93. *Triacetone Dialcohol and its Dehydration Products.*

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Triacetone dialcohol has been isolated from the products of the alkaline condensation of acetone, and some of its physical properties have been determined.

Phorone is easily prepared from this alcohol in almost theoretical yield by dehydration with acid catalysts under certain conditions. Under other conditions, dehydration is carried only half way, giving either an almost quantitative yield of "semiphorone," a dimethylheptenolone, or a 30—40% yield of 2 : 2 : 6 : 6-tetramethyltetrahydro-γ-pyrone.

The 2 : 4-dinitrophenylhydrazones of these ketones have been prepared from acid solutions.

Symmetrical triacetone dialcohol, $CMe_2(OH)\cdot CH_2\cdot CO\cdot CH_2\cdot CMe_2\cdot OH$, the parent alcohol of triacetonamine, triacetonediamine, etc., has been described only by Leopold and Schacke (D.R.-P. 481,290, 1929), who prepared it by condensing together acetone and diacetone alcohol in the presence of phthalic anhydride. In a subsequent patent (D.R.-P. 483,823, 1929) the dehydration of the dialcohol to "semiphorone" and phorone was described.

The vacuum-distillation residues, from the large-scale production of diacetone alcohol, on cooling to room temperature deposit large crops of impure triacetone dialcohol; when purified by recrystallisation or vacuum distillation, this corresponds in its properties to the substance described by Leopold and Schacke. Examination of products through the various stages of the process of manufacture of diacetone alcohol, *viz.*, autocondensation of acetone by means of sodium hydroxide, followed by neutralisation, removal of excess of acetone and vacuum distillation of the crude product, indicates that triacetone dialcohol is formed during the condensation.

The controlled dehydration of the substance has been found to give excellent yields of "semiphorone" (2 : 6-dimethyl-Δ^2-hepten-6-ol-4-one) or phorone at will. In addition, the inner anhydride, probably the hitherto unknown 2 : 2 : 6 : 6-*tetramethyltetrahydro-γ-pyrone*, has been prepared.

Some observations have been made on the 2 : 4-dinitrophenylhydrazones of ketones of the above types and it has been found that, under the usual conditions of their preparation, dehydration or possibly other changes may occur.

Experimental.

Purification of Triacetone Dialcohol.—The vacuum-still residues mentioned contained, besides diacetone and triacetone alcohols, small amounts of higher ketones and inorganic salts. The crystalline mass was centrifuged to remove most of the organic impurities, and the dry crystals were freed from sodium acetate and sodium sulphate by recrystallisation from water. An alternative method was to melt the crystals, allow any solid to settle, or filter the liquid hot, and distil the clear liquid under reduced pressure.

A twice-recrystallised product was soluble in water, alcohol, acetone, or benzene. If it was distilled while slightly alkaline, it gave acetone and diacetone alcohol at reduced pressures, and broke down completely to acetone at normal pressure. The crystals, which can be grown to a large size, are colourless and odourless; m. p. 56·4°, b. p. 128°/15 mm. (Leopold and Schacke give m. p. 57°, b. p. 138°/37 mm.) (Found: C, 62·1; H, 10·5. Calc. for $C_9H_{18}O_3$: C, 62·0; H, 10·4%).

Dehydration of Triacetone Dialcohol.—(i) *To "semiphorone,"* $CMe_2{:}CH\cdot CO\cdot CH_2\cdot CMe_2\cdot OH$. Leopold and Schacke (*loc. cit.*) described a method in which 5% of concentrated sulphuric acid was added dropwise to triacetone dialcohol, and the mixture heated to 75° for 1 hr., neutralised with sodium hydroxide, and vacuum distilled. In our hands this procedure afforded only a 30% yield of semiphorone, much phorone being produced. It was found preferable to distil 100 g. of triacetone dialcohol with 0·1 g. of syrupy phosphoric acid at 20 mm. pressure. This gave 79 g. of semiphorone together with some water; if allowance is made for a residue of 9 g., the yield is 97%.

The same substance is also described by Grignard and Fluchaire (*Ann. Chim.*, 1928, **9**, 5) as occurring among the products of the prolonged action of butoxymagnesium bromide on acetone. When purified by repeated fractionation at low pressure, "semiphorone" is an oily, pale yellow liquid having a pleasant orange-like odour; m. p. $< -70°$, b. p. 101°/15 mm., $d_{4°}^{20°}$ 0·9350, $n_D^{20°}$ 1·4666, r_D 0·2965 (Found: C, 69·2; H, 10·5. Calc. for $C_9H_{16}O_2$: C, 69·2; H, 10·3%). Leopold and Schacke give b. p. 105—110°/20 mm. and Grignard and Fluchaire give b. p. 95°/5 mm., $d_{4°}^{15°}$ 0·9432.

The oil readily adds 2 atoms of bromine but does not form an oxime or a bisulphite compound under the usual conditions.

(ii) *To phorone.* Either (1) the crude vacuum-still triacetone dialcohol, containing residue, or (2) centrifuged crystals can be used.

(1) 200 G. of residue were heated under reflux with 1 c.c. of concentrated sulphuric acid. The mesityl oxide produced from the 55% of diacetone alcohol present in the crude dialcohol acted as an entrainer for removing the water of reaction. Subsequent vacuum fractionation gave 68 g. of phorone, m. p. 24°, *i.e.*, a yield of approximately 80% by weight on the initial pure dialcohol. There were also 12 g. of high-boiling residue.

(2) 100 G. of dialcohol crystals were heated under reflux with 100 c.c. of benzene and 0·05 c.c. of sulphuric acid, the water again being removed by entrainment; vacuum fractionation then afforded 5 g. of mesityl oxide and 67 g. of phorone (m. p. 25°; yield approx. 85% by wt.).

Similar dehydration of "semiphorone" gives equally good yields of phorone.

Redistillation and recrystallisation of the products gave bright yellow crystals of phorone; m. p. 27·5°, b. p. 81°/15 mm., $d_{15\cdot5°}^{29°}$ 0·880.

(iii) *To* 2 : 2 : 6 : 6-*tetramethyltetrahydro-γ-pyrone.* 200 G. of crude centrifuged triacetone dialcohol crystals were heated under reflux with 75 g. of water and 4 g. of sulphuric acid for 1 hr. The oils were steam-distilled from the acid solution and finally fractionated in a vacuum. The products were 48 g. of 2 : 2 : 6 : 6-*tetramethyltetrahydro-γ-pyrone*, 74 g. of phorone, and 20 g. of semiphorone. The new ketone (Found: C, 69·1; H, 10·5; *M*, cryoscopic in benzene, 155, 158. $C_9H_{16}O_2$ requires C, 69·2; H, 10·3%; *M*, 156) combines with sodium hydrogen sulphite, and readily forms an oxime, m. p. 101°, quantitatively in the cold. It has a camphor-like odour and is water white; m. p. 12·8°, b. p. 70°/15 mm.

Elizarova and Nazarov (*Bull. Acad. Sci. U.R.S.S.*, 1940, 189) find that hydration of vinyl *iso*propenyl ketone affords a dimethyltetrahydropyrone.

The tetramethyltetrahydro-γ-pyrone is dehydrated to phorone, and appears to be formed either by hydration of phorone or by removal of 1 mol. of water from the two hydroxyl groups in triacetone dialcohol with ring closure in either case.

The properties of tetrahydropyrone and its 2 : 2-dimethyl and its 2 : 2 : 6 : 6-tetramethyl derivative are compared below :

	Tetrahydro-γ-pyrone.	Dimethyl deriv.	Tetramethyl deriv.
d	1·0795 (24·5°)	—	0·9485 (20°)
n_D	1·4529 (24·5°)	1·4473 (20°)	1·4432 (20°)
r_D	0·2503	—	0·2797
B. p.	164·7°	178·5—179°	186°

Observations on certain 2 : 4-*Dinitrophenylhydrazones*.—These hydrazones were prepared from seven ketones by adding the ketone to a moderate excess of 0·4% solution of 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid. Di- and tri-acetone alcohols afforded precipitates only slowly, but in all cases the reaction mixtures were kept for 24 hrs. with occasional shaking. The hydrazones were filtered off, washed, and recrystallised from alcohol. No. 1 was yellow,

No.	Ketone.	M. p. of deriv., etc.	No.	Ketone.	M. p. of deriv., etc.
1.	Acetone	127—128°	6.	Semiphorone	171—172·5°
2.	Diacetone alcohol	197—198	7.	Tetramethyltetrahydropyrone	171—173
3.	Mesityl oxide	198—199	8.	5 + 6	171—172
4.	2 + 3	197—198	9.	5 + 6 + 7	171—172·5
5.	Triacetone dialcohol	171—172	10.	Phorone	118—118·5

(The values found for acetone, diacetone alcohol, and mesityl oxide agree to within ±1° with the published values.)

Nos. 2, 3, 4, and 10 red, and the others orange. It is clear that both diacetone alcohol and mesityl oxide yield the same product. From its colour there can be little doubt that this is the mesityl oxide derivative. From triacetone dialcohol and its two partial dehydration products the same hydrazone is produced but this is clearly not that of phorone.

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