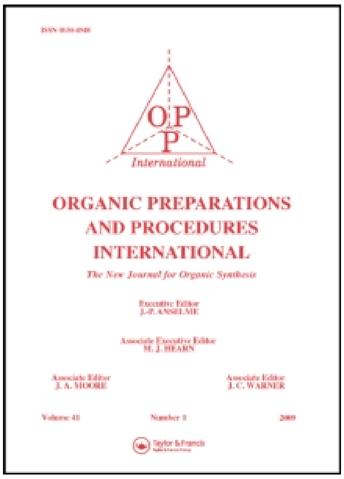

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SYNTHESIS OF 4-ETHYL-2,6-DINITRO-N,N-DIPROPYLANILINE-
A NEW PLANT-GROWTH REGULATOR AND SELECTIVE HERBICIDE

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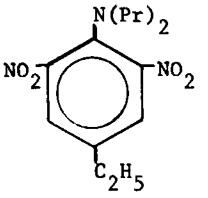
In the course of our studies on the structure - herbicidal activity of the nitroanilines, we found that 4-ethyl-2,6-dinitro-N,N-dipropylaniline (I) exhibited plant-growth regulating activity. The mode of action of this compound appears to be similar to <u>trifluralin</u> (α,α,α-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine).[1-8] At low concentrations it prevents the inition of lateral roots, and at higher concentrations it stunts and enlarges the hypocotyl and tap root; a detailed account of its biological properties will be published elsewhere. Although this compound was covered generally in a patent,[1] its synthesis and properties have not been reported. Furthermore, the preparation of the intermediate, 4-chloro-2,6-dinitroethylbenzene (II), is also unknown. We present



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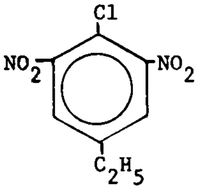

II

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their synthesis and the precautions in handling them.

EXPERIMENTAL

4-Ethyl-2,6-dinitrophenol. - A solution of 4-ethylphenol (25 g) in glacial acetic acid (70 ml) was added dropwise and with stirring (over a period of 45 min), to a mixture of conc. HNO_3 (50 ml) and glacial acetic acid (75 ml).[9] The reaction mixture was maintained at 5°C during the entire reaction; it was then allowed to warm to room temperature (1 hr.) and held at this temperature for another 30 min. The reaction was then quenched by pouring the mixture onto cracked ice (250 g). 4-Ethyl-2,6-dinitrophenol precipitated, and was filtered while the precipitate was still cold. The crude dinitrophenol was purified as the piperidine salt, mp. 233-234°C (95% EtOH, lit.[10] 234°C). The pure phenol, mp. 36°C (lit.[10] 36°C), was obtained by acidifying the piperidine salt in water, and extracting the liberated phenol with benzene. We recommend that the phenol be purified in this manner rather than by vacuum distillation,[10] because this compound exploded violently in spite of a careful attempt to distill it. The yield of 4-ethyl-2,6-dinitrophenol (24 g) was 55%.

4-Chloro-3,5-dinitroethylbenzene. - 4-Ethyl-2,6-dinitrophenol (20 g) was converted to 4-chloro-3,5-dinitroethylbenzene by heating with a mixture of benzene-sulfonyl chloride (35 ml) and N,N-diethylaniline (80 ml) in a sealed tube at 100°C for 20 hr.[11] The resultant dark blue tar was dissolved in benzene and washed twice with 6 N H_2SO_4 to remove unreacted N,N-diethylaniline. The unreacted phenol was then removed by washing the benzene solution with 10% Na_2CO_3 until the aqueous wash was colorless. The benezene solution was dried ($MgSO_4$), and then passed through an activated alumina column. The benzene was removed under vacuum at room temperature, and 4-chloro-2,6-dinitroethybenzene isolated from the oily residue by recrystallization from methanol-water mixture. Subsequent recrystallization from hexane gave pure 4-chloro-2,6-dinitroethylbenzene, 11.6g (52% yield), mp 79.5 - 80.5°C. Nmr (CCL_4), δ 7.85(s, 2H, Aromatic-H); δ, 2.84 (q, 2H, -CH -); δ, 1.36 (t, 3H, $-CH_3$). High resolution mass spectral analysis, calc. $C_8H_7N_2O_4Cl$: 230.0072; found 230.0094.

<u>4-Ethyl-2,6-dinitro-N,N-dipropylaniline</u>. - 4-Ethyl-2,6-dinitro-N,N-dipropylaniline was prepared by heating 4-chloro-3,5-dinitroethylbenzene with a solution of di-n-propylamine and ethanol in a sealed tube. The tube was heated at 95-100°C for 5 hr. Its contents were then dissolved in an equal volume of hexane, and washed several times with dilute H_2SO_4 and 10% Na_2CO_3. The solvent was evaporated leaving 4-ethyl-2,6-dinitro-N,N-dipropylaniline as a red viscous oil. This compound was purified by vacuum distillation (bp. 144-145°/0.25 mm). Nmr (CCl_4), δ, 7.57 (s, 2H, Aromatic H); δ, 2.73 (q, 2H, $-CH_2-$ of C_2H_5), δ, 2.90 (t, 4H $-N-CH_2-$); δ, 1.50 (m, 4H, $-CH_2-$); δ, 0.84 (t, 6H, $-C-CH_3$). High resolution mass spectral analysis, calc. $C_{14}H_{21}N_3O$: 295.1532; found 295.15401.

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