

Effect of Ultrasound on the Benzil—Benzilic Acid Rearrangement under Phase-Transfer Conditions

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Benzil—benzilic acid rearrangement under phase-transfer conditions has been studied. No rearrangement was observed using 50 % KOH solution—toluene and benzyltriethylammonium chloride as the catalyst with or without sonication. Considerable acceleration of the rearrangement by ultrasound was observed at the solid—liquid phase-transfer conditions, especially when a horn technique was used or when the powdered KOH was used.

Generally it is accepted [1] that the Cannizzaro reaction and benzil—benzilic acid rearrangement have similar rate-determining steps, that is hydroxide anion attack on the carbonyl carbon atom. On the other hand, recently it was proved that the Cannizzaro reaction is a SET (single electron transfer) reaction [2], and SET reactions can be accelerated by ultrasound [3]. We reported [4] that the Cannizzaro reaction under PTC (phase-transfer conditions) is considerably accelerated by ultrasound. Therefore it was of interest to examine the effect of ultrasound on the benzil—benzilic acid rearrangement.

EXPERIMENTAL

Sonochemical experiments were carried out in the ultrasonic cleaning bath Tesson 1 Ultrasonic (Tesla, Vrable) (37—42 kHz, 150 W) and in the ultrasonic horn reactor UUA 001 ULTRAGEN (Nitra) (20 kHz, 300 W) that worked in 50 % cycle. Efficiency of sonication was characterized by the $KI \rightarrow KI_3$ test [5]. Sonication of 50 cm³ of 1 M-KI solution in water gave after 3 min 4.7×10^{-6} mol dm⁻³ or 5.1×10^{-6} mol dm⁻³ of KI_3 , respectively. The reactions were performed under the argon atmosphere.

General Procedure for the Benzil—Benzilic Acid Rearrangement

To the solution of benzil (0.5 g; 2.4 mmol) in 10 cm³ of toluene 0.024 mmol of benzyltriethylammonium chloride (TEBA) and 2.4 mmol or 8.9 mmol of solid KOH (pellets) is added. The reaction mixture is then sonicated (stirred or shaken) for appropriate time and the formation of benzilic acid potassium salt

is monitored by the white powder formation. Diethyl ether is added into the reaction mixture, after the reaction was stopped, potassium salt of benzilic acid is extracted into water and benzil into diethyl ether. Benzil was recovered by evaporation of ether, and benzilic acid was, after acidification of aqueous solution, extracted into diethyl ether and isolated by evaporation of the solvent. No side products were isolated or detected by GLC. The results of the experiments are given in Table 1.

RESULTS AND DISCUSSION

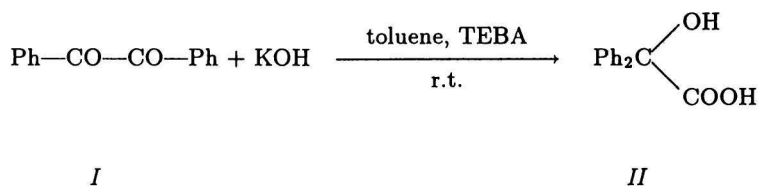
Benzil—benzilic acid rearrangement is a long known and well studied reaction [6—8]. This rearrangement is usually performed by refluxing the appropriate α -diketone in KOH or NaOH—ethanol—water mixture. We decided to examine this reaction under milder phase-transfer conditions.

From the results given in Table 1 it follows that no reaction was observed when the mixture was stirred or shaken at room temperature for 1 h. After prolonged 10 h shaking just 4.5 % of the benzilic acid was isolated when the mole ratio x_r (benzil—KOH) was 1:1, but 51 % of benzilic acid was isolated when the excess of KOH ($x_r = 1:3.7$) was used. Similar dependence of the yields on the x_r (benzil—KOH) can be observed also in the sonochemical experiments.

Sonochemical experiments have been carried out using two types of ultrasonic equipment, *i.e.* an ultrasonic cleaning bath and a horn-type reactor, the efficiency of which was characterized by the $KI \rightarrow KI_3$ test. The reaction was very sluggish in ultrasonic bath, even when the excess of KOH was used. Just 12.8 % of the benzilic acid was isolated after 1 h sonication

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Table 1. Results of Benzil—Benzilic Acid Rearrangement under Different Conditions



Conditions	Time/h	Yield/%			
		$x_r(\text{I—KOH}) = 1:1$		$x_r(\text{I—KOH}) = 1:3.7$	
		I	II	I	II
Stirring	1	98	—	98	—
Shaking	10	93	5	48	51
Ultrasonic bath	1	91	8	76	13
Ultrasonic horn reactor	0.25	81	12	12	84
Ultrasonic horn reactor ^{a,c}	1	—	—	75	20
Ultrasonic bath ^a	1	—	—	30	60
Ultrasonic bath ^b	1	—	—	95	—

a) Powdered KOH was used instead of the KOH pellets; b) 50 % aqueous solution of KOH was used; c) without TEBA (no PTC).

in the case when KOH pellets were used in the reaction. The yields raised considerably (60 %) when a powdered KOH was used instead of pellets. Ultrasonic reactor with the horn immersed into the reaction mixture proved to be much more effective, and 84 % of the benzilic acid was isolated after 15 min sonication even when KOH pellets were used. Differences between the effectiveness of an ultrasonic bath and a horn-type reactor could be explained by a higher power of the horn reactor (see Experimental) and by the fact that transmission of the ultrasonic energy is focused on the pellets which are directly under the horn.

As similar enhancement of the Cannizzaro reaction [4] and benzil—benzilic acid rearrangement was observed, one can speculate if this rearrangement is not also a SET reaction.

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REFERENCES

1. March, J., *Advanced Organic Chemistry*. Fourth Edition. Wiley, New York, 1992.
2. Fuentes, A. and Marinas, J. M., *Tetrahedron Lett.* 28, 2947 (1987).
3. Luche, J. L., Einhorn, C., Einhorn, J., and Sinisterra-Gago, J. V., *Tetrahedron Lett.* 31, 4125 (1990).
4. Poláčková, V., Tomová, V., Elečko, P., and Toma, Š., *Ultrasonics, Sonochemistry*, accepted for publication.
5. Weissler, A. and Cooper, H. W., *J. Am. Chem. Soc.* 72, 1769 (1950).
6. Selman, S. and Eastham, J. F., *Quart. Rev. Chem. Soc.* 14, 221 (1960).
7. Gilman, H. (Editor), *Organic Synthesis*, Col. Vol. 1, p. 89. Wiley, New York, 1941.
8. Vogel, A. I., *Textbook of Practical Organic Chemistry*. Fourth Edition. Longman, London, 1978.

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