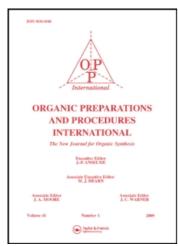
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SYNTHESES WITH AMMONIUM PEROXYDISULPHATE. α,β -DIAZIDOETHYLBENZENE AND α -CHLORO- β -AZIDOETHYLBENZENE

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The addition of two azido groups to olefinic double bonds has been accomplished by means of azido radicals generated by oxidation of the corresponding ion.

$$N_3^- \longrightarrow N_3 + \bullet$$

t-Butylhydroperoxyde, hydrogen peroxyde with ferrous salts, potassium permanganate and ceric sulphate have been used as oxidizing agents.

The radical anion $S0_4^{\bullet\bullet}$, from ammonium peroxydisulphate, is particularly suitable for oxidations <u>via</u> electron transfer. By using it in the present reaction, with the proper choice of solvents, we were able to obtain up to 85% yield (based on unrecovered styrene) of α,β -diazidoethylbenzene from styrene.

Actually the reaction proceeds through oxidation of the azido ion to the corresponding radical, followed by its attack on the double bond and transfer of the second azido group from the ferric azide to the resulting carbon radical, according to the scheme below.

$$S_{2}O_{8}^{2-}$$
 + Fe^{2+} \longrightarrow SO_{4}^{*-} + SO_{4}^{2-} + Fe^{3+}
 SO_{4}^{*-} + $(FeN_{3})^{2+}$ \longrightarrow $(FeSO_{4})^{2+}$ + N_{3}
 N_{3}^{*-} + $CH_{2}=CH-Ph$ \longrightarrow $N_{3}-CH_{2}-CH-Ph$

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$$N_3 - CH_2 - CH - Ph$$
 + $(FeN_3)^{2+} \rightarrow N_3 - CH_2 - CHN_3 - Ph$ + Fe^{2+}

Less than the stoichiometric quantity of ferrous salt is required to complete the reaction, thus supporting the outlined possibility of a chain reaction as outlined in the equation.

In the presence of ferric chloride, the transfer of chlorine prevails over that of the azide group, so that in a quite similar way we also performed the azido-chlorination of styrene to α -chloro- β -azido-chlorination of styrene to α -chloro- β -azido-chloro- β -a

$$N_3 - CH_2 \dot{C}H - Ph + (FeC1)^{2+} \rightarrow N_3 - CH_2 - CHC1 - Ph + Fe^{2+}$$

EXPERIMENTAL

a, β-Diazidoethylbenzene.- In a 11. 3 necked round bottomed flask flushed with nitrogen were placed in order, acetic acid (100 ml), water (50 ml), styrene (10.4 g; 0.1 mole), $Fe_2(SO_4)_3$ (8.4 g; 0.021 mole), NaN₃ (16.3 g; 0.25 mole) and $(NH_4)_2S_2O_8$ (46 g; 0.2 mole). The stirred mixture quickly turned to a blood red colour. A solution of FeSO .7H O (5.6 g; 0.02 mole) in water (50 ml) was added dropwise to the stirred mixture over a period of 5 min. and the temperature rose from 18 to 25°. By the further addition of small portions of finely powdered $FeSO_A$.7 H_2O (5.6 g), the temperature reached 32°. Additional FeSO, caused no further increase in temperature. Stirring was continued for 30 min. while the temperature slowly decreased to ambient. Water (500 ml) was added and the mixture extracted with three 150 ml. portions of ethyl ether. The ethereal layer was washed with saturated NaHCO3 aq. solution until evolution of CO2 ceased. After drying (Na SO), the solvent was removed using a retary evaporator. The residue was distilled under water pump vacuum to recover unreacted styrene (3.3 g). Then, with mechanical pump (CAUTION. Distillation should be carried out cautiously behind a safety plexiglas screen)

SYNTHESES WITH AMMONIUM PEROXYDISULPHATE.

a pale yellow oil was collected at $112^{\circ}/1.5$ mm (11.4 g; 8% yield calcd. on reacted styrene). Distillation was interrupted when the temperature of the vapours tended to increase (130°), to avoid possible dangerous decompositions (residue: 0.4 g). The oil proved to be a,β -diazideethylbensene by comparison with an authentic sample, and by its spectral data, IR: strong azide band at 2110 cm⁻¹, NMR (δ , CDCl₃): signals centered at 3.41 (d,2, J = 6.5 Hz, CH₂), 4.65 (t,1,CH), 7.40 (s,5, aromatic hydrogens).

a-Chloro- β -azidoethylbenzene. This compound was obtained in a similar way starting from the same quantities as above, except that FeCl₃. 6 H₂O (11.2 g; 0.42 mole) was used instead of Fe₂(SO₄)₃. A pale yellow oil was collected at 90°/3 mm (5.3 g;78% yield calcd. on reacted styrene). The spectroscopic data are in accordance with the assigned structure. IR: strong azide band at 2100 cm⁻¹, NMR (δ , CDCl₃): signals centered at 3.38 (d,2, J = 6.5 Hz, CH₂), 4.60 (t,1,CH), 7.35 (s,5, aromatic protons), MS: molecolar ion at m/e 181; major peaks at m/e 139 (181-N₃), 104 (139-Cl), 91, 77.

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