ORGANOMETALLIC SYNTHESIS IN AQUEOUS MEDIA.
SYNTHESIS OF VINYLALLYLCARBINOLS

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Petrier and Luche [1] have recently described the reaction of allyl halides with aldehydes and ketones in the presence of zinc in aqueous NH_4Cl. However, we have obtained low product yields with α,β-unsaturated aldehydes (I)-(IV) and (VI) under these conditions.

We have established that acetic acid and other organic acids are good activators for zinc in the reaction of allyl halides with unsaturated aldehydes in aqueous media. In this case, the corresponding vinylallylcarbinols are formed in high yields.

$$\underset{(I)}{MeCH{=}CHCHO} + \underset{(II)}{CH_2{=}CHCH_2Br} \xrightarrow[H_2O,\text{activator}]{\text{Zn powder}} \underset{(III)}{MeCH{=}CHCH(OH)CH_2CH{=}CH_2} \quad (1)$$

$$\underset{(IV)-(VI)}{R^1R^2C{=}CR^3CHO} + \underset{(II)}{CH_2{=}CHCH_2X} \xrightarrow[H_2O,\ MeCOOH]{\text{Zn powder}} \underset{(VII),\ (VIII),\ (X)}{R^1R^2C{=}CR^3CH(OH)CH_2CH{=}CH_2} + \underset{(IX),\ (XI)}{(R^1R^2C{=}CR^3CHOH)_2}$$

$$R^1 = R^2 = Me,\ R^3 = H\ (IV),\ (VII);\ R^1 =$$
$$= R^2 = H,\ R^3 = Me\ (V),\ (VIII),\ (IX);$$
$$R^1 = R^2 = R^3 = H\ (VI),\ (X),\ (XI).$$

The results given in Table 1 show that this reaction likely proceeds through alkylation of the aldehyde radical-anion. The lack of enantioselectivity upon the use of chiral acids supports the hypothesis that protonation occurs at a later reaction step. This method is much simpler than the synthesis through the Grignard reagent [2] and the product yield is comparable or higher.

EXPERIMENTAL

Typical Procedure. A sample of 44 g (0.58 g-atom) zinc powder was added gradually to a mixture of 48.8 ml (42 g, 0.6 mole) crotonaldehyde, 51.9 ml (72.6 g, 0.6 mole) allyl bromide, 40 ml acetic acid and 160 ml water with cooling. The temperature was maintained at from 22 to 30°C. At the end of the exothermal reaction (about 30 min), the mixture was

TABLE 1. Reaction of α,β-Unsaturated Aldehydes with Allyl Halides in Aqueous Media

Aldehyde		Activator	Product	Yield, %
(I)	Br	MeCOOH	(III)	75
(I)	»	D-Tartaric acid	(III) *	81
(I)	»	D-Alanine	(III) *	63
(I)	»	MeCOOH – $TiCl_4$	(III)	72
(I)	»	MeCOOH – Hg	(III) †	70
(I)	NEt_3^+	MeCOOH	–	–
(I)	Br	$NEt_3 \cdot HCl$ – MeCOOH	(III)	3
(I)	»	$NH_2OH \cdot HCl$	Polymer	–
(I)	»	NH_4Cl	(III)	26
(IV)	»	MeCOOH	(VII)	77 ‡
(V)	I	MeCOOH	(VIII)and(IX)	52 and 15
(V)	Br	MeCOOH – Hg	(VIII)and(IX)	23 and 47
(VI)	»	MeCOOH	(X)and(XI)	18 and 25 **

*$[\alpha]_D = 0$.

†Amalgamation of the Zn slows the reaction.

‡(VII), bp 70-71°C (20 mm).

**(X), bp 36°C (22 mm); (XI), bp 76-82°C (22 mm).

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stirred for an additional 1 h and then aqueous ammonia was added with cooling until the precipitate completely dissolved (250 ml). The organic layer was separated and the aqueous layer was extracted with ether. The combined extract was dried over K_2CO_3 and distilled to give 50.5 g (75%) 1,5-heptadien-4-ol (III), bp 52-54°C (20 mm), which was identical to a sample prepared in our previous work [2].

By analogy, the reaction with methacrylaldehyde (V) gave alcohol (VIII) in 52% yield, bp 44-48°C (22 mm). PMR spectrum in $(C_3)_2CO$ (δ, ppm): 1.62-1.80 m (3H, CH_3), 2.02-2.36 m (2H, CH_2 C=C), 3.58-4.17 (2H, $C\underline{H}OH$), 4.62-5.16 m (4H, $=CH_2$), 5.42-6.03 m (1H, CH=). Found: C, 75.26; H, 11.25%. Calculated for $C_7H_{12}O$: C, 74.9; H, 10.7%. Glycol (IX) was obtained in 15% yield, bp 110-115°C (22 mm). PMR spectrum CCl_4 (δ, ppm): 1.63 m (6H, CH_3), 3.32 br. s (2H, OH), 3.81-4.03 d (2H, CH, J = 6 Hz), 4.65-4.93 m (4H, CH_2). Found: C, 67.43; H, 9.91%. Calculated for $C_8H_{14}O_2$: C, 67.57, H, 9.92%.

CONCLUSIONS

A method has been proposed for the synthesis of vinylallylcarbinols by the reaction of allyl halides with α,β-unsaturated aldehydes with zinc in aqueous acetic acids.

LITERATURE CITED

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GENERATION OF SINGLET OXYGEN FROM THE ADSORPTION AND DECOMPOSITION OF OZONE ON SILICA GEL

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A number of chemical sources for singlet oxygen ($^1O_2$) have been reported [1-4]. Singlet oxygen ($^1\Delta_g$ or $^1\Sigma_g$) is also formed directly from ozone upon UV and visible irradiation [5].

In the present work, the formation of $^1O_2$ was detected upon the absorption and decomposition of O_3 on silica gel (SG).

EXPERIMENTAL

Ozone was obtained using an ozonizer, in which the gases contacted only the walls, in order to exclude the introduction of organic impurities into the mixture of 1-1.5% O_3 in O_2 formed. Solutions of O_3 in CCl_4 were prepared by bubbling of the O_2—O_3 mixture. Carbon tetrachloride was purified according to a standard technique [6]. The ozone concentration was monitored spectrophotometrically. Silica gel L 5/40 μm roasted for 3 h at 400°C was used to prepare the suspensions. The concentration of the suspension in the experiments was 0.5 g/ml. The reaction was carried out in a glass cell equipped with a stirrer. The chemiluminescence (CL) in the IR region was detected through an IKS-7 filter using a cooled FÉU-83 photomultipler. All the experiments were carried out at about 20°C.

RESULTS AND DISCUSSION

Pouring a solution of O_3 in CCl_4 into a cell containing a stirred suspension of SG in CCl_4 leads to an emission flash. In this case, 85-90% of the emission is concentrated at 1000-1300 nm (the boundaries of this region are determined by the transmission of the IKS-7 filter and the limiting sensitivity of the FÉU-83 photomultiplier). In order to identify the emitting species, we compared the observed CL with a standard emission arising in the reaction between H_2O and NaClO in which $^1O_2$ emits at 1270 nm [7]. About 90% of the emission

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