[Contribution from the Department of Chemistry, University of Maryland]

Pyrolysis of Esters. VIII. Effect of Methoxy and Dimethylamino Groups on the Direction of Elimination[1]

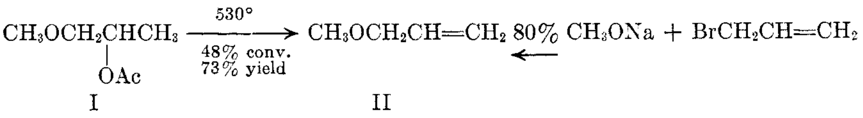
WILLIAM J. BAILEY and LOUIS NICHOLAS[2]

Received February 2, 1956

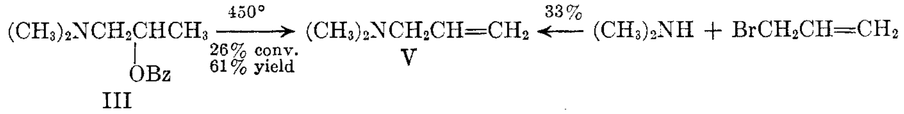
The introduction of a β-methoxy or β-dimethylamino group in the alkyl portion of an ester does not change the direction of elimination. Thus the pyrolysis of β-methoxyisopropyl acetate (I) produced allyl methyl ether and the pyrolysis of β-dimethylaminoisopropyl benzoate (III) produced allyldimethylamine. The use of the pyrolysis of esters to distinguish between isomers was illustrated by the structure determination of III and the isomeric 2-dimethylaminopropyl benzoate (IV).

It was shown previously that the pyrolysis of esters of simple secondary[3] and tertiary[4] alcohols proceeds in a highly selective manner to give almost entirely the least highly alkylated olefin. The direction of elimination was always such that the hydrogen was abstracted in the order $CH_3 > CH_2 > CH$. Thus the pyrolysis of methylisopropylcarbinyl acetate gave primarily 3-methyl-1-butene and the pyrolysis of *tert*-amyl acetate, 2-methyl-1-butene. It was of interest, therefore, to determine what effect, if any, polar groups would have on the direction of elimination. It was felt that the largest effect would be exhibited by a polar group if it were located in the β-position to the acetoxy group.

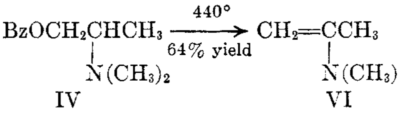
For this reason β-methoxyisopropyl acetate (I) was pyrolyzed at 530° under such conditions that only 58% of the theoretical amount of acetic acid was liberated. These conditions were selected so that no charring would occur in the pyrolysis tube and promote side reactions. Under these conditions, a 48% conversion to allyl methyl ether (II) was observed. An authentic sample of II was prepared from sodium methoxide and allyl bromide. The physical properties of the two samples were identical, as were their infrared absorption spectra, which had strong bands at 914, 942, 972, 1005, 1094, 1150, 1197, 1370, 1428, 1460, 1635, and 2950 cm.$^{-1}$ and medium bands at 694, 1275, 1515, 1530, 1555, 1680, 1840, 2035, 2350, and 3600 cm^{-1}. From the spectral as well as the physical data one would conclude that the allyl methyl ether from the pyrolysis of I was at least 95% pure.



$$\underset{\text{I}}{\underset{\text{OAc}}{\underset{|}{CH_3OCH_2CHCH_3}}} \xrightarrow[\substack{48\%\text{ conv.}\\ 73\%\text{ yield}}]{530°} \underset{\text{II}}{CH_3OCH_2CH{=}CH_2} \xleftarrow{80\%} CH_3ONa + BrCH_2CH{=}CH_2$$



$$\underset{\text{III}}{\underset{\text{OBz}}{\underset{|}{(CH_3)_2NCH_2CHCH_3}}} \xrightarrow[\substack{26\%\text{ conv.}\\ 61\%\text{ yield}}]{450°} \underset{\text{V}}{(CH_3)_2NCH_2CH{=}CH_2} \xleftarrow{33\%} (CH_3)_2NH + BrCH_2CH{=}CH_2$$



$$\underset{\text{IV}}{\underset{N(CH_3)_2}{\underset{|}{BzOCH_2CHCH_3}}} \xrightarrow[64\%\text{ yield}]{440°} \underset{\text{VI}}{\underset{N(CH_3)_2}{\underset{|}{CH_2{=}CCH_3}}}$$

A similar study was undertaken with a dimethylamino group located in the β-position to the ester group. In this case, the benzoate was chosen to simplify the preparation of the amino ester through the Schotten-Bauman reaction with benzoyl chloride. However, when a commercial sample of Dowanol 22B, β-dimethylaminoisopropyl alcohol, was treated under these conditions, two benzoates were obtained, a solid ester IV in a 26% yield and a liquid ester III in a 64% yield. Since the Dowanol 22B undoubtedly was prepared by the reaction of dimethylamine and propylene oxide, the two benzoates are very probably β-dimethylaminoisopropyl benzoate and the isomeric 2-dimethylaminopropyl benzoate. β-Dimethylaminoisopropyl benzoate was described in a patent[5] but no physical properties were given, although a derivative was described. It was felt that the structures of these two esters, III and IV, could be established through pyrolysis.

Thus the liquid ester was pyrolyzed at 450° under such conditions that only 42% of the theoretical

---

(1) Previous paper in this series, *J. Org. Chem.*, **21**, 543 (1956).

(2) Office of Naval Research Fellow, 1951–1954.

(3) Bailey and King, *J. Am. Chem. Soc.*, **77**, 75 (1955).

(4) Bailey, Hewitt, and King, *J. Am. Chem. Soc.*, **77**, 357 (1955).

(5) Chemische Fabrib auf Aktien (vorm. E. Schering), German Patent 189,482 (1905) [*Zentr.*, **78 II**, 2004 (1907)].

amount of benzoic acid was liberated. These mild conditions were necessary in order to minimize charring. Under these conditions, a 26% conversion to allyldimethylamine (V) was obtained. Since 58% of the starting benzoate was recovered, the yield of V, based on unrecovered material, was 61%. An authentic sample of V was prepared by the reaction of allyl bromide and dimethylamine. The two samples of V were indistinguishable; both samples possessed strong bands in their infrared absorption spectra at 880, 980, 1280, and 2000 cm.$^{-1}$, and medium bands at 810, 947, 1080, 1145, 1213, 1270, and 2090 cm.$^{-1}$. Since of the two possible isomers only β-dimethylaminoisopropyl benzoate (III) could yield allyldimethylamine (V), the liquid ester must be assigned this structure.

The solid ester was pyrolyzed at 440° under such conditions that 85% of the theoretical amount of benzoic acid was liberated and very little charring occurred. From this pyrolysis there was obtained a 64% yield of a vinyl amine, which is very likely 2-dimethylamino-1-propene (VI). The structure of VI was indicated by analysis and by its infrared absorption spectrum, which was unlike that of V and had strong bands at 816, 890, 945, 985, 1082, 1160, 1210, 1302, and 2000 cm.$^{-1}$ and medium bands at 910, 1035, 1053, 1260, 1427, and 2090 cm.$^{-1}$. One can conclude that the structure of the solid ester IV is 2-dimethylaminopropyl benzoate. With the aid of information concerning the direction of elimination, the pyrolysis of esters should become a useful tool for the determination of structure.

Ash, Carlson, Koslin, and Vaughn[6] developed a method for the production of allyl alcohol by the pyrolysis of propylene diacetate followed by hydrolysis. The pyrolysis of propylene diacetate at 500° in an unpacked Pyrex tube gave a 75% yield of allyl acetate and a 2% yield of propenyl acetate. Burchfield[7] found that apparently slightly more vigorous conditions gave 75% allyl acetate and 25% propenyl acetate. These results can be explained by the assumption that the secondary ester group would be eliminated the more easily[4] and the remaining primary acetoxy group would influence the direction of elimination so that the hydrogen would be abstracted preferentially from the methyl group. Thus the acetoxy group has the same influence as the methoxy and dimethylamino groups on the direction of elimination in the pyrolysis of esters.

Olsen[8] found also that the pyrolysis of β-acetoxytetrahydrofuran gave 1,4-dihydrofuran plus furan. The ether group apparently directed the elimination to the 2,3-position.

Previous work[3,4] indicated that the direction of elimination in the pyrolysis of esters might be determined by the relative acidities of the β-hydrogen atoms. It appears that a simple polar group $(-I+T)$ will not reverse the direction of elimination. The inductive effect of the electron-withdrawing methoxy group does not seem to activate the adjacent hydrogen atoms for removal during pyrolysis. The fact that the apparent nucleophilic attack of the carbonyl oxygen on the β-hydrogen is not aided by the ether group suggests the presence of a transient intermediate, such as a carbanion, that is deactivated by the $+T$ effect of the methoxy group. If a free radical or a carbonium ion were involved as a transient intermediate, the ether group would be an activating influence. The effect of other types of polar groups will be reported later.

EXPERIMENTAL[9]

β-Methoxyisopropyl acetate (I). To 1500 g. (14.7 moles) of acetic anhydride heated under reflux was added 245 g. (2.72 moles) of 1-methoxy-2-propanol (Dowanol 33B)[10] over a 2-hour period. After the mixture had been heated under reflux for an additional 15 hours, it was carefully stirred into a cold saturated sodium bicarbonate solution. The aqueous mixture was extracted with 500 ml. of ether and then with two 250-ml. portions of ether. After the combined ether solutions were dried over magnesium sulfate, the ether was removed by distillation, and the residue was fractionated through a 12-inch, helix-packed column to yield 249 g. (70%) of β-methoxyisopropyl acetate (I), b.p. 145–146°, n_{D}^{25} 1.3991 [reported[11] b.p. 145.5–146°, n_{D}^{20} 1.4028].

Methyl allyl ether (II). To 30 g. (0.55 mole) of solid sodium methoxide was added in small portions, while the cooled reaction mixture was vigorously shaken, 60 g. (0.5 mole) of allyl bromide. The precipitated salt was removed by filtration, and the filtrate was fractionated through an 18-inch, helix-packed column to yield 28.8 g. (80%) of methyl allyl ether (II), b.p. 42° (752 mm.), n_{D}^{25} 1.3764 [reported[12] b.p. 42.5–43° (757 mm.), n_{D} 1.3778–1.3803].

Pyrolysis of β-methoxyisopropyl acetate (I). At the rate of 1.2 g. per minute, 72.5 g. (0.54 mole) of β-methoxyisopropyl acetate (I) was dropped through a vertical Vycor tube packed with Pyrex helices and externally heated at 530°, as described previously.[13] The pyrolysis apparatus was continuously swept out with a slow stream of oxygen-free nitrogen. The pyrolysate was condensed in a 6-inch spiral condenser and collected in a side-arm flask cooled in a Dry Ice-chloroform-carbon tetrachloride bath. The pyrolysate, to which had been added 25 mg. of *tert*-butylcatechol, was extracted with four 50-ml. portions of water and dried over-

---

(6) Ash, Carlson, Koslin, and Vaughn, U.S. Patent 2,441,540 (1948).

(7) Burchfield, U.S. Patent 2,485,694 (1949).

(8) Olsen, *Acta Chem. Scand.*, **4**, 473 (1950).

(9) The authors are indebted to Dr. Mary Aldridge and Kathryn Gerdeman for the microanalyses and to Dr. Robert A. Spurr, Dr. Joseph Wenograd, and Kathyrn Gerdeman for the infrared absorption spectra. A Perkin-Elmer model 12-C infrared spectrophotometer, modified for double-pass operation, was used.

(10) The authors are indebted to the Dow Chemical Company, Midland, Michigan, for a generous supply of this material.

(11) Petrov, *J. Gen. Chem.* (*U.S.S.R.*), **14**, 1038 (1944).

(12) Irvine, Macdonald, and Soutar, *J. Chem. Soc.*, **107**, 337 (1915).

(13) Bailey and Golden, *J. Am. Chem. Soc.*, **75**, 4780 (1953).

night with potassium carbonate and magnesium sulfate. (Titration of an aliquot of the aqueous washings indicated that 58% of the theoretical amount of acetic acid had been liberated.) Distillation of the dried solution through a 6-inch, helix-packed column yielded 18 g. (48%) of allyl methyl ether (II), b.p. 42–43° (745 mm.), n_{D}^{25} 1.3764, and 24.6 g. (34% recovery) of β-methoxyisopropyl acetate (I). The yield of ether II, based on unrecovered starting material, was 73%.

β-Dimethylaminoisopropyl benzoate (III) *and 2-dimethylaminopropyl benzoate* (IV). In a 2-liter, three-necked flask, equipped with a stirrer, a condenser, and a dropping-funnel, were placed 175 g. (1.7 moles) of Dowanol 22B[10] (shown to be a mixture of 1-dimethylamino-2-propanol and 2-dimethylamino-1-propanol) and 500 ml. of 6 *N* sodium hydroxide. The mixture was cooled in an ice-bath while 240 g. (1.71 moles) of benzoyl chloride was added dropwise over a 1-hour period. The organic layer was washed with five 250-ml. portions of water. After the crude benzoates had been allowed to remain overnight at room temperature, a solid crystallized out. The solid was removed by filtration and recrystallized from an ether-petroleum ether mixture to yield 89.5 g. (26%) of 2-dimethylaminopropyl benzoate (IV), m.p. 54–55°.

Anal. Calc'd for $C_{12}H_{17}NO_2$: C, 69.56; H, 8.21. Found: C, 69.40; H, 8.07.

The filtrate from the crude ester was fractionated through a 12-inch, helix-packed column to yield 225 g. (64%) of β-dimethylaminoisopropyl benzoate (III), b.p. 85° (0.8 mm.), n_{D}^{25} 1.4970 (reported[5] in a patent but with no physical properties).

β-Dimethylaminoisopropyl benzoate hydrochloride. Dry hydrogen chloride was bubbled through a solution of 0.5 g. of liquid β-dimethylaminoisopropyl benzoate (III) in 5 ml. of alcohol and 15 ml. of ether until no more precipitate formed. The precipitate was removed by filtration and was recrystallized from an alcohol-ether mixture to yield 0.52 g. (91%) of β-dimethylaminoisopropyl benzoate hydrochloride, m.p. 127–128° (reported[5] m.p. 127–128°).

2-Dimethylaminopropyl benzoate hydrochloride. By a similar procedure 0.5 g. of 2-dimethylaminopropyl benzoate (IV) gave 0.45 g. (78%) of 2-dimethylaminopropyl benzoate hydrochloride, m.p. 141–142°.

Anal. Calc'd for $C_{12}H_{18}ClNO_2$: C, 59.38; H, 7.40. Found: C, 59.21; H, 7.10.

Allyldimethylamine (V). A sealed tube containing 540 g. of a 25% aqueous solution of dimethylamine (135 g.), 72 g. of allyl bromide, and 4.5 g. of sodium hydroxide was shaken overnight on a mechanical shaker. The reaction mixture was extracted with a solution of 15 g. of potassium hydroxide in 20 ml. of water and the organic layer was dried over potassium hydroxide. The crude amine was fractionated through a 12-inch, helix-packed column to yield 16.9 g. (33%) of allyldimethylamine (V), b.p. 64° (752 mm.), n_{D}^{25} 1.3977 [reported[14] b.p. 64° (743 mm.), n_{D}^{25} 1.3981].

The *picrate* of allyldimethylamine, prepared with a saturated solution of picric acid in alcohol plus V, melted at 95–96° (reported[15] m.p. 95°).

Pyrolysis of β-dimethylaminoisopropyl benzoate (III). At the rate of 1.2 g. per minute, 89.7 g. (0.43 mole) of β-dimethylaminoisopropyl benzoate (III) was pyrolyzed at 450° by the use of the apparatus and procedure described previously. To the pyrolysate were added 25 mg. of *tert*-butylcatechol and 30 ml. of ether. This mixture was extracted with several portions of a saturated sodium bicarbonate solution and then with water to remove the benzoic acid. Acidification of the aqueous extracts produced 22 g. (42%) of benzoic acid, m.p. 119–121°. After the ether layer was dried over magnesium sulfate, the ether was removed by distillation and the residue was fractionated through a 6-inch, helix-packed column to yield 9.4 g. (26%) of allyldimethylamine (V), b.p. 63–64° (744 mm.), n_{D}^{25} 1.3978 and 51 g. (56% recovery) of β-dimethylaminoisopropyl benzoate (III). The yield of V, based on unrecovered starting material, was 61%.

This sample of V was treated with a saturated solution of picric acid in alcohol to produce the allyldimethylamine picrate, m.p. 95–96°. A mixture melting point determination with the picrate prepared from the authentic sample of allyldimethylamine showed no depression.

Pyrolysis of 2-dimethylaminopropyl benzoate (IV). The same apparatus and procedure were used for the pyrolysis of 2-dimethylaminopropyl benzoate (IV), as described previously, with the exception that the solid ester was placed in a dropping-funnel and melted with aid of an infrared heat lamp. At the rate of 1.2 g. per minute, 36 g. (0.175 mole) of the molten ester IV was dropped through the pyrolysis tube, which was heated at 440° and flushed with a slow stream of oxygen-free nitrogen. Distillation of the untreated pyrolysate through a 6-inch, helix-packed column produced 9.4 g. (64%) of 2-dimethylamino-1-propene, b.p. 41° (756 mm.), n_{D}^{25} 1.3988. The residue in the distillation flask was extracted with a saturated sodium bicarbonate solution. The aqueous solution was acidified and the mixture was filtered to yield 18 g. (85%) of benzoic acid. No attempt was made to recover any starting material.

Anal. Calc'd for $C_5H_{11}N$: C, 70.59; H, 12.94. Found: C, 70.27; H, 12.71.

COLLEGE PARK, MARYLAND

---

(14) Cope and Towle, *J. Am. Chem. Soc.*, **71**, 3423 (1949).

(15) Knorr and Roth, *Ber.*, **39**, 1420 (1906).