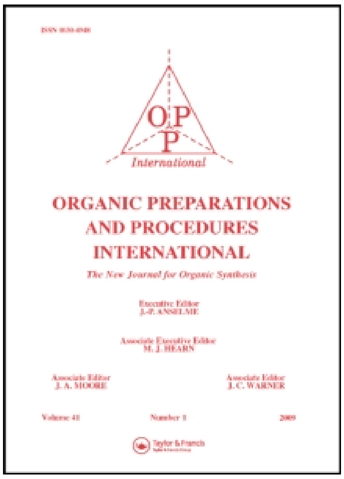

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AN IMPROVED SYNTHESIS OF α-CHLORODIPHENYLACETIC ACID

J. B. Maciel[a]; R. A. S. San Gil[a]; A. C. Neto[a]
[a] Department of Organic Chemistry, Institute of Chemistry, Federal University of Rio de Janeiro, Rio de Janeiro, RJ, Brazil

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AN IMPROVED SYNTHESIS OF α-CHLORODIPHENYLACETIC ACID

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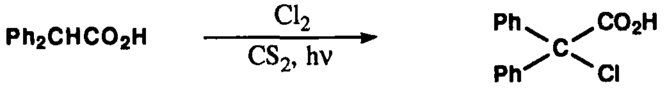
J. B. Maciel, R. A. S. San Gil* and A. C. Neto

Department of Organic Chemistry
Institute of Chemistry
Federal University of Rio de Janeiro
Rio de Janeiro, RJ 21941 BRAZIL

α-Chlorodiphenylacetic acid, an intermediate in the FriedelCrafts synthesis of 9-fluorenecarboxylic acid from trichloroacetic acid and benzene,[1] has also been used in the synthesis of pharmaceuticals such as *Estocin* and *Etpenal.*[2] It has also been prepared from benzilic acid and POCl$_3$ or SOCl$_2$,[3] albeit not in very good yields. This route requires long reaction times (about 24 hrs) and furnishes a mixture of products which is difficult to purify. We now report an improved procedure which involves chlorination of diphenylacetic acid in carbon disulfide, using a 250W mercury lamp as a light source. The yield of α-chlorodiphenylacetic acid is better than those previously reported. The effect of varying the chlorine gas flow rate (range 20-80ml/min),[4] temperature (20-80°, reaction times (0.5 hr to 10 hrs), solvents and light sources has been studied. The best results were obtained at 28-32° with a solution that had been saturated with chlorine.



EXPERIMENTAL SECTION

Melting points were taken with a Mettler FP5 melting point apparatus. Gas chromatographic (GC) analyses were done on a Hewlett Packard 5790 instrument using a 20m SE-52 glass capillary column. The carrier gas was hydrogen at a flow rate of 2 mL/mbn The injector and detector temperatures were maintained at 280° and the program used was 80-280°, 6°/min. Mass spectra were obtained using a Hewlett Packard Model 5987A (CG-MS). Ionization was performed at 70 eV electrons with 300 μA emission current.

α-Chlorodiphenylacetic Acid.- Diphenylacetic acid (4.24 g, mp. 147-149°, Matheson, Coleman & Bell) was placed in a 200 mL three-necked flask fitted with a thermometer, a gas inlet tube and a condenser fitted with a gas trap. Freshly distilled carbon disulfide (80 mL, Grupo Química, 99.5%) was added and the resulting solution was stirred with a magnetic stirrer while nitrogen was passed into the system for 15 min. The mercury lamp, employed as light source was turned on. Chlorine gas was then passed into the solution at the rate of 60mL/min until it had been saturated, whereupon the flow was reduced to 5 mL/min during the rest of the time (6 hrs). The effluent gas was collected in a trap of 20% NaOH solution. After the reaction was completed, the system was purged with nitrogen for 30 min. Carbon disulfide was removed *in vacuo* on a rotavapor (CAUTION: CS_2 is a very poisonous compound) to yield 3.9 g (70-90%) of α-chlorodiphenylacetic acid, mp. 121-123°, lit.[5] mp. 120-122°.

The progress of the reaction was monitored by high resolution gas chromatography and mass spectrometry after derivatization of the sample with an ethereal solution of diazomethane (MS m/e: 262, 260 (M^+), 225, 203, 201, 167, 165).

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