Terminally Phenylated Conjugated Unsaturated Ketones II.[1] *Silver Acetate on Dibenzylidenecycloalkanone Tetrabromides*

Ping-Yuan YEH

(Received August 4, 1953)

In the course of a study of the aromatization of 2,6-dibenzylidenecyclohexanone[2] the action of silver acetate on dibenzylidenecycloalkanone tetrabromides was studied.

Diacetoxy - dibromo - 2, 5 - dibenzylidenecyclopentanone was obtained by the action of silver acetate on 2,5-dibenzylidenecyclopentanone tetrabromide in acetic acid even when 4 mole equivalents of silver acetate were used. The corresponding tetraacetoxy-derivative was obtained, however, when 4 mole equivalents of silver acetate were reacted with 2,6-dibenzylidenecyclohexanone tetrabromide. On using 2 mole equivalents of silver acetate and heating them at 85~90° for an hour, both diacetoxydibromo- and triacetoxymonobromo-derivatives were obtained with a 10% recovery of 2, 6 - dibenzylidenecyclohexanone tetrabromide. If the temperature was maintained at 85~90° for more than 2 hours or the reaction mixture was refluxed for half an hour the only crystalline product identified was 2,6-dibenzylidenecyclohexanone. By refluxing half an hour in acetic acid, however, tetraacetoxy- and tetrabromo-2,6-dibenzylidenecyclohexanone did not give 2,6-dibenzylidenecyclohexanone.

Two isomers of diacetoxy-dibromo-2,5-dibenzylidenecyclopentanone, m.p. 213~214° (decomp.), colorless plates, and m.p. 185~186°, colorless prisms, and two isomers of tetraacetoxy-2,6-dibenzylidenecyclohexanone, m.p. 227~228° (decomp.), colorless needles, and m.p. 220~221° (decomp.) colorless polygonal crystals, were obtained in the present work.

Experimental[3]

Materials. 2, 5-Dibenzylidenecyclopentanone tetrabromide and 2, 6-dibenzylidenecyclohexanone tetrabromide were prepared according to the published methods[4][5] and had m.p. 175° (with decomposition) and 193°, respectively.

Action of silver acetate on 2, 5-dibenzylidenecyclopentanone tetrabromide. A mixture of 20 g. (0.034 mole) of 2, 5-dibenzylidenecyclopentanone tetrabromide, 24.2 g. (0.136 mole) of silver acetate, and 180 ml. of glacial acetic acid was refluxed for 3 hours under mechanical stirring. After removing the silver bromide and adding water the crude diacetoxydibromo-derivative separated out as a white precipitate (14.0 g., 76%) which was recrystallized from ethanol; colorless plates, m.p. 213–214° (decomp.). It gave positive Beilstein test. *Anal.* Calcd. for $C_{23}H_{22}O_5Br_2$: C, 51.32; H, 4.12. Found: C, 51.78 and 51.63; H, 4.27 and 3.96.

From the mother liquor of the above recrystallization, a small number of colorless prismatic crystals, m.p. 185–186°, were obtained. These also gave positive Beilstein test. *Anal.* Calcd. for $C_{23}H_{22}O_5Br_2$: C, 51.32; H, 4.12. Found: C, 50.84; H, 3.70.

Action of silver acetate on, 2, 6-dibenzylidenecyclohexanone tetrabromide. a) 2, 6–Dibenzylidenecyclohexanone tetrabromide (15 g., 0.025 mole), silver acetate (8.4 g., 0.05 mole), and 70 cc. of glacial acetic acid were heated at 85–90° for an hour and treated in the same manner as in the above experiment. By extracting the silver bromide precipitate with benzene, 10% (1.5 g.) of the unreacted tetrabromide was recovered. The crude product (12.7 g., 90%) was recrystallized from ethanol. Colorless needles, m.p. 210–211° (decomp.). Yield 5.7 g. (40%). It gave positive Beilstein test. *Anal.* Calcd. for $C_{24}H_{24}O_5Br_2$: C, 52.19; H, 4.38. Found: C, 52.52 and 51.94; H, 4.50 and 4.38.

From the mother liquor of the above recrystallization colorless polygonal crystals melting at 200–201° (0.2 g.) were obtained which gave positive Beilstein test. *Anal.* Calcd. for $C_{26}H_{27}O_7Br$: C, 58.76; H, 5.12. Found: C, 58.28; H, 4.78.

When the reaction mixture was refluxed for half an hour or heated at 85–90° for more than 2 hours, instead of heating for an hour, the crystalline product was 2, 6–dibenzylidenecyclohexanone, (m.p. and mixed m.p. with authentic specimen, 117–118°, no depression) and no diacetoxydibromo-derivative could be obtained. *Anal.* Calcd. for $C_{20}H_{18}O$: C, 87.56; H, 6.61. Found: C, 87.23; H, 6.51.

b) A mixture of 15 g. (0.025 mole) of 2, 6–dibenzylidenecyclohexanone tetrabromide, 16.8 g. (0.1 mole) of silver acetate, and 200 ml. of glacial acetic acid was refluxed for an hour under mechanical stirring and treated in the same manner as in the above experiment. The precipitate (3.8 g.) thus obtained was recrystallized from benzene. Colorless needles, m.p. 227–228° (decompn.), yield 3.3 g. (26%). This gave negative Beilstein test. *Anal.* Calcd. for $C_{28}H_{30}O_4$: C, 65.87; H, 5.92. Found: C, 66.32; H, 5.95.

---

1) Ping-Yuan Yeh, "Isomerization and dimerization of 2,6-dibenzylidenecyclohexanone" J. Taiwan Pharmaceutical Association, **5**, 2 (1953).

2) Ping-Yuan Yeh, "Aromatization of 2, 6-dibenzylidenecyclohexanone". In this series of manuscript.

3) All melting points are corrected.

4) D. Vorländer and K. Hobohm, *Ber.*, **29**, 1837 (1896).

5) C. E. Garland and E. E. Reid, *J. Am. Chem. Soc.*, 2336 (1925).

Besides this product, some colorless polygonal crystals (less soluble in benzene than the needles, m.p. 220-221° (decomp.), yield 0.3 g. (2.3%), were obtained. These also gave negative Beilstein test. *Anal.* Calcd. for $C_{28}H_{30}O_4$: C, 65.87; H, 5.92. Found: C, 66.19; H, 5.83.

Summary

The action of silver acetate on 2,6-dibenzylidenecyclohexanone tetrabromide and 2,5-dibenzylidenecyclopentanone tetrabromide was studied.

The author wishes to express his gratitudes to Prof. Tetsuo Nozoe, Tohoku University, and Prof. Eigai Sebe, Kumamoto University for their advice.

Department of Chemistry,
National Taiwan University,
Formosa, China