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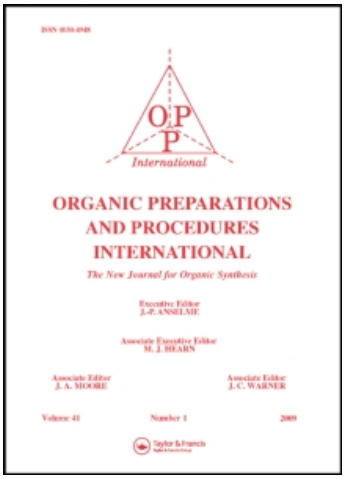

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A FACILE SYNTHESIS OF 4-ALKYL-2,6-DINITROCHLOROBENZENES

C. S. Giam[a]; R. C. Hall[a]
[a] Department of Chemistry, Texas A&M University, College Station, Texas

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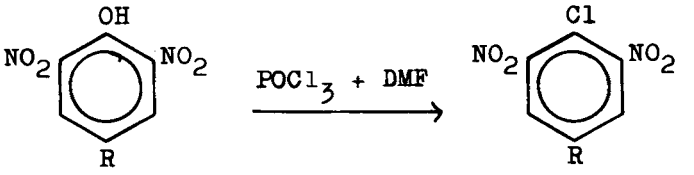
A FACILE SYNTHESIS OF 4-ALKYL-2,6-DINITROCHLOROBENZENES

C. S. Giam[1] and R. C. Hall
Department of Chemistry
Texas A&M University
College Station, Texas 77843

Some 4-substituted-2,6-dinitroanilines (e.g., Trifluralin[2] and Planavin[3]) were reported to exhibit good plant-growth regulating activity. In the course of our study on the structure-activity relationship of 4-alkyl-2,6-dinitroanilines, we sought a general procedure for the preparation of 4-alkyl-2,6-dinitrochlorobenzenes (II, R=alkyl) from which the required alkyl dinitroanilines could be obtained.



I II

Although several procedures are available, none were satisfactory. The direct nitration of 4-alkylchlorobenzenes yields a mixture of mono- and dinitro isomeric products from which the desired product may be isolated but only with considerable difficulty.[4] The conversion of alkyl dinitrophenols either gave poor yields[5] or involved elaborate procedures.[6-8] Furthermore, when we applied some of these procedures to the synthesis of II, the desired product was not easily isolated from the oily reaction mixture. We wish to report a simple procedure employing N,N-dimethylformamide (in amounts larger than catalytic quantities) and phosphorus oxychloride for the conversion of I to II. The desired products were

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easily isolated and in a high degree of purity; the yields were 75% or better. The method has been used successfully to prepare various alkyl analogues (methyl, ethyl, propyl and butyl). A typical procedures for the preparation of 4-t-butyl-2,6-dinitrochlorobenzene is described.

EXPERIMENTAL

4-t-Butyl-2,6-dinitrochlorobenzene

A solution of 4-t-butyl-2,6-dinitrophenol in phosphorus oxychloride (15 ml $POCl_3$/g. of phenol) was placed in a round bottom flask fitted with a reflux condenser and drying tube. To this stirred solution was added dropwise dimethylformamide (5 ml/g. of phenol). The mixture was heated over a steam bath for 18 hours, allowed to cool and then poured over crushed ice. After the $POCl_3$ was completely hydrolyzed, the crude precipitate of 4-t-butyl-2,6-dinitrochlorobenzene was filtered and dissolved in benzene (ca. 10 ml/g. of phenol). The benzene solution washed twice with dil. sulfuric acid, water, and finally with aqueous (10%) sodium carbonate until the aqueous layer was colorless. Further purification was achieved by eluting the benzene solution through a column of activated alumina; additional solvent benzene was employed to completely elute the product. Removal of the solvent gave a residue which was recrystallized from n-hexane to yield a 76% yield of 4-t-butyl-2,6-dinitrochlorobenzene, mp. 116.5-117.5°, lit.[4] mp. 116-117°.

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