A mixture of 2.4 g. (0.015 mole) of 6-methoxy-1-indanone, 50 ml. of absolute ethanol, and 0.55 g. of platinum oxide[26] were shaken under 3 atm. of hydrogen for 3.5 hr. The ethanol was removed from the filtered mixture, and the residue was dehydrated by distillation from a crystal of potassium bisulfate. A yellow oil was collected, b.p. 220–240°, $n_D^{24.3}$ 1.5746, wt. 1.2 g. (55%) (lit.[4] for 5- or 6-methoxyindene, b.p. 236°). It gave a positive potassium permanganate test in acetone.

When the reduction and dehydration was repeated using 2.4 g. (0.015 mole) of 5-methoxy-1-indanone, 1.4 g. of a yellow oil was collected, b.p. 230–245°, $n_D^{24.5}$ 1.5730. Its infrared spectrum was identical to that of the first methoxyindene. Boiling this compound with 20 ml. of 5% potassium hydroxide solution for 15 min. did not change its infrared spectrum.

Preparation of 6-methoxy-1-indenylmagnesium bromide and subsequent treatment with 5-methoxy-1-indanone. Ethylmagnesium bromide was prepared from 0.25 g. (0.01 mole) of magnesium, 1.1 g. (0.01 mole) of ethyl bromide, and 10 ml. of dry ether in the usual manner. A solution of 1 g. (0.007 mole) of 6-methoxyindene and 10 ml. of dry ether was added at such a rate as to keep the Grignard mixture refluxing vigorously. The mixture was refluxed for 15 min. and then 1.1 g. (0.007 mole) of 5-methoxy-1-indanone and 40 ml. of dry ether were added. No obvious reaction was observed and the mixture was refluxed for 0.5 hr. A saturated solution of ammonium chloride was added dropwise, the ether solution separated and the solvent was removed. The residue (1.6 g.) consisted of recovered 5-methoxy-1-indanone, m.p. 98.0–107.5°, and an oil which was probably recovered 6-methoxyindene.

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TROY, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HOLLINS COLLEGE]

Aromatic and Hindered Ketals[1]

ALEXEJ B. BOŘKOVEC

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A series of aromatic and aliphatic ketals containing bulky alkoxy groups was synthesized. The interaction of ketals with Lewis acids was studied and the effect of α-hydrogen upon the stability and reactivity of ketals was demonstrated.

The alcohol interchange and the ketone interchange reactions[2] are suitable for the preparation of a wide variety of ketals. The method is particularly useful for ketals of secondary alcohols[3] although the yields tend to diminish with the increasing size of the alkoxy group.

In the present work the effect of the size of the groups attached to the central carbon atom of the ketal upon the ease of preparation and reactivity of the product was studied. Ketals of aliphatic ketones are easily pyrolyzed especially in the presence of an acid catalyst[4,5] to unsaturated ethers. This reaction depends upon the presence of a hydrogen attached to the carbon next to the central carbon of the ketal (α-hydrogen). A ketal without an α-hydrogen, dimethoxydiphenylmethane, was prepared by the ketone interchange reaction and its properties were compared to those of a ketal with an α-hydrogen, 2,2-dimethoxypropane. While the latter decomposes to a significant extent on distillation at 80°,[6] the dimethoxydiphenylmethane can be distilled without extensive decomposition at 290°.

The interaction of the two ketals with Lewis acids at moderate temperatures is even more instructive. 2,2-Dimethoxypropane forms a crystalline addition compound with both ferric chloride and antimony pentachloride, but the two oxonium compounds decompose rapidly even at room temperature to complex mixtures containing polymers of isopropenyl methyl ether. Dimethoxydiphenylmethane, on the other hand, forms with the same reagents crystalline addition products which are stable at room temperature and decompose only in contact with moisture to benzophenone, methanol, and the Lewis acid.

The effect of the alkoxy groups upon the reactivity of the ketal is much less obvious. The introduction of an amino group in the alkoxy moiety increased the stability of the ketal, which was apparently due to the basicity of the nitrogen. The amino ketals can be precipitated as dihydrochlorides from their ethereal solutions by dry hydrogen chloride.[7] 2,2-Bis(β-chloroethoxy)propane was used as a starting material for the preparation of the amino ketal.

$$(CH_3)_2C(OCH_2CH_2Cl)_2 + 4\,HNR_2 \longrightarrow (CH_3)_2C(OCH_2CH_2NR_2)_2 + 2\,NHR_2{\cdot}HCl \quad (1)$$

Several reactions were attempted with ammonia (R = H), but although good yields of ammonium

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[1] Presented in part before the Virginia Academy of Science on May 12, 1961 in Lexington, Va.

[2] N. B. Lorette and W. L. Howard, *J. Org. Chem.*, **25**, 521 (1960).

[3] W. L. Howard and N. B. Lorette, *J. Org. Chem.*, **25**, 525 (1960).

[4] D. B. Killian, G. F. Hennion, and J. A. Nieuwland, *J. Am. Chem. Soc.*, **57**, 544 (1935).

[5] H. P. Crocker and R. H. Hall, *J. Chem. Soc.*, 2052 (1955).

[6] The pyrolysis can be prevented by the addition of a small amount of a base to the ketal; however, in the presence of an acid or a Lewis acid, it can be quantitative.

[7] F. F. Blicke and G. R. Toy, *J. Am. Chem. Soc.*, **76**, 4615 (1954).

chloride were obtained, the isolation of the free amine was not achieved and viscous, polymeric materials were obtained. It appears that when one of the chloro groups is replaced by the amino group, the latter can readily react with the chloroethoxy groups of other ketal molecules and thus form polymers of varying molecular weight. This possibility was substantiated by a hydrolysis of the polymeric material which resulted in the formation of acetone, a mixture of ethanolamines, and a small amount of unidentified material. When di-*n*-butylamine ($R = CH_2CH_2CH_2CH_3$) was used in reaction (1), the corresponding amino ketal was obtained in a good yield.

The introduction of a nitro, phenyl, benzyl, and other groups (Table I) on the carbon attached to the alkoxy oxygen presented no difficulties, but all attempts to prepare 2,2-diphenoxypropane by the alcohol interchange reaction were unsuccessful. Phenol is apparently sufficiently acidic to catalyze the decomposition of the ketal, especially at a higher temperature. The 2-methoxy-2-phenoxypropane was obtained by G. R. Martin by the addition of phenol to methyl isopropenyl ether and a vacuum distillation of the mixture below 50°.[8] This ketal decomposed readily at a temperature above 60° even in the presence of a base. In contrast to aliphatic phenoxy ketals, analogous ketals derived from benzophenone are quite stable. Methoxyphenoxydiphenylmethane was prepared in a good yield according to Equation 2a, and the symmetrical diphenoxydiphenylmethane was obtained from methoxyphenoxydiphenylmethane and phenol (2b).

$$(C_6H_5)_2C(OCH_3)_2 + C_6H_5OH \xrightarrow{H^+} (C_6H_5)_2C(OCH_3)(OC_6H_5) + CH_3OH \quad (2a)$$

$$(C_6H_5)_2C(OCH_3)(OC_6H_5) + C_6H_5OH \xrightarrow{H^+} (C_6H_5)_2C(OC_6H_5)_2 + CH_3OH \quad (2b)$$

Although attempts were made in reaction (2a) to induce the formation of the symmetrical ketal by a large excess of phenol, high temperature and long reaction time, only the mixed ketal was isolated.

In accord with the increasing degree of hindrance on the central carbon atom in dimethoxydiphenylmethane, methoxyphenoxydiphenylmethane, and diphenoxydiphenylmethane the yields in the interchange reactions were 92%, 60%, and 14%, respectively.

EXPERIMENTAL

The ketals 1-5 (Table I) were prepared by the interchange reaction of the corresponding alcohol and 2,2-dimethoxy propane according to the procedure of Lorette and Howard.[2,3] The ketal 7 was prepared by a ketone interchange method (2,2-dimethoxypropane and benzophenone in the

TABLE I

KETALS[a]

$R_2C(OR')(OR'')$

	R	R′	R″	Yield, %	B.P.	Mm.	M.P.	n_D (Temp.)	d (Temp.)	Calcd., % C	Calcd., % H	Calcd., % Other	Found, % C	Found, % H	Found, % Other
1	CH_3	CH_2CH_2Br	CH_2CH_2Br	45	64-66	1		1.4886 (25)	1.585 (25)	28.99	4.87	Br 55.11	29.24	4.84	Br 55.27
2	CH_3	$CH_2CH_2CH_2Cl$	$CH_2CH_2CH_2Cl$	40	67-68	1		1.4499 (25)	1.102 (25)	47.17	7.92	Cl 30.95	46.89	7.73	Cl 30.72
3	CH_3	$CH_2C(CH_3)_2NO_2$	$CH_2C(CH_3)_2NO_2$	65	131-132	3	88			47.47	7.97	N 10.07	47.53	7.76	N 10.17
4	CH_3	$CH_2CH_2C_6H_5$	$CH_2CH_2C_6H_5$	84	79-81	3		1.5172 (20)	0.9776 (25)	80.28	8.45		80.24	8.55	
5	CH_3	$CH_2C_6H_5$	$CH_2C_6H_5$	75	125	1	<10[b]	1.5343 (22)	1.033 (25)	79.65	7.86		79.41	7.61	
6	CH_3	$CH_2CH_2N(n\text{-}C_4H_9)_2$	$CH_2CH_2N(n\text{-}C_4H_9)_2$	95	125	2		1.4322 (21.5)	0.8566 (21)	71.44	13.04	N 7.25	71.24	13.25	N 7.48
7	C_6H_5	CH_3	CH_3	92	102-105	1	106.5[c]								
8	C_6H_5	CH_2CH_2Cl	CH_2CH_2Cl	75	150-152	0.5	57.0-57.7			62.78	5.58	Cl 21.80	63.08	5.76	Cl 21.94
9	C_6H_5	CH_3	C_6H_5	60			117.5			82.73	6.25		82.54	6.23	
10	C_6H_5	C_6H_5	C_6H_5	14			135-136.5[d]			85.20	5.72		85.28	5.79	

[a] Infrared spectra of all the ketals listed were consistent with the proposed structure. [b] Reported by J. E. Mackenzie, *J. Chem. Soc.*, **69**, 987 (1896) to have m.p. 104-105°. The compound prepared in the present work crystallized from its methanolic solution cooled to −40°, but the crystals melted somewhat above 0°. [c] J. E. Mackenzie, *J. Chem. Soc.*, **69**, 987 (1896), m.p. 106.5-107.0°. [d] M.p. 132° reported by H. Wieland, *Ber.*, **44**, 2550 (1904), and M. Gomberg and R. L. Jickling, *J. Am. Chem. Soc.*, **37**, 2575 (1915).

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[8] G. R. Martin, The Dow Chemical Co., Freeport, Tex., personal communication.

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. 0.1*N* 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 0.1*N* 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.

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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).