1-indanone[10] in 400 ml of dry chloroform was refluxed for 1.5 hr. After removal of the solvent *in vacuo*, the solid product was recrystallized from chloroform–hexane to give 42.0 g (66.3%) of **4**, mp 130–131°, as a yellow solid: ir, 5.88 (C=O), 6.28 (phenyl), 6.65, and 7.52 μ (NO_2).

Anal. Calcd for $C_{15}H_{11}NO_3S$: C, 63.16; H, 3.89. Found: C, 63.32; H, 3.73.

5a,6-Dihydroindeno[2,1-*b*]-1,4-benzothiazine (6).—To a boiling solution of 56.4 g (0.198 mol) of **4** in 500 ml of glacial acetic acid was slowly added with stirring a hot solution of 140 g (0.521 mol) of stannous chloride dihydrate in 150 ml of concentrated hydrochloric acid. After the addition was completed (about 15 min), the solution was boiled an additional 30 min before cooling. The golden yellow solid which had crystallized was washed with 95% ethanol followed by ether, then dried to give 64.0 g (80.1%) of bis(5a,6-dihydroindeno[2,1-*b*]-1,4-benzothiazinium) hexachlorostannate (**5**), mp 170° dec. As **5** was only sparingly soluble in water and organic solvents, it was not further purified but used directly in the next step: ir, ν 6.12 μ (C=N).

A mixture of 30.4 g (0.0376 mol) of **5** in 500 ml of 10% sodium hydroxide solution was shaken intermittently for 1 hr. The yellow-tan solid which formed was washed with dilute sodium hydroxide until free of tin salts, then with water until free of base. After drying, 16.8 g (94.2%) of **6** was obtained as a light tan solid. Recrystallization of a small portion of this solid from chloroform gave pure **6**: mp 100–105° dec; ir, 3.30 and 3.52 (C–H), 6.12 μ (C=N).

Anal. Calcd for $C_{15}H_{11}NS$: C, 75.93; H, 4.67. Found: C, 75.56; H, 4.81.

6-Bromoindeno[2,1-*b*]-1,4-benzothiazine (7).—To a solution of 16.0 g (0.0675 mol) of **6** in 200 ml of carbon tetrachloride was added slowly with swirling a solution of 21.6 g (0.135 mol) of bromine in 50 ml of carbon tetrachloride. A brown precipitate formed initially, but after one-third of the bromine was added, the mixture turned dark green. Hydrogen bromide evolution did not begin until over half of the bromine was added. The mixture was warmed and allowed to stand overnight at room temperature. The dark green solid (hydrobromide of **7**) which had precipitated was dried and added to 500 ml of 10% sodium hydroxide. After intermittent shaking for 1 hr, a deep purple solid formed. This was washed with water and dried to give 18.0 g (84.8%) of **7**, mp 205–206°. Compound **7** was soluble in concentrated hydrochloric acid, giving a green solution: ir, 3.37 (C–H), 6.26, 6.58, 7.01, 8.01, 8.17, 10.60, 13.1 (broad), and 13.3 μ (broad). The analytical sample was purified by sublimation, mp 205–206°.

Anal. Calcd for $C_{15}H_8BrNS$: C, 57.34; H, 2.57; N, 4.46. Found: C, 57.12; H, 2.59; N, 4.18.

The **hydrobromide of 7** had mp 155° dec.

Anal. Calcd for $C_{15}H_9Br_2NS$: C, 45.57; H, 2.28; N, 3.54. Found: C, 45.58; H, 2.33; N, 3.28.

Nucleophilic Substitution Reactions of 7. A. 6-Phenylthioindeno[2,1-*b*]-1,4-benzothiazine (8a).—A solution of sodium thiophenoxide was prepared by adding a solution of 0.36 g (3.3 mmol) of thiophenol in 5 ml of absolute ethanol to a solution of 0.18 g (3.3 mmol) of sodium methoxide in 10 ml of absolute ethanol. To this solution was added a solution of 1.0 g (3.2 mmol) of **7** in 10 ml of absolute ethanol, and the mixture was refluxed overnight under nitrogen. Water was added to the cooled mixture to precipitate a purple solid, which was recrystallized from ethanol–water to give 0.8 g (73%) of **8a**: mp 114–116°; ir, 3.38 (C–H), 6.26, 6.36, 6.68, 6.81, 6.88, 7.01, 7.68, 8.01, 8.17, 13.4 (very broad), and 14.58 μ; mass spectrum (low ionizing voltage), 343.

Anal. Calcd for $C_{21}H_{13}NS_2$: C, 73.46; H, 3.82; N, 4.08. Found: C, 73.21; H, 3.85; N, 4.19.

B. **6-Cyanoindeno[2,1-*b*]-1,4-benzothiazine (8b).**—A mixture of 1.0 g (3.2 mmol) of **7**, 0.35 g (3.9 mmol) of cuprous cyanide, and 10 ml of dimethylformamide was refluxed for 4 hr.[4] After cooling, the mixture was poured into a ferric chloride–hydrochloric acid solution and warmed for 30 min. The precipitated solid was washed successively with dilute hydrochloric acid, dilute sodium hydroxide, and water, then dried to give 0.8 g (96%) of **8b**, mp 215–220°, as a deep purple solid: ir, 3.43 (C–H), 4.63 (C≡N), 6.29, 6.68, 6.92, 7.06, 7.68, 7.93, 8.12, 8.99, 13.1 (broad), and 13.3 μ (broad); mass spectrum, 260. The analytical sample was purified by sublimation, mp 215–220°.

Anal. Calcd for $C_{16}H_8N_2S$: C, 73.84; H, 3.10; N, 10.77. Found: C, 74.18; H, 3.17; N, 10.93.

C. **6-Oxo-5a,6-dihydroindeno[2,1-*b*]-1,4-benzothiazine (9).**—A solution of 1.0 g (3.2 mmol) of **7** in 30 ml (303 mmol) of piperidine was refluxed under nitrogen for 5 days. The excess piperidine was removed *in vacuo* and the residue was taken up in ether. The precipitated piperidinium bromide was removed by filtration (recovered 0.4 g, 75% of theoretical). The ethereal filtrate was extracted with dilute hydrochloric acid to give a blue aqueous solution. The purple ether layer containing unreacted **7** was discarded. The aqueous acidic solution was extracted with ether until all unreacted **7** was removed. When the solution was made basic with dilute sodium hydroxide, a deep blue solution was obtained, from which no organic material could be extracted with ether. However, when the solution was carefully neutralized by adding dilute hydrochloric acid, a greenish blue substance precipitated, which was extracted with ether. The ether solution was washed with water and dried over anhydrous sodium sulfate, and the ether was removed *in vacuo*. Recrystallization of the residue from ether–ethanol gave 0.2 g (25%) of **9**, mp 210–212°, as a blue-green solid. Compound **9** was readily soluble in dilute acid, giving a blue solution, and in dilute base, giving a deep blue solution: ir, 3.24 and 3.43 (C–H), 5.91 (C=O), 6.10 (C=N), 6.27, 6.35, 6.61, 6.83, 7.02, 7.32, 7.78, 8.26, 11.7, and 13.5 μ.

Anal. Calcd for $C_{15}H_9NOS$: C, 71.71; H, 3.61; N, 5.57. Found: C, 71.97; H, 3.71; N, 5.67.

Indeno[2,1-*b*]-1,4-benzothiazinyl-6-carboxylic Acid (8c).—A mixture of 0.50 g (1.9 mmol) of **8b** in 15 ml of glacial acetic acid, 15 ml of concentrated hydrochloric acid, and 5 ml of water was refluxed for 4 hr. The solvents were removed *in vacuo* and the residue was taken up in ether. The ether solution was extracted with dilute hydroxide until the extracts were colorless. The ether solution containing unreacted **8b** was discarded. The combined basic extracts were acidified with dilute hydrochloric acid, and the product was extracted with ether. After the ether washing layer was washed with water and dried over anhydrous sodium sulfate, the ether was removed *in vacuo* to give less than 0.1 g of **8c**, mp >250°, as a dark purple solid. Compound **8c** was soluble in dilute base: ir, 3.3–3.7 (COOH), 6.07 (conjugated C=O), 6.64, 6.85, 7.04, 7.63, 7.98, 8.13, 13.12, and 13.44 μ.

Anal. Calcd for $C_{16}H_9NO_2S$: N, 5.02. Found: N, 4.82.

Registry No.—**4**, 16888-88-3; **6**, 16888-89-4; **7**, 16888-90-7; **7** HBr, 16888-91-8; **8a**, 16888-92-9; **8b**, 16888-93-0; **8c**, 16888-94-1; **9**, 16888-95-2.

Acknowledgment.—This investigation was supported by Public Health Research Grant No. CA-07351 from the National Cancer Institute.

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(10) K. L. Rinehart, Jr., and D. H. Gustafson, *J. Org. Chem.*, **25**, 1836 (1960).

Tishchenko Reaction of Chloral by Aluminum Haloalcoholates

Takeo Saegusa and Takashi Ueshima

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan

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The Tishchenko reaction of trichloroacetaldehyde (chloral) by the usual aluminum alcoholate catalyst is very sluggish.[1,2] In this communication, we report our finding that some aluminum haloalcoholates cause a rapid Tishchenko reaction of chloral to produce trichloroethyl trichloroacetate. The results are sum-

$$Cl_3CCHO \longrightarrow Cl_3CCOOCH_2CCl_3 \qquad (1)$$

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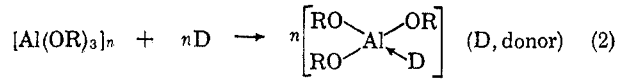
(1) I. Lin and A. R. Day, *J. Amer. Chem. Soc.*, **74**, 5133 (1952).

(2) R. Dworzak, *Monatsch.*, **47**, 11 (1927).

marized in Table I. The catalyst activity is expressed in two ways, the reaction time (minutes) required for 30% conversion and the conversion per cent after 1 hr of reaction.

The results clearly demonstrate that $Al(OCH_2CCl_3)_3$ (I), $Al(OCH_2CBr_3)_3$ (II), and $Al[OCH(CH_2Cl_2)_2]_3$ (III) as well as alkylaluminum compounds are distinguished by high catalyst activity among aluminum compound catalysts in the Tishchenko reaction of chloral. $Al(OCH_2CHCl_2)_3$ and $Al(OCH_2CH_2Cl)_3$ are also aluminum haloalcoholates, but they are less active. The high catalytic activity of II has also been observed in the Tishchenko reaction of tribromoacetaldehyde (bromal).

The characteristic activities of I, II, and III in the Tishchenko reactions may be due, at least partly, to *their marked tendencies of dissociation into monomeric form in the presence of donors* such as carbonyl compounds (eq 2).



$$[Al(OR)_3]_n + nD \longrightarrow n\left[\begin{matrix}RO & & OR\\ & Al & \\ RO & & D\end{matrix}\right] \quad (D, donor) \qquad (2)$$

In our previous studies[3,4] the dissociation tendencies (which are quoted in Table I) of several aluminum alcoholates in the presence of carbonyl compound in hydrocarbon solvent were examined by nmr spectroscopy. The association of the usual aluminum alcoholates of unsubstituted alcohols is strong and is not broken even by strong donors.[3]

TABLE I

TISHCHENKO REACTION OF ALDEHYDES IN THE PRESENCE OF VARIOUS ALUMINUM CATALYSTS

	Catalyst	T_{30}, min[a]	% conversion after 1 hr	Structure in the presence of xanthone[b]
Cl_3CCHO[c]				
	$Al(OCH_2CCl_3)_3$	6	99	Dissociated
	$Al(OCH_2CBr_3)_3$	3	50[d]	
	$Al[OCH(CH_2Cl)_2]_3$	6	92	
	$Al(C_2H_5)_3$	5	84	. . .
	$Al(C_2H_5)_2Cl$	5	94	
	$Al(OC_2H_5)_3$	310	2	*e*
	$Al[OCH(CH_3)_2]_3$	30,600	0.06	Associated[f]
	$Al[OC(CH_3)_3]_3$		0	Associated
	$Al(OCH_2CHCl_2)_3$	150	7	Associated
	$Al(OCH_2CH_2Cl)_3$	1,420	0.67	
Br_3CCHO[g]				
	$Al(OCH_2CBr_3)_3$	2	98	Dissociated
	$Al(OC_2H_5)_3$	14,200	0 (4.6)[h]	Associated
n-C_3H_7CHO[i]				
	$Al(OCH_2CBr_3)_3$	2	92	Dissociated
	$Al[OCH(CH_3)_2]_3$	64	26	Associated

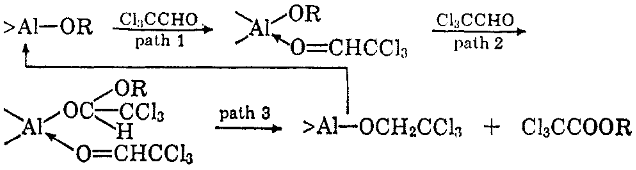
[a] T_{30} is the reaction time required for 30% conversion. [b] See ref 4. [c] Reaction conditions were Cl_3CCHO, 0.05 mol; aluminum compound, 0.0015 mol; benzene, 10 ml; naphthalene, 0.2 g; 30°. [d] The yield did not increase at a prolonged reaction time. [e] Insoluble (highly associated). [f] Acetone was used as a carbonyl compound: V. J. Shiner, Jr., and D. Whittaker, *J. Amer. Chem. Soc.*, **85**, 2337 (1963). [g] Reaction conditions were Br_3CCHO, 0.01 mol; aluminum compound, 0.0003 mol; benzene, 2 ml; dibenzyl, 0.2 g; 20°. [h] Reaction time, 46 hr. [i] Reaction conditions were n-C_3H_7CHO, 0.01 mol; aluminum compound, 0.0003 mol; benzene, 2 ml; diisopropylbenzene 0.2 ml; 20°.

$Al(OCH_2CHCl_2)_3$ and $Al(OCH_2CH_2Cl)_3$ are also strongly associated and, therefore, poor in catalytic activity. The superior catalytic activities of $Al(C_2H_5)_3$ and $(C_2H_5)_2AlCl$ may be explained by the rapid reaction of the ethylaluminum group with chloral[5] to produce a trichloroethoxyaluminum species.

$$>AlC_2H_5 + Cl_3CCHO \longrightarrow >AlOCH_2CCl_3 + CH_2{=}CH_2 \qquad (3)$$

According to the mechanistic scheme presented in our previous studies,[6,7] the Tishchenko reaction consists of three processes (Scheme I), the coordination of aldehyde with aluminum (path 1), the transfer of the alkoxyl group from aluminum to the aldehyde (path 2), and the transfer of hydride from the hemiacetal alcoholate to the aldehyde (path 3). After the first cycle of three processes, the so-called Tishchenko ester is continuously produced. The coordination of aldehyde with the aluminum alcoholate, which is essential in the Tishchenko reaction, has been demonstrated by infrared studies.[8] Thus, the dissociation tendency of aluminum alcoholates is directly related to the catalytic activity for the Tishchenko reaction.

SCHEME I



The high catalytic activity of II is also observed in the Tishchenko reaction of unsubstituted aldehydes, *e.g.*, *n*-butyraldehyde (Table I). However, the effect of halogen in the alkoxyl group upon the catalyst activity is less conclusive. It may be explained by the difference in donating power between chloral and unsubstituted aldehyde. Chloral is a much weaker donor because of the electron-withdrawing nature of three chlorine atoms. *n*-Butyraldehyde is a stronger donor, which can coordinate even with aluminum alkoxide having no halogen in the alkoxyl group. Therefore, the coordination of chloral with aluminum catalyst is more facilitated by the ease of dissociation of catalyst. Further, as the reaction proceeds, the haloalkoxyl groups of the aluminum species are gradually replaced by the *n*-butoxyl group derived from *n*-butyraldehyde. The effect of haloalkoxyl groups of the initial catalyst is thus reduced.

Experimental Section

Catalysts.—Aluminum haloalcoholates were prepared and purified by the procedure described previously.[3,4]

Reaction of Aldehydes.—To a mixture of 1.5 mmol of aluminum catalyst and 10 ml of benzene containing naphthalene as the internal standard for glpc analysis (usually about 0.2 g), 50 mmol of anhydrous chloral was added with shaking while keeping the reaction mixture at 30°. At appropriate intervals, a small amount of reaction mixture was removed and analyzed by glpc using a combination of silicon DC 550 and PEG 20,000 columns.

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(4) T. Ueshima and T. Saegusa, *Bull. Chem. Soc. Jap.*, in press.

(5) H. Meerwein, G. Hinz, and H. Majart, *J. Prakt. Chem.*, **147**, 236 (1937).

(6) J. Furukawa, T. Saegusa, and H. Fujii, *Makromol. Chem.*, **44/46**, 398 (1961).

(7) T. Saegusa, K. Hirota, E. Hirasawa, and H. Fujii, *Bull. Chem. Soc. Jap.*, **40**, 967 (1967).

(8) H. Fujii, T. Saegusa, and J. Furukawa, *Kogyo Kagaku Zasshi*, **65**, 695 (1962).

A similar procedure was used in the Tishchenko reactions of bromal and *n*-butyraldehyde.

Registry No.—Chloral, 75-87-6; bromal, 115-17-3; *n*-butylaldehyde, 123-72-8.

Aluminum Chloride Induced Cleavage and Alkylation of Ferrocene in Dichloromethane[1]

EBERHARD W. NEUSE

Missile & Space Systems Division, McDonnell Douglas Corporation, Santa Monica, California

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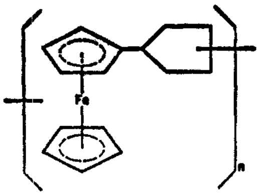
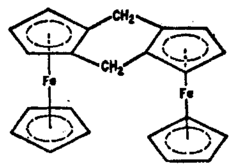
Nesmeyanov and coworkers[2] were the first to study the action of anhydrous aluminum chloride on ferrocene in boiling dichloromethane. The authors, using Lewis acid and metallocene in approximately equimolar quantities, obtained polynuclear alkylation products whose structures were assumed to comprise ferrocenylene units interlinked by a multiplicity of methylene bridges, these bridges being generated by action of the solvent as the alkylating species. However, no structural proof for any of the reaction products was established at that time. Later investigations[3] cast some doubt on these reports as one of the "alkylated" products from a related system involving 1,2-dichloroethane solvent[4] was found to arise in benzene solution as well and was identified[3b,c] as a diferrocenyldicyclopentyl. The proposed mechanism of formation involved Lewis acid induced cleavage of the metal–ring bond in the metallocene and intermediacy of cyclopentenyl and ferrocenyl cyclopentyl cations. Consistent with this concept of metal–ring bond fission, a reinvestigation[3c] of Nesmeyanov's earlier work[2] on the ferrocene–aluminum chloride–dichloromethane system revealed the presence of cyclopentylene groups in the polymeric products of this reaction, analytical results suggesting structure I.



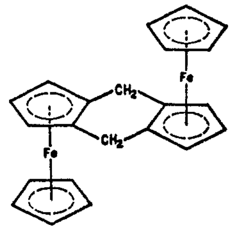
I

In a related investigation, Valot,[5] using a considerable Lewis acid excess, obtained polymers with an appreciably larger content of ferrocene cleavage products; the average repeat unit corresponded in composition to a ferrocenylenecyclopentylene skeleton plus three additional cyclopentenyl groups and one hydroxycyclopentyl moiety. No evidence of concurrent alkylation by the solvent as originally proposed[2] was found in these two later studies.[3c,5] In hopes of achieving the synthesis of [1.1]ferrocenophanes II,[6] of interest as prototype structures of double-bridged segments postulated in earlier polymer studies,[7] we have independently investigated the reaction of ferrocene with aluminum chloride in dichloromethane, using somewhat milder experimental conditions (12–24 hr, 0–25°) than previously employed. The results of this study have shown that, while the sequence of reactions based on metal–ring bond fission predominates, the alkylation of ferrocene by dichloromethane is, indeed, a competitive process. Consequently, the arising polymeric products possess structures appreciably more complex than originally[3b,c,5] assumed.

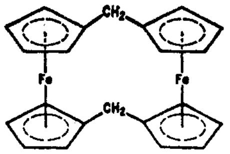
Typical experiments, employing equimolar quantities of ferrocene and aluminum chloride, resulted in the recovery of 50–60% ferrocene. Additionally, the following ferrocene derivatives were isolated: a dinuclear [1.1]ferrocenophane likely to possess structure IId (in addition to other unidentified isomers II);[8] 1,1′-(1,3-cyclopentylene)ferrocene (III);[9] 1,1′-(1-methyl-1,3-cyclopentylene)ferrocene (IV); diferrocenylmethane (V);[10] a 1,3-diferrocenylcyclopentane VI assumed previously[11] to possess the *cis* configuration; and a mixture, not further separated, essentially consisting of diferrocenylmethylcyclopentane isomers VII. In addition to these mono- and dinuclear com-



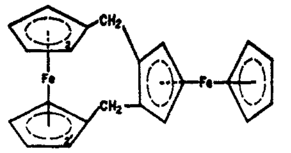
IIa



IIb



IIc



IId

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[1] Metallocene Polymers. XXIII. Part XXII: E. W. Neuse, *J. Macromol. Sci.*, in press. The denotation of the open bond on the left-hand side in structures I and VIII is the same as in previous parts of this series and implies attachment to the preceding recurring unit *via* any one position 2, 3, or 1′.

[2] A. N. Nesmeyanov, V. V. Korshak, V. V. Voevodskii, N. S. Kochetkova, S. L. Sosin, R. B. Materikova, T. N. Bolotnikova, V. M. Chibrikin, and N. M. Bazhin, *Dokl. Akad. Nauk SSSR*, **137**, 1370 (1961).

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[4] (a) A. N. Nesmeyanov and N. S. Kochetkova, *Dokl. Akad. Nauk SSSR*, **126**, 307 (1959); (b) A. N. Nesmeyanov, N. S. Kochetkova, and R. B. Materikova, *ibid.*, **136**, 1096 (1960); **147**, 113 (1962).

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[6] The nomenclature and chemistry of ferrocenophanes has been reviewed most knowledgeably by W. E. Watts, *Organometal. Chem. Rev.*, **2**, 231 (1967).

[7] (a) E. W. Neuse and D. S. Trifan, *J. Amer. Chem. Soc.*, **85**, 1952 (1963); (b) E. W. Neuse and E. Quo, *J. Polym. Sci., Part A-3*, 1499 (1965).

[8] The all-heteroannular IIc was recently synthesized by W. E. Watts, *J. Organometal. Chem.*, **10**, 191 (1967). Also known is the 1,12-dimethyl derivative: W. E. Watts, *J. Amer. Chem. Soc.*, **88**, 855 (1966). We are most grateful to Dr. Watts for submitting copies of the ir, pmr, and mass spectra of both compounds for comparative purposes.

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[10] (a) K. Schlögl and A. Mohar, *Monatsh. Chem.*, **92**, 219 (1961); (b) P. L. Pauson and W. E. Watts, *J. Chem. Soc.*, 3880 (1962); (c) E. W. Neuse and K. Koda, *Bull. Chem. Soc. Jap.*, **39**, 1502 (1966); (d) E. W. Neuse and E. Quo, *ibid.*, **39**, 1508 (1966).

[11] E. W. Neuse, R. K. Crossland, and K. Koda, *J. Org. Chem.*, **31**, 2409 (1966).