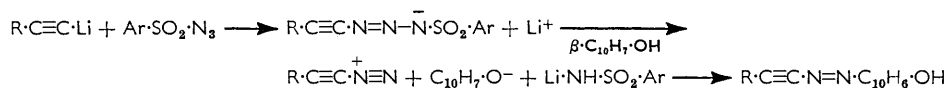


346. *The Reaction between Toluene-*p*-sulphonyl Azide and Lithium Acetylides to yield 1,2,3-Triazolediazonium Salts.*

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Hex-1-ynyl-lithium, when treated successively with 2 mol. of toluene-*p*-sulphonyl azide and an excess of β -naphthol, yielded 1-(4-butyl-1,2,3-triazol-5-ylazo)-2-naphthol. A similar reaction has been observed with phenylacetylene. Attempts to prepare acetylenylazo- β -naphthols by using a deficiency of toluene-*p*-sulphonyl azide were not successful.

COUPLING of arenesulphonyl azides with carbanions, first observed by Curtius *et al.*,¹ has more recently been adapted to the synthesis of diazocyclopentadiene² and the direct preparation of diazo-oxides from phenols.³ The present work was initiated with the object of using this reaction for the preparation of the then unknown acetylenediazonium salts. These compounds have recently been synthesised in these laboratories by another route and the use of arenesulphonyl azides for this purpose has been abandoned. However we feel that the results obtained in this investigation are of general interest. The following sequence of reactions was originally expected:



Ether solutions of hex-1-yne, toluene-*p*-sulphonyl azide, and β -naphthol were added successively to an ethereal solution of phenyl-lithium. Each addition was followed by a

¹ Curtius and Klavehn, *J. prakt. Chem.*, 1926, **112**, 65.

² Doering and De Puy, *J. Amer. Chem. Soc.*, 1953, **75**, 5955.

³ Tedder and Webster, *J.*, 1960, 4417.

an atmosphere of nitrogen. The resulting suspension of hexynyl-lithium was cooled to 0° and a solution of toluene-*p*-sulphonyl azide (20.7 g.) in ether (15 c.c.) was added dropwise while the mixture was stirred. Then the orange-yellow mixture was allowed to warm to room temperature and a solution of β-naphthol (14.4 g.) in ether (50 c.c.) was added; a deep red colour developed rapidly. The complete mixture was filtered through glass wool into water (500 c.c.). The ether layer was separated and extracted with *n*-sodium hydroxide and the aqueous washing were added to the main aqueous layer. The combined aqueous solution was extracted with ether and then acidified. A yellow precipitate was formed, consisting of an azo-dye and unchanged β-naphthol. The precipitate was isolated by ether-extraction, and, after the extract had been dried (Na₂SO₄) and the solvent evaporated, the residue was chromatographed on deactivated alumina. The column was eluted first with benzene and then with chloroform. The main material eluted was unchanged β-naphthol. The dye adhered firmly to the top of the column and could not be eluted in any organic solvent. The alumina was extruded and the top portion was extracted with 2*N*-sodium hydroxide. The dye was recovered by acidification of the alkaline extract followed by ether-extraction. The crude dye (5.07 g.) recrystallised from benzene as orange-yellow needles (4.6 g.), m. p. 136° (Found: C, 65.1; H, 5.7; N, 24.1. C₁₆H₁₇N₅O requires C, 65.1; H, 5.8; N, 23.7%). These are assigned the structure 1-(4-*butyl*-1,2,3-triazol-5-ylazo)-2-naphthol on the basis of (i) analysis, (ii) chemical reactions, (iii) ultra-violet and infrared spectra. The important chemical properties were solubility in alkali (indicating very acidic NH) and the formation of very stable complexes with transition-metal ions (which indicated that the acidic NH and the phenolic OH must flank the azo-link). The spectra confirmed the azo-link and were consistent with the other structural features.

In another experiment, with double quantities, the original ether layer obtained when the mixture was poured into water was dried and evaporated. The residue was chromatographed on activated alumina. Elution with benzene yielded some unidentified coloured fractions in traces but the main fraction was 2-naphthyl toluene-*p*-sulphonate (3.5 g.), m. p. 123—124°.⁵ The aqueous phase in this experiment was treated as above, but the top of the deactivated alumina cut off after extrusion was extracted (Soxhlet) with methanol for 12 hr. Evaporation of the methanol yielded red crystals (0.03 g.), m. p. 126—127°. On the basis of analysis only, it is believed to be 1-*butyl*naphtho[1',2'-ε]-[1,2,3]-triazolo[4,3-*c*]-[1,2,4]-triazine (I) (Found: C, 63.3; H, 6.0; N, 25.2. C₁₆H₁₅N₅ requires C, 69.3; H, 5.4; N, 25.3%). The same compound was prepared by heating the triazolazonaphthol *in vacuo* just below its m. p.: the azo-dye (0.31 g.) was heated *in vacuo* at 130° for 3 hr. The residue was taken up in ether and then extracted exhaustively with alkali. Evaporation of the ether left an orange residue which after chromatography on activated alumina and recrystallisation from ether yielded dark red crystals (0.025 g.), m. p. alone or in admixture with the above product 124—125° (Found: C, 69.9; H, 5.5%).

In a further experiment involving hexyne (8.2 g.) a solution of toluene-*p*-sulphonyl azide (20.3 g.) in ether (50 c.c.) was added in 1 hr. at 0° as before. A solution of hydrogen chloride (5 g.) in dry ether (100 c.c.) was then added and a bright yellow precipitate was formed. The mixture was poured into water, but the aqueous layer when separated contained no diazonium salt. The reaction was repeated with acetic acid but again no diazonium salt was formed. In both cases the ether layer was also investigated but no diazonium salt was present.

1-(4-*Phenyl*-1,2,3-triazol-5-ylazo)-2-naphthol.—Phenylacetylene (5.1 g.) was added to an ether solution of phenyl-lithium [prepared from bromobenzene (7.9 g.) and lithium (0.7 g.) in ether (25 c.c.)] in an atmosphere of nitrogen. Toluene-*p*-sulphonyl azide (20.7 g.) in ether (50 c.c.) was added to the cooled suspension of the lithium acetylide. The mixture was then allowed to warm to room temperature and a solution of β-naphthol (14.4 g.) in ether was added. The dye was isolated as before, and the crude product (1.62 g.) was recrystallised from acetone to yield 1-(4-*phenyl*-1,2,3-triazol-5-ylazo)-2-naphthol, m. p. 193—194° (Found: C, 68.5; H, 4.3; N, 21.8. C₁₈H₁₃N₅O requires C, 68.6; H, 4.1; N, 22.2%).

Both the butyl- and the phenyl-triazolazonaphthol dye formed stable chelates with the common transition-metal ions, and both dyes gave intense colours (red and purple, respectively) in concentrated sulphuric acid.

⁵ Reverdin and Crépeux, *Ber.*, 1901, **34**, 2999.