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Exo-7-ethyl-5-methyl-6,8-dioxabicyclo[3.2.1]oct-3-ene (3). To a refluxed solution of *t*-butoxide (0.54 g) in *t*-butyl alcohol (8 m*l*) was added 0.23 g of **2** and refluxed overnight. After cooling, *t*-butyl alcohol was removed and H_2O (10 m*l*) was added to this reaction mixture which was then extracted with diethyl ether (20 m*l*×4) and dried ($MgSO_4$), followed by filtration, evaporation and chromatography gave 0.095 g of the product **3** (63% yield).

^{1}H-NMR ($CDCl_3$): δ 5.77 (br, s, 2H), 4.20 (br, s, 1H), 3.82 (m, 1H), 2.8-1.3 (m, 4H), 1.60 (s, 3H), 0.90 (t, 3H); IR (neat): 2934, 1664, 1459, 1391, 1317, 1251, 720 cm^{-1}.

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A Facile Synthetic Route to 1,2-Dicarbomethoxy-1,2-dicyanocyclopropanes

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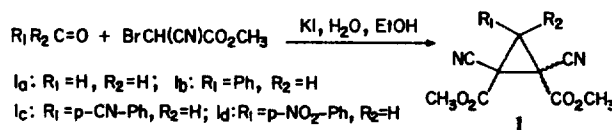*Department of Chemistry, Inje University, Kimhae 621-749*

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Although there are several reports on the synthesis of 1,1,2-trior 1,1,2,2-tetracyanocyclopropanes, examples on the preparation of 1,2-dicyanocyclopropanes are rare. 1,1,2-Tricyanocyclopropanes can be prepared from bromomalononitrile and ylidenecyanoacetate.[1] 1,1,2,2-Tetracyanocyclopropanes can be prepared by the reaction of formaldehyde and malononitrile,[2] tetracyanoethylene and diazomethane,[3] or tetracyanoethylene with bromoketene acetals.[4] A large number of substituted 1,1,2,2-tetracyanocyclopropanes are available by the Wideqvist reaction,[5,6] in which a carbonyl compound reacts with 2 equiv of bromomalononitrile. Hart and his coworkers reported a similar cyclopropanation procedure.[7,8]

In the present report, we extended the Wideqvist reaction to prepare 1,2-dicarbomethoxy-1,2-dicyanocyclopropanes. A series of aldehydes and ketones were condensed with methyl bromocyanoacetate in the presence of potassium iodide.[9] The

Table 1. Synthesis of 1,2-Dicarbomethoxy-1,2-dicyanocyclopropane $(1_{a-d})^a$

Compd	R_1	R_2	temp, °C	time, hr	yield, %	mp, °C
1_a	H	H	25	60	21	119-120
1_b	Ph	H	25	10	45	135-136
1_c	*p*-CN-Ph	H	25	10	50	114-115
1_d	*p*-NO$_2$-Ph	H	25	10	54	116-117
	p-CH$_3$O-Ph	H	25	10	b	
	p-OH-Ph	H	25	10	b	
	CH$_3$	H	25	48	b	
	CCl$_3$	H	25	10	b	
	CH$_3$	CH$_3$	25	10	b	
	—(CH$_2$)$_5$—		25	10	b	
	Ph	CH$_3$	25	10	b	
	Ph	CH$_2$CN	25	10	b	
	p-CN-Ph	CH$_3$	25	10	b	
	p-Cl-Ph	CH$_3$	25	10	b	

^{a} All the cyclopropans were mixtures of *cis*- and *trans*-isomers, which was confirmed by ^{1}H-NMR and IR spectra. ^{b} Small amount of methyl cyanoiodoacetate was formed.

$R_1R_2C=O$ + $BrCH(CN)CO_2CH_3$ $\xrightarrow{KI, H_2O, EtOH}$

1_a: R_1=H, R_2=H; 1_b: R_1=Ph, R_2=H

1_c: R_1=*p*-CN-Ph, R_2=H; 1_d: R_1=*p*-NO$_2$-Ph, R_2=H

results are summarized in Table 1. As shown in Table 1, formaldehyde, benzaldehyde, and substituted benzaldehydes react readily with methyl bromocyanoacetate to give mixtures of *cis*- and *trans*-1,2-dicarbomethoxy-1,2-dicyanocyclopropanes (1_{a-d}) in a moderate yield. Most of the common ketones such as acetone, cyclohexanone, benzophenone, and 4-acetylbenzonitrile are inert to the condensation. In the case of *p*-substituted benzaldehydes, electron-withdrawing on benzene ring accelerated the reaction. However, benzaldehydes with electron-releasing group such as −OCH$_3$ failed to give cyclopropanes. These results are reasonable in view of the electrophilicity of carbonyl carbon. Chemical structures of the resulting cyclopropanes 1_{a-d} were identified by ^{1}H-NMR, IR, and elemental analysis data.[10] All the spectral and elemental analysis data confirmed the expected structures.

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9. A representative propanation procedure is as follows: A solution of potassium iodide (7.0 g, 42 mmol) in 20 ml of water was added slowly to the solution of benzaldehyde (2.12 g, 20 mmol) and methyl bromocyanoacetate (7.12 g, 40 mmol) in 20 ml of ethanol at 25°C. After stirring for 10 hr at 25°C, the product was filtered and rinsed with 20 ml of cold ethanol. The obtained product was dried and recrystallized from 95% ethanol to give 2.6 g (45% yield) of 1_b.

10. Analytical data of 1_{a-d} are as follows: 1_a: ^{1}H-NMR (acetone-d_6) δ 2.63 (s, 2H), 3.93 (s, 6H); IR (KBr) 3105, 3008 (propane ring C-H), 2240 (CN), 1745 (*trans* C=O), 1734 (*cis* C=O) cm^{-1}. Anal. Calcd for $C_9H_8N_2O_4$: C, 51.92; H, 3.85; N, 13.46. Found: C, 51.82; H, 3.83; N, 13.48. 1_b: ^{1}H-NMR (acetone-d_6) δ 3.86 (s, 6H), 3.93-4.10 (m, 1H), 7.30-7.71 (m, 5H); IR (KBr) 3023 (cyclopropane ring C−H), 2245 (CN), 1750 (*trans* C=O), 1737 (*cis* C=O) cm^{-1}. Anal. Calcd for $C_{15}H_{12}N_2O_4$: C, 63.38; H, 4.23; N, 9.86. Found: C, 63.30; H, 4.28; N, 9.80. 1_c: ^{1}H-NMR (acetone-d_6) δ 3.87 (s, 6H), 4.23 (s, 1H), 7.67-7.99 (m, 4H); IR (KBr) 3075 (cyclopropane ring C−H), 2240, 2220 (CN), 1748 (C=O) cm^{-1}. Anal. Calcd for $C_{16}H_{11}N_3O_4$: C, 62.14; H, 3.56; N, 13.59. Found: C, 62.08; H, 3.51; N, 13.51. 1_d: ^{1}H-NMR (acetone-d_6) δ 3.78-4.05 (m, 6H), 4.30 (s, 1H), 7.70-8.43 (m, 4H); IR (KBr) 3090, 3050 (cyclopropane ring C−H), 2250 (CN), 1758 (*trans* C=O), 1742 (*cis* C=O) cm^{-1}. Anal. Calcd for $C_{15}H_{11}N_3O_6$: C, 54.71; H, 3.34; N, 12.77. Found: C, 54.63; H, 3.39; N, 12.70.

Vibrational Relaxation of Asymmetric Stretching Levels of Water Molecules in H_2O+Ar Collision

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In the vibrational relaxation of H_2O molecules, following the excitation to the asymmetric stretching level (v_3), relaxation can proceed through several different energy transfer pathways.[1-3] The equilibration of the v_3 and v_1 levels is very fast, being as fast as the gas kinetic collision rate.[2,4] The dominant path for the collisional deexcitation of these equilibrated stretching levels by a collision partner is relaxation down to the bending overtone ($2v_2$) level followed by relaxation of a single bending quantum to the bending fundamental (v_2) level, which finally returns to the ground level. In recent paper, we reported the 001→020, 020→010, 010→000 transi-

tion probabilities in H_2O+Ar over the temperature range of 200-1000 K based on the vibration-to-rotation (VR) model,[5] where the energy release ΔE is removed by rotation. Calculated transition probabilities agree well with the recent experimental data[2] over the entire temperature range. Another path for the relaxation of stretching levels is down to the bending fundamental level, *i.e.*, 001→010 relaxation, which also finally returns to the ground level. The other path, *i.e.*, the direct relaxation to the ground level (001→000) involves a large energy mismatch ($\Delta E = 3755$ cm^{-1}), and is expected to be much less efficient than the first two paths. The latter two paths are, of course, expected to be less efficient at low temperatures, but become more efficient at higher temperatures. Therefore, it is interesting to examine the relaxation rate for these different processes. For the latter two processes, the application of the model developed in Ref. 5 is so straightforward, that it is simple to study the effects of the relaxation. In this paper, we report such a study over the temperature range 200-1000 K and compare the results with those obtained for 001→020 relaxation rate.

In Ref. 5, we have shown the derivation of the VR energy transfer probability, for the 001→010 transition, the time evolution of oscillator state is

$$|\psi(t)> = \exp[g_1(t)a_2a_3^+]\exp[g_2(t)a_2^+a_3]\exp[g_3(t)a_2^-a_2]$$
$$\times \exp[g_4(t)a_3^+a_3]\exp[g_5(t)I]|001>, \quad (1)$$

where I is the identity operator and $g_i(t)$ is a complex valued function of time. Here a_i and a_i^+ are ladder operators. The probability of 001→010 vibrational deexcitation is

$$P_{001\to010} = \lim_{t\to\infty} |g_2(t)\exp[g_4(t)+g_5(t)]|^2, \quad (2)$$

the following five differential equations have to be solved to calculate the transition probability,

$$i\hbar\dot{g}_1(t) = -g_1(t)\hbar(\omega_2-\omega_3)-g_1^2(t)F'_{11}(t)+F'_{11}(t) \quad (3a)$$

$$i\hbar\dot{g}_2(t) = g_2(t)\hbar(\omega_2-\omega_3)+2g_1(t)g_2(t)F'_{11}(t)+F'_{11}(t) \quad (3b)$$

$$i\hbar\dot{g}_3(t) = g_1(t)F'_{11}(t)+\hbar\omega_2 \quad (3c)$$

$$i\hbar\dot{g}_4(t) = -g_1(t)F'_{11}(t)+\hbar\omega_3 \quad (3d)$$

$$i\hbar\dot{g}_5(t) = \frac{1}{2}\hbar(\omega_2+\omega_3). \quad (3e)$$

Here $F'_{11}(t) = (\hbar/2\omega_2)^{\frac{1}{2}}(\hbar/2\omega_3)^{\frac{1}{2}}F_{11}(R, \theta)$, which is the interaction potential responsible for 001→010 transition and defined in Ref. 5. The function $g_5(t)$ is simply $\exp[-i(\omega_2+\omega_3)t]$ and others are obtained numerically.

For the 001→000 transition, the quantum state needed in determining the transition probability is

$$|\psi(t)> = \exp[g_1(t)a_3^+]\exp[g_2(t)a_3]\exp[g_3(t)a_3^+a_3]$$
$$\times \exp[g_4(t)I]|001>, \quad (4)$$

where I is also the identity operator. The transition probability is

$$P_{001\to000} = \lim_{t\to\infty} |g_2(t)\exp[g_3(t)+g_4(t)]|^2. \quad (5)$$

where g_i's are the solutions of

$$i\hbar\dot{g}_1(t) = \hbar\omega_3 g_1(t)-F'_{01}(t) \quad (6a)$$

$$i\hbar\dot{g}_2(t) = -\hbar\omega_3 g_2(t)+F'_{01}(t) \quad (6b)$$