BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 594—596 (1967)

The Hunsdiecker Reaction of Silver Acrylate and Methacrylate

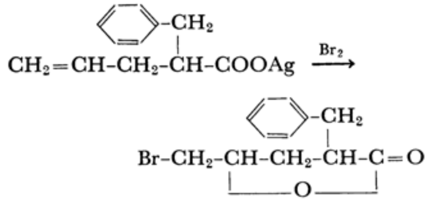
Shu FURUKAWA, Kiyoshi NARUCHI, Shigetake MATSUI and Michio YUUKI

Department of Industrial Chemistry, Faculty of Engineering, Chiba University, Yayoicho, Chiba

(Received June 8, 1966)

The Hunsdiecker reaction of silver acrylate and methacrylate has been investigated; 1, 1, 2-tribromoethane was obtained from the former, and bromoacetone from the latter. Since bromoacetone has also been obtained by the reaction of 2-bromopropene-1 with acetyl hypobromite, it is conceivable that, in the case of the Hunsdiecker reaction of silver methacrylate, methacryloyl hypobromite (the intermediate of the Hunsdiecker reaction) oxidized 2-bromopropene-1 (the primary product of the Hunsdiecker reaction) to bromoacetone, with an accompanying rearrangement of the bromine atom.

In lower series of unsaturated fatty acids, no normal Hunsdiecker reaction has ever been reported to occur by the reactions of the silver salts of the carboxylic acids with bromine. Silver allylacetate¹⁾ gave bromolactone, and silver allylbenzylacetate gave α-benzyl-δ-bromo-γ-pentano-lactone,²⁾ as follows:



Moreover, silver fumarate and maleate gave³⁾ no Hunsdiecker reaction products.

Conly¹⁾ obtained the polymer and no halide from silver methacrylate by reacting it with bromine, but he observed no evolution of carbon dioxide.

The present authors studied the structure of the polymer and examined the reaction of bromine with silver acrylate and methacrylate; they obtained 1, 1, 2-tribromoethane from the former and bromoacetone from the latter, together with polymers in large portions in both cases. In this paper, the details of the Hunsdiecker reaction will be described.

Results and Discussion

When a suspension of silver acrylate in carbon tetrachloride was added to a carbon tetrachloride solution of bromine at -5—-2°C, about 1.5% of carbon dioxide was observed to evolve; some 1, 1, 2-tribromoethane was obtained as a normal product of the Hunsdiecker reaction, together with a substantial portion of the polymer.

In the case of silver methacrylate, the reaction was carried out under various conditions. A suspension of silver methacrylate in carbon tetrachloride was added drop by drop to a carbon tetrachloride solution of bromine at -10—-23°C, or a bromine solution in carbon tetrachloride was added to a suspension of silver methacrylate in carbon tetrachloride at various temperatures. In every case, about 2—4% of carbon dioxide

---

1) J. C. Conly, *J. Am. Chem. Soc.*, **75**, 1148 (1953).

2) S. Furukawa and B. Kubota, unpublished.

3) R. G. Johnson and R. K. Ingham, *Chem. Revs.*, **56**, 219 (1956).

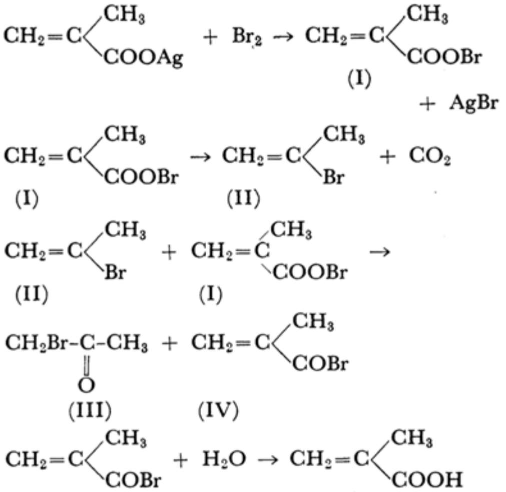
TABLE 1. HUNSDIECKER REACTION OF SILVER METHACRYLATE

Expt	Ag-salt mol	Br_2 mol	$Ag{:}Br_2$[a] mol	Method of dropping	Reaction temp. °C	Reaction time, hr b) c)	CO_2[d] %	Yield[e] %
1	0.480	0.722	1 : 1.5	Ag[f]	−10—−20	6.5+2.0	3.87	3.97
2	0.596	0.576	1 : 0.96	Ag	−21—−23	4.0+7.5	4.11	4.55
3	0.347	0.330	1 : 0.96	Br[g]	−21—−23	4.7+4.7	3.92	3.92
4	0.400	0.248	1 : 0.62	Br	−20	6.5+1.5	2.63	3.85
5	0.300	0.468	1 : 1.56	Br	1—3	7.5+2.0	2.71	2.82
6	0.300	0.284	1 : 0.95	Br	76.4	8.0+2.0	2.08	3.39

a) Mol ratio of silver salt to bromine. b) Time of addition. c) Duration of additional stirring (kept at the temp.). d) Mol% of CO_2 evolved (based on silver salt). e) Yield of bromoacetone (based on silver salt), calculated from gas chromatogram (column: tricresyl phosphate on Shimalite B, 3 m, column temp. 120°C, carrier gas He 100 m*l*/min). f) Silver salt was added (reverse addition). g) Bromine was added (normal addition).

was detected to evolve; a 3—4.5% yield of bromoacetone was obtained, together with some methacrylic acid and a polymeric substance. The results and the conditions of the reaction are summarized in Table 1.

In the reaction of methacrylate, 2-bromopropene-1 is produced first by the Hunsdiecker reaction, and then 2-bromopropene-1 (II) is oxidized to bromoacetone (III) by methacryloyl hypobromite (I), the intermediate of the Hunsdiecker reaction; thus methacryloyl bromide (IV) is also produced. The latter reaction was confirmed in a separate experiment.



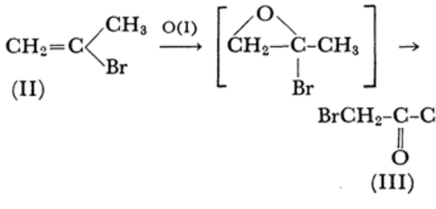
$$CH_2{=}C(CH_3)COOAg + Br_2 \rightarrow \underset{(I)}{CH_2{=}C(CH_3)COOBr} + AgBr$$

$$\underset{(I)}{CH_2{=}C(CH_3)COOBr} \rightarrow \underset{(II)}{CH_2{=}C(CH_3)Br} + CO_2$$

$$\underset{(II)}{CH_2{=}C(CH_3)Br} + \underset{(I)}{CH_2{=}C(CH_3)COOBr} \rightarrow \underset{(III)}{CH_2Br{-}CO{-}CH_3} + \underset{(IV)}{CH_2{=}C(CH_3)COBr}$$

$$\underset{(IV)}{CH_2{=}C(CH_3)COBr} + H_2O \rightarrow \underset{(V)}{CH_2{=}C(CH_3)COOH} + HBr$$

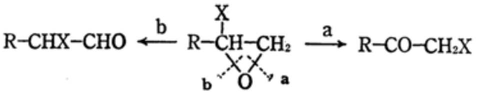
The bromoacetone may be derived from 2-bromopropene-1 through the following oxidative rearrangement mechanism:



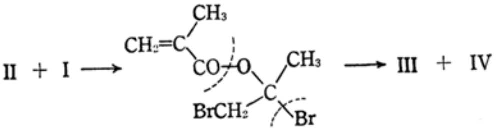
$$\underset{(II)}{CH_2{=}C(CH_3)Br} \xrightarrow{O(I)} [\text{epoxide}] \rightarrow \underset{(III)}{BrCH_2{-}CO{-}CH_3}$$

A few analogous oxidative rearrangements may be seen in the literature. Demole[4] obtained bromoacetyl bromide from 1, 1-dibromoethylene, and Bachman[5] obtained α-bromopropionyl bromide from 1, 1-dibromopropene-1, by oxidation with molecular oxygen. Furthermore, Henry[6] obtained 1, 3-dichloroacetone and 1, 2, 2, 3-tetrachloropropane from 2, 3-dichloropropene-1 by oxidation with hypochlorous acid.

Recently, Kirrman *et al.*[7] have described the rearrangement of α-epoxide with nucleophilic substituents. The rearrangement proceeds according to the following scheme:



The possibility of another mechanism, that through the addition of methacryloyl hypobromite to 2-bromopropene, followed by the splitting of methacryloyl bromide from the resulting ester according to the following scheme, can not be denied:



Experimental

Materials. Carbon tetrachloride and bromine were purified and dried by usual methods. Commercial methyl acrylate and methyl methacrylate were purified by distillation and converted into their sodium salts.[8]

---

4) E. Demole, *Ber.*, **11**, 315 (1878).

5) G. B. Bachman, *J. Am. Chem. Soc.*, **57**, 1088 (1935).

6) L. Henry, *J. Chem. Soc.*, **42**, 1039 (1882).

7) A. Kirrman, P. Duhamel and R. Nouri-Bimorghi, *Ann.*, **691**, 33 (1966).

8) S. Suzuki and H. Ito, Japanese Pat. application No. 29-5522 (1954).

Silver salts were prepared by the double decomposition of the sodium salts with aqueous silver nitrate; then they were recrystallized from water and dried in a vacuum.

Reaction of Silver Methacrylate with Bromine. A four-necked 1-*l* flask equipped with a stirrer, a dropping funnel, a reflux condenser, a thermometer, and a nitrogen gas inlet was connected through the top of the reflux condenser with a glass tube packed with calcium chloride and then with a bromine absorber (red phosphorus+glass wool) and a carbon dioxide absorber (a barium hydroxide solution). After the flask had been dried overnight, dry nitrogen was introduced to expel the air. A solution of 91.2 g (0.576 mol) of bromine in 325 m*l* of carbon tetrachloride was placed in the flask and cooled to −22°C (dry ice in methanol) under a slow stream of nitrogen; then a suspension of 115.6 g (0.596 mol) of fine-powdered silver methacrylate in 280 m*l* of carbon tetrachloride was added, drop by drop, over a 4 hr period. The flask was then maintained for 7.5 more hr at −21—−23°C under a slow stream of nitrogen.

After the reaction, the solution was separated by filtration from the solid reaction products (AgBr+polymer), and the filtrate was washed with a 0.5 N sodium thiosulfate solution to remove the excess bromine. The organic layer was dried over anhydrous sodium sulfate and distilled to remove the crabon tetrachloride; the 71 g of a reddish brown liquid which remained was fractionally distilled. The 1st fraction bp 76.0—76.5°C/760 mmHg, 40 g; the 2nd fraction bp 70—75.5°C/45 mmHg, 5.9 g; the 3rd fraction bp 75.5—120°C/45 mmHg, 3.3 g; the 4th fraction bp 120—125°C/25 mmHg, 1.5 g; the 5th fraction bp 100—115°C/15 mmHg, 1.0 g; viscous residue, 18 g.

Identification of the Products. Bromoacetone was present in the second and third fractions; it was separated by gas chromatography (column: tricresyl phosphate on Shimalite B, 3 m; column temp.: 120°C; He 100 m*l*/min). It was identified by the retention time of the gas chromatography and by comparing its IR spectrum with that of an authentic specimen.

Found: C, 26.16; H, 3.87; Br, 57.97%. Calcd for C_3H_5OBr: C, 26.30; H, 3.56; Br, 58.33%.

Methacrylic acid was obtained from the second fraction by fractionation with gas chromatography; it was identified by a comparison of its IR spectrum with that of an authentic sample.

Reaction of 2-Bromopropene-1 with Acetyl Hypobromite.[9] Dried silver acetate (8.5 g, 0.051 mol) and 65 m*l* of carbon tetrachloride were placed into a four-necked flask, and the air was replaced by nitrogen. The flask was then cooled to 1°C with ice, and a solution of bromine (7.9 g, 0.0495 mol) in 20 m*l* of carbon tetrachloride was added, drop by drop, over a 2 hr period. After 30 min, a solution of 2.24 g (0.0185 mol) of 2-bromopropene-1 dissolved in 10 m*l* of carbon tetrachloride was added, drop by drop. The precipitated silver bromide was separated by filtration; when the filtrate was distilled, 3.776 g of a liquid residue was obtained. It was fractionated by gas chromatography, and thus bromoacetone was separated and identified by means of gas chromatography and a study of its IR spectrum. In all, 0.4772 g (12.5% yield) of bromoacetone was obtained (calculated from the gas chromatogram).

Reaction of Silver Acrylate with Bromine. Powdered silver acrylate (Found: Ag, 60.21%, Calcd for $C_3H_3O_2Ag$: Ag, 60.29%) was suspended in carbon tetrachloride, and the suspension was added, drop by drop, to the carbon tetrachloride solution of bromine at −5—−2°C. The reaction apparatus was the same as that employed in the case of silver methacrylate. About 1.5% of carbon dioxide was observed to evolve. Silver bromide and a part of the polymer were separated by filtration, and carbon tetrachloride was removed from the filtrate. About 30 m*l* of the reddish brown liquid thus obtained was fractionated under reduced pressure. The fraction (10 g, bp 60—120°C/18 mmHg) was further rectified, and three fractions, namely, bp 64—77°C/18 mmHg, 1.3 g; bp 77—80°C/18 mmHg, 3 g and bp 80—110°C/16 mmHg, 4 g, were obtained. From the first and second fractions, 1, 1, 2-tribromoethane was isolated by fractionation with gas chromatography (column, tricresyl phosphate on Shimalite B, 3 m; column temp. 120°C; He 100 m*l*/min).

Found: Br, 90.18%. Calcd for $C_2H_3Br_3$: 89.86%.

This was further identified by a comparison of its IR spectrum with that of the authentic compound synthesized.

Preparation of 1, 1, 2-Tribromoethane. This was synthesized by the reaction of vinyl bromide with bromine in the presence of water. D_4^{19} 2.62331, $n_D^{18.5}$ 1.5908, bp 82—83°C/18 mmHg.

---

[9] S. G. Levine and M. E. Wall, *J. Am. Chem. Soc.*, **81**, 2826 (1959).