The Dimerization of 3-Methyl-3-penten-2-one

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(Received August 23, 1957)

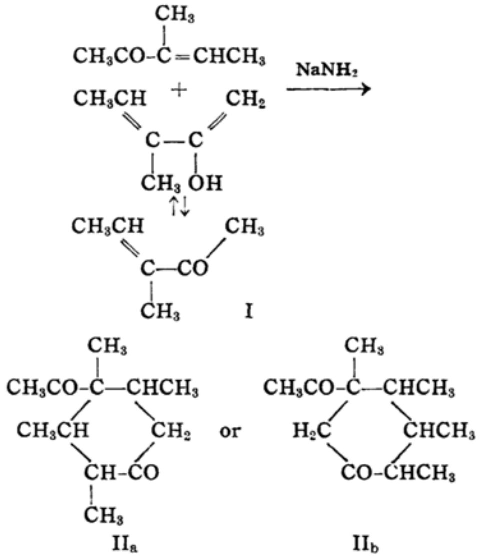
In an attempt to prepare an ethynylcarbinol from 3-methyl-3-penten-2-one (I) and acetylene by the action of sodium amide in ethereal solution, we encountered a characteristic crystalline product (II) which proved to be a dimer of I. This reaction is considered to be of the same class as that of acetylcyclohexene which was reported by Jones and Koch[1)].

In the present experiment I was treated with sodium amide in ethereal solution in the cold. From the reaction mixture, colorless crystals (II) were obtained in ca. 30% yield in addition to other oily products.

II had no unsaturated nature and the existence of two carbonyl groups in its molecule was presumed on the basis of its diketonic derivatives. Together with analyses and molecular weight determined, a cyclic structure corresponding to a dimer of I was considered for it. Its one carbonyl group seemed to be in the ring and the other in the exocyclic position because of the following facts.

On treatment with hypobromite it gave bromo-derivatives instead of the corresponding acid, and at most, trisubstituted derivative could be obtained though the reagent was applied in great excess. From these bromo-derivatives certain materials having unsaturated nature could easily be formed. Further, II gave positive reaction toward acetyl test[2)]. On these evidences, a six-membered ring was proposed and the three hydrogen atoms which are easily replaceable were considered to be in some special positions, perhaps on the two carbon atoms adjacent to the endocyclic carbonyl group.

Thus structure II_a or II_b was proposed for the dimer in question. Structure II_a (4-acetyl-2,3,4,5-tetramethyl-1-cyclohexanone) seems probable, on the basis of the results obtained in the case of acetylcyclohexene[1)]. The reaction seems to follow the mode of diene synthesis.



It may be noted that mesityl oxide gave a dimer of different nature when treated with sodium amide in a manner similar to that in the above case. The crystalline substance obtained here had unsaturated nature and its melting point was almost identical with 2-acetyl-1,3,3,5-tetramethyl-5-cyclohexen-1-ol reported by Braude et al.[3)] who obtained the compound from mesityl oxide in the presence of lithium.

Experimental

3-Methyl-3-penten-2-one (I).—The preparation followed the method of Hinkel et al.[4)] with some modifications. Paraldehyde was used in place of acetaldehyde, and pyridine was substituted for quinoline to eliminate hydrogen chloride in the crude product. B.p. 136~138°.

Dimerization of I.—The yield of the dimer was rather dependent upon the reaction temperature and other trivial conditions. A typical run is described below.

Fifty grams of I was added dropwise to a suspension of 25 g. of powdered sodium amide in 300 cc. of dry ether in a course of ca. 40 min. at $-2\sim6°$, and kept stirred for ca. 4 hr. at the same temperature. The reaction mixture was

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1) E. R. H. Jones and H. P. Koch, *J. Chem. Soc.*, **1942**, 393.

2) J. Adachi, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zassi)*, **71**, 566 (1950); *J. Anal. Chem.*, **23**, 1491 (1951).

3) E. A. Braude, B. F. Gofton, G. Lowe and E. S. Waight, *J. Chem. Soc.*, **1956**, 4054.

4) L. E. Hinkel, E. E. Ayling, J. F. J. Dippy and T. H. Angel, ibid., **1931**, 814.

poured onto crushed ice containing acetic acid; the ethereal portion was separated, washed with a solution of potassium carbonate and dried over calcium chloride. Ether was then removed and the residue was distilled under reduced pressure to yield the following fractions: (1) b. p. ca. 50°/30 mmHg, ca. 4.5 g.; (2) b.p. ca. 140~164°/23 mmHg, ca. 26.5 g., somewhat viscous yellowish oil; residue, ca. 5 g., dark resinous material.

Fraction (2) was kept cooled overnight in an ice-box and the colorless crystals (II) separated out were collected, ca. 11 g., yield, ca. 22%.

In another experiment, II was obtained in ca. 30% yield, in which the reaction was held at 2~12° for 6 hr. (after the addition of I) and the whole was allowed to stand for 10 hr. at room temperature.

The crude crystalline product was crystallized twice from methanol; colorless square plates or needles, fairly easily soluble in ethanol, methanol and ether, insoluble in cold water, somewhat soluble in hot water, m. p. 80~81.5°.

Anal. Found: C, 73.56; H, 10.10; mol. wt. (Rast), 192. Calcd. for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27%; mol. wt., 196.3.

II did not decolorize bromine water and gave red coloration on heating with potassium hypobromite solution and pyridine, suggesting the presence of acetyl group[2].

The remaining oil of fraction (2), from which the above crystals were separated, seemed still to contain a fair amount of II or its isomers; this was inferred from the amount of the corresponding semicarbazone obtained from it. Likewise, this oil instantly decolorized bromine water indicating the presence of another unsaturated material.

Derivatives of II. — *Semicarbazone.* — The semicarbazone was prepared in aqueous ethanolic solution and recrystallized from ethanol, colorless long plates, m. p. 217° (with frothing; slowly heated), 240° (with frothing; rapidly heated).

Anal. Found: C, 61.25; H, 8.97; N, 16.45. Calcd. for $C_{13}H_{23}O_2N_3$: C, 61.63; H, 9.15; N, 16.59%.

2, 4-Dinitrophenylhydrazone. — The derivative was recrystallized from pyridine; orange-yellow crystals, m.p. 200~201°.

Anal. Found: C, 57.47; H, 6.19; N, 14.83. Calcd. for $C_{18}H_{24}O_5N_4$: C, 57.43; H, 6.43; N, 14.89%.

Bis-2, 4-dinitrophenylhydrazone.—An excess of a solution of 2, 4-dinitrophenylhydrazine in methanolic sulfuric acid was added to II and refluxed for ca. 30 min. The orange crystals formed, which were sparingly soluble in boiling methanol, were crystallized twice from hot pyridine; orange crystals, m.p. 263~264° (with decomposition; rapidly heated) and 236~237° (with decomposition; slowly heated (ca. 1° per 30 sec.)).

Anal. Found: C, 52.11; H, 5.17; N, 20.15. Calcd. for $C_{24}H_{28}O_8N_8$: C, 51.79; H, 5.07; N, 20.14%.

Phenylhydrazone.—One and a half grams of II was refluxed in a mixture of 3 g. of phenylhydrazine, 5 cc. of ethanol and 1 cc. of water for ca. 20 min., and, after being cooled, the product was collected. Recrystallization from pyridine-ethanol gave almost colorless (faintly pale) plates, m.p. 155~156° (in sealed tube).

Anal. Found: C, 75.36; H, 9.05; N, 9.77. Calcd. for $C_{18}H_{26}ON_2$: C, 75.48; H, 9.15; N, 9.78%.

Bisphenylhydrazone.—A solution of 1.8 g. of II and 2.7 g. of phenylhydrazine in a mixture of ca. 3 cc. of 50 per cent. acetic acid and ca. 4 cc. of methanol was refluxed for ca. 1 hr. The crude product was recrystallized from methanol-pyridine, almost colorless (faintly greenish yellow) needles, m.p. 155~156° (in sealed tube).

Anal. Found: C, 76.24; H, 8.53; N, 14.96. Calcd. for $C_{24}H_{32}N_4$: C, 76.55; H, 8.57; N, 14.88%.

Hydrazone.—Two grams of II was refluxed with a mixture of excessive hydrazine hydrate and 3 cc. of ethanol for several minutes. Colorless long needles (ca. 2 g.) which readily separated out on standing, were crystallized twice from a small amount of ethanol; colorless needles or prisms, somewhat soluble in water and in ether, much more soluble in hot water, easily soluble in ethanol and methanol, m.p. 130~131°.

Anal. Found: C, 68.46; H, 10.54; N, 13.41; mol. wt. (Rast), 202. Calcd. for $C_{12}H_{22}ON_2$: C, 68.53; H, 10.55; N, 13.32%; mol. wt., 210.3.

Bromo-derivatives of II. — An attempt to oxidize II by hypobromite for the purpose of obtaining the corresponding acid resulted in bromination.

Tribromo-derivative (III). — Five grams of II was shaken with hypobromite solution, made from 24 g. of bromine, 28 g. of potassium hydroxide and 250 cc. of water, for ca. 4 hr. at room temperature, and left overnight. The reaction product which weighed ca. 3 g. was separated and recrystallized from ethanol; colorless needles or prisms, m. p. 81° (with partial decomposition), 100~101° (with partial decomposition; rapidly heated).

Anal. Found: C, 33.29; H, 3.94; Br, 54.92; mol. wt. (Rast), 455. Calcd. for $C_{12}H_{17}O_2Br_3$: C, 33.28; H, 3.96; Br, 55.37%; mol. wt., 433.0.

2, 4-Dinitrophenylhydrazone of III.—Recrystallization from ethanol-pyridine gave long orange plates, m. p. 145° (with decomposition), 157~158° (with decomposition; rapidly heated).

Anal. Found: C, 35.20; H, 3.43; N, 9.03; Br, 38.97. Calcd. for $C_{18}H_{21}O_5N_4Br_3$: C, 35.26; H, 3.45; N, 9.14; Br, 39.11%.

Dibromo-derivative. — On applying a smaller amount of hypobromite another bromo-derivative containing one bromine atom less was obtained from II together with III. However its rigid separation from III was difficult, its 2, 4-dinitrophenylhydrazone being obtained in fairly pure state; orange plates or fine yellowish orange needles from pyridine, m. p. 160° (with decomposition), 174° (with decomposition; rapidly heated).

Anal. Found: C, 40.66; H, 4.11; N, 10.43. Calcd. for $C_{18}H_{22}O_5N_4Br_2$: C, 40.47; H, 4.15; N, 10.49%.

Some Notes on the Bromo-derivatives of

II.—(a) III was warmed with ethanolic potassium hydroxide for ca. 1 hr., the reaction mixture was acidified with sulfuric acid and extracted with ether. After the ether was evaporated, a small amount of yellow needles was formed. A similar substance was obtained from the aqueous portion in the case of the hypobromite reaction mentioned above. In both cases the amount was insufficient for characterization purposes.

(b) When the bromo-derivatives were recrystallized from hot ethanolic acetic acid containing a little water, they turned into an oily material which instantly decolorized bromine water. Further, the bromo-derivatives, on warming with pyridine for ca. 1.5 hr., gave almost colorless crystals which also decolorized bromine water.

Dimerization of Mesityl Oxide.—The reaction was carried out in the same manner as in the case of I. A considerable amount of colorless needles or prisms was obtained, which on recrystallization from ethanol had m. p. 74~75°. It instantly decolorized bromine water and was positive toward acetyl test[2)].

Anal. Found: C, 73.31; H, 10.17; mol. wt. (Rast), 184. Calcd. for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27%; mol. wt., 196.3.

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