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Studies on Formaldehyde-Condensation Resin. VII.[*1] Isolation of Mono-, Di-, Tri-, and Tetramethylolacetoguanamines

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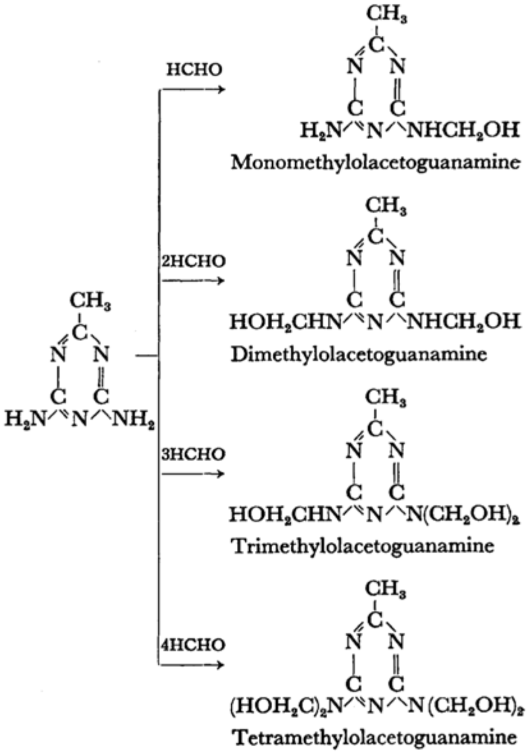
The reaction of acetoguanamine with formaldehyde was carried out in the presence of basic catalyst under various conditions, and mono-, di-, tri-, and tetramethylol derivatives of acetoguanamine were purely isolated. Their structures were identified by elemental analyses, infrared absorption spectra, NMR spectra, and chemical analyses of methylol groups.

The isolation of some intermediates of phenol, urea, melamine, and guanamine resins, well-known as the addition-condensation resin, has been studied by many workers.[1–9] Recently, there have been interesting presentations[10,11] on the syntheses of some kinds of benzoguanamine-formaldehyde resin intermediates, but no reports on any detailed studies of the methylol derivatives of acetoguanamine.

Acetoguanamine can be hydroxymethylated to form mono-, di-, tri-, tetramethylolacetoguanamines as follows:



Monomethylolacetoguanamine

Dimethylolacetoguanamine

Trimethylolacetoguanamine

Tetramethylolacetoguanamine

The present paper deals with the isolation of the methylol derivatives which were obtained from the base-catalyzed reaction of acetoguanamine with formaldehyde under various conditions.

Experimental

Materials. Nippon Gosei Chem. Ind. Co. best grade acetoguanamine was recrystallized from water, mp 269—271°C. Commercial formaline (*ca.* 37 wt%) was used. Pure commercial dimethylsulfoxide (DMSO) was purified by the usual method[12]: bp 88°C/25 mmHg.

[*1] Part VI: T. Uragami and M. Oiwa, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **71**, 596 (1968).

1) M. Imoto, H. Kakiuchi and K. Kō, "Formaldehyde," Asakura-Shoten, Tokyo (1965), p. 209 and others.

2) H. Kakiuchi, "Urea Resin," Kobunshibunko 19, Kobunshi-Kankokai, Kyoto (1965), p. 35 and others.

3) S. Seto, *Osaka-Shiritsu Kogyo Kenkyusyo Hokoku* (*Bull. Osaka Mun. Tech. Research Institute*), Vol. **24** (1960); *Kobunshi Tenbo*, No. **11**, 13 (1954).

4) K. Koeda, *Kobunshi Tenbo*, No. **11**, 39 (1954).

5) H. Ohno, *Kobunshi Kagaku* (*Chem. High Polymers Japan*), **20**, 443 (1963).

6) T. Tashiro and R. Murase, *Sen'i Kogyo Shikensyo Hokoku* (*Bull. Textile Research Institute of Japanese Government*), **56**, 65 (1961).

7) M. Gordon *et al.*, *Soc. Chem. Ind.* (*London*), *Monograph*, No. **20**, 187 (1966).

8) M. Tajima and R. Shiba, Preprint for the 17th Annual Meeting of the Thermosetting Resin Lecture Discussion of Japan (September, 1967), p. 107.

9) S. Takeuchi and E. Ninagawa, Preprint for the 21th Annual Meeting of the Chemical Society of Japan (April, 1968), No. 4, p. 2772.

10) B. Ogaki, A. Yotsutsuji and Y. Sato, Preprint for the 15th Annual Meeting of the Thermosetting Resin Lecture Discussion of Japan (September, 1965), p. 5, *ibid.* (September, 1966), p. 99.

11) B. Ogaki, A. Yotsutsuji and T. Nakamura, *ibid.* (September, 1968), p. 239.

12) C. A. Kingsbury, *J. Org. Chem.*, **29**, 3262 (1964).

Hydroxymethylation of Acetoguanamine. In a four-necked flask equipped with a reflux condenser and a stirrer, formaline was added to 1 mol of acetoguanamine in the formaldehyde/acetoguanamine molar ratio of 1—8 (in some cases, water was added), and the pH was adjusted to the desired value with sodium hydroxide solution (the pH was measured with a glass electrode using Hitachi Horiba M-5 pH meter.). This mixture was heated for an hour with stirring in a thermostat regulated at 80°C, and then the flask containing the reaction products was cooled in ice-water or allowed to stand at room temperature until crystals precipitated. The obtained crystals [A] were collected on a Büchner funnel and the filtrate was allowed to stand for 1—2 days (in the cases of the formaldehyde/acetoguanamine molar ratio of 7 and 8, the filtrate was allowed to stand for a week) in a refrigerator. The crystals [B] deposited from the filtrate were filtered off, and the filtrate was treated again as mentioned above.

The conditions for preparation of methylol acetoguanamines are shown in Table 1.

TABLE 1. THE CONDITIONS FOR PREPARATION OF METHYLOLACETOGUANAMINES

No.	AG g	F m*l*	Water m*l*	Molar ratio AG: F	pH
1	90	54.1	360	1 : 1	9.04
2	31	22	50	1 : 1.2	9.40
3	125	150.1	287	1 : 2	8.81
4	125	225.2	0	1 : 3	9.00
5	87.5	210	0	1 : 4	9.20
6	75	270	0	1 : 6	9.01
7	50	210	277	1 : 7	9.00
8	50	240	309	1 : 8	9.00

Acetoguanamine and formaldehyde are abbreviated as AG and F respectively.

Monomethylolacetoguanamine. To a suspension of 31 g (0.248 mol) of acetoguanamine in 50 m*l* of water was added 22 m*l* (0.2976 mol) of formaline. The mixture was adjusted to pH 9.40, heated at 80°C for about an hour after complete dissolution, and then cooled to 10°C. The deposited crystals were collected and dissolved in methyl cellosolve to remove unreacted acetoguanamine monomer. The crystals 2-A (see Table 2) recrystallized from acetone were separated, washed with cold water, air-dried and then dried at room temperature *in vacuo*.

Dimethylolacetoguanamine. A mixture of 125 g (1 mol) of acetoguanamine and 225.2 m*l* (3 mol) of formaline was adjusted to pH 9.00. This mixture became a transparent solution within a few minutes, and after 20 min, the reaction solution changed into a milky turbid solution, and then the reaction was continued for 40 min. The separated product 4-A was washed with petroleum ether and dried *in vacuo* (room temperature). The pure crystals 4-A′ were obtained by repeated crystallization from DMSO.

Trimethylolacetoguanamine. A mixture of 87.5 (0.7 mol) of acetoguanamine and 210 m*l* (2.8 mol) of formaline was heated for an hour at pH 9.20 and 80°C. This mixture became homogeneous after 10 min, and the reaction solution was clear until the reaction came to an end. The resulting solution was allowed to stand at room temperature until crystals formed, then the crystalline product 5-A was separated by filtration and the filtrate was kept to stand for 2 days in a refrigerator. The crystals 5-B obtained from this filtrate were collected, washed with cold water and methanol, and air-dried.

Tetramethylolacetoguanamine. Acetoguanamine (50 g, 0.4 mol) was suspended in 240 m*l* (3.2 mol) of formaline and about 310 m*l* of water. This mixture immediately became clear by heating at 80°C and pH 9.00. The product 8-A was obtained by setting the reaction solution for a week in a refrigerator. The

TABLE 2. THE QUANTITATIVE ESTIMATION OF METHYLOL GROUPS IN METHYLOLACETOGUANAMINES

No.	Cryst. No.	Methylol F%		Methylol + Methylene F%	Observed F/AG ratio	Mp (°C)	N%		Yield (%)
		Found	Calcd				Found	Calcd	
1	1-A	18.03	19.35	—	0.92	—	46.64	45.13	—
2	2-A	19.45		19.36	1.01	193—194	45.14		65.54
	2-B	20.61		—	1.07	—	44.56		—
	2-C	21.09		—	1.11	—	44.08		—
3	3-A	29.17	32.42	—	1.71	—	38.73	37.81	—
	3-B	29.68		—	1.82	—	38.35		—
	3-C	30.83		—	1.89	—	35.81		—
4	4-A	31.86		32.33	1.95	—	37.93		—
	4-A′	32.11		32.59	1.98	175—176	37.89		46.71
	4-B	35.37		—	2.28	—	32.76		—
5	5-A	39.39	41.85	—	2.74	—	34.53	32.54	—
	5-B	41.56		41.41	2.97	170—172	32.62		56.05
6	6-A	44.65	48.97	—	3.51	—	30.55	28.56	—
	6-B	46.95		—	3.69	—	29.76		—
7	7-A	46.96		—	3.69	—	29.78		—
	7-B	47.71		—	3.80	—	29.36		—
8	8-A	48.95		48.93	3.99	166—167	28.59		—
	8-B	48.87		48.88	3.98	166—167	28.59		20.96

Calcd % of methylol F and N are for pure mono-, di-, tri-, and tetramethylolacetoguanamines.

yield of crystals 8-A was lower than those of crystals 2-A, 4-A′, and 5-B. The filtrate, after the crystals 8-A were separated off, was kept for a week in a refrigerator and a small amount of the product 8-B was obtained.

Analyses of the Products. The products were analyzed by the iodometric[13] and the Levenson (phosphoric acid decomposition[14–16]) methods; the molar ratio of the hydroxymethylated formaldehyde and the combined total formaldehyde to acetoguanamine were calculated respectively. The amount of the methylene linkage was estimated from the difference between the two values obtained by the two methods. The infrared absorption spectra were observed by KBr disk method using the IR-27G infrared spectrophotometer of Shimadzu Co., Ltd. The NMR spectra of acetoguanamine derivatives in DMSO were recorded on a Japan Electron Optics Lab. NMR spectrometer, model JNM-3H (60 Mc), using tetramethylsilane as an internal reference.

The analyses of No. 2-A, 4-A′, 5-B, and 8-A crystals and their yields and melting points are shown in Table 2.

Results and Discussion

Chemical Analysis of Methylol Derivatives. It may be first considered from Table 2 that in products No. 2-A, 4-A′, 5-B, and 8-A the methylene linkage is not found at all, because the content of the methylol group agrees very closely with that of the combined total formaldehyde. Tollens reagent was reduced by these compounds, indicating the presence of the methylol groups. The molar ratio of the hydroxymethylated formaldehyde of these compounds were 1.01, 1.98, 2.97, and 3.99 respectively. It was also recognized that the agreement between the calculated and found values (elemental analyses) of No. 2-A, 4-A′, 5-B, and 8-A is within the error of the analysis and that the sharp melting point of each compound indicates a good quality. Accordingly, each of the crystals No. 2-A, 4-A′, 5-B, and 8-A was assumed to be a pure methylol derivative of mono-, di-, tri-, and tetramethylolacetoguanamines, respectively. Henceforth, they will be represented as AGF, AG2F, AG3F, and AG4F respectively.

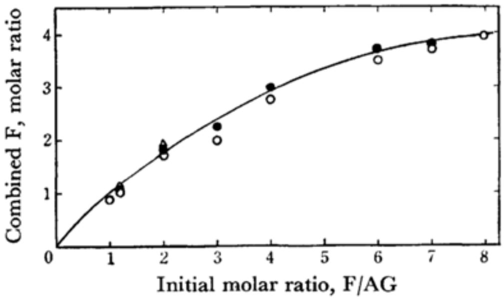


Fig. 1. The relationship between the initial molar ratio, F/AG and the observed molar ratio in methylol compounds.
○: crystal A, ●: crystal B, △: crystal C

The relationship between the initial molar ratios of formaldehyde and acetoguanamine and the observed molar ratios in methylol compounds is plotted in Fig. 1 based on data in Table 2. As can be seen from Fig. 1, the molar number of the combined formaldehyde to acetoguanamine increases with the increase of the reaction molar ratio. But in all the above results, each expected methylol compound is formed when an excess amount of formaldehyde is present in the reaction system, and especially in the preparation of AG4F, 8 mol of formaldehyde is needed which corresponds to two equivalents of acetoguanamine. This fact may easily be understood from the presence of four equilibriums in the formation of AG4F.

An increase of the content of the methylol group in the order of crystals [A], [B], and [C] in Table 2 indicates the formation of the higher order methylol compound.

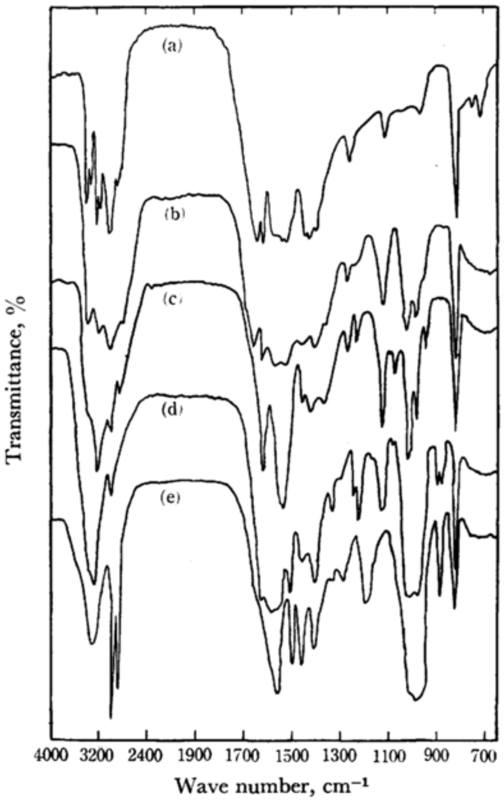


Fig. 2. Infrared absorption spectra of acetoguanamine (a), mono- (b), di- (c), tri- (d), and tetramethylolacetoguanamine (e).

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[13] A. Takahashi and I. Yamazaki, *Kobunshi Kagaku* (*Chem. High Polymers Japan*), **15**, 232 (1958).

[14] I. J. Levenson, *Ind. Eng. Chem. Anal. Ed.*, **12**, 332 (1940).

[15] T. Kitagawa, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **53**, 181 (1950).

[16] K. Koeda, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **75**, 571 (1954).

Infrared Absorption Spectra of Mono-, Di-, Tri-, and Tetramethylolacetoguanamines. In Fig. 2 are shown the infrared absorption spectra of acetoguanamine and its methylol derivatives, AGF, AG2F, AG3F, and AG4F. In these spectra, the absorption bands near 3000 cm^{-1} can not definitely be assigned, because in acetoguanamine (Fig. 2(a)) the $-NH_2$ and C–H stretching vibrations overlap with each other and in methylol derivatives (Fig. 2(b)—(e)) the N–H and O–H stretching bands[17,18] additionally overlap. The characteristic absorption bands at 1655 and 1626 cm^{-1} are assigned to the $-NH_2$ scissor vibration[19] and decreased with an increase of the number of methylol groups. The absorption at 1620 cm^{-1} shown in Fig. 2(c) (AG2F) is due to the N–H deformation vibration. The variation of the characteristic bands in the region of 1655 to 1620 cm^{-1} in Fig. 2(a)—(c) indicate that $-NH_2$ and –NH– groups on acetoguanamine take part in a series of reactions leading to the formation of methylol compounds, especially in Fig. 2 (e) (AG4F) where these peaks disappeared completely. The absorption in 1555—1400 cm^{-1} region seems to be due to the overlaps of the C–H stretching vibrations[19-21] of the triazine ring system and the side chain, and the C–H deformation band of the substituent group, $-CH_3$ on the triazine ring. It is known[22] that the bands of the C–H stretching vibration corresponding to primary, secondary, and tertiary amines appear at 1360—1250 cm^{-1}, but in these spectra, it is difficult to distinguish each peak clearly. The absorption near 1000 cm^{-1} due to the C–O stretching[23,24] indicates the presence of methylol group, which has been known[25] in the infrared absorption spectra of *o*- and *p*-methylolphenol. The intensity of this peak shows a prominent increase in proportion to the number of methylol groups. This fact suggests in connection with the absorption bands of

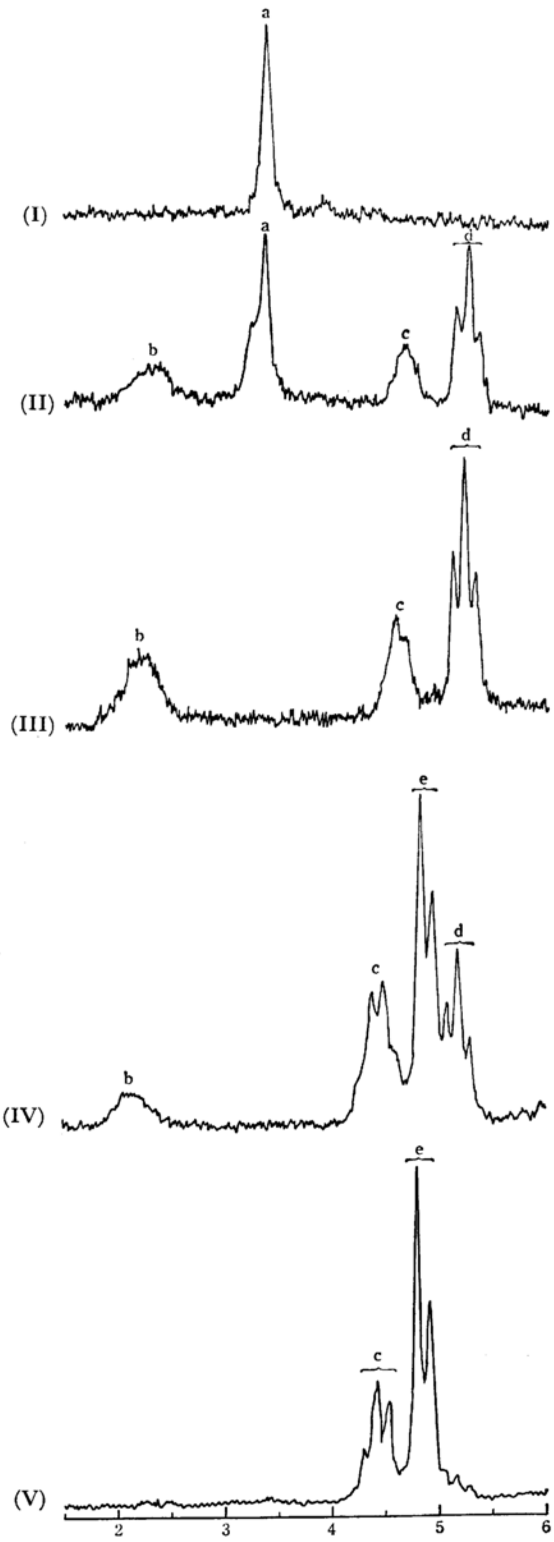

Fig. 3. NMR spectra of acetoguanamine (I), mono- (II), di- (III), tri- (IV), and tetramethylolacetoguanamine (V).

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[17] Y. Ogata, Y. Izawa, T. Itoh and S. Matsui, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **70**, 124 (1967).

[18] R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, Inc., New York (1963), p. 56.

[19] G. Morimoto, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **87**, 797 (1966).

[20] W. F. Jones and W. J. Orivelle-Tomas, *Trans. Faraday Soc.*, **55**, 208 (1957).

[21] M. Takimoto, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **85**, 168 (1964).

[22] A. D. Cross, "An Introduction to Practical Infrared Spectroscopy," published by Butterworth & Co., Ltd. Copyright, London (1964).

[23] L. J. Bellamy, "The Infrared Spectra of Complex Molecules" (1958).

[24] K. Nakanishi, "The Infrared Absorption Spectra," Nankodo, Tokyo (1960), p. 66 and others.

[25] N. Yoshimi, M. Yamano and M. Tanaka, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **66**, 286, 1602 (1963).

TABLE 3. NMR DATA OF ACETOGUANAMINE AND ITS METHYLOL DERIVATIVES

Peak No.	a	b	c	d	e
ppm \ Compound	3.4	2.3	4.3	5.1—5.4	4.7—5.0
AG	○	×	×	×	×
AGF	○	○	○	○	×
AG2F	×	○	○	○	×
AG3F	×	○	○	○	○
AG4F	×	×	○	×	○
Assignment proton	$-N\underline{H}_2$	$-N\underline{H}-$	$-NHCH_2O\underline{H}$	$-NHC\underline{H}_2OH$	$-N(C\underline{H}_2OH)_2$

Where the circle and saltire-cross marks indicate the presence and absence of the signals respectively.

the $-NH_2$ scissor and the N–H deformation that the number of methylol groups increases in the order of Fig. 2(a)—(e). It has been known[20,21,26] that the sharp band at 815 cm^{-1} is assigned to out-of-plane deformation vibration of the triazine ring.

The results of the infrared spectra may allow us to conclude, at least qualitatively, that the characteristic absorption bands, especially the peaks in 1655—1620 cm^{-1} region and at 1000 cm^{-1}, can be used as a measure of the degree of hydroxymethylation of acetoguanamine with formaldehyde.

NMR Spectra of Mono-, Di-, Tri-, and Tetramethylolacetoguanamine. The measurements of NMR spectra were also carried out to identify the above results. Since the signals of the methylene protons from acetoguanamine and DMSO (solvent) overlapped with each other, the signals of $-NH_2$ groups, $-NH-$, $-CH_2-$, and $-OH$ on $-NHCH_2OH$ groups, and $-CH_2-$ on $-N(CH_2OH)_2$ were inquired. These spectra are shown in Fig. 3 and their chemical shifts are given in Table 3, in which the circle and saltire-cross marks indicate the presence and absence of the signals, respectively.

The signal at 3.4 ppm is observed both in the spectrum of acetoguanamine and AGF but not in that of the other compounds, and acetoguanamine has only this peak (Fig. 3(I)). Therefore, this singlet signal can be identified due to protons of primary amine. The protons which are possessed in AGF, AG2F, and AG3F, but not in acetoguanamine and AG4F, correspond to the imino proton and methylene protons of $-NHCH_2OH$ groups. It has been revealed[27] that the broad signal centered at 2.5 ppm can be assigned to a proton of secondary amine. From these results, the peak at about 2.3 ppm mentioned above may be assigned to the imino proton. On the other hand, the appearance of the triplet in the region of 5.1 to 5.4 ppm is due to the absorption for the methylene protons on $-NHCH_2OH$. The signal near 4.5 ppm can be identified with the hydroxyl group proton on methylol group, because this signal does not appear in acetoguanamine (Fig. 3(I)) but appears in AGF, AG2F, AG3F, and AG4F possessing the methylol group (Fig. 3(II)—(V)). The doublet signal in the region of 4.7 to 5.0 ppm appears in AG3F and AG4F as shown in Fig. 3(IV) and (V), in the spectrum of AG4F, the other absorption other than this doublet peak (e) and the hydroxyl group proton peak (c) can not be detected. Thus the peak (e) may be assigned as coming from the methylene protons on $-N(CH_2OH)_2$. It has become apparent that if the methylene protons on the methylol groups are the same, the methylene protons on $-NHCH_2OH$ and on $-N(CH_2OH)_2$ give the different signals respectively, and from the difference of these signals that the AG2F isomer of $-N(CH_2OH)_2$ type is not contained in the AG2F, *i.e.* the AG2F isomer is very difficult to be formed compared with AG2F bonding two methylol groups on both sides of amino groups. This fact may be explained by the difference of the reactivity of $-NH_2$ and $-NH-$ groups as found by Jong and Jonge[28] on urea resin. If this isomer exists in the obtained AG2F compound, the absorption peaks of a primary amine should remain and that of the methylene on $-N(CH_2OH)_2$ should appear in Fig. 3(III).

The assignment of each proton in acetoguanamine and its methylol derivatives is shown in Table 3. The ratio of the absorption intensities of the signals is recognized to be in reasonable harmony with the calculated one for pure methylol compounds. It may be concluded that the results of the NMR spectra can be used as an indicator of the degree of hydroxymethylation by observing the characteristic absorption signals.

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26) W. M. Padgett and N. F. Hammer, *J. Am. Chem. Soc.*, **80**, 803 (1958).

27) N. Yasaku and J. Kumanotani, Preprint for the 16th Annual Meeting of the Thermosetting Resin Lecture Discussion of Japan (September, 1966), p. 23.

28) J. I. de Jong and J. de Jonge, *Rec. Trav. Chim.*, **72**, 88 (1953).

From results of chemical analysis, infrared absorption spectra and NMR spectra analyses, it was found that four kinds of pure methylol derivatives of acetoguanamine, *i.e.*, mono-, di-, tri-, and tetramethylolacetoguanamines, can easily be synthesized by selecting the reaction conditions, especially the molar ratio of formaldehyde and acetoguanamine.

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