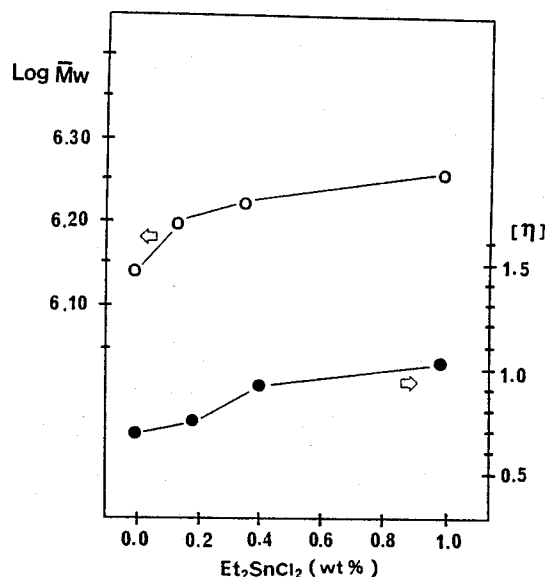


Table 3. Molecular Weights and Thermal Properties of Polydichlorophosphazene^a Depending on the Amounts of Catalysts

Catalysts	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	\bar{M}_w/\bar{M}_n	T_{10}^b (°C)
Blank ^c	167	34	4.9	395
0.2% AlCl ₃	138	43	3.2	388
0.2% AlCl ₃ + 0.2% Et ₂ SnCl ₂	162	48	3.4	391
0.2% AlCl ₃ + 0.4% Et ₂ SnCl ₂	164	43	3.8	395
0.2% AlCl ₃ + 1.0% Et ₂ SnCl ₂	183	44	4.2	400

^aMelt polymerized at 240 °C for 7 h. ^bT₁₀: Temperature of 10% degradation from TGA. ^cMelt polymerized without catalyst at 255 °C for 5 h.

**Figure 1.** Molecular weights and intrinsic viscosities of polyphosphazenes depending on the contents of Et₂SnCl₂.

responding thermal stability compared with the blank polymer prepared without catalyst. Also, all the chromatograms of the polymers formed in the presence of the catalysts have shown a monomodal and narrow molecular weight distribution in contrast to the well-known bimodal molecular weight distribution of the blank polymer. Figure 1 shows that the molecular weight and the intrinsic viscosity of the polymers are slightly increasing as the content of diethyltin dichloride increases.

Organotin(IV) compounds have already been demonstrated by the authors to act as a negative catalyst by inhibiting effectively the cross-linking reactions during the thermal polymerization reaction of the phosphazene trimers.⁴ It is generally known that Lewis acids such as boron and aluminum trihalides acting as initiation catalyst for ring-opening polymerization of the phosphazene trimer accelerate the polymerization reaction, but beyond a certain degree of polymerization cross-linking reaction is also induced resulting in limited product yields.^{5,11} However, addition of a relatively large amount of diethyltin dichloride seems to inhibit such a cross-

linking reaction allowing the chain-growing reaction to proceed for a enough period of time until high molecular weight is attained.

In conclusion, the catalytic melt polymerization of the phosphazene trimer using a combined catalytic system of aluminum trichloride and diethyltin dichloride affords high molecular weight poly(dichlorophosphazene) ($\bar{M}_w > 10^6$) in high yield (>90%). The molecular weights of the polymers are approximately proportional to the content of diethyltin dichloride in the catalytic system.

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Deoxygenation and Decomposition of Cyclic Ethers by Molybdenum Atoms

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Metal atoms have been utilized to effect insertion of a metal atom into carbon-hydrogen^{1,2} and carbon-carbon bonds.¹ The reactivity of metal atoms has also been studied for

Table 1. Cocondensation Reaction Conditions and Yields

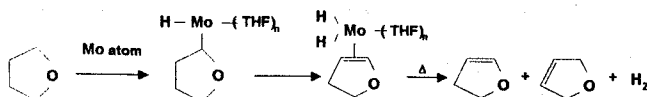
	Molybdenum vaporized (mmol)	Substrates (mmol)	Cocondensation time (min)	Yields (%) ^a	
				Hydrogen & methane ^b	Hydro- carbons ^c
THF	0.87	97	80	245	12.8
2-MeTHF	0.88	101	92	142	5.9
2,5-diMeTHF	0.79	101	106	90	3.4
oxepane	0.65	92	90	67	7.3

^aYields are based on the mole of Mo atoms vaporized. ^bTotal yields of hydrogen and methane were obtained from the pressure expressed after warming up the reaction matrix to room temperature and then trapping other hydrocarbons at liquid nitrogen temperature, with the known volume of the vacuum line. ^cThe samples are trapped at $-196\text{ }^{\circ}\text{C}$.

Table 2. Composition* of hydrocarbons gathered during warming up the cocondensation matrices of Mo atoms with various cyclic ethers in mole %

Composition substrates	ethylene	ethane	propylene	propane	butenes	iso-butane	n-butane	pentanes	hexanes
THF(1)	—	14.2	13.8	15.9	—	24.6	32.4	—	—
2-MeTHF(2)	—	7.8	8.2	24.0	—	10.7	44.5	—	—
2,5-diMeTHF(3)	4.4	51.9	21.9	21.7	—	—	—	—	—
oxepane(4)	1.0	2.3	7.5	9.7	8.1	1.0	6.9	39.1	24.5

*expressed as mole % of the total hydrocarbons gathered.

**Scheme 1.**

the deoxygenation and/or desulfurization from some organic compounds.³⁴ In this report, we present the results obtained from the cocondensation of molybdenum atoms with various cyclic ethers, such as tetrahydrofuran (1), 2-methyltetrahydrofuran (2), 2,5-dimethyltetrahydrofuran (3), and oxepane (4). Table 1 lists conditions of cocondensation experiments of molybdenum atoms with various substrates, *i.e.*, cyclic ethers. Throughout the cocondensation reactions, hydrogen and methane, and other hydrocarbons were produced in 67-245% and 3.4-12.8% yield, respectively, based on the mole of the molybdenum atoms vaporized. Table 2 shows the composition of the hydrocarbons generated from the cocondensation reactions.

Shevlin and co-workers⁵ have reported that C1, C2 hydrocarbons, and relatively large amount of hydrogen are formed in the cocondensation of molybdenum atoms with 1. It has been proposed⁵ that the hydrogen results from insertion of the Mo into a C-H bond of 1 to form the molybdenum hydride complexes and subsequent β -hydrogen transfer as shown in Scheme 1. They also have found that cocondensation of Mo with 1 followed by addition of the alkene to the matrix after condensation of the metal brings about hydrogenation of the alkene.

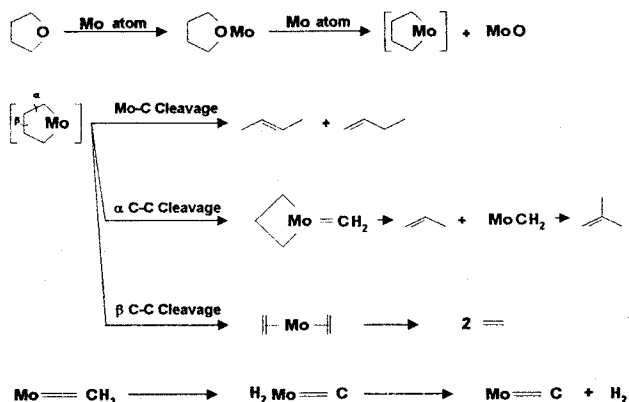
However, we have identified the formation of C2, C3 and C4 hydrocarbons from the above cocondensation reaction with 1. As shown in Table 2, besides the generation of C2

and C3 hydrocarbons, bigger hydrocarbons, such as C4 or C5 and C6, are generated by the cocondensation reaction of Mo atoms with 1, 2, and 4. Surprisingly, in the cocondensation reaction of molybdenum atoms with 3, any bigger hydrocarbons are not generated but C2 and C3. These results suggest that there would be two reactions occurring while warming up the matrix of the cocondensation, one is the insertion reaction of Mo into a C-H bond to generate the hydrogen and the other is the deoxygenation reaction to produce various hydrocarbons.

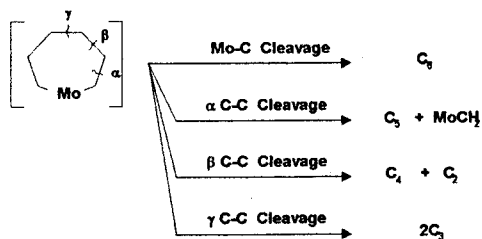
Based on the composition of hydrocarbons given in Table 2, we propose the mechanism of deoxygenation as shown in schemes 2, 3, 4, and 5 for the reaction systems of 1, 4, 2, and 3, respectively.

The Mo atom coordinates to the oxygen atom of the cyclic ether to form an unstable complex which decomposes to "MoO"⁶ and forms a metalacyclic compound with another Mo atom. Metal-carbon bond cleavages or α or β C-C bond cleavages of the metalacyclic compound produce unsaturated hydrocarbons and the molybdenum carbene. As shown in scheme 2 for using substrate 1, Mo-C bond cleavages of the metalacyclic intermediate produce 1-butene and 2-butene. The molybdenum carbene produced from α C-C bond cleavage reacts with propylene to yield isobutene, while a part of molybdenum carbene decompose to molybdenum carbides⁶ and hydrogen. According to yields for the reaction of Mo atoms with substrate 1, C3 and C4 hydrocarbons are produced as major products, and C2 hydrocarbons as minor products due to β C-C bond cleavage. The Mo-C bond cleavages produce a good amounts of *n*-butane. These results suggest that the bond cleavages occurred in the order of α C-C > Mo-C > C-C for the metalacyclic compounds.

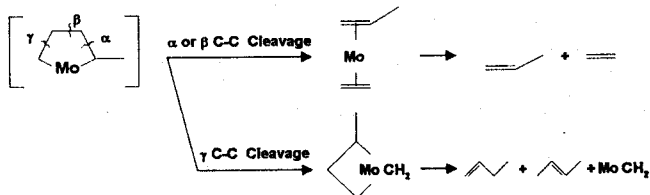
In the case of substrate 4 (see Scheme 3), Mo-C and α ,



Scheme 2.



Scheme 3.

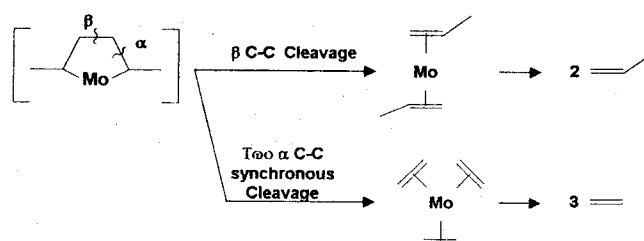


Scheme 4.

β , and γ C-C bond cleavages produce C6 unsaturated hydrocarbons, C5 and molybdenum carbene, C4 and ethylene, and C3 hydrocarbons, respectively, as similar ways shown in scheme 2. In this reaction, the ease of bond cleavages also appears in the order of α C-C > Mo-C > β C-C ~ γ C-C.

However, as shown in schemes 4 and 5, Mo-C bond cleavages do not occur for the substrates 2 and 3, while α , β , or γ C-C bond cleavages produce unsaturated hydrocarbons and molybdenum carbene. In the case of substrate 3, β C-C bond cleavage and synchronous cleavages of two α C-C bonds occur with the similar probability and yield only C3 and C2 unsaturated hydrocarbons. These results suggest that the Mo-C bonds are strengthened by the electron donation effects of the methyl groups in 2- and/or 5-positions of the metalacyclic intermediates.

The unsaturated hydrocarbons produced by the above processes are hydrogenated to the saturated hydrocarbons by the molybdenum hydrides generated from the insertion reaction of the Mo atom into a C-H bond of the cyclic ether, according to the mechanism proposed by Shevlin and co-workers.⁵ A similar mechanism has also been proposed for the deoxygenation reaction of 1 with organometallic cluster



Scheme 5.

compounds produced from the reaction of MoCl_3 with Mg and 1.⁷

Experimental

Molybdenum atoms were produced by electric resistive heating in a metal atom reactor similar to that described by Skell and co-workers.⁸ A sample of molybdenum wire, about 10 cm length with 1 mm diameter, was bent into a "U" shape and bolted to the two water-cooled brass electrodes. A current of about 50 ampere was applied to the electrodes to vaporize molybdenum in the rate of about 0.7 mmole/hr. The cocondensation was carried out on the wall of the reactor at 77 K with the internal pressure of the reactor being kept below 10^{-4} torr. After the cocondensation, the matrix allowed to warm up to room temperature for more than half an hour and the volatiles were pumped into a cold trap. The volatiles were subsequently removed by vacuum distillation through a series of slush baths at various temperatures and analyzed. IR spectra were recorded on a JASCO IRA-1 spectrometer. A HITACHI 064 gas chromatograph (Column: 20% BEEA on Chromosorb P AW, 6 m \times 1/8" stainless steel, Detector: TCD) and a JEOL JMS-DX303 mass spectrometer equipped with JMA-DA5000 data system (ionization mode: EI, 70 eV, ionmultiplier voltage: 1 kV) were used for quantitative analysis and for qualitative analysis of hydrocarbons, respectively. Esca Lab MKII, VG Scientific Ltd., was used for analysis of nonvolatile residue.

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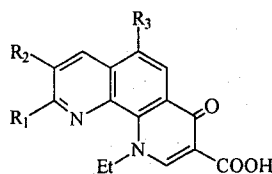
Quinolone(III): Synthesis of Pyrido[2,3-h]quinolone and Pyrido[2,3-g]quinolone-3-carboxylic Acid Derivatives as Potential Antibacterials

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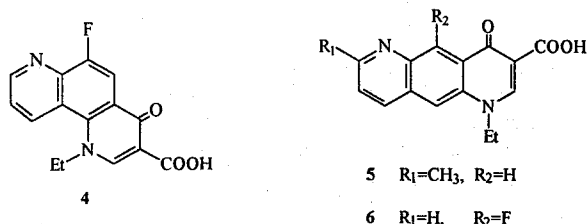
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In earlier paper,¹ we reported the synthesis of 1-ethyl-6-fluoro-4-oxo-pyrido[3,2-h]quinoline-3-carboxylic acid (**1**), 1-ethyl-9-(4-methylpiperazin-1-yl)-4-oxo-pyrido[3,2-h]quinoline-3-carboxylic acid (**2**) and 1-ethyl-8-fluoro-9-(4-methylpiperazin-1-yl)-4-oxo-pyrido[3,2-h]quinoline-3-carboxylic acid (**3**) as potential antibacterial compounds.



- 1** R₁=R₂=H, R₃=F
2 R₁=4-methyl-1-piperazinyl
R₂=R₃=H
3 R₁=4-methyl-1-piperazinyl
R₂=F, R₃=H

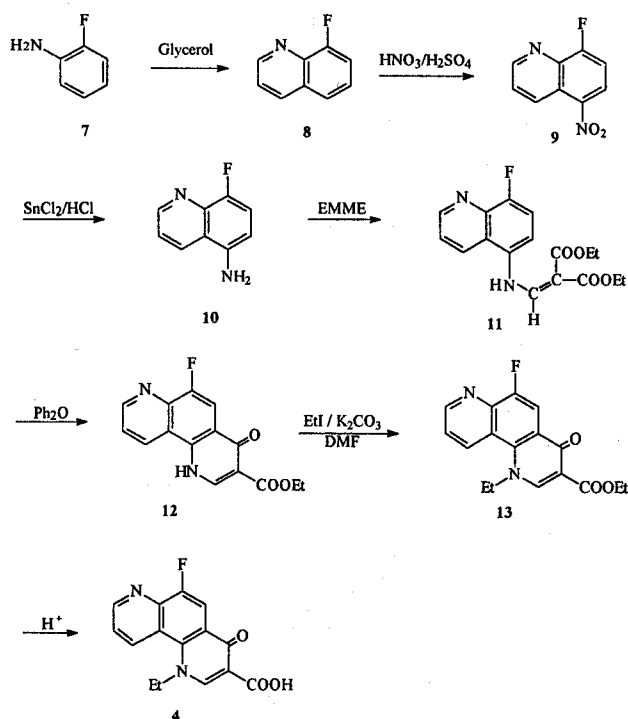
These potent antibacterial compounds belong to 4-quinolones, an important new class of synthetic antibacterial agents.²⁻⁴ Among the above three compounds, **1** was found to be the most active. Considering the structure activity relationship of quinolone antibacterials,²⁻⁴ 4-oxo-3-carboxyl group are essential.



- 5** R₁=CH₃, R₂=H
6 R₁=H, R₂=F

The substituents on N₁ are mostly to be small alkyl groups, e.g. ethyl or cyclopropyl. Besides 6-fluoro and 7-amine are known to be the magic groups.

Comparing the structural similarity of **1** to norfloxacin, it is understandable that 6-fluoro is the main reason to make it the most active. This result prompted us to synthesize



Scheme 1.

compound **4**, which has 7-amine and 6-fluoro.

Considering the proposed stacking model, the tetramer of quinolone, for the interaction of quinolone and DNA gyrase,⁴ substituted 1-ethyl-4-oxo-pyrido[2,3-g]quinoline-3-carboxylic acids (**5** and **6**), which are the linear form of quinolones, are expected to form the better stacking tetramer than the previous bent quinolones (**1**, **2** and **3**). Thus we tried also to synthesize **5** and **6**, and tested their activities.

Skraup reaction with 2-fluoroaniline (**7**), glycerol and sodium m-nitrobenzenesulfonate as oxidizing agent gave high yield of 8-fluoroquinoline (**8**).⁵ 8-Fluoroquinoline (**8**) was nitrated with HNO₃/H₂SO₄ to 8-fluoro-5-nitroquinoline (**9**).⁶ 8-Fluoro-5-nitroquinoline (**9**) was easily reduced to 5-amino-8-fluoroquinoline (**10**) with SnCl₂/HCl.⁷ The synthesis of 1-ethyl-6-fluoro-4-oxo-pyrido[2,3-h]quinoline-3-carboxylic acid (**4**) was achieved by reaction of 5-amino-8-fluoroquinoline (**10**) with diethyl ethoxymethylenemalonate (EMME), followed by thermal cyclization, N-ethylation and successive hydrolysis of the obtained ester **13** in mild acidic condition (Scheme 1).⁸⁻¹⁴

Strangely enough, we could not get the carboxylic acid **4**, through the hydrolysis in basic condition. When the last step, the hydrolysis of ethyl ester **13** to carboxylic acid **4** was carried out in basic condition, the N₁-ethyl group was also disappeared together with COO-CH₂CH₃.

2-Methyl-6-nitroquinoline (**14**) was reduced to 6-amino-2-methylquinoline (**15**) with H-reduced Fe/AcOH.¹⁵ The next steps of EMME cyclization, N-ethylation and hydrolysis were carried out by the well known methods (Scheme 2). Thermal cyclization of the malonate **16** was carried out in diphenyl ether to give the mixture of ethyl 7-methyl-4-oxo-pyrido[2,3-g]quinoline-3-carboxylate (**17**) and ethyl 7-methyl-4-oxo-pyrido[3,2-f]quinoline-3-carboxylate (**18**), which was successfully separated by recrystallization. Ethylation of **17** and hy-