

CHEMISTRY

THE REACTION OF DIPHENYLDIAZOMETHANE WITH SULPHUR DIOXIDE

BY

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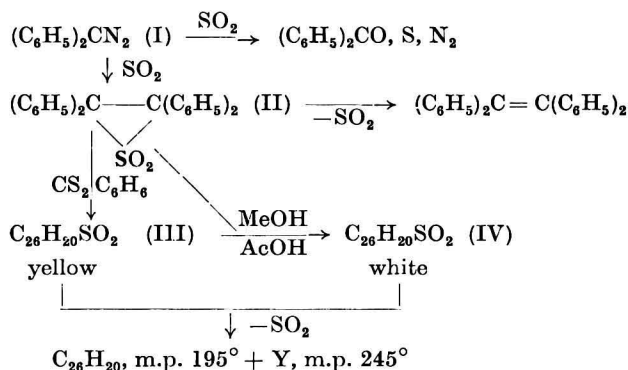
(Communicated at the meeting of October 28, 1950)

STAUDINGER and PFENNIGER¹⁾ examined in 1916 the reaction of diphenyldiazomethane (I) with sulphur dioxide. In the presence of SO₂ in excess, benzophenone, nitrogen and sulphur are formed. An excess of diphenyldiazomethane, however, leads to a compound C₂₆H₂₀O₂S, which they regard as tetraphenylethylenesulphone (II), because it splits, on heating, into SO₂ and tetraphenylethylene.

When heated with indifferent solvents (CS₂, benzene) the sulphone II is transformed into a yellow isomer (III). In the presence of methyl alcohol or acetic acid, however, it gives a white isomer (IV), which may also be obtained from the yellow product by means of the same solvents.

The two isomers (III, IV) are also sulphones. When heated "in vacuo", they lose SO₂ and give rise to the formation of a hydrocarbon C₂₆H₂₀ (m.p. 195°), isomeric with tetraphenylethylene; its structure was not established. By heating the yellow sulphone for a long time in boiling acetic acid, S. and P. got a product melting at about 245°, which was not analysed.

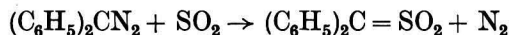
In 1930 BERGMANN²⁾ synthesized 9,9-diphenyl-9,10-dihydroanthracene (V). In a foot note he suggested, that it might be identical with STAUDINGER's hydrocarbon (m.p. 195°).



¹⁾ H. STAUDINGER and F. PFENNIGER, Ber. **49**, 1941 (1916).

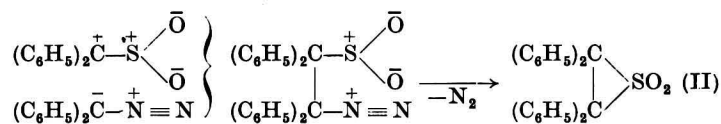
²⁾ E. BERGMANN, Ber. **63**, 1628 (1930).

STAUDINGER studied the reaction of diphenyldiazomethane with SO_2 in the hope of obtaining diphenylsulphene:

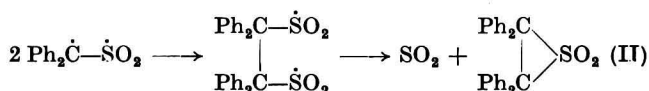


This hypothetical sulphene might give rise to two reactions:

A. By virtue of the electron attracting power of the sulphonyl group, the sulphene may show a limiting structure with a positive charge on the central carbon atom. This might combine with the negative carbon atom of a second molecule of diazo compound in its most probable limiting structure; then the product might lose nitrogen and give the sulphone II:



B. Another possibility is a combination of two sulphene molecules in their bi-radical form, followed by the loss of SO_2 :



Tetraphenylethylenesulphone (II) has several reasons for being unstable.

1. The ethylenic group carries four phenyl groups.
2. It belongs to an unstable ring of three atoms.
3. The sulphur atom is strongly electro attracting.
4. The molecule has a plane of symmetry vertical to the ethylenic bond.

Thus all conditions are present for breaking this bond and forming a bi-radical: $\text{Ph}_2\dot{\text{C}}-\text{SO}_2-\dot{\text{C}}\text{Ph}_2$ (VI).

Formula VI is only one type of the possible limiting structures. One of the unpaired electrons or both may occupy the *o* or *p* position in the available phenyl groups. Among these there are several equivalent structures of type VII. If the two electrons form together a new bond, a stable five membered ring is formed; the product will be 1,1,3-triphenyl-1,8-dihydro-isothianaphtene-2,2-dioxide (III). The presence of three conjugated double bonds and the conjugated phenyl group explain the yellow colour of this isomer.

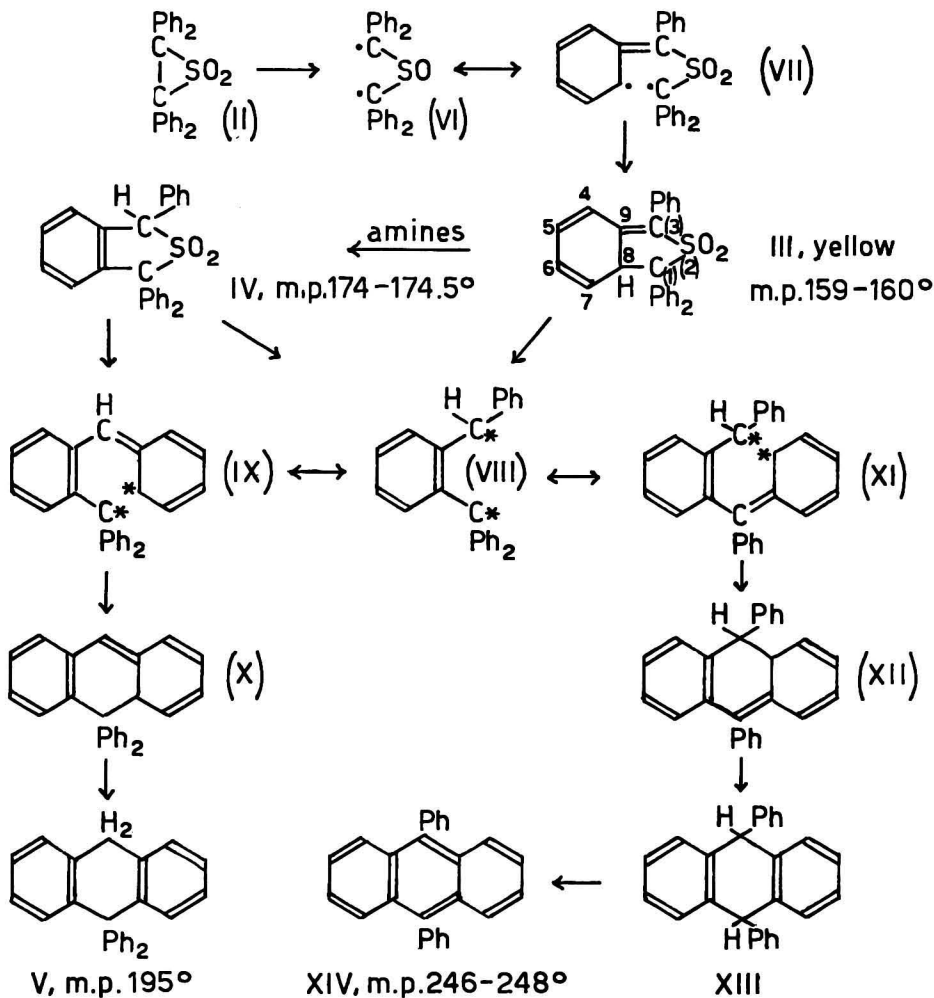
This compound (III) can stabilize itself by aromatisation of the hexadiene ring. This prototropic three carbon tautomerism will occur in polar solvents. STAUDINGER used methyl alcohol or acetic acid. A much better isomerizing agent is an amine. The product has recovered the original benzene ring and the conjugation has disappeared. The new isomer (IV) is colourless.

When heated, this isomer (IV) loses SO_2 and gives the intermediate compound VIII; in the formula the two asterisks represent unpaired electrons (bi-radical) or possibly a positive and a negative charge.

Formula VIII is only one representative of a number of mesomeric forms. The forms IX and XI can close to give six-membered rings. The products X and XII will isomerise to stable anthracene derivatives, respectively:

V, 9,9-diphenyl-9,10-dihydroanthracene,

XIII, 9,10-diphenyl-9,10-dihydroanthracene.



Compound V is the hydrocarbon $\text{C}_{26}\text{H}_{20}$ (m.p. 195°), obtained by STAUDINGER¹) and prepared by BERGMANN²) by a different method.

Compound XIII will easily lose a molecule of hydrogen and pass into 9,10-diphenylanthracene, for which substance melting points from 240° to 250° have been recorded. This may be STAUDINGER's compound Y (245°).

By decomposing IV "in vacuo" we have got a few crystals of V (m.p. 195°), 6 % of XIII and 65 % of XIV (m.p. 246–248°).

By their melting point and crystalline form the latter compounds (XIII, XIV) were identified with the products which HAACK ³⁾ obtained by reducing 9,10-diphenylanthracene. The structure of XIV was further proved by chlorination to 9,10-dichloro-9,10-dihydroanthracene ⁴⁾ and by oxidation to *o*-dibenzoylbenzene ⁵⁾ (mixed melting point).

The experimental part of this research will be published elsewhere.

³⁾ E. HAACK, Ber. 62, 1771 (1929).

⁴⁾ C. K. INGOLD and P. G. MARSHALL, J. Chem. Soc. 3083 (1926).

⁵⁾ H. SIMONIS and P. REMMERT, Ber. 48, 208 (1915). R. ADAMS and M. H. GOLD, J. Am. Chem. Soc. 62, 56 (1940).