presence of methanol). The ketals 8–10 were prepared from the corresponding alcohol and dimethoxydiphenylmethane.

Interaction of 2,2-dimethoxypropane with ferric chloride and antimony pentachloride. A solution of 10.4 g. (0.1 mole) of 2,2-dimethoxypropane in 50 ml. of hexane was cooled to −40° and 16.2 g. (0.1 mole) of sublimed ferric chloride was added. Anhydrous conditions were maintained throughout the experiment. The mixture was stirred and the temperature was allowed to increase slowly. At −10° the mixture turned yellow and the black crystals of suspended ferric chloride turned red-brown.[9] Above 0°, an exothermic reaction started, and a black, viscous, oily layer separated. The hexane layer was decanted and the oil was treated with 100 ml. $0.1N$ hydrochloric acid. About 80% of the iron was extracted as ferric chloride and ferrous chloride (1:1). The same experiment was repeated with 29.9 g. (0.1 mole) of antimony pentachloride. The oxonium compound which formed initially was white, and it decomposed slowly at 25° to a black tar. The antimony was not extensively reduced and the tarry polymer was similar to that obtained in the ferric chloride experiment.

Interaction of dimethoxydiphenylmethane with ferric chloride and antimony pentachloride. A solution of 22.8 g. (0.1 mole) of dimethoxydiphenylmethane in 100 ml. of hexane was mixed with 16.2 g. (0.1 mole) of anhydrous ferric chloride. Reddish needles, which decomposed slowly in contact with moisture but remained unchanged in the hexane solution, were hydrolyzed quantitatively with $0.1N$ hydrochloric acid to benzophenone, methanol, and ferric chloride. A similar experiment with antimony pentachloride yielded a white, crystalline oxonium compound which hydrolyzed easily in the same manner.

Preparation of 2,2-bis(β-di-n-butylaminoethoxy)propane. A mixture of 44 ml. (0.25 mole) of 2,2-bis(β-chloroethoxy)propane and 205 ml. (1.25 mole) of di-*n*-butylamine was refluxed for 12 hr. The reaction mixture was extracted with ether, leaving 78.1 g. (yield 94.5%) butylamine hydrochloride. The ether extract was fractionated *in vacuo* and a colorless fraction, b.p. 123–128° (2 mm.), was collected. An analytical sample was obtained by redistilling this fraction, b.p. 125° (2 mm.), molar refraction 74.07 (calculated 74.02).

Preparation of 2,2-bis(β-aminoethoxy)propane. A mixture of 25 ml. of (0.14 mole) of 2,2-bis(β-chloroethoxy)propane, 15 ml. (0.71 mole) of liquid ammonia, and 15 ml. of methanol was heated in a Carius tube at 90° for 3 hr. The precipitated 10.8 g. (yield 70%) of ammonium chloride was filtered out and the filtrate was fractionated at 0.5 mm. Evolution of gases and discoloration indicated decomposition above 100°. An acid hydrolysis of the residue yielded acetone and a mixture of ethanolamines.

Acknowledgment. The author is grateful to Judy B. Chapman, Elizabeth A. Greene, and George B. Clemans who synthesized some of the ketals, and to the National Science Foundation and the Hollins College Faculty Research Fund for financial support.

HOLLINS, VA.

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(9) When this solid, believed to be an oxonium compound of the ketal, was filtered in a separate experiment, it quickly decomposed to a tarry material.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DEFENSE ACADEMY]

Solvent-Catalyzed Alkylations of Active Methylene Groups in Liquid Ammonia

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A new modification of the alkylation reaction was investigated. It was found that some active methylene compounds, such as malononitrile, cyanoacetamide, and substituted cyanoacetamide, could be successfully alkylated with alkyl halide to form the corresponding C-alkylation products without the condensing agent in liquid ammonia. The high yields were generally obtained with very reactive benzyl and allyl halides. Six new compounds were prepared in this investigation.

In our previous paper[1,2] a new modification of the Michael reaction was reported wherein the reactions between active methylene groups and acrylic acid derivatives proceeded without the condensing agent in liquid ammonia to produce the corresponding addition products. The reaction was probably attributed to the basic character of liquid ammonia compared with the common organic solvent usually employed, and it was suggested that the base-catalyzed ionic organic reactions in general would be promoted to a great extent by the use of liquid ammonia as solvent.

From this viewpoint, in the present investigation we have attempted the reaction between the active methylene group and the alkyl halide without the condensing agent in liquid ammonia. We have now found that some active methylene compounds, such as malononitrile, cyanoacetamide, and substituted cyanoacetamide, which have the enhanced acidity resulting from the substitution of phenyl or acetamido group on the α-carbon atom are successfully alkylated with the alkyl halide to give the corresponding C-alkylation products in liquid ammonia. In general, the high yields are obtained with very reactive halogen compounds such as benzyl halide and allyl halide. Attempted alkylations of less acidic monoalkyl cyanoacetamide, and phenyl- or acetamidomalonamide have been unsuccessful even with a halide of allyl type under the same reaction conditions. The results of the alkylation reactions are shown in Tables I and II. Table III

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(1) S. Wakamatsu, *Bulletin of the Chemical Research Institute of Non-Aqueous Solutions Tohoku University*, **10**, 111 (1961).

(2) K. Shimo and S. Wakamatsu, *J. Org. Chem.*, **26**, 3788 (1961).

TABLE I

Alkylation of Malononitriles and Cyanoacetamides with Alkyl Halides in Liquid Ammonia

Compound Alkylated	Alkyl Halide[a]	Method[b]	Product	Yield, %[c]
$CH_2(CN)_2$	$CH_2{=}CH{-}CH_2Br$	B	$(CH_2{=}CH{-}CH_2)_2C(CN)_2$	91
$CH_2(CN)_2$	$C_6H_5CH_2Cl$	A	$(C_6H_5CH_2)_2C(CN)_2$	74
$CH_2(CN)_2$	$C_6H_5CH_2Cl$	B	$(C_6H_5CH_2)_2C(CN)_2$	75
$CH_2(CN)_2$	C_2H_5I	A	$(C_2H_5)_2C(CN)_2$	44
$CH_2(CN)_2$	C_2H_5I	B	$(C_2H_5)_2C(CN)_2$	72
$CH_2(CN)CONH_2$	$CH_2{=}CH{-}CH_2Br$	B	$CH_2{=}CH{-}CH_2CH(CN)CONH_2$	21
			$(CH_2{=}CH{-}CH_2)_2C(CN)CONH_2$	43
$CH_2(CN)CONH_2$	C_2H_5I	B	$C_2H_5CH(CN)CONH_2$	24

[a] Two molar equivalents were used per mole of malononitrile and cyanoacetamide. [b] See Experimental. [c] Based on the starting active methylene compound.

TABLE II

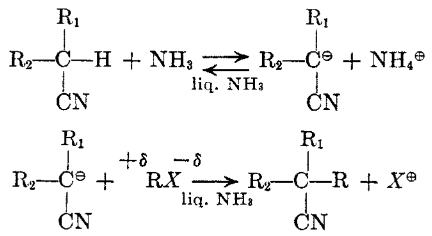
Alkylation of Phenyl- and Acetamidocyanoacetamides with Alkyl Halides in Liquid Ammonia

$R_1CH(CN)CONH_2$			$RR_1C(CN)CONH_2$		Yield, %[c]
R_1	Alkyl Halide[a]	Method[b]	R	R_1	
C_6H_5	$CH_2{=}CH{-}CH_2Br$	B	$CH_2{=}CH{-}CH_2$	C_6H_5	91
C_6H_5	$C_6H_5CH_2Cl$	B	$C_6H_5CH_2$	C_6H_5	74
C_6H_5	$C_2H_5\ I$	B	C_2H_5	C_6H_5	69
C_6H_5	$C_2H_5\ I$	A	C_2H_5	C_6H_5	45
C_6H_5	$C_2H_5\ Br$	A	C_2H_5	C_6H_5	43[d]
C_6H_5	$C_2H_5\ Br$	B	H	C_6H_5	(79)
C_6H_5	$C_3H_7\ Br$	A	C_3H_7	C_6H_5	42[d]
C_6H_5	$C_3H_7\ Br$	B	H	C_6H_5	(86)
C_6H_5	$i\text{-}C_3H_7\ Br$	A	$i\text{-}C_3H_7$	C_6H_5	40
C_6H_5	$i\text{-}C_3H_7\ Br$	B	H	C_6H_5	(94)
C_6H_5	$C_4H_9\ Br$	A	C_4H_9	C_6H_5	33
C_6H_5	$C_4H_9\ Br$	B	H	C_6H_5	(91)
C_6H_5	$i\text{-}C_4H_9\ Br$	A	$i\text{-}C_4H_9$	C_6H_5	30
CH_3CONH	$CH_2{=}CH{-}CH_2Br$	B	$CH_2{=}CH{-}CH_2$	CH_3CONH	91
CH_3CONH	$C_6H_5CH_2Cl$	B	$C_6H_5CH_2$	CH_3CONH	71
CH_3CONH	$C_6H_5CH_2Cl$	A	$C_6H_5CH_2$	CH_3CONH	65[d]
CH_3CONH	$C_2H_5\ I$	B	C_2H_5	CH_3CONH	71
CH_3CONH	$C_2H_5\ I$	A	C_2H_5	CH_3CONH	41[d]
CH_3CONH	$C_2H_5\ Br$	B	C_2H_5	CH_3CONH	21
CH_3CONH	$C_3H_7\ Br$	A	C_3H_7	CHCONH	21[d]

[a] One molar equivalent per mole of $R_1CH(CN)CONH_2$ was used unless otherwise specified. [b] See Experimental. [c] Yields based on the starting cyanoacetamides. Parenthesized figures indicate recovered $R_1CH(CN)CONH_2$ unchanged. [d] Two molar equivalents per mole of $R_1CH(CN)CONH_2$ were used.

gives melting points and analyses of the reaction products.

The new alkylation reaction in liquid ammonia will include the following stages (*X* is halogen atom, R_1 and R_2 are both electrophilic groups or one of them hydrogen) which may be quite characteristic of the effective catalytic action of the solvent



$$R_2{-}\overset{\overset{\large R_1}{|}}{\underset{\underset{\large CN}{|}}{C}}{-}H + NH_3 \underset{\text{liq. }NH_3}{\rightleftarrows} R_2{-}\overset{\overset{\large R_1}{|}}{\underset{\underset{\large CN}{|}}{C}}{}^{\ominus} + NH_4^{\oplus}$$

$$R_2{-}\overset{\overset{\large R_1}{|}}{\underset{\underset{\large CN}{|}}{C}}{}^{\ominus} + \overset{+\delta}{R}\overset{-\delta}{X} \xrightarrow[\text{liq. }NH_3]{} R_2{-}\overset{\overset{\large R_1}{|}}{\underset{\underset{\large CN}{|}}{C}}{-}R + X^{\ominus}$$

to form the enolate of the active methylene compound.

The reaction temperature had a serious effect on the alkylation reaction in liquid ammonia. When the alkyl halide was relatively less reactive, the reaction was best carried out at room temperature under pressure. On the other hand, in most cases, the desired reaction did not proceed at atmospheric pressure below the boiling point of liquid ammonia (−50°). However, not only the enolate of active methylene compound but also the ammonia itself can react with the alkyl halide to form the alkylation product. It was found that this undesirable side reaction competed remarkably with the normal alkylation when the reaction temperature was increased. Actually, by the use of very reactive allyl halide at room temperature none of the desired C-alkylated product could have been obtained.

EXPERIMENTAL[3]

The reactions were carried out by two general methods; (A) the use of a pressure vessel at room temperature and (B)

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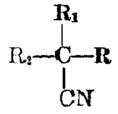
[3] Melting points are uncorrected. Microanalyses were performed by The Institute of Physical and Chemical Research, Tokyo, Japan.

TABLE III

PHYSICAL PROPERTIES OF ALKYLATION PRODUCTS



$$R_2{-}\overset{\displaystyle R_1}{\underset{\displaystyle CN}{C}}{-}R$$

R	R_1	R_2	M.P.	Reported M.P.	Formula	Carbon, %		Hydrogen, %		Nitrogen, %	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
$CH_2{=}CH{-}CH_2$	$CH_2{=}CH{-}CH_2$	CN	36[a,i]		$C_9H_{10}N_2$	73.94	73.67	6.89	6.93	19.16	19.00
$C_6H_5CH_2$	$C_6H_5CH_2$	CN	130–131	131[b]	$C_{17}H_{14}N_2$					11.37	11.28
C_2H_5	C_2H_5	CN	46–47	44–45[c]	$C_7H_{10}N_2$					22.93	22.63
$CH_2{=}CH{-}CH_2$	H	$CONH_2$	101–104		$C_6H_8N_2O$	58.05	58.97	6.50	6.53	22.57	21.84
$CH_2{=}CH{-}CH_2$	$CH_2{=}CH{-}CH_2$	$CONH_2$	128–129[a,j]	113[e]	$C_9H_{12}N_2O$	65.83	65.85	7.37	7.26	17.06	17.10
C_2H_5	H	$CONH_2$	112.5–113.5	98[d]	$C_5H_8N_2O$					24.99	24.87
$CH_2{=}CH{-}CH_2$	C_6H_5	$CONH_2$	115–116[a,k]		$C_{12}H_{12}N_2O$	71.98	71.58	6.04	5.89	13.99	13.82
$C_6H_5CH_2$	C_6H_5	$CONH_2$	135.5–136	135[f]	$C_{16}H_{14}N_2O$					11.19	11.08
C_2H_5	C_6H_5	$CONH_2$	117–117.5	117[g]	$C_{11}H_{12}N_2O$					14.88	14.72
C_3H_7	C_6H_5	$CONH_2$	115–116	120[g]	$C_{12}H_{14}N_2O$					13.85	13.82
i-C_3H_7	C_6H_5	$CONH_2$	125.5–126.5	130[g]	$C_{12}H_{14}N_2O$					13.85	13.77
C_4H_9	C_6H_5	$CONH_2$	127.5	126[g]	$C_{13}H_{16}N_2O$					12.95	13.15
i-C_4H_9	C_6H_5	$CONH_2$	97.5–100	100[g]	$C_{13}H_{16}N_2O$					12.95	13.12
$CH_2{=}CH{-}CH_2$	CH_3CONH	$CONH_2$	194–198[a,k]		$C_8H_{11}N_3O_2$	53.03	52.76	6.12	5.82	23.19	23.22
$C_6H_5CH_2$	CH_3CONH	$CONH_2$	205–206	208.5–209.5[h]	$C_{12}H_{13}N_3O_2$					18.17	17.72
C_2H_5	CH_3CONH	$CONH_2$	205[a,j]		$C_7H_{11}N_3O_2$	49.69	49.00	6.55	6.25	24.84	25.20
C_3H_7	CH_3CONH	$CONH_2$	210–211[a,j]		$C_8H_{13}N_3O_2$	52.44	52.43	7.15	7.04	22.94	22.79

[a] New compound. [b] J. C. Hessler, *Am. Chem. J.*, **22**, 188 (1899). [c] **Beilsteins** *Handbuch Der Organischen Chemie*, **Vierte Auflage, Band II,** p. 689. [d] Beilsteins *Handbuch Der Organischen Chemie*, Vierte Auflage, Band II, p. 776. [e] J. C. Hessler, *Am. Chem. J.*, **22**, 170 (1899). [f] Chemische Fabrik von Heyden, Aktien-Gesellschaft, *Chem. Centr.*, 1921, IV, 126. [g] T. J. Thompson, H. L. Bedell, and G. M. Buffett, *J. Am. Chem. Soc.*, **47**, 875 (1925). [h] K. Shimo and S. Wakamatsu, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **64**, 303 (1961). [i] Recrystallized from ligroin. [j] Recrystallized from water. [k] Recrystallized from ethanol-water.

the reaction at atmospheric pressure below the boiling point of liquid ammonia (−50°). These are illustrated by the following instances.

Dibenzylmalononitrile (*Method A*). To a mixture of 3.3 g. (0.05 mole) of malononitrile and 12.7 g. (0.1 mole) of benzyl chloride contained in a glass pressure vessel[4] was added 50 cc. of liquid ammonia. In a moment the exothermic reaction occurred,[5] and a great deal of crystalline solids began to separate. The reaction mixture was allowed to stand at room temperature for about 24 hr.; then the ammonia was evaporated. The remaining solids were washed with water and recrystallized from ethanol; yield, 9.1 g. (74%) of dibenzylmalononitrile, m.p. 127.5–129°. An additional recrystallization from ethanol raised the m.p. to 130-131°.

2-Allyl- and 2,2-diallylcyanoacetamide (*Method B*). Allyl bromide (36.3 g., 0.3 mole) was added dropwise to a stirred solution of 12.6 g. (0.15 mole) of cyanoacetamide in 150 cc. of liquid ammonia contained in a three necked flask equipped with a mechanical stirrer and a Dewar reflux condenser over a period of 1 hr. while maintaining the reaction temperature at −50°. After the addition was completed, the mixture was stirred for 3 hr., and then the ammonia was evaporated. The residue was washed with water. The remaining solids were dissolved in boiling water, and the solution was allowed to stand at room temperature. 2,2-Diallylcyanoacetamide was precipitated rapidly from the still warm solution; yield, 10.5 g. (43% based on cyanoacetamide) which melted at 128–129°. 2-Allylcyanoacetamide was isolated thereafter as a crystalline product from the filtrate by cooling with ice water; it melted at 101–104°, 4.0 g. (21% based on cyanoacetamide).

2-Acetamido-2-ethylcyanoacetamide (*Method B*). To a stirred solution of 7.1 g. (0.05 mole) of 2-acetamidocyanoacetamide and 150 cc. of liquid ammonia, 7.8 g. (0.05 mole) of ethyl iodide was added dropwise at −50°. Stirring was continued for 2 hr.; then the ammonia was evaporated. The resulting mixture was washed with water and recrystallized from water. The yield of 2-acetamido-2-ethylcyanoacetamide, m.p. 204–205° dec., was 6.0 g. (71%). Upon repeated recrystallization from water it melted at 205° dec.

YOKOSUKA, JAPAN

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(4) K. Shimo and S. Wakamatsu, *J. Org. Chem.*, **24,** 19 (1959).

(5) External cooling with cold water was desired until the reaction was completed (for about 0.5 hr.).

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, NATIONAL RESEARCH CENTRE]

The Stobbe Condensation with *o*- and *p*-Chlorobenzaldehyde

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o- and *p*-Chlorobenzaldehyde condense with methyl succinate to give methyl hydrogen *cis*-γ-*o*-chlorophenyl-, and methyl hydrogen *cis*-γ-*p*-chlorophenylitaconate together with di-*o*-chlorobenzylidene-, and di-*p*-chlorobenzylidenesuccinic acid. The itaconates are cyclized by acetic anhydride and sodium acetate to methyl 4-acetoxy-8-, and -6-chloro-2-naphthoate which are converted into 5-, and 7-chloro-1-naphthol, respectively. The anhydride of the di-*o*-chlorobenzylidenesuccinic acid is cyclized by the action of heat to the corresponding 1-phenylnaphthalene derivative.

Continuation of the investigation of the Stobbe condensation on substituted aromatic aldehydes,[1] *cis*-β-half esters, methyl hydrogen *cis*-γ-*o*-(Ia;$R_3 = CH_3$) and *cis*-γ-*p*-chlorophenylitaconate (Ib; $R_3 = CH_3$) together with di-*o*-chlorobenzylidene-(VIa) and di-*p*-chlorobenzylidenesuccinic acid (VIb)[2] were obtained in about 52% and 14% yield respectively by Stobbe condensation of *o*- and *p*-chlorobenzaldehyde with dimethyl succinate and *t*-butyl alcohol potassium *t*-butoxide.[3] In the case of *p*-chlorobenzaldehyde, a small amount of *p*-chlorobenzoic acid was also isolated. Repeating the reaction under nitrogen atmosphere gave no such acid. The structure and the *cis* configuration of the half esters (Ia and b) were confirmed by their cyclization with fused sodium acetate in acetic anhydride[1,4] to methyl 4-acetoxy-8-(IIa;$R_3 = CH_3$, R_4 = Ac) and -6-chloro-2-naphthoate (IIb; $R_3 = CH_3$, R_4 = Ac) in a good yield. Alkaline hydrolysis of the acetoxy esters gave 8-, and 6-chloro-4-hydroxy-2-naphthoic acid (IIa and b; $R_3 = R_4 =$ H), respectively.

These phenolic acids were converted by methyl sulfate and potassium carbonate in acetone into the corresponding methoxy esters (IIa and b; $R_3 = R_4 = CH_3$) which were hydrolyzed to the methoxy acids (IIa and b; R_3 = H, $R_4 = CH_3$) and then decarboxylated by quinoline and copper-bronze to give 5-, and 7-chloro-1-methoxynaphthalene, respectively.

The structure of these naphthol ethers was confirmed by their cleavage with hydriodic acid to the known 5-, and 7-chloro-1-naphthol.[5]

Hydrolysis of the *cis*-β-half esters (Ia and b; $R_3 = CH_3$) with boiling barium hydroxide solution gave the *cis*-itaconic acids (Ia and b; R_3 = H). These were converted into their *cis*-anhydrides (IVa and b), which on boiling with methanol gave the *cis*-α-half esters (Va and b) which were different from the *cis*-β-half esters (Ia and b; $R_3 = CH_3$) obtained by the Stobbe condensation.

The anhydride (VII) was cyclodehydrogenated

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(1) A. M. El-Abbady and Lanson S. El-Assal, *J. Chem. Soc.*, 1024 (1959).

(2) F. G. Baddar, L. S. El-Assal, N. A. Doss, and A. H. Shehab, *J. Chem. Soc.*, 1016 (1959).

(3) *Cf.* W. S. Johnson and G. H. Daub, *Org. Reactions*, VI, 1 (1951).

(4) W. Borsche, S. Kettner, M. Gillies, H. Kuhn, and R. Manteuffel, *Ann.* **526,** 1 (1936).

(5) H. Erdmann and R. Kirchhoff, *Ann.* **247,** 366 (1888).