α,β-Unsaturated Hydroxyketones

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α,β-Unsaturated hydroxyketones, $R^1R^2C(OH)—CO—CH=CH—Ar$, were prepared by the Claisen-Schmidt condensation of α-hydroxyketones, $R^1R^2C(OH)—CO—CH_3$ with aromatic aldehydes.

THE AVAILABILITY of α-hydroxyketones, $R^1R^2C(OH)—CO—CH_3$, prepared as described earlier, (*1*), prompted a study of the Claisen-Schmidt condensation (*2*) of these compounds with a variety of aromatic aldehydes. The physical properties of the reaction products are summarized in Table I. All compounds, whether liquid or crystalline, had a yellow color.

The infrared spectra of these compounds were characteristic of β-aryl-α,β-unsaturated ketones. The carbonyl stretching vibrations appeared as strong bands at 5.92 to 5.98 microns, while the carbon to carbon double bond stretching vibrations appeared as stronger, broader bands at 6.20 to 6.25 microns. The Ar—CH=CH— vibrations showed as medium, sharp bands at 6.35 to 6.40 microns, and the olefinic C—H out-of-plane deformations were represented by strong bands at 10.2 to 10.3 microns. The O—H stretching vibrations appeared as medium, broad bands at 2.8 to 2.9 microns.

EXPERIMENTAL

Melting points were determined using a Mel Temp capillary melting point apparatus. The infrared spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer.

General Procedure. An 80% ethanol solution of the hydroxyketone (0.20 mole), aldehyde (0.20 mole), and 15 ml. of 10% aqueous sodium hydroxide solution was stirred at room temperature for 16 to 18 hours. The reaction mixture was poured onto crushed ice and diluted with water. If a solid precipitate was obtained, it was collected, air-dried, and recrystallized from either a 1 to 1 hexane-ether mixture or aqueous methanol. If an oil was produced, it was extracted into ether, and the ether solution was dried over anhydrous magnesium sulfate. The product was then isolated by reduced pressure distillation.

Table I. α,β-Unsaturated Hydroxyketones

$R^1R^2C(OH)COCH=CH—Ar$

Compd. No.	R^1	R^2	Ar	Physical[a] Constants	Yield[b], %
1	CH_3	CH_3	C_6H_5	(113–16/0.35)	80
2	CH_3	CH_3	4-Br-C_6H_4	69–70[c]	81
3	CH_3	CH_3	2-ClC_6H_4	(148–51/0.65)	60
4	CH_3	CH_3	4-ClC_6H_4	(125–8/0.20)	74
5	CH_3	CH_3	2,4-$Cl_2C_6H_3$	113–115[c]	47
6	CH_3	CH_3	2,6-$Cl_2C_6H_3$	(151–4/0.55)	51
7	CH_3	CH_3	4-Cl-3-$NO_2C_6H_3$	108–109[c]	51
8	CH_3	CH_3	3-$NO_2C_6H_4$	91–3[c]	56
9	CH_3	CH_3	2-$CH_3OC_6H_4$	61–2[c]	78
10	CH_3	CH_3	3-$CH_3OC_6H_4$	(156–8/0.70)	62
11	CH_3	CH_3	2,3-$(CH_3O)_2C_6H_3$	(171–4/0.55)	53
12	CH_3	CH_3	2,4-$CH_3O)_2C_6H_3$	82–3[c]	58
13	CH_3	CH_3	2,5-$(CH_3O)_2C_6H_3$	(173–6/0.5)	50
14	CH_3	CH_3	3,4-$(CH_2O_2)C_6H_3$-	103–104.5[d]	59
15	CH_3	CH_3	4-$CH_3C_6H_4$	53–4[c]	68
16	CH_3	CH_3	4-$(CH_3)_2NC_6H_4$	93–98[d]	45
17	CH_3	CH_3	4-$(C_2H_5)_2NC_6H_4$	104–8[d]	33
18	CH_3	CH_3	4-$(C_2H_5)_2N(CH_2)_2OC_6H_4$-	45–7[d]	77
19	CH_3	CH_3	1-Naphthyl	87–88[c]	71
20	CH_3	CH_3	2-Furyl	(135–6/6.0)	71
21	CH_3	CH_3	2-Thienyl	(122–3/0.55)	39
22	C_6H_5	CH_3	4-Cl-C_6H_4	103–104.5[c]	11
23	C_6H_5	CH_3	3,4-$Cl_2C_6H_3$	98–101[c]	39
24		$—CH_2—(CH_2)_3—CH_2—$	2-ClC_6H_4	62–3[c]	66
25		$—CH_2—(CH_2)_3—CH_2—$	4-ClC_6H_4-	101–102[c]	50
26		$—CH_2—(CH_2)_3—CH_2—$	2,4-$Cl_2C_6H_3$-	92–3[c]	66
27		$—CH_2—(CH_2)_3—CH_2—$	2,6-$Cl_2C_6H_3$	70–1[c]	52
28		$—CH_2—(CH_2)_3—CH_2—$	4-Cl-3-$NO_2C_6H_3$	126–9[d]	25
29		$—CH_2—(CH_2)_3—CH_2—$	3,4-$(CH_2O_2)C_6H_3$	115–117[c]	77
30		$—CH_2—(CH_2)_3—CH_2—$	3-$CH_3OC_6H_4$	(175–9/0.35)	45
31		$—CH_2—(CH_2)_3—CH_2—$	4-$CH_3OC_6H_4$	88.5–90[c]	68
32		$—CH_2—(CH_2)_3—CH_2—$	1-Naphthyl	116–117[d]	91
33		$—CH_2—(CH_2)_3—CH_2—$	3-Pyridyl	118–20[c]	26
34		$—CH_2—(CH_2)_3—CH_2—$	2-Thienyl	87–9[c]	78

[a] Numbers in parentheses are for boiling points (° C./mm.). Others represent melting points in ° C. [b] Yields are for once distilled or recrystallized materials. [c] Recrystallized from 1 to 1 hexane-ether. [d] Recrystallized from aqueous methanol.

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Synthesis of 1-Amino-2-alkanols

3-(2-Propeneoxy)-1-amino-2-propanols and 4,4,4-Trichloro-1-amino-2-butanol Hydrochlorides

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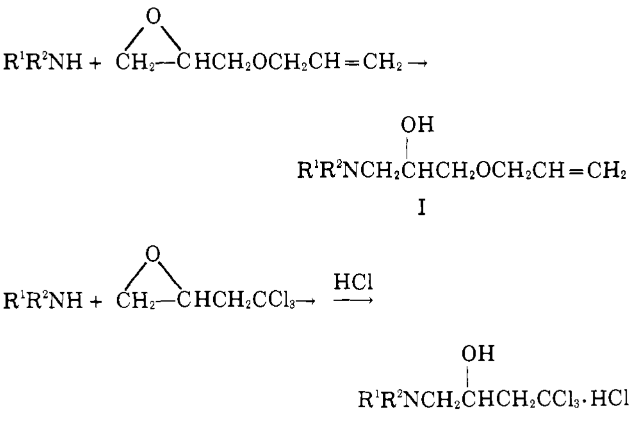
New 3-(2-propeneoxy)-1-amino-2-propanols and 4,4,4-trichloro-1-amino-2-butanol hydrochlorides have been synthesized by the reactions of allyl glycidyl ether and 4,4,4-trichloro-1,2-epoxybutane with primary and secondary amines.

THE REACTIONS of allyl glycidyl ether with a variety of primary and secondary amines in the absence of a solvent yielded the corresponding 3-(2-propeneoxy)-1-amino-2-propanols (I) in good to excellent yields. These compounds (Table I), which were colorless to pale yellow oils, were obtained by reduced pressure distillation of the reaction mixtures. Several compounds of this type have been described (*1*).

The reactions of 4,4,4-trichloro-1,2-epoxybutane with primary and secondary amines (*2*) proceeded smoothly in either boiling toluene or ethanol solutions to yield the corresponding 4,4,4-trichloro-1-amino-2-butanols (II). These compounds were isolated as their hydrochlorides, since the free bases apparently decomposed on attempted reduced pressure distillation. The physical properties of these nicely crystalline colorless salts are listed in Table II.



$$R^1R^2NH + \overset{O}{CH_2{-}CH}CH_2OCH_2CH{=}CH_2 \rightarrow R^1R^2NCH_2\overset{OH}{C}HCH_2OCH_2CH{=}CH_2$$

I

$$R^1R^2NH + \overset{O}{CH_2{-}CH}CH_2CCl_3 \rightarrow \xrightarrow{HCl} R^1R^2NCH_2\overset{OH}{C}HCH_2CCl_3 \cdot HCl$$

II

Table I. 3-(2-Propeneoxy)-1-amino-2-propanols[a]

$R^1R^2NCH_2CH(OH)CH_2OCH_2CH{=}CH_2$

Compd. No.	R^1	R^2	Yield,[b] %	B.P., ° C./Mm.	n_D^{25}	Molecular Formula
1	$CH_3O(CH_2)_3$—	H	64	121-3/0.7	1.4587	$C_{10}H_{21}NO_3$
2	Allyl	Allyl	83	112-4/2.6	. . .	$C_{12}H_{21}NO_2$
3	*n*-C_3H_7	*n*-C_3H_7	90	99-100/1.1	1.4451	$C_{12}H_{25}NO_2$
4	Iso-C_3H_7	Iso-C_3H_7	77	103-4/2.4	1.4482	$C_{12}H_{25}NO_2$
5	*n*-C_4H_9	CH_3	89	94-6/1.5	1.4469	$C_{11}H_{23}NO_2$
6	*n*-C_4H_9	*n*-C_4H_9	92	105-7/0.4	1.4461	$C_{14}H_{29}NO_2$
7	Iso-C_4H_9	Iso-C_4H_9	88	106-9/1.3	1.4445	$C_{14}H_{29}NO_2$
8	Iso-C_5H_{11}	Iso-C_5H_{11}	90	116-20/0.9	1.4475	$C_{16}H_{33}NO_2$
9	$\overline{CH_2(CH_2)_2OCH}CH_2$—	CH_3	90	120-1/0.5	1.4674	$C_{12}H_{23}NO_3$
10	Cyclohexyl	CH_3	90	126-7/1.0	1.4740	$C_{13}H_{25}NO_2$
11		—$(CH_2)_2$—CH—(CH_3)—$(CH_2)_2$—	85	112-5/1.5	1.4677	$C_{12}H_{23}NO_2$
12		—CH_2—$(CH_2)_4$—CH_2—	84	101-4/0.5	1.4767	$C_{12}H_{23}NO_2$
13	2-ClC_6H_4	H	70	142-4/0.1	1.5513	$C_{12}H_{16}ClNO_2$
14	3-$CF_3C_6H_4$	H	12	. . .	[c]	$C_{13}H_{16}F_3NO_2$
15	C_6H_5	C_2H_5	89	138-41/0.6	1.5373	$C_{14}H_{21}NO_2$
16	C_6H_5	Iso-C_3H_7	83	119-21/0.07	1.5264	$C_{15}H_{23}NO_2$
17	$C_6H_5CH_2$—	H	64	132-5/0.2	1.5240	$C_{13}H_{19}NO_2$
18	C_6H_5—CH_2—	CH_3	83	116-9/0.15	1.5120	$C_{14}H_{21}NO_2$

[a] Confirming elemental analyses have been obtained for all compounds and deposited with the American Documentation Institute.
[b] Yields for once distilled products. [c] M.p. 39-41°.