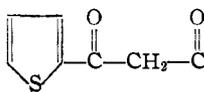


TABLE I
 β -DIKETONES OF THE TYPE  ACYL-2-THIENYLMETHANES

R	2-Thienyl- methane	B. p.		Mm.	Yield, %		S Analyses ^b		Cu salt m. p., °C.
		°C.			LiNH ₂	NaNH ₂ ^c	Calcd.	Found	
Methyl	Acetyl	129-131		8	57.4	80.7	19.06	18.85	228-230
Ethyl	Propionyl	124-126.5		4	49.2	62.2	17.58	17.58	192-194
<i>n</i> -Propyl	<i>n</i> -Butyryl	135-139.5		4	37.2	62.1 (18.7)	16.34	16.14	140-142
Isopropyl	Isobutyryl	133-136		5	30.1	49 (6.3)	16.34	16.38	159-161
<i>n</i> -Amyl	Caproyl	163-166		4	42.1	69.3 (24.4)	14.29	14.34	108-109
Phenyl	Benzoyl	198-201		4	45.2	58.1	13.92	13.80	276-278
2-Thienyl	2-Thienyl	78-78.5 (m. p.)				(16.1) [(61.1)] ^c			
		99-100 (m. p.)			..	63.8	27.14	27.10	259-263

^a The values in parentheses are from experiments carried out by Method B. All other experiments were carried out by Method A. ^b These analyses were performed by Mr. George Stragand of the University of Pittsburgh Microanalytical Laboratory. ^c Refluxed eight hours. In this experiment, since a crystalline copper salt could not be obtained, the product was isolated by distillation. In addition to the β -diketone, there was obtained 2.2 g. (8.5%) of benzamide, m. p. 130°, and a considerable non-distillable boiler residue which may have consisted of self-condensed 2-acetylthiophene.

reaction mixture is refluxed two hours. However, when the reflux time is increased to eight hours, the yield is increased to 61%.

Experimental

The Use of Sodium Amide as the Condensing Agent.—

The apparatus used in these reactions consisted of a 1000-ml., three-necked, round-bottomed flask equipped with ground-glass joints, a mercury-sealed stirrer, a reflux condenser, and an addition funnel (protected from atmospheric moisture by a drying tube filled with Drierite). The reactions were carried out in a well-ventilated hood. Using a method previously described,⁴ 0.4 mole (9.2 g.) of sodium metal was converted to sodium amide and the amide was then suspended in 300 ml. of absolute ether. To the rapidly stirred suspension of the sodium amide, 0.2 mole (Method A) or 0.4 mole (Method B) of 2-acetylthiophene, dissolved in 50 ml. of absolute ether, was added. Four tenths of a mole (Method A) or 0.2 mole (Method B) of the appropriate ester dissolved in 50 ml. of absolute ether was then added and the reaction mixture was then stirred and refluxed for two hours on a water-bath. The reaction mixture was poured onto a mixture of ice and 125 ml. of concentrated hydrochloric

acid, and then was extracted several times with ether. The combined ethereal solutions were dried over Drierite and the ether distilled. The β -diketones were isolated by the copper salt method which has been described previously.^{4,5,6} A sample of each β -diketone was analyzed. The yields of the β -diketones are given in Table I.

The Use of Lithium Amide as the Condensing Agent.—Four-tenths of a mole (9.2 g.) of commercially available lithium amide was used in each of these experiments and the reactions were carried out as described above with sodium amide.

Summary

The acylation of 2-acetylthiophene with a series of esters has been studied in the presence of sodium amide and lithium amide.

Two methods for synthesizing these β -diketones are described.

Sodium amide is superior to lithium amide for the acylation of 2-acetylthiophene with the esters used in the present investigation.

PITTSBURGH, PA.

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[CONTRIBUTION FROM THE WHITMORE LABORATORY OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Dehydration of Isopropyl-*t*-butylcarbinol¹

By J. A. DIXON, N. C. COOK AND F. C. WHITMORE

As a portion of the research on the dehydration of aliphatic alcohols being conducted at The Pennsylvania State College, a group of carbinols containing the neopentyl system has been investigated.² Isopropyl-*t*-butylcarbinol contains such a structure and in 1932 Whitmore and Houk³ published a preliminary report on its dehydration. Although they reported only the isolation and identification of 2,4,4-trimethyl-1-pentene, they

suggested that 2,4,4-trimethyl-2-pentene, 2,3,4-trimethyl-1-pentene, 2,3,4-trimethyl-2-pentene and 3-methyl-2-isopropyl-1-butene might be present in the complex mixture of dehydration product. Houk⁴ later reported that upon ozonolysis of the distillation fractions, he obtained fragments whose precursors should have been the two 2,4,4-trimethylpentenes and the two 2,3,4-trimethylpentenes.

In the present study the alcohol was dehydrated over alumina at 340-375°. The olefins found and their amounts are shown in Table I.

(1) Paper XX on dehydration of alcohols. For paper XIX see Whitmore, Rowland, Wrenn and Kilmer, THIS JOURNAL, **64**, 2970 (1942).

(2) Whitmore, *et al.*, *ibid.*, **54**, 4011 (1932); **55**, 1119 (1933); **55**, 1528 (1933); **55**, 3721 (1933); **55**, 3732 (1933); **55**, 4153 (1933).

(3) Whitmore and Houk, *ibid.*, **54**, 3714 (1932).

(4) A. L. Houk, Ph.D. Thesis, The Pennsylvania State College, 1933.

which by loss of a proton from the adjacent methylene group gives (I) or from one of the adjacent methyl groups gives (II). These two olefins are the diisobutylenes, which are obtained in a 1:4 ratio by dimerizing isobutylene,⁹ and dehydrating 2,4,4-trimethyl-2-pentanol.¹ The latter processes go through carbonium ion (2).^{10,2} Thus, the formation of (I) and (II) in a 1:1 ratio indicates that a considerable amount of dehydration takes place through carbonium ion (1) without rearrangement through (2).

(c) With a methyl from the *t*-butyl group to give (3) which can give olefins (III) and (IIIa) by loss of a proton from an adjacent methyl group or from the adjacent tertiary carbon.

(d) With a methyl from the isopropyl group to give the carbonium ion of 3,4,4-trimethyl-2-pentanol, which could undergo the rearrangement of the tertiary :H to give the carbonium ion of 2,2,3-trimethyl-3-pentanol. Rearrangement of :Me from the *t*-butyl group would convert this to the carbonium ion of 2,3,3-trimethyl-2-pentanol. No indication was found of any of the four octenes obtainable from these three carbonium ions.

Returning to carbonium ion (3), it can undergo the rearrangement of the tertiary :H to give (4). This can lose a proton to form olefins (IIIa) and (IV). The formation of (III), (IIIa) and (IV) in 29, 18 and 3% yields, respectively, indicates that the loss of a proton by (3) is easier than its rearrangement.

The rearrangement of (4) to (5) involves the formation of a neo carbon atom comparable to the conversion of pinacol to pinacolone. Carbonium ion (5) is formed by the migration of any one of the four :Me groups in (4). Olefin V, formed to the extent of 2%, represents the end of the long series of rearrangements. Rearrangement of (5) would give only the carbonium ions already indicated.

We believe that the presence of 3-methyl-2-isopropyl-1-butene (IV) and 3,3,4-trimethyl-1-pentene (V) show that any alcohol dehydration study where the analysis of the olefin products is based only on fractional distillation and ozonolysis techniques is open to question. These olefins which were present in such small amounts and yet are of great significance to the work would be extremely difficult to identify and quantitative information would be almost impossible to obtain. When it is

realized that five of the six olefins found boil within a range of six degrees, the improbability of clean separation by fractional distillation becomes apparent.¹¹

Experimental

2,4,4-Trimethyl-3-pentanol.—The alcohol was prepared from *t*-butylmagnesium chloride and isobutyraldehyde by the method of Conant and Blatt.¹² Its b. p. (uncor.) and *n*_D²⁰ were, respectively, 112.5° (218 mm.) and 1.4290.

Dehydration of 2,4,4-Trimethyl-3-pentanol.—Four hundred and thirty grams (3.3 moles) was dehydrated over alumina at 340–375° to produce 328 g. (2.93 moles) of olefins, 31 g. of unreacted carbinol (0.24 mole) and 55 g. (3.06 moles of water). This is a 95% yield of olefins based on unrecovered carbinol. The olefins and alcohol were separated from the water and dried over anhydrous potassium carbonate. They were then charged to a 60 by 1.1-cm. fractionating column packed with 3/64 inch single turn stainless steel helices. Two olefins, 2,4,4-trimethyl-1-pentene and 2,3,4-trimethyl-2-pentene, were isolated. The intermediate cuts were combined to form six samples. Each of these samples represented 11–17% of the initial charge and contained no more than three components. The samples were then analyzed by means of their Raman spectra.

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Summary

1. The alcohol 2,4,4-trimethyl-3-pentanol was dehydrated over alumina at 340–375°.
2. The product was quantitatively analyzed by means of a Raman spectral analysis of the fractionated olefins. The olefins and their percentages are 2,4,4-trimethyl-1-pentene, 24; 2,4,4-trimethyl-2-pentene, 24; 2,3,4-trimethyl-1-pentene, 29; 2,3,4-trimethyl-2-pentene, 18; 3,3,4-trimethyl-1-pentene, 2; and 3-methyl-2-isopropyl-1-butene, 3.
3. The mechanism for the formation of the olefins is discussed.
4. It is suggested that a reliable method for the analysis of alcohol dehydration products consists of careful fractional distillation followed by spectral analysis of distillation fractions.
5. Previous alcohol dehydration studies which depended on distillation and ozonolysis for the analysis may not be reliable, especially in regard to the olefins which might be present in small amounts.

(9) Whitmore and Wrenn, *THIS JOURNAL*, **53**, 3136 (1931); Tongberg, Pickens, Fenske and Whitmore, *ibid.*, **54**, 3706 (1932); Whitmore and Church, *ibid.*, **54**, 3710 (1932).

(10) Whitmore, *Ind. Eng. Chem.*, **26**, 94 (1934).

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(11) Whitmore, *et al.*, *THIS JOURNAL*, **62**, 795 (1940).

(12) Conant and Blatt, *ibid.*, **51**, 1227 (1929).