

Figure 1. Variations of initial rate of ethylene dimerization with composition of catalysts and evacuation temperature. ● evacuated at 400°C; ○; equimolar mixture catalyst of nickel oxide and titanium oxide.

catalyst composition in the figure. The catalytic activity for ethylene dimerization was determined at 20°C by a conventional static system following pressure change from an initial pressure of 280 torr. Fresh catalyst sample of 0.2g was used for every run and the catalytic activity was calculated as the amount of ethylene consumed in the initial 3 minutes. Reaction products were analyzed by gas chromatography with a VZ-7 column at room temperature.

Different mole ratios of nickel oxide-titanium oxide were tested for their activities. It can be seen that the maximum rate is obtained at around equimolar composition. An equimolar coprecipitate of nickel hydroxide and titanium hydroxide was decomposed at different evacuation temperature and tested for

its activity. It can be seen that the activity appears above 200°C reaching a maximum at 400°C. On all the catalysts of NiO-TiO₂ treated with H₂SO₄, ethylene was selectively dimerized to *n*-butenes. In the composition of *n*-butenes analyzed by gas chromatography, 1-butene was found to predominate exclusively at the initial reaction time as compared with *cis*-butene and *trans*-butene. However, it was shown that the amount of 1-butene decreases with the elapse of reaction time, while the amount of 2-butene increases with that of reaction time. It was also observed that the specific surface area attained a maximum by the equimolar mixture of nickel oxide and titanium oxide, and the evacuation at 400°C. On the other hand, a series coprecipitated samples as well as nickel oxide, and titanium oxide by themselves which were not treated with H₂SO₄ were nearly inactive as catalyst for ethylene dimerization. Nickel oxide treated with H₂SO₄ exhibited very low activity for ethylene dimerization, while titanium oxide treated with H₂SO₄ exhibited low activity for ethylene polymerization, as shown in the figure.

According to the IR spectra, the catalyst treated with H₂SO₄ possessed the bidentate sulphate ion coordinated to the metal.⁵ The existence of both Brønsted and Lewis acid sites was shown by the IR spectra of pyridine adsorbed on the catalyst. In respect of crystalline structure, it was different depending on the evacuation temperature. They showed amorphous structure up to 400°C, rutile and nickel titanium oxide at 450°C, rutile, anatase and nickel titanium oxide at 500°C, and only anatase after the evacuation of 550°C.

References

- (1) A. Ozaki, *Nippon Kagaku Zasshi*, **75**, 1 (1954).
- (2) J. P. Hogan, R. L. Banks, W. C. Lanning, and A. Clark, *Ind. Eng. Chem.*, **47**, 752 (1955).
- (3) J. R. Sohn and A. Ozaki, *J. Catal.*, **59**, 303 (1979).
- (4) J. R. Sohn and A. Ozaki, *J. Catal.*, **61**, 29 (1980).
- (5) K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd Edition, John Wiley & Sons, New York, 1978.

Development of Catalysts for the Synthesis of Some Intermediate Fine Chemicals. (I) An Efficient Method for the Di-C-Ethylation of Ethyl Acetoacetate. Alkylation of Crowded Carbanions*

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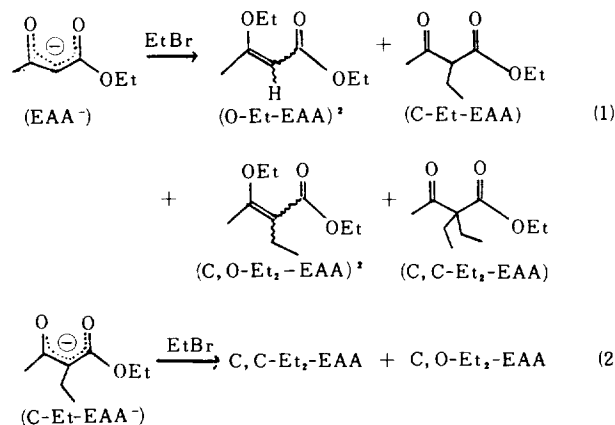
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Factors governing the reactivity of bimolecular nucleophilic substitution (*S_N2*) reactions are well known. For example, dipolar aprotic solvents greatly enhances the reactivity of anionic nucleophiles toward neutral substrates.¹ Introduction of bulkier

groups at the reaction center of the substrate retards the reaction. The reactivity of a nucleophile is greatly reduced when it becomes more crowded.

In this study, the ethylation of ethyl acetoacetate anion (EAA⁻) with ethyl bromide is investigated. Various products obtained by the reaction are indicated in eq 1 and 2.

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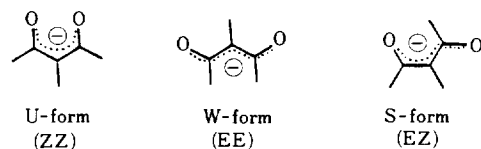


The anionic carbons of EAA^- and, especially, C-Et-EAA^- are very crowded. If the conformation of EAA^- or C-Et-EAA^- is influenced so that these carbon atoms are more exposed to the ethylating reagents, the reactivity would be enhanced. For this purpose, we have examined the effects of solvents and various reagents on the yield and the product distribution of the ethylation of EAA^- and C-Et-EAA^- . The most significant results obtained with a crown ether are described in this report.

The results obtained in dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), and ethanol (EtOH) in the presence and absence of added 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane) are summarized in Table 1 and Table 2. The yield and product distribution listed in these tables were measured by ^1H nmr and gas chromatography according to the literature.³

The overall yields for the production of $\text{C,C-Et}_2\text{-EAA}$ by stepwise diethylation of EAA^- are 72%, 4%, and 18% in DMSO, THF, and EtOH, respectively. In the presence of the crown ether, the yields are improved to 100%, 65%, and 26%, respectively. The high yield in DMSO parallels the high S_N2 reactivity of anionic nucleophiles in dipolar aprotic solvents.¹ The yield in THF or EtOH in the absence of the crown ether is particularly poor for the ethylation of C-Et-EAA^- . This may be related to the much more crowded conformation around the anionic carbon atom in C-Et-EAA^- compared with EAA^- .

Like other nonrigid β -dicarbonyl anions, EAA^- and C-Et-EAA^- would exist in three major conformations: U-, W-, and S-shapes.⁴



The steric environment of the anionic carbon atoms of these shapes is best estimated by using a space-filling model. Examination of a space-filling model indicates that the anionic carbon of the metal-free form of C-Et-EAA^- is most exposed in the W-conformation and least exposed in the U-conformation to the attack of external reagents.

Association of the carbanions with a metal ion lowers the nucleophilicity of the anionic centers. Moreover, the metal association prefers the U-form, decreasing the amount of the anions in W- or S-form. Addition of the crown ether to DMSO or THF leads to the dissociation of the carbanion from the counter-cation (Na^+ in the present study). This would result in

TABLE 1: Ethylation of EAA^-

| condition | yield(%) | Product distribution ^b (%) | | |
|-------------------|----------|---------------------------------------|----|----|
| | | C | O | CC |
| DMSO | 100 | 71 | 18 | 11 |
| THF | 83 | 100 | 0 | 0 |
| EtOH | 83 | 89 | 2 | 9 |
| DMSO + 15-crown-5 | 100 | 87 | 0 | 13 |
| THF + 15-crown-5 | 94 | 98 | 1 | 1 |
| EtOH + 15-crown-5 | 98 | 92 | 2 | 6 |

^a The reaction mixtures contained 7.8 mmole of thoroughly dried sodium salt of EAA^- (soluble in the solvents) and either 7.8 mmole or 23 mmole of ethyl bromide in 20 ml solvent. The yield represents the amount of ethyl groups attached to the substrate in comparison with the initial amount of the anionic substrate. Attachment of an ethyl group destroys one molecule of the anionic form of the substrate, and, therefore, the maximum yield attainable is 100%. The change in the amount of ethyl bromide did not affect the yield and the product distribution appreciably. When 15-crown-5 was added, its amount was 7.8 mmole. The reaction mixtures were incubated for 3 days at 25°C prior to the analysis of the products. The reaction in DMSO reached the maximum yield within three hours, and those in THF or EtOH within three days. ^b C, O, and CC stand for C-Et-EAA, O-Et-EAA, and C,C-Et₂-EAA, respectively.

TABLE 2: Ethylation of C-Et-EAA^-

| condition | yield(%) | Product distribution (%) | |
|-------------------|----------|--------------------------|----|
| | | CC | CO |
| DMSO | 88 | 97 | 3 |
| THF | 5 | 100 | 0 |
| EtOH | 24 | 100 | 0 |
| DMSO + 15-crown-5 | 100 | 100 | 0 |
| THF + 15-crown-5 | 71 | 100 | 0 |
| EtOH + 15-crown-5 | 27 | 100 | 0 |

^a The reaction conditions and the symbols are the same as those of TABLE 1, except that the substrate is the sodium salt of C-Et-EAA^- (soluble in the solvents) and CO stands for C,O-Et₂-EAA.

the enhanced nucleophilicity of the carbanion. In addition, a greater portion of C-Et-EAA^- would take the conformation of W-form, which is best suited for the C-alkylation. In non-polar solvents like THF, association of Na^+ to the carbanion is very strong. Thus, the effect of the crown ether is most prominent in THF. In protic solvents like EtOH, the carbanion should be associated with the solvent more than with the metal ion, and the effect of the crown ether would be small as observed in the present study.

For the ambident anions like EAA^- or C-Et-EAA^- , it is generally believed⁵ that the alkylation of the oxygen atom, the more electronegative site, increases as the anion becomes freer. For example, a dipolar aprotic solvent would make the anion freer by dissociating it from the counter-cation to a larger extent. The greater portions of the O-alkylation products in DMSO compared with THF or EtOH in the present study (Table 1 and 2) are in accordance with this prediction. The addition of crown ethers also dissociate the metal ion from the carbanion, expecting the increased extent of O-alkylation compared with C-alkylation. The present results, however, contradict this prediction. The addition of the crown ether to DMSO led to exclusive C-alkylation of both EAA^- and C-Et-EAA^- . The

predominating effect of the crown ether, therefore, is the conformational factor to produce more exposed carbon centers.

References and Notes

- (1) A. J. Parker, *Adv. Phys. Org. Chem.*, **5**, 173 (1967).
- (2) The two geometric isomers were not separately estimated in the

present study.

- (3) W. J. le Noble and H. F. Morris, *J. Org. Chem.*, **34**, 1969 (1969).
- (4) E. V. Dehmlow and S. S. Dehmlow, "Phase transfer catalysis," 2nd Edn., pp. 144, Verlag-Chemie, Weinheim (1983).
- (5) W. J. le Noble, "Highlights of organic chemistry," p. 821, Marcel Dekker, New York (1974).

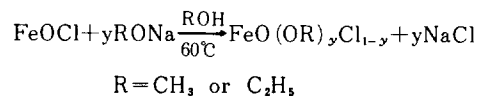
Formation of Layered Compounds of $\text{FeO}(\text{OCH}_3)_y\text{Cl}_{1-y}$ and $\text{FeO}(\text{OC}_2\text{H}_5)_y\text{Cl}_{1-y}$ by Topochemical Reaction

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Organic molecules can be included in the interlayer space of layered transition metal chalcogenohalides which are maintained together only by van der Waals forces.¹ In the case of FeOCl which belongs to the orthorhombic space group P_{mnm} with $a = 378.0$ pm, $b = 330.2$ pm, $c = 791.7$ pm and $Z = 2$,² it was shown that the chemical behavior towards polar neutral guests like ammonia, amines,^{3,4} aromatic heterocycles^{5,6} and alkali metals⁷ or organometallic cations⁸⁻¹¹ can be attributed to two kinds of reactions; namely, intercalation by the partial reduction of Fe^{3+} centers and/or substitution of Cl^- layers by NH_2^- , RNH^- or RO^- , etc. Such compounds are of interest because of their unusual chemical and physical properties such as large enhancement of chemical reactivity in partially reduced FeOCl to neutral guests¹⁶ and increase of electrical conductivity from semiconducting FeOCl to conductor on intercalation reaction by $10^7 \Omega \cdot \text{cm}^{12}$. Substitution of chloride layers in FeOCl lattice with methoxide has been reported by Kikkawa, *et al.*^{13,14} Surprisingly the chloride ions were totally substituted by methoxide ions and b-axis of unit cell was expanded from 330 pm to 399 pm for methoxy derivative assigned as FeOOCH_3 . But this total substitution is scarcely expected because the methoxy groups on the Fe atom are sufficiently bulky, and presumable tend to sweep out large volumes as they rotate randomly. As an evidence, *n*-alkanols or *n*-alkylamines can be intercalated into FeOCl lattice as much as ca. 0.54 mole per 1 mole of FeOCl.^{4,15} From this reason, there has been a great expectation that the value of y in $\text{FeO}(\text{OR})_y\text{Cl}_{1-y}$ should be less than

0.54, or slightly greater in the case of methoxy substituent and approaches to any constant values as the chain length of alkoxide increases. To certify our presupposition to be true or not we have prepared the methoxy and ethoxy derivatives of FeOCl as follows:



The host lattice, FeOCl, was prepared by heating the mixture of $\alpha\text{-Fe}_2\text{O}_3$ and FeCl_3 with the mole ratio of 3:4 in a sealed pyrex tube at $370 \sim 300^\circ\text{C}$ for 5 days according to chemical vapor transport technique.^{3,4} For intercalation and successive substitution reaction in the alkoxide/alcohol solution, the concentration of alkoxides were chosen as 1 mole per 1 mole of FeOCl which was controlled by adding sodium into the excess alcohol and all the batches were incubated at 60°C for about 4 days. The color of reaction products was changed from lustrous dark brown to gold tint, but somewhat different depending upon the number of carbon atoms in alkoxide. The resulting intercalates were washed with the corresponding water free alcohol and dried in vacuo.

The elemental analyses are not only consistent with those of theoretically calculated for iron oxyalkoxide $\text{FeOOC}_x\text{H}_{2x+1}$ but also with the values reported by Kikkawa, *et al.*¹³ as shown in Table 1. If the methoxide ions are fully substituted, the bond angle of $\text{Cl}(1)\text{-Fe-Cl}(1)$ in distorted octahedron of *cis*- FeCl_2O_4 ($= 88.42^\circ$)² must be changed to ca. 143° of $\text{CH}_3\text{O-Fe-OCH}_3$

TABLE 1: Elemental Analyses Data for *n*-alkoxy Substituents of Iron(III) Oxychloride; $\text{FeO}(\text{OCH}_3)_y\text{Cl}_{1-y}$ and $\text{FeO}(\text{OC}_2\text{H}_5)_y\text{Cl}_{1-y}$ (weight percent)

| Compound | C | H | Cl | Remarks |
|--|--------------|--------------------------|--------------|---|
| $\text{FeO}(\text{OCH}_3)_y\text{Cl}_{1-y}$ | 8.24 (0.71) | 2.05 (0.71) | 9.20 (0.73) | this work |
| | 9.29 (0.80) | 2.43 (0.84) ^b | 4.20 (0.88) | Kikkawa, <i>et al.</i> ¹³ |
| | 11.70 (1.00) | 2.94 (1.00) | 0.00 (0.00) | theoretical values for FeOOCH_3 ($y = 1$) |
| $\text{FeO}(\text{OC}_2\text{H}_5)_y\text{Cl}_{1-y}$ | 6.85 (0.31) | 1.45 (0.32) | 21.01 (0.35) | this work |
| | 20.50 (1.00) | 4.31 (1.00) | 0.00 (0.00) | theoretical values for FeOOC_2H_5 ($Y = 1$) |

^aThe approximate chemical compositions derived from these data were chosen as $\text{FeO}(\text{OCH}_3)_y\text{Cl}_{1-y}$ and $\text{FeO}(\text{OC}_2\text{H}_5)_y\text{Cl}_{1-y}$. Values in parentheses denote the extent of substitution (y).