

ADDITION OF METHYL DIBROMOACETATE TO METHYL  
CROTONATE IN THE PRESENCE OF IRON PENTACARBONYL  
AND DIMETHYLANILINE

F. K. Velichko, T. A. Pudova,  
and R. Kh. Freidlina

UDC 542.955:547.464:547.391.3

The usual initiators used in free-radical addition reactions, like peroxides and azo compounds, are ineffective in the case of the addition of electrophilic bromine-containing addenda to electron-acceptor acrylic compounds [1, 2]. Previously it was shown that  $\text{Fe}(\text{CO})_5$  is an effective initiator for the addition of methyl dibromoacetate to methyl acrylate and methyl methacrylate [3]. It is known that olefins with a nonterminal double bond usually enter with difficulty into free-radical addition and give lower yields of the desired reaction products [4].

In the present paper we studied the addition of methyl dibromoacetate to methyl crotonate. The formation of addition products is practically not observed when either photoinitiation or thermal initiation ( $140^\circ$ ), as well as azobisisobutyronitrile, is used as the initiator. In the case of initiation with either benzoyl peroxide or tert-butyl peroxide at  $140^\circ$ , based on the GLC data,  $\sim 6\%$  of the adduct is formed (Table 1).  $\text{Fe}(\text{CO})_5$  without a nucleophilic cocatalyst also proved ineffective; under conditions analogous to those given in [1, 3], the yield of the adduct was less than  $4\%$ . As initiators we investigated initiating systems that contained  $\text{Fe}(\text{CO})_5$  and a cocatalyst;  $\text{Fe}(\text{CO})_5 + \text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$ ;  $\text{Fe}(\text{CO})_5 + (\text{CH}_3)_2\text{NCHO}$ ;  $\text{Fe}(\text{CO})_5 + (\text{C}_6\text{H}_5\text{O})_3\text{P}$ ;  $\text{Fe}(\text{CO})_5 + (\text{C}_2\text{H}_5\text{O})_3\text{P}$ . Only the system  $\text{Fe}(\text{CO})_5 + \text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$  proved effective at  $140^\circ$ , which gave (based on GLC) a  $27\%$  yield of the adduct, or  $80\%$  when based on reacted dibromoacetate (see Table 1). At  $100^\circ$  the yield of the adduct was  $4\%$ . An increase in the amount of  $\text{Fe}(\text{CO})_5$  from 0.25 to 0.8 M (here the  $\text{Fe}(\text{CO})_5$  : cocatalyst ratio was kept constant) lowered the yield of the adduct at  $140^\circ$  to  $5\%$ .

Based on the NMR and GLC data, both isomers are formed:  $\text{CH}_3\text{CH}(\text{CHBrCOOCH}_3)_2$  (I) and  $\text{CH}_3\text{CHBr} \cdot \text{CH}(\text{COOCH}_3)\text{CHBrCOOCH}_3$  (II) in a 5:1 ratio. Based on the NMR data, (I) is a mixture of two stereo forms in a ratio of  $\sim 3:2$ .

EXPERIMENTAL

The experiments were run as described in [1], using 5 ml and 10 ml ampules, respectively, filled with 0.4 and 3 ml of the reaction mixture. The yield of the adduct and the conversion of the starting compounds were determined by GLC using the standards: dimethyl phthalate for the adduct, and chlorobenzene for the methyl dibromoacetate and methyl crotonate. The results are given in Table 1. See [1] for the chromatography conditions. In order to isolate the adduct the experiment was run in a flask in an argon atmosphere.

Dimethyl Ester of  $\beta$ -Methyl- $\alpha,\alpha'$ -dibromoglutaric Acid [Adduct (I)]. To a flask fitted with a reflux condenser, and immersed in a bath at a temperature of  $140^\circ$ , was added in 2 h a mixture of 34.6 g of  $\text{CHBr}_2 \cdot \text{COOCH}_3$ , 7.5 g  $\text{CH}_3\text{CH}=\text{CHCOOCH}_3$ , 2.8 g  $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$ , and 1.3 g of  $\text{Fe}(\text{CO})_5$  in drops. On conclusion of addition the heating was continued for another hour at  $140^\circ$ . Then the methyl dibromoacetate was distilled off at 10 mm (16 g), and the residue was extracted with boiling petroleum ether, the extract was evaporated, and the residue was fractionally distilled at 4 mm. We obtained 3.8 g of the adduct with a purity of  $97\%$ . (GLC); yield  $16\%$ ; bp  $142\text{--}143^\circ$  (4 mm) (with partial decomposition);  $n_D^{20}$  1.5039;  $d_4^{20}$  1.6835. From [5]: bp  $179\text{--}180^\circ$  (20 mm). Found: C 28.65; H 3.55; Br 48.58%; MR 58.39.  $\text{C}_8\text{H}_{12}\text{Br}_2\text{O}_4$ . Calculated: C 28.91; H 3.61;

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 1, pp. 159-160, January, 1973. Original article submitted March 9, 1972.

© 1973 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. All rights reserved. This article cannot be reproduced for any purpose whatsoever without permission of the publisher. A copy of this article is available from the publisher for \$15.00.

TABLE 1. Addition of Methyl Dibromoacetate to Methyl Crotonate\*

Initiating system	Yield of adduct, % of theory	Conversion, % †	
		CHBr <sub>2</sub> COOCH <sub>3</sub>	CH <sub>3</sub> CH=CHCOOCH <sub>3</sub>
Azobisisobutyronitrile‡	0,5	1	1
tert-Butyl peroxide‡	6	8	21
Benzoyl peroxide‡	7	8	25
Fe(CO) <sub>5</sub>	4	15	12
Fe(CO) <sub>5</sub> + (C <sub>6</sub> H <sub>5</sub> O) <sub>3</sub> P	0	**	**
Fe(CO) <sub>5</sub> + (C <sub>6</sub> H <sub>5</sub> O) <sub>3</sub> P	3	26	62
Fe(CO) <sub>5</sub> + (CH <sub>3</sub> ) <sub>2</sub> NCHO	6	45	25
Fe(CO) <sub>5</sub> + C <sub>6</sub> H <sub>5</sub> N(CH <sub>3</sub> ) <sub>2</sub>	27	17	60

\* Sealed ampuls, 140°, 4 h; concentration, M, CHBr<sub>2</sub>COOCH<sub>3</sub> : CH<sub>3</sub>CH=CHCOOCH<sub>3</sub> : Fe(CO)<sub>5</sub> : cocatalyst = 5 : 2.5 : 0.25 : 0.8.

† Based on charged starting compound.

‡ Concentration 0.3 M.

\*\* The reaction mixture turned to a tar.

Br 48.19%; MR 57.98. NMR spectrum (in CCl<sub>4</sub>) (60 MHz,  $\delta$ , ppm): singlet at 3.82 (COOCH<sub>3</sub>), multiplets at 1.15 (CH<sub>3</sub>), 2.73 (C-CH-C), and 4.45 (CHBr). A multiplet with  $\delta$  1.53-2.13 is also present in the spectrum, which, by analogy with the spectrum of CH<sub>3</sub>CH<sub>2</sub>CHBrCH<sub>3</sub> [6], was assigned to the CH<sub>3</sub> group of isomer (II). The signals of the CHBr group in the CH<sub>3</sub>CHBr fragment of isomer (II) are superimposed on the signals of the CHBr grouping of isomer (I).

## CONCLUSIONS

1. The adduct was obtained in 16-27% yield when methyl dibromoacetate was added to methyl crotonate in the presence of the system: Fe(CO)<sub>5</sub>-dimethylaniline.

2. Peroxides, azobisisobutyronitrile, and Fe(CO)<sub>5</sub> without a nucleophilic cocatalyst, are ineffective as initiators for the free-radical addition of methyl dibromoacetate to methyl crotonate.

## LITERATURE CITED

1. R. Kh. Freidlina, F. K. Velichko, and R. A. Amriev, Dokl. Akad. Nauk SSSR, 187, 350 (1969).
2. M. S. Kharasch, P. S. Skall, and P. Fischer, J. Amer. Chem. Soc., 59, 407 (1937).
3. R. A. Amriev, F. K. Velichko, and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Ser. Khim., 1172 (1970).
4. Organic Reactions [Russian translation], Vol. 13, Mir (1966), p. 110.
5. C. K. Ingold, J. Chem. Soc., 121/122, 2676 (1922).
6. L. A. Kazitsyna and N. B. Kupletskaya, Application of Ultraviolet, Infrared and NMR Spectroscopy in Organic Chemistry [in Russian], Vysshaya Shkola (1971), pp. 133, 198.