ACTA CHEMICA SCANDINAVICA 21 (1967) 1737–1740

The Preparation and Structure of Some Halogenosubstituted Unsaturated Aliphatic Acids

CHRISTOFFER RAPPE and KURT ANDERSSON

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

By NMR it has been proved that the structure of the dibromo acid described by Cahours in 1861 is 3,3-dibromomethacrylic acid (II). The bromination of II yielded a tribromo acid, 3,3-dibromo-2-(bromomethyl)acrylic acid (VIII). When VIII was treated with base, 3,3-dibromo-2-(hydroxymethyl)acrylic acid (IX) was the product.

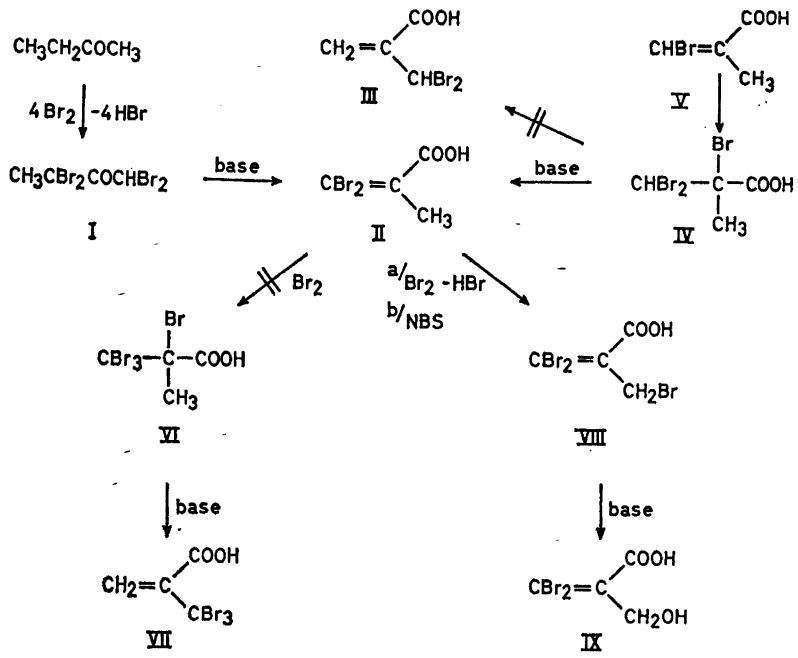
In connection with studies on the Favorsky rearrangement, the present authors studied the rearrangement of 1,1,3,3-tetrabromo-2-butanone (I). From this ketone we obtained 3,3-dibromomethacrylic acid (II), the structure of which was determined by NMR-analyses.[1]

This acid, or the isomeric 2-(dibromomethyl)acrylic acid (III) has previously been described by Cahours.[2,3] In his paper Cahours also described some other bromosubstituted acids, prepared from 3,3-dibromomethacrylic acid (II). However, no melting points, yields, or structural proofs are given for any of these acids. During the century which has passed since Cahours' work was published, no investigations have been published to clarify the structure of these acids.

As starting material for the preparation of 3,3-dibromomethacrylic acid (II) Cahours used 2,3,3-tribromoisobutyric acid (IV), which in turn was prepared from one of the isomeric 3-bromomethacrylic acids (V).[2]

The preparation of *cis*- and *trans*-3-bromomethacrylic acids (V) will be treated in a separate paper.[4] Both isomers gave the same addition product with bromine, 2,3,3-tribromoisobutyric acid (IV). The best way to prepare IV is by addition of bromine to *trans*-3-bromomethacrylic acid in carbon tetrachloride catalyzed by direct sunlight for one hour. When acid IV was treated with base, a dibromo substituted unsaturated acid was obtained, which was proved to be identical with the 3,3-dibromomethacrylic acid (II) prepared from the Favorsky rearrangement.[1]

When acid II was treated with bromine, Cahours reported that he could isolate a tetrabromo product.[2] As we now know the correct structure of the starting acid, the structure of the tetrabromo product would be 2,3,3,3-tetra-



bromoisobutyric acid (VI).[5] By treating this tetrabromo acid with base, Cahours isolated a tribromosubstituted unsaturated acid, which would be 2-(tribromomethyl)-acrylic acid (VII).[2,3]

As pointed out above, it is very difficult to really establish the identity of the acids prepared by Cahours.[2] No physical data are given and the analytical data are of very limited value due to impure analytical reagents.[6,7]

When we treated acid II with one equivalent of bromine in a sealed tube at 125°C for 5 h (the conditions used in Ref. 2), the bromine colour disappeared, but a strong evolution of hydrogen bromide was observed. In experiments, not described here, we found that a solution of bromine and acid II in carbon tetrachloride kept in sunlight at room temperature resulted in a brisk evolution of hydrogen bromide. The same result was obtained when the reaction was catalyzed by benzoyl peroxide. From the ampoule syntheses we obtained a 55 % yield of an acid, with the empirical formula $C_4H_3Br_3O_2$. Furthermore, the same acid was obtained in a 59 % yield (after recrystallization) by treating one equivalent of acid II with one equivalent of N-bromosuccinimide in boiling carbon tetrachloride with a peroxide as initiator. This result is consistent with a substitution and not with an addition of bromine. From IR (strong band at 1558 cm^{-1}) and NMR (two singlets, ratio 2:1) its structure was established as 3,3-dibromo-2-(bromomethyl)acrylic acid (VIII).

When acid VIII was treated with base, we obtained an acid with the empirical formula $C_4H_4Br_2O_3$. By its reaction with diazobenzenesulfonic acid

it could be established that it contained an OH-group (IR weak band at 3430 cm^{-1}). A double bond could be identified by IR (bands at 1595 and 1620 cm^{-1}). The NMR-spectrum contained two singlets, ratio 1:1. From these data it could be concluded that the structure was 3,3-dibromo-2-(hydroxymethyl)acrylic acid (IX).

EXPERIMENTAL

The NMR-spectra were recorded on a Varian model A-60 spectrometer. The syntheses were performed in duplicate (a minimum) and the yields given are mean values. The micro analyses were performed by the Analytical Department, Chemical Institute, University of Uppsala.

trans-*3-Bromomethacrylic acid* (V), was prepared according to Ref. 4, m.p. 64.0—64.5°C.

2,3,3-Tribromoisobutyric acid (IV). A. A mixture of 3.3 g (0.020 mole) of *trans*-3-bromomethacrylic acid and 3.2 g (0.020 mole) of bromine was heated for 16 h in a sealed tube in an oil bath at 110°C. When cooled, the red-brown liquid crystallized at about 80°C. A trace of hydrogen bromide was observed when the sealed tube was opened. The crystals were dissolved in 50 ml of ether, the ether phase washed with water (2 × 10 ml), dried ($CaCl_2$), and evaporated. The ether left 6.3 g of white crystals, which were dissolved in 50 ml of boiling hexane, treated with activated carbon, filtered hot, and left for crystallization. 4.1 g (63 %) of white crystals, m.p. 97.0—98.0°C, were collected. Repeated recrystallizations raised the melting point to 97.5—98.0°C. The NMR-spectrum (carbon tetrachloride) showed three singlets at δ 2.12, 6.22, and 11.84 ppm, respectively (TMS = 0), with the ratio 3:1:1. (Found: C 14.92; H 1.56; Br 74.06. Calc. for $C_4H_5Br_3O_2$: C 14.79; H 1.55; Br 73.82).

B. A solution of 2.65 g (0.016 mole) of *trans*-3-bromomethacrylic acid and 2.6 g (0.016 mole) of bromine in 40 ml of carbon tetrachloride was placed in direct sunlight. The bromine colour rapidly disappeared and the reaction was complete within 30 min. Hydrogen bromide could be detected and the yellow-brownish solution was washed with 10 ml of water, dried ($CaCl_2$), and evaporated. The carbon tetrachloride left 5.0 g of white crystals. Recrystallization from 30 ml of boiling hexane (activated carbon) yielded 3.3 g (63 %) of white crystals, m.p. 97.0—98.0°C. By NMR, IR, and mixed melting points this acid was established to be identical with the acid obtained from the procedure outlined in A.

C. 0.2 g (0.0012 mole) of *cis*-3-bromomethacrylic acid and 0.2 g (0.0012 mole) of bromine treated in a sealed tube as above (100°C, 2.5 h) yielded 0.2 g (50 %) of white crystals, m.p. 97.0—98.0°C. By NMR, IR, and mixed melting points the identity with 2,3,3-tribromoisobutyric acid was established.

3,3-Dibromomethacrylic acid (II).[1] A solution of 4.2 g (0.013 mols) of 2,3,3-tribromoisobutyric acid and 1.8 g (0.032 mole) of potassium hydroxide in 50 ml of water was rapidly heated to boiling. When the solution had just come to boil (after about 8 min), the reaction was quenched by rapid chilling. The solution was then extracted with ether (2 × 20 ml), acidified with diluted hydrochloric acid, and extracted with ether (3 × 20 ml) again. The acidic ether phase was washed with 10 ml of water and dried ($CaCl_2$). Evaporation of the ether yielded 3.0 g of white crystals, which were recrystallized from hot water. 2.0 g (63 %) of white, glasswool-like crystals were collected, m.p. 98.0—99.0°C. By NMR- and IR-analyses and mixed melting points this acid was established to be identical with 3,3-dibromomethacrylic acid obtained from the Favorsky rearrangement of 1,1,3,3-tetrabromo-2-butanone.[1]

3,3-Dibromo-2-(bromomethyl)acrylic acid (VIII). A. A mixture of 2.45 g (0.010 mole) of 3,3-dibromomethacrylic acid and 1.60 g (0.010 mole) of bromine in a sealed tube, was heated in an oil bath at 125°C for 5 h. A vigorous evolution of hydrogen bromide resulted when opening the sealed tube. The residual crystals were dissolved in 50 ml of ether, the ethereal solution washed with water (2 × 15 ml), dried ($CaCl_2$), and evaporated. The ether left 3.3 g of white crystals, which were recrystallized from 40 ml of boiling heptane (activated carbon). 1.80 g (55 %) of white crystals were collected, m.p. 124—

125°C. (Found: C 14.80; H 0.93; Br 74.21. Calc. for $C_4H_3Br_3O_3$: C 14.88; H 0.94; Br 74.27). Acidimetric titration gave the equivalent weight 321.8; calc. for VIII 322.8. The NMR-spectrum shows two singlets, ratio 2:1, and the IR-spectrum shows a strong band at 1558 cm^{-1}.

B. To a solution of 1.22 g (0.005 mole) of 3,3-dibromomethacrylic acid and 0.80 g (0.005 mole) of bromine in 30 ml of carbon tetrachloride, was added 0.10 g of benzoyl peroxide. The sealed flask was kept at room temperature. After 17 h the bromine colour had completely disappeared and hydrogen bromide was evolved when opening the flask. The solution was evaporated, the residue extracted with ether and worked up as above. Recrystallization yielded 0.80 g (50 %) of 3,3-dibromo-2-(bromomethyl)acrylic acid. A blank solution without the peroxide kept in darkness did not show any change.

C. 2.44 g (0.010 mole) of 3,3-dibromomethacrylic acid was refluxed for 24 h with 1.80 g (0.010 mole) of N-bromosuccinimide in 60 ml of dry carbon tetrachloride with a trace of benzoyl peroxide added. After completed reaction, the mixture was cooled, filtered to remove the solid succinimide, and the solution washed with water and dried ($CaCl_2$). Evaporation and recrystallization of the residual crystals from 40 ml of boiling heptane (activated carbon) yielded 1.90 g (59 %) of white crystals, m.p. 124—125°C. From mixed melting points, IR-, and NMR-spectra it was established that the products from procedures A, B, and C were identical.

3,3-Dibromo-2-(hydroxymethyl)acrylic acid (IX). A solution of 1.61 g (0.005 mole) of 3,3-dibromo-2-(bromomethyl)acrylic acid and 0.70 g (0.012 mole) of potassium hydroxide in 10 ml of water was refluxed for 10 min. After cooling, the solution was washed with ether, acidified with concentrated hydrochloric acid, and extracted with ether (4 × 10 ml). The ether phase was washed with 10 ml of water, dried ($MgSO_4$), and evaporated. From the ether was collected 1.3 g of pale yellow crystals which, in lack of a suitable solvent for recrystallization, were washed by boiling in heptane to remove the starting material. After repeated washings, 1.15 g (89 %) of white crystals, m.p. 128.0—129.5°C, were collected. 1.0 g of the acid was recrystallized from 200 ml of boiling carbon tetrachloride yielded 0.18 g of white crystals, m.p. 128.5—129.5°C. Reaction with diazobenzenesulfonic acid showed that it contained an OH-group. (Found: C 18.51; H 1.49; Br 61.55. Calc. for $C_4H_4Br_2O_3$: C 18.49; H 1.55; Br 61.50). Acidimetric titration gave the equivalent weight 262.7; calc. for IX 259.9. NMR-spectrum (D_2O) showed two singlets, ratio 1:1, and IR spectrum bands at 3430 (weak), 1595 and 1620 cm^{-1}.

Acknowledgements. The authors are indebted to Professor Arne Fredga for all facilities placed at their disposal. Grants from the *Swedish Natural Science Research Council* to C. R. and from the *Faculty of Mathematics and Natural Sciences*, University of Uppsala to K. A. are gratefully acknowledged.

REFERENCES

1. Rappe, C. and Andersson, K. *Arkiv Kemi* **24** (1965) 303.
2. Cahours, A. *Ann. Suppl.* **2** (1861) 345.
3. *Beilsteins Handbuch der Organischen Chemie*, Band II, Springer, Berlin 1920, p. 425.
4. Rappe, C. and Andersson, K. *Acta Chem. Scand.* **21** (1967) 1741.
5. Ref. 3, p. 297.
6. Cahours, A. *Ann. Suppl.* **2** (1861) 80.
7. Kekulé, A. *Ann. Suppl.* **2** (1861) 107.

Received March 23, 1967.