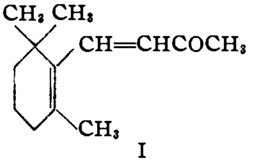
TABLE I

AMINATIVE HYDROGENATION OF KETONES[a]

Carbonyl compound	Wt., g.	Moles	NH₃ sol.,[b] cc.	Cat.,[c] g.	Product	Yield, %	B. p., °C.	B. p., Mm.	% N Calcd.	% N Found
Phenylacetone[d]	118	0.89	400	22	$C_9H_{13}N$[e]	85	80	10	10.4	10.1
Benzalacetone[f]	29.2	.21	400	5	$C_{10}H_{15}N$[g]	67	80	4	9.4	9.4
Furfuralacetone[h]	100	.74	300	7	$C_8H_{13}ON$[i]	50	190	760[j]	10.0	10.3
β-Ionone[k]	130 (I)	.67	400	5	$C_{13}H_{25}N$[l]	93	78	0.3[m]	7.2	7.2
Diethylamino-acetone[n]	25.4	.20	100	5	$C_7H_{18}N_2$[o]	65	154	760[p]		
4-Diethylamino-2-butanone[q]	14.3	.10	100	1.5	$C_8H_{20}N_2$[r]	72	70	10		
5-Diethylamino-2-pentanone	15.7	.10	150	15	$C_9H_{22}N_2$[s]	85	196–198	755	17.8	17.9

[a] Hydrogen pressure at 1 atm. or slightly above; temperature at 20° or slightly above. [b] 17% NH_3 in ethanol. [c] Raney nickel. [d] "Organic Syntheses," Coll. Vol. II, p. 487; Bobranskii and Drabik, *C. A.*, **36**, 2531 (1942). [e] Hydrochloride, m. p. 146°. By-product: 10.2 g. (8%) bis-(1-phenylpropyl-2)-amine, $C_{18}H_{23}N$, b. p. 154° (2 mm.). Calcd.: N, 5.5. Found: N, 5.5. [f] B. p. 153° (25 mm.). [g] Previously prepared by reduction of the oxime (Harries and de Osa, *Ber.*, **36**, 2999 (1903); Bargellini, Beilstein, **12**, 1165) or phenylhydrazone [Schlenk, *J. prakt. Chem.*, **78**, 57 (1908)] of benzalacetone. Hydrochloride, from ethyl acetate, m. p. 148°. [h] Leuck and Cejka, "Organic Syntheses," Coll. Vol. I, p. 283. See also *Chem. Zentr.*, **103**, II, 2183 (1932). [i] $n^{28}D$ 1.4730. Calcd.: C, 69.0; H, 9.3; mol. wt., 139. Found: C, 68.5; H, 9.4; mol. wt., 142. By-product, 18 g. (19%) of di-(1-α-furylbutyl-3)-amine, $C_{16}H_{23}O_2N$, b. p. 128° (0.05 mm.), $n^{29}D$ 1.4942. Calcd: C, 73.5; H, 8.8; N, 5.4. Found: C, 74.0; H, 8.3; N, 5.0. [j] B. p. 102° (25 mm.). [k] B. p. 100–102° (2 mm.). [l] $n^{27}D$ 1.4800. Calcd.: C, 80.0; H, 12.8; mol. wt., 195. Found: C, 79.9; H, 12.6; mol. wt., 185. Hydrochloride, m. p. 212°, very soluble in water; chloroplatinate, m. p. 216° (dec.); picrate (from 60% ethanol), m. p. 176°. [m] B. p. 115° (30 mm.). [n] Stoermer and Dzimski, *Ber.*, **28**, 2220 (1895). [o] By-product, 1.4 g. of bis-(3-diethylaminopropyl)-2-amine, $C_{14}H_{33}N_3$, b. p. 150° (20 mm.). Calcd.: N, 17.3. Found: N, 17.3. [p] B. p. 70° (20 mm.). [q] Mannich, *Arch. Pharm.*, **255**, 261 (1917); Sohl and Shriner, THIS JOURNAL, **55**, 3828 (1933); Emerson, *ibid.*, **60**, 2023 (1938); **65**, 471 (1943); du Feu, McQuillin and Robinson, *J. Chem. Soc.*, 56 (1937); Tuda, Hukusima and Oguri, *C. A.*, **36**, 3154 (1942). Yield, 60%, b. p. 80° (18 mm.), $n^{16}D$ 1.463, d^{24}_4 0.863. [r] d^{20}_{20} 0.826; $n^{18}D$ 1.4430. By-product, 1.1 g. of bis-(4-diethylaminobutyl-2)-amine, $C_{16}H_{37}N_3$, b. p. 152–155° (22 mm.). Calcd.: N, 15.5. Found: N, 15.5. [s] d^{20}_4 0.8296, $n^{20}D$ 1.4442. Calcd.: C, 68.3; H, 13.9. Found: C, 68.0; H, 14.0. Chloroaurate, m. p. 157°, lit. 155°. By-product, small amount of bis-(5-diethylaminopentyl-2)-amine, $C_{18}H_{41}N_3$, b. p. 152° (3 mm.). Calcd.: N, 14.0. Found: N, 14.6.

No exact proof of formula (II), however, has so far been obtained.



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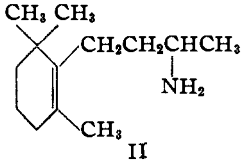
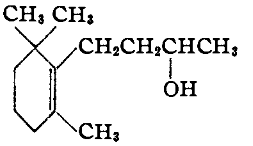


II



III

The amines of the general formula $(C_2H_5)_2N(CH_2)_n$-$CH(NH_2)CH_3$ are usually prepared by reduction of the corresponding ketoximes.[4] It has been found that they can be obtained directly from the ketones by catalytic hydrogenation in presence of ammonia under fairly mild conditions.[5] In the case of 5-diethylamino-2-aminopentane (from 5-diethylamino-2-pentanone), the product was characterized by its known[6] chloroaurate; it is believed that the products obtained from 4-diethylamino-2-butanone and diethylaminoacetone are, analogously, 4-diethylamino-2-aminobutane and 3-diethylamino-2-aminopropane, respectively.

In each of the three cases, a higher-boiling by-product was observed in small quantities, which analyzed for the corresponding secondary amine $[(C_2H_5)_2N(CH_2)_nCH(CH_3)]_2NH$. For $n = 3$, the structure was proved by conversion into 5-diethylamino-2-aminopentane according to Grigorowski, Margolina and Magidsson[7] with 40% yield. Assignment of the analogous structures in the other two cases appears justified.

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(4) (a) Magidson and Grigorowsky, *Ber.*, **69**, 401 (1936); (b) Magidson, Grigorovsky, Melnikov and Klein, *Prom. Org. Khimji*, 596 (1936); Knunyantz, Chelintzev and Osetroua Russian Patent 35,837 [*C. A.*, **29**, 8007 (1936)]; Grigorowki Russian Patent 48,203 [*Chem. Zentr.*, **108**, II, 472 (1937)]; (c) Breslow, *et. al.*, THIS JOURNAL, **66**, 1921 (1944).

(5) Breslow, Walker, Yost, Shivers and Hauser [THIS JOURNAL, **68**, 100 (1946)] carried out this reaction under high pressure.

(6) Knunjanz, Toptschijew and Tschelinzew, *Chem. Zentr.*, **106**, I, 1896 (1935).

(7) Grigorowski, Margolina and Magidsson, *ibid.*, **109**, **II**, 768 (1938).

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The Reaction of Benzyl Bromide with Ethyl α-Acetoxyacetoacetate

BY NATHAN GREEN AND F. B. LAFORGE

Dimroth and Schweitzer[1] have described the preparation of ethyl α-acetoxyacetoacetate and state that the sodium derivative reacts with halogen compounds, giving substitution products. The resulting compounds were not further investigated, however.

The present investigation is a study of the reaction of benzyl bromide with the sodium derivative of ethyl α-acetoxyacetoacetate, and of the behavior of the product.

The reaction with benzyl bromide proceeded normally, giving ethyl α-acetoxy-α-benzylaceto-

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(1) Dimroth and Schweitzer, *Ber.*, **56**, 1381 (1923).

acetate. An acetyl determination on the product showed two acetyl groups. Attempted ketone cleavage with sodium ethylate, or even with cold dilute aqueous barium hydroxide, removed two acetyl groups and gave β-phenyllactic acid as the end-product. The reaction had therefore proceeded exclusively in the sense of the acid cleavage with simultaneous saponification of the acetoxy group. Attempts at acid hydrolysis were also unsuccessful, where the compound showed great resistance to this treatment.

It is probable that the reaction of halides with α-acetoxyacetoacetates may be generally useful in the preparation of α-hydroxy acids.

Experimental Part

Ethyl α-Acetoxyacetoacetate.[1]—Eighty-four grams of ethyl acetoacetate (0.65 mole) was dissolved in 320 ml. of benzene, and 88 g. of lead tetraacetate (0.6 mole calculated on a 100% basis) was added in several small portions with stirring, the temperature being kept below 35°. The mixture was stirred for one-half hour after the last addition, and then ice-water was added and the layers were separated. The benzene solution was washed with ice water and sodium bicarbonate solution, dried, and distilled from a modified Claisen flask. Forty-one grams (34%) of product was obtained boiling at 125–127° at 17.5 mm., n^{25}D 1.4280.

The compound distills as a pale yellow liquid, which becomes colorless upon standing. It readily reduces Fehling solution in the cold. *Anal.* Calcd. for $C_8H_{12}O_5$: C_2H_5O, 23.9. Found: C_2H_5O, 23.8.

Ethyl α-Acetoxy-α-benzylacetoacetate.—Two and four-tenths grams (0.1 mole) of sodium hydride was placed in a nitrogen-swept flask with 100 ml. of dioxane, and 18.8 g. (0.1 mole) of the acetoxy compound in 40 ml. dioxane was added dropwise to the stirred mixture over a period of thirty minutes. After an additional thirty minutes 17.1 g. (0.1 mole) of benzyl bromide was added slowly, and the mixture was then refluxed for one and a half hours. The reaction mixture was poured into 1 liter of water containing sufficient acetic acid to neutralize the alkali. The heavy oil which separated was extracted twice with ether, and the ethereal solution was washed with water and then with saturated sodium chloride solution. The solution was dried, the solvent removed, and the product distilled from a modified Claisen flask. The yield was 18.6 g. (67%) of product boiling at 118–122° at 0.5 mm., n^{25}D 1.4916.

Anal. Calcd. for $C_{15}H_{18}O_5$: C, 64.73; H, 6.52; C_2H_5O, 16.2; $2CH_3CO$, 30.9. Found: C, 64.02; H, 6.72; C_2H_5O, 16.0; CH_3CO, 26.7.

Hydrolysis of Ethyl α-Acetoxy-α-benzylacetoacetate.—The compound was unchanged by refluxing with water for one hour. Refluxing with glacial acetic acid containing a little concentrated hydrochloric acid also failed to hydrolyze the compound. Although some carbon dioxide was evolved by the process, the starting material was recovered almost quantitatively. The same was true when the compound was refluxed with 20% sulfuric acid. The products of these experiments were identified, by boiling points, refractive indices and ethoxyl analyses, as the original material.

Hydrolysis with Sodium Ethylate.—Five and one-half grams (0.02 mole) of ethyl α-acetoxy-α-benzylacetoacetate was added to 2 g. of sodium dissolved in 35 ml. of ethanol and the solution was refluxed for one hour. Most of the alcohol was removed under diminished pressure, and the residue was acidified to congo red with dilute hydrochloric acid. The solution was then saturated with sodium chloride and extracted several times with ether. On evaporation of the solvent on the steam-bath and subsequently under reduced pressure, 3.3 g. of crystalline material was obtained, which was recrystallized from benzene. The product melted at 95–96°, neutralization equivalent 166, and was identified as β-phenyllactic acid.[2]

Hydrolysis with Barium Hydroxide.—Five and one-half grams of ethyl α-acetoxy-α-benzylacetoacetate was added to 250 ml. of a 2.5% aqueous solution of barium hydroxide, and the suspension was shaken for forty-eight hours. Carbon dioxide was then passed into the solution to remove the excess alkali. After the barium carbonate had been filtered off, most of the water was removed under reduced pressure. On addition of ethanol, 5.8 g. of crude barium salt of β-phenyllactic acid was obtained.

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[2] *Ber.*, **42** [4], 4892 (1909).

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Preparation of 1,2-Dichloropropene-1

BY ERNEST H. HUNTRESS AND F. SANCHEZ-NIEVA[1]

In view of the extent of recent studies of chloro- and polychloro-olefins the paucity of reports on 1,2-dichloropropene is remarkable. This compound should exist in two geometrically stereoisomeric forms. The only record of the lower boiling stereomer is an ancient report[2] claiming its preparation from 1,2,2-trichloropropane by dehydrochlorination with alcoholic potassium hydroxide. A liquid regarded as the higher boiling stereomer was subsequently obtained[3] from α,β,β-trichloro-*n*-butyric acid by solution and heating in aqueous sodium carbonate. None of the cited papers give satisfactory details.

We have developed the preparation of the lower boiling stereomer to give readily 55–58% yields, have established certain needed physical constants, have shown that upon ozonolysis the compound yields formic and acetic acids, and that with methanol it gives an azeotrope. We did not, in this work, study the preparation of the supposed higher boiling stereomer[3] but all attempts to isomerize the lower boiling material were unsuccessful. The configuration of the two stereomers is still undetermined.

1,2-Dichloropropene-1 (*lower boiling stereomer*).—One mole of 1,2,2-trichloropropane (b. p. 123–125° at 762.4 mm., n^{25}D 1.4609, obtained from 2-chloropropene-1 by addition of chlorine) was added dropwise with frequent shaking to a 25% solution of sodium methoxide (1.3–1.5 moles) in methanol kept cold in ice water. After completion of the vigorous reaction the solution was poured into a large volume of water, and the heavy insoluble layer washed, dried and distilled. Because of its much higher boiling point any unreacted trichloropropane was easily separated from the desired dichloropropene (55–58% yield).

Redistillation of the crude product through a ten theoretical plate column gave the lower boiling 1,2-dichloropropene-1, b. p. 76.8–77.0° at 757.0 mm.; d^{25}_4 1.1755, d^{20}_4 1.1818, n^{25}D 1.4451, n^{20}D 1.4471.

This product formed with anhydrous methanol an azeo-

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[1] From part of a thesis submitted by Mr. Sanchez-Nieva in October, 1945, in partial fulfillment of the requirements for the degree of Master of Science at M. I. T.

[2] Friedel and Silva, *Compt. rend.*, **74**, 807 (1872); **75**, 81 (1872); *Bull. soc. chim.*, [2] **17**, 386 (1872); *Jahresber.*, 322, 329 (1871).

[3] Szenic and Taggesell, *Ber.*, **28**, 2667–2668 (1895).