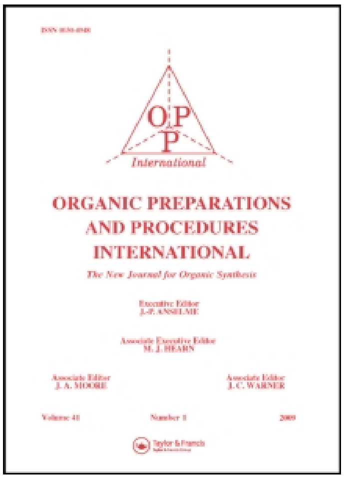

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

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To cite this Article Galli, R. and Malatesta, V.(1971) 'SYNTHESES WITH AMMONIUM PEROXYDISULPHATE. α,β-DIAZIDOETHYLBENZENE AND α-CHLORO-β-AZIDOETHYLBENZENE', Organic Preparations and Procedures International, 3: 5, 231 — 233

To link to this Article: DOI: 10.1080/00304947109356780

URL: http://dx.doi.org/10.1080/00304947109356780

ORGANIC PREPARATIONS AND PROCEDURES INT. 3(5), 227-230 (1971)

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.[1-3]

$$N_3^- \longrightarrow {}^{\bullet}N_3 + e^-$$

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

The radical anion $SO_4^{\bullet-}$, from ammonium peroxydisulphate, is particularly suitable for oxidations *via* electron transfer.[4] By using it in the present reaction, with the proper choice of solvents, we were able to obtain up to 89% 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.

$$S_2O_8^{2-} + Fe^{2+} \longrightarrow SO_4^{\bullet-} + SO_4^{2-} + Fe^{3+}$$

$$SO_4^{\bullet-} + (FeN_3)^{2+} \longrightarrow (FeSO_4)^{2+} + {}^{\bullet}N_3$$

$${}^{\bullet}N_3 + CH_2{=}CH-Ph \longrightarrow N_3-CH_2-\dot{C}H-Ph$$

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

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,[2,5] so that in a quite similar way we also performed the azido-chlorination of styrene to α-chloro-β-azidoethylbenzene.

$$N_3{-}CH_2\dot{C}H{-}Ph \quad + \quad (FeCl)^{2+} \longrightarrow N_3{-}CH_2{-}CHCl{-}Ph \quad + \quad Fe^{2+}$$

EXPERIMENTAL

α,β-Diazidoethylbenzene.- In a 1l. 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), NaN_3 (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 $FeSO_4.7H_2O$ (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 $FeSO_4.7\ H_2O$ (5.6 g), the temperature reached 32°. Additional $FeSO_4$ 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 $NaHCO_3$ aq. solution until evolution of CO_2 ceased. After drying (Na_2SO_4), the solvent was removed using a rotary 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) a pale yellow oil was collected at 112°/1.5 mm (11.4 g; 89% 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 α,β-diazidoethylbenzene by comparison with an authentic sample[2] and by its spectral data, IR: strong azide band at 2110 cm^{-1}, NMR (δ, $CDCl_3$): signals centered at 3.41 (d,2, J = 6.5 Hz, CH_2), 4.65 (t,1,CH), 7.40 (s,5, aromatic hydrogens).

α-Chloro-β-azidoethylbenzene.-This compound was obtained in a similar way starting from the same quantities as above, except that $FeCl_3 \cdot 6H_2O$ (11.2 g; 0.42 mole) was used instead of $Fe_2(SO_4)_3$. 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 , $CDCl_3$): signals centered at 3.38 (d,2, J = 6.5 Hz, CH_2), 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-N_3), 104 (139-Cl), 91, 77.

REFERENCES

1. F.Minisci and R.Galli, Tetrahedron Letters, N°12,533 (1962).
2. F.Minisci, R.Galli and M.Cecere, Gazz. Chim. Ital., 94, 67 (1964).
3. F.Minisci, R.Galli and M.Cecere, Chimica industria (Milano) 48, 347 (1966).
4. G.P.Gardini, F.Minisci, G.Palla, A.Arnone and R.Galli, Tetrahedron Letters, N°1, 59 (1971).
5. F.Minisci and R.Galli, Tetrahedron Letters, N°6, 357 (1963).

(Received July 16, 1971)