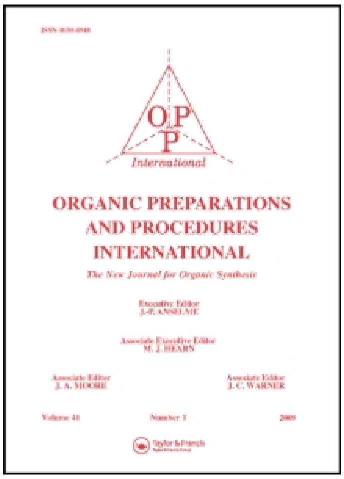

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AN IMPROVED SYNTHESIS OF β-TETRALONE

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these conditions, none of the possible dilactones (derived from intermolecular reactions) was found. The products were characterized by IR and analyzed by VPC (internal standard, octadecane) and then isolated by chromatography on Florisil column. Lactone 3 is rather unstable and very sensitive to both base and acid which induce ring opening[6] [VPC conditions: Carbowax 2 m; P_{N2} = 1.2 kg; retention time 3 = 7.0 min., standard = 5.6 min.].

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AN IMPROVED SYNTHESIS OF β-TETRALONE

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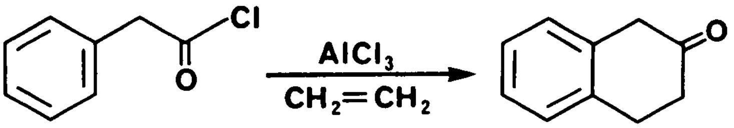
An urgent need for β-tetralone in quantities larger than commercial sources could supply led us to investigate methods for preparing this compound. The many literature methods of synthesis discussed by Soffer[1] are laborious and thus rather expensive. A more promising synthesis developed by Burckhalter[2] utilizes a Friedel-Crafts cyclization, but suffers from long reaction times and the use of carbon disulfide as the reaction solvent. Aside from one obscure note,[5] there has been no literature reference describing a more efficient synthesis of β-tetralone itself, although chloro,[3] methyl,[4] and methoxy[5] substituted β-tetralones have been reported.



We now report in detail the facility with which β-tetralone can be prepared following a modification of Sims' method.[5] The key involves the use of one molar equivalent of aluminum chloride at low temperature. Use of larger amounts of aluminum chloride results in the formation of larger quantities of ethyl β-tetralone and other unwanted polyethylene derivatives of β-tetralone.

EXPERIMENTAL SECTION

β-Tetralone.- A 22 L 4-neck round-bottomed flask fitted with a mechanical stirrer, a suitable thermometer, a $CaCl_2$ drying tube and a 2 L addition funnel with a nitrogen inlet adapter at the top, was charged with 1078 g (8.11 mol) of $AlCl_3$ and 11 L of CH_2Cl_2. While under N_2, the vessel and its contents were cooled to 0°, then a solution of 1250 g (8.11 mol) of phenylacetyl chloride in 4 L of CH_2Cl_2 was rapidly added in a dropwise manner; the temperature was maintained near 0° throughout. After the addition, the orange solution which contained small bits of undissolved $AlCl_3$ was cooled to -55°. At this point, the addition funnel with N_2 inlet was replaced with a long inlet tube (unfritted) extending deep into the cold solution and the $CaCl_2$ tube was replaced with a suitably sized (25 mm dia) bent tube adapter pointed to the rear of the hood or connected to a high volume gas scrubber. Ethylene gas was then bubbled into the solution *via* the long partially submerged tube at a rapid rate (70 L/min) thus returning the temperature to approximately 0^o within a 3-4 minute period. The temperature dropped slowly to about -15^o at which time the flow of ethylene was shut off; the total addition time was 7-8 minutes (considerable volumes of HCl as well as ethylene are evolved from the exit tube during the ethylene addition). The cold bath was drained and the reaction mixture was stirred at approximately -15^o while N_2 was bubbled into it for 15-30 minutes. A hot water bath was then used to raise the temperature rapidly to $30-35^o$. This temperature was held for approximately 15 minutes and the reaction mixture was cooled again to 0^o. Three kg of ice were added portionwise to the reaction mixture; the temperature was kept between 0^o to 15^o and several color changes occured as the ice was added. Enough water was then added to dissolve the heavy white precipitate remaining after the ice had melted.

The top layer (aqueous) was separated and washed with CH_2Cl_2 (2x500 ml) and discarded. The CH_2Cl_2 washes were combined with the original CH_2Cl_2 reaction layer and washed with 1N HCl (2x2 L) followed by saturated $NaHCO_3$ solution (4x2 L). After drying over $MgSO_4$, concentration *in vacuo* gave the crude product as a dark yellow oil, weighing nearly 1200 g; the theoretical yield is 1184 g. The crude β-tetralone is suitable for use in many reactions.

NMR ($CDCl_3$): δ 0.8 to 2.4 (series of very low humps corresponding to polyethylene derivatives), 2.40 (t, 2H), 2.95 (t, 2H), 3.48 (s, 2H), 4.1 (s, residual acid chloride), 5.2 (s, residual CH_2Cl_2), 6.90 to 7.30 (m, 4H). Tlc: [SiO_2, Toluene-ethyl acetate (9:1), UV or I_2], 1 spot, Rf = 0.5. GLC: OV-1 column 150 to 260° at 10°/min. or XE-60 column 200 to 240° at 10°/min., indicates 98% purity.

The yield of colorless liquid, bp. 80-85°/0.2 mm, lit.[1] 131°/11 mm after distillation varies between 70-80% depending on amounts of acid chloride and polyethylene materials present during distillation. The product, crude or distilled, is quite stable if stored frozen (lit.[1] mp. 18°) under nitrogen.

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