regeneration methods of oximes and hydrazones have received much attention to organic chemists.¹ These nitrogenous derivatives could be converted to its original carbonyl compounds by a variety of oxidative and reductive methods.² And, hydrolytic cleavage method by equilibrium exchange with other carbonyl 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 equilibrium 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 TFPA) proved to be effected in the regeneration of carbonyl compounds from their nitrogenous derivatives (eq. 1).⁶ We also reported that some dicarbonyl compounds



X = OH, NH₂, NMe₂, NHSO₂C₂H₅

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

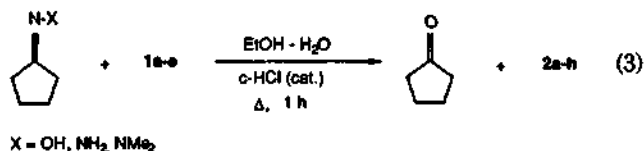


In continuation of our studies on the regeneration of carbonyl compounds, we report herein the chemical transformation of the dicarbonyl compounds in the exchange reaction to pursue the reason for why the equilibrium reaction goes

completely by using only moderate excess (1.5-2.0 equiv) of the dicarbonyl compounds.

Results and Discussion

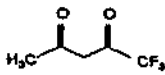
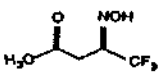
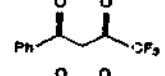
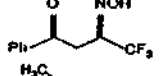
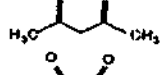
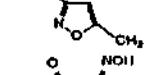
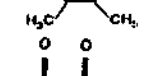
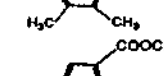
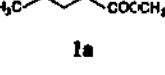
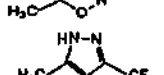
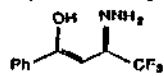
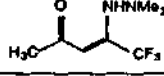
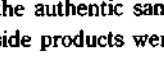
We have examined regeneration of cyclopentanone from its various nitrogenous derivatives with some selected dicarbonyl compounds **1** as reagents (eq. 3). The yield of cyclo-



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 nitrogenous 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 ¹H-NMR, ¹³C-NMR, and IR spectra, we assumed the structures like below.

In ¹H-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 ¹³C-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

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

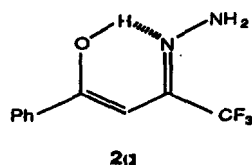
Entry	X	1	2 ^a
1	OH	 (1a)	 (2a)
2	OH	 (1b)	 (2b)
3	OH	 (1c)	 (2c)
4	OH	 (1d)	 (2d) ^b
5	OH	 (1e)	 (2e) ^b
6	NH ₂	1a	 (2f) ^b
7	NH ₂	1b	 (2g) ^b
8	NMe ₂	1a	 (2h)

^aThese compounds were identical with the authentic samples by GC and TLC. ^bSome 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 us⁶ 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.



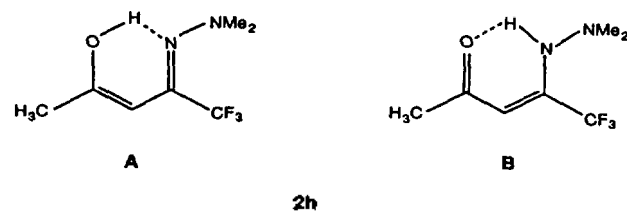
But in the case of compound 2g, it is interesting to note that the carbonyl group remains in the enol form both in solution and in solid state as depicted below. In ¹H-NMR



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



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 nitrogenous 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 equilibrium¹² 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. ¹H and ¹³C-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 nitrogenous derivatives of cyclopentanone (1 mmol) and dicarbonyl compounds 1a-e (1 mmol) in 50% aq. ethanol (3 ml), 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 identified by compa-

ribose 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 ml) was added 0.5 N HCl (100 ml) and a solution of hydroxylamine hydrochloride (5.34 g, 76 mmol) in water (20 ml). After stirred for 20 h, the solvents were removed by evaporation up to ~100 ml. Extraction with EtOAc (2×100 ml), washed with water (50 ml), dried with $MgSO_4$, and evaporation of the solvents gave the desired product. Flash column chromatography (CH_2Cl_2) afforded analytically pure white solid, 5.31 g (81%). mp. 89–91°C (lit.¹³ 86–87°C); 1H -NMR ($CDCl_3$) 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); ^{13}C -NMR ($CDCl_3/acetone-d_6$, 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 $C_5H_5F_3NO_2 \cdot 1/4 H_2O$: 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-butanedione (**1b**, 10.8 g, 50 mmol) and hydroxylamine hydrochloride (7.0 g, 100 mmol) in aqueous methanol (H_2O 30 ml, MeOH 100 ml) was added dropwise a solution of potassium carbonate (6.9 g, 50 mmol) in water (20 ml) at room temperature. After stirred for 20 h, methanol was removed and the aqueous phase was extracted with ethyl acetate (2×100 ml). After washing with water (100 ml), dried with $MgSO_4$, and evaporated to dryness. The product was recrystallized from benzene to give white needles, 9.82 g (85%). mp. 144–145°C (lit.¹³ 143–144°C); 1H -NMR ($CDCl_3$) 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 ($DMSO-d_6$) 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 $C_{10}H_8F_3NO_2$: 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 acetoacrylate (**1e**, 1.44 g, 10 mmol) in methanol (20 ml) 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 ml), and extracted with ether (2×100 ml). The organic layers were washed with water (50 ml), dried with $MgSO_4$, and removal of the solvents gave a white solid, 0.8 g (57%). mp. 93–94°C; 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 ml) 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 chromatographic separation (CH_2Cl_2) of the residue afforded pure product as a white solid, 5.21 g (80%). mp. 92–94°C; 1H -NMR ($CDCl_3$) δ 2.32 (s, 3H), 5.64 (s, 1H), 13.04 (brs, 1H); ^{13}C -NMR ($CDCl_3$) 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 $C_5H_5F_3N_2$: C, 40.00; H, 3.33; N, 18.67. Found: C, 39.71; H, 3.25; N, 18.73.

4,4,4-Trifluoro-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 ml) 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 (CH_2Cl_2) of the residue afforded pure product as a white solid, 10.6 g (92%). mp. 132–135°C; 1H -NMR ($CDCl_3/acetone-d_6$, 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 $C_{10}H_9F_3N_2O$: 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 ml) 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 (CH_2Cl_2) 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°C; 1H -NMR ($CDCl_3$) δ 2.20 (s, 3H), 2.61 (s, 6H), 5.23 (s, 1H), 11.50 (s, 1H); ^{13}C -NMR ($CDCl_3$) 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 $C_7H_{11}F_3N_2O$: C, 42.86; H, 5.61; N, 14.29. Found: C, 42.79; H, 5.68; N, 14.36.

Acknowledgement. We wish to thank the Korea Science and Engineering Foundation for financial support of this work.

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Etching of Al and Cu Solids by SiCl₄ Molecules

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Received December 18, 1991

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 reported¹⁵⁻²⁴ 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 paper¹, 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