## ADDITION OF METHYL TRIBROMOACETATE AND METHYL MONOBROMACETATE TO ACRYLIC COMPOUNDS

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UDC 542.955:547.464.2:547.391

The methyl esters of the bromoacetic acids  $CH_3OOCCH_nBr_{3-n}$  (n = 0-2), with their gradation in the electrophilicity of the  $CH_nBr_{3-n}$  group and the stability of the C-Br bond, represent a convenient object for studying homolytic addition and telomerization reactions, which go under the conditions of an unfavorable polar factor, in particular, addition to electrophilic acrylic compounds. Peroxide initiation is inefficient in these cases, since cleavage of a bromine atom from the electrophilic brominated methyl acetate by the electrophilic growing  $CH_3OOCCH_nBr_{2-n}CH_2CHX$  radical is difficult (see scheme below), as a result of which the main direction of the process becomes polymerization of the acrylic compound. The use of initiating systems based on  $Fe(CO)_5$  makes it possible to reduce the difficulties in the chain transfer step [1-3].

In the present paper we studied the addition of methyl tribromoacetate (MTBA) to acrylonitrile (AN) and methyl acrylate (MA), and of methyl monobromoacetate to MA, in the presence of coordination complexes (CC) that contain  $Fe(CO)_5$ . The obtained results are given in Tables 1-3, and they fit within the framework of the general scheme of the chain radical reactions of addition and telomerization involving CC, both in the initiation step and in the chain transfer step [4].

Initiation

$$\mathrm{CH_{3}OOCCH}_{n}\mathrm{Br}_{3^{-n}} \xrightarrow{\mathrm{CC}} \mathrm{CH_{3}OOC\dot{C}H}_{n}\mathrm{Br}_{2^{-n}} + (\mathrm{FeBr})^{2^{+}} - \mathtt{complex}$$

Addition

 $\begin{array}{rl} \mathrm{CH_{3}OOC\dot{C}H_{n}Br_{2-n}} &+ \mathrm{CH_{2}=CHX} &\rightarrow \mathrm{CH_{3}OOCCH_{n}Br_{2-n}CH_{2}\dot{C}HX} & \mathrm{(I)} \\ &n = 0,2; \ \mathrm{X} = \mathrm{CN}, \ \mathrm{COOCH_{3}} \end{array}$ 

Chain transfer

$$(I) + CH_{3}OOCCH_{n}Br_{3-n} \xrightarrow{(PeBr)^{\mu+}-complex} \rightarrow CH_{3}OOCCH_{n}Br_{2-n}CH_{2}CHBrX + CH_{3}OOCCH_{n}Br_{2-n} (T_{1})$$

Further growth of the (I) radical is also possible, with the formation of the addition product of two monomeric units (telomer  $T_2$ ).

 $(I) + CH_2 = CHX \xrightarrow{CH_3OOCCH_nBr_{3-n}} CH_3OOCCH_nBr_{2-n}(CH_2CHX)_2Br (T_2)$ 

The reaction result, which depends primarily on the chain transfer steps (they have a higher activation energy than the chain growth steps), is affected mainly by two factors, namely the electrophilicity of the two reactants and the stability of the C-Br bond in the addendum. A decrease in the electrophilicity of the addendum in the series:  $CBr_3COOCH_3 > CHBr_2COOCH_3 > CH_2BrCOOCH_3$  increases the reactivity of the addendum toward the acrylic compound. But the stability of the C-Br bond also increases in the same order, which hinders the reaction. As a result, the extreme members in the bromoacetate series, namely methyl tribromoacetate, which is characterized by the highest electrophilicity of the reaction center (at the bromine-carrying C atom), and at the same time the lowest energy of the C-Br bond, and methyl monobromoacetate, for which the reverse picture is true, are least efficient in the chain transfer step,

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1575-1580, July, 1975. Original article submitted August 28, 1974.

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	Components of CC (amount,	MTBA con- version, %		Yield, % of theory					
Exper-				adduct*		II		MDBA	
		AN	MA	AN	MA	AN	MA	AN	MA
1 2 3 4 5 6 7 8 9 ‡ 10 ‡ 11 ‡ 12 ‡	$\begin{array}{c} Fe(CO)_{5}(50) \\ Fe(CO)_{5}(300) \\ Fe(CO)_{5}(300) + CH_{3}CN(3000) \\ Fe(CO)_{5}(300) + DMFA (150) \\ Fe(CO)_{5}(150) + DMFA (150) \\ Fe(CO)_{5}(150) + I_{2} (75) \\ Fe(CO)_{5}(150) + I_{2} (150) \\ Fe(CO)_{5}(50) + DMFA (50) \\ Fe(CO)_{5}(50) + DMFA (50) \\ Fe(CO)_{5}(50) + I_{2} (25) \\ \end{array}$	42 77 64 96 97 95 92 83 29 32 30 30	64 95 80 83 73 88 86 93 — — — —	26 39 26 35 40 37 55 60 19 18 18 20	53 60 49 44 50 53 66 70 — — — — — —	$ \begin{array}{ c c c c c } 3 & 11 \\ 11 & 11 \\ 21 & 10 \\ 7 & 8 \\ 5 & 6 \\ 2 & 1 \\ 0,5 \\ \end{array} $	4 11 18 19 13 6 9 7 — — —	$ \begin{array}{c} 4 \\ 6 \\ 4 \\ 5 \\ 6 \\ 14 \\ 6 \\ 4 \\ 0,8 \\ 0,5 \\ 1 \\ 0 \\ \end{array} $	4 7 9 7 23 12 13 — —

TABLE 1. Reaction of  $CBr_3COOCH_3$  (MTBA) with  $CH_2 = CHCN$  (AN) or  $CH_2 = CHCOOCH_3$  (MA) in Presence of Initiating Systems (CC). 1 Mole of MTBA, 2 Moles of AN; 2 h, 80°C

\*The adduct from acrylonitrile is  $CH_3OOCCBr_2CH_2CHBrCN$ ; and  $CH_3OOCCBr_2CH_2CHBr-COOCH_3$  from methyl acrylate.

tNot determined. Much tarring was observed in the experiment.

 $\pm$  AN: MTBA mole ratio = 5; the yield of  $T_2(CH_3COOCCBr_2(CH_2CHCN)_2Br)$  is less than 0.1% of theory.

which is expressed in a comparatively low yield of the adducts and a substantial contribution by the side reactions.

In a series of studies involving the use of iron compounds in the chain transfer step, which was carried out on other examples [4], it was observed that the cocatalyst plays an important role when homolytic addition is initiated by  $Fe(CO)_5$ . It was also shown [2] that the presence of compounds with an ester grouping (whether it is the addendum, monomer, or solvent) in the reaction mixture activates  $Fe(CO)_5$  as an initiator of free-radical addition to the C—Hal bond, so that the addition of an additional cocatalyst (DMFA, dimethylaniline (DMA)) no longer exerts a noticeable effect on the efficiency of the CC. From Table 1 it can be seen (Expts. 2, 5, 6, and 9-11) that this phenomenon also takes place in the studied case: when  $CBr_3COOCH_3$  is present the addition of DMFA or DMA does not increase the yield of the adduct. As a result, it can be said that the indicated rule has a general character.

The experimental data obtained by us further show that, as could be expected, starting with the least stable C-Br bond in methyl tribromoacetate (MTBA), when compared with the C-Br bond in methyl dibromoacetate (MDBA) and methyl monobromoacetate (MMBA), methyl tribromoacetate proved to be a sufficiently efficient chain transfer agent so as to not form  $T_2$  under the conditions of a fivefold excess of AN. However, both with a fivefold, as well as with a twofold excess of the monomer the yields of the adduct ( $T_1$ ) were far from quantitative, due to the contribution by the side reactions, which will be discussed below (see, for example, Expts. 4-7, in which the MTBA conversion is close to 100%). A substantial portion of the reaction MTBA (up to 34% in individual cases, see Expt. 4) is not consumed in the step of transfer of the bromine atom to the growing radical (I), but in various side reactions, in particular debromodimerization (up to 21%, see Table 1, Expt. 4). Analogous transformations of bromine-containing compounds

$$\begin{array}{c} \text{CH}_{3}\text{OOCCBr}_{3} \xrightarrow{\text{Fe}(\text{OO})_{5}} \text{CH}_{3}\text{OOCCBr} = \text{CBrCOOCH}_{3} + \text{FeBr}_{2} + \text{CO} \\ (\text{II}) \end{array}$$

under the influence of  $Fe(CO)_5$  were mentioned in [5, 6]. The initiation efficiency also decreases for the reason that a substantial portion (up to 26% of the reacted MTBA, Expt. 6) of the CH<sub>3</sub>OOCCBr<sub>2</sub> radicals, which are formed in the initiation and chain transfer steps, is reduced to CHBr<sub>2</sub>COOCH<sub>3</sub>, and even to

$$CH_{3}OOCCBr_{3} \longrightarrow CH_{3}OOCCBr_{2}$$

$$(I)$$

$$(I)$$

$$(I)$$

$$(I)$$

$$(I)$$

$$(I)$$

BrCH<sub>2</sub>COOCH<sub>3</sub>, via hydrogen cleavage from the hydrogen-containing components of the reaction medium.

$$CH_{2}OOCCBr_{2} \xrightarrow{RH} CH_{2}OOCCHBr_{2} \xrightarrow{\dot{R}} CH_{3}OOCCHBr \xrightarrow{RH} CH_{3}OOCCH_{2}Br$$

TABLE 2. Addition of  $BrCH_2$ -COOCH<sub>3</sub> (MMBA) to  $CH_2 =$ CHCOOCH<sub>3</sub> (MA) in Presence of System Fe(CO)<sub>5</sub> + DMFA. MMBA and MA 0.1 Mole Each; 2 h. 135°

Fe(GO)₅	DMFA	Yield of ad-	
mo	les	of theory*	
$0,02 \\ 0,01 \\ 0,02 \\ 0,02 \\ 0,02 \\ 0,02$	None 0,03 0,02 0,04 0,06	Traces 4 7 6 3	

•Marked tarring of the reaction mass was observed in all cases.

TABLE 3. Ratio of Addition and Substitution as a Function of Initial Concentration of  $Fe(CO)_5$  and DMA. MMBA and MA 0.1 Mole Each; 2 h, 135°C

Fe(CO)s	DMA	Yield of	Amount*			
moles		theory	.(III)	(IV)		
0,05 0,1 0,1 0,2	$ \left \begin{array}{c} 0,15\\ 0,1\\ 0,3\\ 0,2 \end{array}\right  $	$ \begin{array}{ } 4\\2\\0,8\\0,5\\\end{array} $	$     \begin{array}{r}       65 \\       44 \\       20 \\       4     \end{array}   $	35 56 80 96		

The sum (III) + (IV) was taken as 100.

In all of the experiments the addition of MTBA is accompanied to more or less degree by the polymerization of the acrylic compound, which is initiated by all of the types of radicals formed in the reaction. A tarry or glassy residue remained in most of the experiments on distillation. This direction of the reaction becomes the main one under peroxide initiation conditions, and the adduct is practically not formed.

As the data in Table 1 show,  $Fe(CO)_5$  alone makes it possible to obtain the adduct in up to 60% yield (Expts. 1-3). The fraction of side products, mainly (II), increases with increase in the  $Fe(CO)_5$  concentration. Consequently, despite the low conversion, the mole ratio  $Fe(CO)_5$ :  $(CBr_3COOCH_3 + CH_2 = CHX) = 0.015-0.02$  (Expt. 1) is practically more feasible than a higher ratio (0.1-0.3). Although the addition of a solvent (CH<sub>3</sub>CN) increased the reaction rate (cf. the conversion of Expts. 3 and 4), still it did not materially change the adduct; (II) ratio in the reaction products.

Besides such known cocatalysts as DMA and DMFA, we also studied iodine. It is known [7] that iodine easily enters into the coordination sphere of iron carbonyls and activates this sphere toward various reactants. In addition, iodine inhibits the polymerization of AN [8]. It proved that in the addition of MTBA, both to AN and to MA (see Table 1, Expts. 7 and 8), the addition of iodine to  $Fe(CO)_5$  accelerates the process as a whole, increases the yield of the adduct, and reduces the amount of (II) (Expts. 2, 7, 8, and 12).

The data in Table 1 show that the same tendencies are manifested in the case of MA as in the case of AN, and specifically: 1) the system  $Fe(CO)_5 + I_2$  gives the best yield of the adduct (Expts. 7 and 8), and the use of this system can have preparative value; 2) in the experiments with  $Fe(CO)_5$  alone (Expts. 1-3) the yield of the adduct depends on the  $Fe(CO)_5$  concentration, and passes through a maximum close to  $[Fe(CO)_5]_0 = \sim 5$  mole % (Expt. 2); 3) the systems  $Fe(CO)_5 + DMA$  and  $Fe(CO)_5 + DMFA$  give approximately the same yield of the adduct, but among the side reactions the formation of (II) is more strongly expressed in DMFA, while in DMA it is the reduction of the addendum (formation of MDBA (Expts. 5 and 6).

Together with this, mention should also be made of a number of differences between AN and MA in the reaction with MTBA. Thus, the reaction is more complicated with AN, and gives a relatively smaller yield of the adduct and a substantially greater amount of tarry products, which is responsible for the lack of agreement in the material balance (up to 40%, Expt. 5) between the MTBA conversion and the sum of identified products. The side processes of reduction are more strongly expressed in the case of MA, which is an argument in favor of the activity of the COOCH<sub>3</sub> group of MA as a hydrogen donor in the formation of MDBA (see Table 1, Expts. 4, 6-8). Dimethylaniline plays an important role in the reduction processes (cf. Expts. 2 and 6), but it is not the sole hydrogen source, as can be concluded from the data of Expts. 6-8.

The efficiency of the above enumerated initiating systems in the case of an addendum that has a fairly unreactive halogen atom was studied by us on the example of the addition of MMBA to MA. It proved that

 $CH_3OOCCH_2Br + CH_2 = CHCOOCH_3 \xrightarrow{CC} CH_3OOCCH_2CH_2CHBrCOOCH_3$  (III)

 $Fe(CO)_5$  alone, and the systems  $Fe(CO)_5 + DMA$ ,  $Fe(CO)_5 + DMFA$ , and  $Fe(CO)_5 + I_2$ , initiate the addition of  $BrCH_2COOCH_3$  to  $CH_2 = CHCOOCH_3$  to give only a slight amount of (III), apparently due to the low activity of  $Fe(CO)_5$  in cleaving a hydrogen atom from  $BrCH_2COOCH_3$ . It was also for the same reason that notice-able differences were not observed in the activity of the initiating systems when one cocatalyst was replaced

by another, or when their ratios were varied (see Tables 2 and 3). The side reactions entered first place. Thus, in the case of using DMA as the cocatalyst the formation of  $C_{6}H_{5}N(CH_{3})CH_{2}COOCH_{3}$  (IV) was predominant, evidently via the intermediate ammonium salt.

 $\begin{array}{l} C_{3}H_{5}N(CH_{3})_{2} + BrCH_{2}COOCH_{3} \rightarrow [C_{6}H_{5}N(CH_{3})_{2}CH_{2}COOCH_{3}]Br^{-} \rightarrow \\ \rightarrow C_{6}H_{5}N(CH_{3})CH_{2}COOCH_{3} \text{ (IV)} \end{array}$ 

The initiating system apparently catalyzes the decomposition of the ammonium salt, because the (IV): (III) ratio in the reaction mixture increases noticeably with increase in the initial concentration of  $Fe(CO)_5$  and DMA (see Table 3).

The reduction products of the intermediately formed radicals  $(CH_3COOCH_3, CH_3OOC(CH_2)_3COOCH_3)$ were not found among the reaction products of MMBA with MA, and  $(CH_3OOCCH_2)_2$ , the doubling product of the  $CH_3OOCCH_2$  radicals, which are formed in the initiation step, is also absent. Together with the low yield of the adduct, the absence of these compounds is an argument in favor of the slight development of radical formation processes in general during the initiation of this reaction, since reduction processes always take place in the homolytic addition reactions of MA and AN at a sufficient concentration of the initiating and growing radicals when using the initiating systems selected by us, as can be seen from Table 1 and was mentioned repeatedly in the literature [9, 10].

#### EXPERIMENTAL

All of the experiments were run in an inert gas atmosphere (N<sub>2</sub>, argon). The GLC analysis was run on a Tswett 1/64 instrument, using the internal standard method. The columns were: stainless steel, 1 m, 5% poly(ethylene glycol adipate)-3000; 1 m, 5% Silicone Elastomer; 2 m, 5% Silicone E-301; Chromosorb (80-100 mesh) was the support in all cases. The temperature was 100, 130, and 150°, the detection was based on the heat conductivity, and helium was the carrier gas. The NMR spectra were taken at 60 MHz, the solvent was  $CCl_4$ , and the chemical shifts are given on the  $\delta$  scale.

<u>Methyl Ester of  $\alpha, \alpha, \gamma$ -tribromo- $\gamma$ -cyanobutyric Acid.</u> To a solution of 1.9 g of iodine in a mixture of 15.5 g of CBr<sub>3</sub>COOCH<sub>3</sub> and 5.3 g of AN was added 1.47 g of Fe(CO)<sub>5</sub>. After heating the stirred reaction mass at 80° for 2 h it was passed through 15 g of Al<sub>2</sub>O<sub>3</sub> in order to remove the iron compounds. The Al<sub>2</sub>O<sub>3</sub> bed was washed with hot petroleum ether. The wash liquor was combined with the reaction mass. After distilling off the solvent the mixture was fractionally distilled in vacuo. Here 5.8 g of unreacted CBr<sub>3</sub>COO-CH<sub>3</sub> distilled at 50° (2 mm), and then were isolated: a) 0.9 g (11%) of dimethyl  $\alpha,\beta$ -dibromofumarate; bp 90° (2 mm); n<sub>D</sub><sup>20</sup> 1.5310; d<sub>4</sub><sup>20</sup> 1.9212. Found: C 23.44; H 1.93; Br 53.50%. MR 48.63. C<sub>6</sub>H<sub>6</sub>Br<sub>2</sub>O<sub>4</sub>. Calculated: C 23.84; H 1.98; Br 53.00%; MR 48.20. NMR spectrum ( $\delta$ , ppm): 3.84 s (COOCH<sub>3</sub>). The Raman spectrum has a band at 1580 cm<sup>-1</sup>, which is characteristic for a symmetrically substituted double bond. This compound was also obtained in 30% yield by heating (1 h, 80°) 3 g of CBr<sub>3</sub>COOCH<sub>3</sub> with 1.9 g of Fe(CO)<sub>5</sub>; b) 7.4 g (40%) of methyl  $\alpha, \alpha, \gamma$ -tribromo- $\gamma$ -cyanobutyrate; bp 130° (2 mm); n<sub>D</sub><sup>20</sup> 1.5540; d<sub>4</sub><sup>20</sup> 2.1241. Found: C 19.91; H 1.70; Br 65.77%; MR 54.92. C<sub>6</sub>H<sub>6</sub>Br<sub>3</sub>NO<sub>2</sub>. Calculated: C 19.81; H 1.66; Br 65.89%; MR 54.68. NMR spectrum (ABX system) ( $\delta$ , ppm): 3.95 s (COOCH<sub>3</sub>), 3.15-3.80 (two quartets of CH<sub>2</sub> with a center at 3.50), and 4.55-4.85 (two doublets of CHBr with a center at 4.70). The integral intensity corresponds to the formula. CH<sub>3</sub>OOCCHBrCH<sub>2</sub>CHBrCN.

The other experiments listed in Table 1 were run in a similar manner.

Dimethyl Ester of  $\alpha, \alpha, \gamma$ -Tribromoglutaric Acid (adduct of MTBA and MA): bp 122-3° (1 mm); n<sub>D</sub><sup>20</sup> 1.5320; d<sub>4</sub><sup>20</sup> 2.0194. Found: C 21.30; H 2.31; Br 60.00%; MR 60.89. C<sub>7</sub>H<sub>9</sub>Br<sub>3</sub>O<sub>4</sub>. Calculated: C 21.18; H 2.28; Br 60.40%; MR 61.13. NMR spectrum ( $\delta$ , ppm): 3.78 s and 3.91 s (CH<sub>3</sub> for CHBrCOOCH<sub>3</sub> and CBr<sub>2</sub>COOCH<sub>3</sub>, respectively.

<u>Dimethyl Ester of  $\alpha$ -Bromoglutaric Acid (III)</u>. To a stirred mixture of 7.6 g of BrCH<sub>2</sub>COOCH<sub>3</sub> and 1.4 g of DMFA at 135° was added in drops, in 1 h, a solution of 1.9 g of Fe(CO)<sub>5</sub> in 4.3 g of MA, after which the mixture was heated for another hour, cooled, passed through a bed of silica gel (20 g) to remove the iron compounds, the silica gel was washed with boiling hot petroleum ether, and the combined filtrate was vacuum-distilled. We isolated 0.8 g (7%) of adduct (III), which, based on the GLC data, is 98.5% pure; bp 124° (12 mm);  $n_D^{20}$  1.4650;  $d_4^{20}$  1.4504, which agrees with [11]. Found MR 45.56, calculated 45.60. NMR spectrum ( $\delta$ , ppm): 2.48 m (CH<sub>2</sub>--CH<sub>2</sub>), 3.75 s (CH<sub>3</sub> in CH<sub>2</sub>COOCH<sub>3</sub>), 3.85 s (CH<sub>3</sub> in CHBrCOOCH<sub>3</sub>), 4.38 t (CHBr). The structure of (III) was confirmed by counter synthesis from glutamic acid by the following scheme.

# $\begin{array}{c} \text{HOOCCH}(\text{NH}_2)\text{CH}_2\text{CH}_2\text{COOH} \xrightarrow[0-5^\circ]{} \text{HOOCCHBrCH}_2\text{CH}_2\text{COOH} \xrightarrow[0-5^\circ]{} \text{HOOCCH}_2\text{CH}_2\text{COOH} \xrightarrow[0-5^\circ]{} \text{HOOCCH}_2\text{CH}_2\text{CH}_2\text{COOH} \xrightarrow[0-5^\circ]{} \text{HOOCCH}_2\text{$

<u>Methyl Ester of N-Phenyl-N-methylglycine (IV)</u>. In a N<sub>2</sub> stream, to a mixture of 15.3 g of BrCH<sub>2</sub>-COOCH<sub>3</sub> and 12.1 g of DMA was added 1.9 g of Fe(CO)<sub>5</sub>. At the end of heat evolution the mixture was heated at 135° for 1 h and then worked up as described for (III). After a double vacuum-distillation we obtained 9.5 g (50%) of amine (IV), which quickly turned blue in the air, bp 90° (2 mm);  $n_2^{D}$  1.5438;  $d_4^{20}$  1.1327. Found: C 66.25; H 7.28; N 8.50%; MR 49.87.  $C_{10}H_{13}NO_2$ . Calculated: C 67.00; H 7.26; N 7.82%; MR 50.37. Picrate, mp 80°. Found: N 13.57%.  $C_{10}H_{13}NO_2 \cdot C_6H_3N_3O_7$ . Calculated: N 13.73%. NMR spectrum of (IV) ( $\delta$ , ppm): 2.85 s (CH<sub>3</sub>), 3.47 s (COOCH)<sub>3</sub>, 3.85 s (CH<sub>2</sub>C), 6.55 m and 6.85 m (monosubstituted benzene ring). The structure of (IV) was confirmed by counter synthesis from 0.2 mole of  $C_6H_5NHCH_3$  and 0.1 mole of BrCH<sub>2</sub>COOCH<sub>3</sub> (3 h, 130°, yield of (IV) = 42%).

### CONCLUSIONS

1. Coordination initiating systems that contain iron pentacarbonyl and a cocatalyst (dimethylaniline, DMFA, iodine) are efficient in the homolytic addition of methyl tribromoacetate to methyl acrylate and acrylonitrile, and are ineffecient in the addition of methyl monobromoacetate to methyl acrylate. In the addition of methyl tribromoacetate to acrylic compounds the system: iron pentacarbonyl + iodine gave the highest yield of the adducts.

2. The main side processes in the addition of methyl tribromoacetate to methyl acrylate and acrylonitrile in the presence of the above enumerated initiators are polymerization of the acrylic compound, reduction of the intermediate free radicals, and debromodimerization of the methyl tribromoacetate. The greatest contribution by the reduction reactions is observed in the case of the iron pentacarbonyl + dimethylaniline system.

3. Iron pentacarbonyl catalyzes the alkylation of dimethylaniline by methyl monobromoacetate to give the methyl ester of N-phenyl-N-methylglycine.

### LITERATURE CITED

- 1. F. K. Velichko and R. A. Amriev, Izv. Akad. Nauk SSSR, Ser. Khim., 592 (1973).
- 2. R. Kh. Freidlina, F. K. Velichko, and R. A. Amriev, Dokl. Akad. Nauk SSSR, 187, 350 (1969).
- 3. R. A. Amriev, F. K. Velichko, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 1172 (1970).
- 4. R. Kh. Freidlina and F. K. Velichko, Methods in Heteroorganic Chemistry. Chlorine. Aliphatic Compounds [in Russian], Nauka (1973), pp. 136-140.
- 5. H. Alper and E. C. H. Keung, J. Org. Chem., 37, 2566 (1972).
- 6. T. Shirafuji, Y. Yamamoto, and H. Nozaki, Bull. Chem. Soc. Japan, 44, 1994 (1971).
- 7. Monograph, "Organic syntheses via metal carbonyls" [Russian translation], Mir (1970), pp.178-179.
- 8. S. U. Mullik, S. A. A. Chishti, and S. B. Kapadia, Sci. Ind. (Karachi), <u>5</u>, 473 (1967); C. A., <u>70</u>, 58340 (1969).
- 9. N. A. Kuz'mina, E. Ts. Chukovskaya, M. A. Rozhkova, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 961 (1972).
- E. Ts. Chukovskaya, M. A. Rozhkova, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 1782 (1973).
- 11. B. Teichmann, Z. Chem., 5, 106 (1965).