OBITUARY NOTICES.

ALAN EDWIN BRADFIELD.

1897—1953.

BORN at Norwich on January 11th, 1897, Alan Edwin Bradfield was educated at King Edward VI Middle School, Norwich, and the City of Norwich School. He was then apprenticed to a pharmacist and meanwhile attended classes at the Norwich Technical College. At the age of 18 he enlisted in the Norfolk Regiment and served on the Western Front from 1916 onwards. He was awarded the Military Medal and Bar and in 1918 was gazetted Second Lieutenant in the East Lancashire Regiment.

After demobilisation in 1919, Bradfield proceeded to the University College of North Wales, Bangor, where he graduated with First Class Honours in Chemistry in 1922. At the close of a three-year period of postgraduate work he was awarded the Ph.D. degree and in the same year, 1925, was appointed to a lectureship in Chemistry at Bangor, which he held until 1939. The University of Wales awarded him the D.Sc. degree in 1933.

In 1926, Bradfield married Cicely, daughter of the late Mr. John Stribling of King Edward VI Middle School, Norwich. Dr. and Mrs. Bradfield were popular members of the College community at Bangor, where they took a prominent part in the social life of staff and students and were among the organisers of the activities of the Old Students' Association.

First as a student, and then as a member of staff, Bradfield came under the inspiring influence of the late Professor Kennedy Orton and, in addition to taking his full share in the teaching and other routine duties of the department, he entered with characteristic energy upon a series of investigations of reaction mechanism, a field in which Orton was a pioneer and a master.* He contributed additional evidence for Orton and Jones's mechanism of the chloramine transformation (*J.*, 1909, 1456) by showing that the proportions of *o*- and *p*-chloro-isomerides formed in the rearrangement of *N*-chloro-anilides were identical with those obtained by the direct chlorination of the anilides (*J.*, 1927, 986) and he further succeeded in obtaining some confirmation of the intramolecular character of the rearrangements of aromatic nitramines (*J.*, 1929, 915).†

Bradfield's main contribution in the field of reaction mechanism was his kinetic study of the halogenation of phenolic ethers and in a series of communications to this *Journal* between 1928 and 1931 (*J.*, 1928, 1006, 3073; 1929, 2810; 1931, 2903, 2907) he showed, for the first time, that such reactions can be interpreted simply in terms of statistical probability and energy requirements. In this work he was associated with a number of postgraduate students, among whom first place must be given to Brynmor Jones, now Professor of Chemistry at the University College, Hull, who continued and extended this work after Bradfield had transferred his principal attention to other fields. Bradfield retained his interest in the subject, however, as is shown by his publication, as recently as 1949, of a study of the mechanism of bromination of phenolic ethers.

Measurement of the speeds of chlorination of a series of phenolic ethers in 99% acetic acid, by the delicate method of chlorination devised by Orton and King (*J.*, 1911, 1185), revealed the highly significant fact that, for compounds of the general formula p-RO·C_6H_4X, where R and X were varied independently, the relative effects of a series of groups R_1, R_2, etc., are independent of the nature of X, the relative effects of a series of groups X_1, X_2, etc., likewise being independent of the nature of R. A preliminary study of the effect of temperature on the reaction velocities gave a very strong indication that the variations are due entirely, or almost entirely, to changes in the energy of activation and not to any significant changes in the non-exponential term of the equation $k = PZe^{-E/RT}$; this was later confirmed by a more stringent test on a large number of phenolic ethers by Brynmor Jones (*J.*, 1942, 418, 676).‡

* Bradfield's first publication (*J.*, 1924, 960; cf. *J.*, 1927, 983) dealt with the purification of acetic acid, and the writer has vivid recollections of the difficulties encountered at Bangor by the presence in post-war commercial acetic acid of impurities which reacted rapidly with halogens. These difficulties were eliminated completely by the use of Bradfield's method of distilling the acid from chromic anhydride and an appropriate quantity of acetic anhydride.

† Proof of this has recently been provided by E. D. Hughes and G. T. Jones (*J.*, 1950, 2678).

‡ Similar results have been obtained for other reactions in aromatic systems, *e.g.*, by Williams and Hinshelwood, *J.*, 1934, 1079.

The general conclusion was thus reached that each group contributes a characteristic amount to the energy of activation (see summary by Bradfield and B. Jones, *Trans. Faraday Soc.*, 1941, **37**, 726), and subsequent work by Brynmor Jones showed that this rule of additivity holds over a wide range of phenolic ethers.

In Bradfield's last paper on this subject (*J.*, 1949, 1389), he showed that the rate of bromination of chlorophenyl ethers in 75% acetic acid may be represented by the expression

$$dx/dt = k_b[\text{Ether}][Br_2] + k_t[\text{Ether}][Br_2]^2$$

where $[Br_2]$ represents the concentration of free bromine (*i.e.*, not combined as HBr_3 which apparently does not brominate); k_t/k_b is constant throughout a series of *p*-chlorophenyl ethers but has a different (though again constant) value for a similar series of *o*-chlorophenyl ethers. The second term may indicate a reaction between the ether and a Br_4 molecule present in very low concentration.

After the death of Professor Orton in 1930, the chair at Bangor was occupied by Professor (now Sir) John L. Simonsen, with whom Bradfield collaborated in the degradative and synthetic investigation of certain sesquiterpene derivatives, including the study of eremophilone and cyperone, the first known sesquiterpene ketones (*J.*, 1932, 2744; 1934, 188, 1810; 1935, 309, 315; 1936, 667, 1137; 1937, 760).

In 1939, Bradfield left Bangor to take up an appointment as Research Officer with the Indian Tea Association (London) and until 1948 worked in the laboratories of Messrs. J. Lyons and Co. These investigations were seriously handicapped by war conditions, but much pioneer work was nevertheless accomplished on the chemical constituents of green tea, and a method was developed for the separation of the polyphenols by partition chromatography (*J.*, 1947, 32; 1948, 2249). Bradfield realised that the problem presented by the fundamental chemistry of tea was in reality a particular case of a far wider problem, *viz.*, the chemistry of green plants in general, and the opportunity of entering this more comprehensive field of study was provided by his appointment, in October 1948, as Senior Organic Chemist in the Biochemical Section of the East Malling Research Station, Kent. His terms of reference were " to study the organic constituents of fruit plants," an almost virgin field of study, and his first tasks were the design of a laboratory for the work and the appointment of staff. These matters having been dealt with satisfactorily, " he threw himself into the attack on the many problems and inspired in his colleagues the same type of enthusiasm. First, he confined his attention to the water- and alcohol-soluble organic constituents of fruit plants and, using modern techniques, sorted the complex mixture into simpler groups—chlorophyll and carotenoids, amino-acids, plant acids, sugars, and an ethyl acetate-soluble fraction. Each group was then examined in detail, the ultimate aim being to identify and isolate each constituent and devise a method for its estimation. The sugar fraction of dormant apple shoots was shown to consist of fructose, glucose, sucrose, raffinose, stachyose, and a sugar alcohol (*Nature*, 1950, **166**, 264), and his last piece of work, completed just before his death, was concerned with quantitative methods for dealing with this mixture. An improvement on Isherwood's method for separating plant acids (chiefly hydroxy-acids) is also unpublished The complex ethyl acetate-soluble fraction, containing the glycosides and many other important metabolic constituents, was also examined. Chlorogenic and *iso*chlorogenic acids were identified in pear shoots and other material, and some glycosides were also recognised; a powerful tool discovered recently was a method for obtaining ultra-violet absorption spectra directly from paper chromatograms (*J.*, 1952, 4740).

" The collaborative spirit was very dear to Bradfield's heart. He was ever ready to find time to discuss with anybody their problems and no-one ever came away from such a *tête-à-tête* without a sense of encouragement and the enthusiasm to push the investigations further along the path to their ultimate goal. It was as if the dark way ahead had been for a moment illuminated by a flash of lightning."

The closing sentences of the above account of Bradfield's work at East Malling, kindly supplied to the writer by Dr. A. E. Flood, describe the experiences of his colleagues and friends at all stages of his career. The possessor of an exceedingly clear and far-seeing mind, he was able quickly to detect the real crux of a problem and, having determined the route which seemed most likely to lead to a solution, he carried the work through with vigour and concentration; or, if he discussed the problem of a colleague, the latter invariably received both inspiration and enlightenment from such an informal conversation. To quote again from Dr. Flood: " Bradfield was a master, not only of his own science, but of the fundamentals of thought. This is why he always had something worthwhile to contribute to any discussion, no matter what the topic. He was the complete natural philosopher."

Bradfield's sudden passing on May 3rd, 1953, has deprived chemistry of a researcher of no mean ability and vision, while his former colleagues both at Bangor and in South-East England, and, indeed, all who knew him, have lost a true and valued friend. He leaves a wife and one daughter; the latter is following in her father's footsteps, being a student of Biochemistry at the University of Bristol.

H. B. WATSON.

GILBERT JOHN FOWLER.

1868—1953.

GILBERT JOHN FOWLER was born in Paris on January 23rd, 1868, and educated at Sidcot School, Somerset, and Owens College Manchester where he obtained a first-class honours degree in chemistry. His early research work was of a metallurgical nature and he was awarded the Dalton Prize and the degree of M.Sc. for a thesis on silver suboxide. He also taught physics, chemistry, and metallurgy in Manchester. It was, however, not until 1896, by his appointment as chemist and bacteriological assistant to the Rivers Committee of the Manchester City Council, that he was introduced to a new type of work which was destined to be of life-long interest and to make his name well known in many countries. He found his duties greatly to his liking and made a special study of bacteriology at Manchester University to enable him to deal with the many complex problems he encountered. Three years later he was appointed superintendent and chemist at the Manchester Corporation sewage works, his association with the Corporation lasting in all for 20 years. From the very earliest days he realised that there were two outstanding problems connected with the efficient treatment of sewage; the first, the prevention of the loss of combined nitrogen, and the second, the coagulation of the colloidal matter to give a clear liquid and a solid which could be handled readily. As far back as 1901 he pointed out that such treatment was likely to depend on the addition of oxygen in the presence of the requisite bacteria, but no immediate developments followed. The improvements in sewage treatment at Manchester, however, attracted world-wide attention, and in 1912 Fowler was invited to New York to help to solve the problem of the growing contamination of the Hudson and East rivers. While in the United States, he was shown some experiments on forced aeration which were in progress at the Lawrence Sewage Experimental Station. These were not entirely successful, and it appeared to him that the correct type of bacteria was not present. On returning to England, in conjunction with Ardern and Lockett, he conducted experiments on similar lines, but retained the precipitated sludge in the aeration tank. This sludge proved to be the home of the missing bacteria, and the activated sludge process, perhaps the most important in the world today, became a commercial possibility.

In 1916 Fowler was appointed Professor of Applied Chemistry at the Indian Institute of Science, Bangalore, his title being changed three years later to that of Professor of Biochemistry. In this capacity he had to deal with a wider range of subjects. When first appointed, he brought with him cultures of the Weizmann bacillus for producing acetone by fermentation, and conducted extensive researches as to the possibility of using mahua flowers as a raw material instead of food grains. He also initiated many investigations on indigenous raw materials and especially the cultivation and improvement of lac. He by no means lost interest in activated sludge, but had a very extensive consulting practice dealing with new installations and the problems associated with them, and also was able to carry out valuable practical scientific experiments on a small plant erected at the Indian Institute of Science. As time went on, it became clear to him that the activated sludge process could only deal with a small fraction of the available material, and his thoughts turned more and more to the possibility of conserving nitrogen in Indian villages. The nitrogen cycle indeed, under the stimulus of a visit to China in 1918, became an obsession. An ardent Christian Scientist, he was profoundly distressed by the waste of combined nitrogen and the resulting loss of foodstuffs and the lowering of the standard of living for the poorest of the poor. In consequence, he welcomed with enthusiasm the composting process originated by the Howards in North India, and by means of lectures and the writing of numerous articles, did his utmost to extend its adoption. His preoccupation with social reform increased when he retired from the Institute of Science in 1924, and one aspect which he considered of vital importance was currency reform. He insisted that payments in any existing currency did not adequately represent the useful work

carried out to earn them, and suggested as a currency basis the "ERN" which was primarily 10 grams of nitrogen in the form of protein, or alternatively 300 calories, the heat produced in the body by this amount of protein. The value of a commodity would thus be its food value or the amount of work expended in its production.

It is not possible in a short notice to give an account of the many-sided activities of Fowler's well-filled life—his widespread consulting work, his lecturing, his tenure of the post of Principal at the Harcourt Butler Technological Institute, his work on committees, his books and his papers on science and economics. One item deserves special mention; his work for many years as honorary corresponding secretary for India of the Royal Institute of Chemistry. This involved his reviewing all applications for membership, a task of no mean order, but one for which he was well suited if only for the high esteem in which he was held by all classes of Indians.

He died peacefully on March 21st, 1953, at the Central Hotel, Bangalore, where he had been living since 1942. His wife Amy Hindmarsh, née Scott, and two sons survive him.

H. E. WATSON.

SAMUEL SMILES.

1877—1953.

SAMUEL SMILES, emeritus Professor of Chemistry in the University of London, died at Tunbridge Wells on May 6th, 1953.

He was born in Belfast on July 17th, 1877, an only son but with one sister. His father, also named Samuel, partner in the firm of Appleton, Machin and Smiles, tea dealers, had married Miss S. A. Pennington, an Australian-born lady who came of an English farming family.

His grandfather was the well-known Samuel Smiles, author of "Self Help," "Lives of the Engineers," and many other works, who had begun life by studying medicine at Edinburgh and Leiden and many years later was made an honorary LL.D. of his original University. Other members of the family were his uncle William Smiles who was manager of the Belfast Ropeworks, and his first cousin Sir Walter Smiles, M.P. for County Down, Northern Ireland, who was one of those who lost their lives in the wreck of the Princess Victoria off the Irish Coast in the storm of January 31st, 1953.

The family moved to London (Blackheath) in 1880 and it was there that Smiles spent a most happy boyhood and youth in the stimulating atmosphere provided by affectionate and sympathetic parents. He was considered to be a rather delicate and backward child; he was left-handed and inclined to stammer, but in fact he had no serious illness and later on he enjoyed games and played cricket and hockey for his House.

He entered Marlborough on the Modern Side in 1890, having already at a preparatory school begun to learn German and to take an interest in natural history. In his last years at school his interest in Chemistry was aroused by the teaching of R. G. Durrant and he became anxious to take up a scientific career. It might have been expected that the young Smiles would enter the family business, but his father gave him every encouragement to take up scientific work when he realised that his son was not temperamentally suited to a business life.

It was intended that he should go to Cambridge, but in the meantime his father met Professor Ramsay and was so impressed by his personality that the plan was altered and Smiles entered University College, London, in October 1894. According to the requirement of the University at that time he took the Pass degree in Chemistry, Physics, and Mental and Moral Science before he obtained 1st Class Honours in November 1897. As an undergraduate he had won the silver medal in Prof. Collie's organic chemistry course and at the time of his graduation he was awarded the Tufnell scholarship in Chemistry, while his performance in the Honours examination won him the Granville scholarship from the University. As a senior student he owed much to Dr. Wallace Walker and to Dr. M. W. Travers who was at that time a demonstrator in the main laboratory.

Little or no research was then being done in organic chemistry at University College, research students being anxious to join in the important work which Sir William Ramsay was developing on the rare gases. Smiles, however, chose to work on the organic side and received most generous help and encouragement from Sir William. Under Dr. Wallace Walker he made a

study of the esters of (−)-phenylchloroacetic acid which provided data for Dr. Walker's demonstration a few years later that the optical rotatory powers of a related group of substances cannot be expressed by a formula depending directly on a factor for each of the substituents on the asymmetric atom.

When Dr. Walker left for Canada in 1898 Smiles started independent work on the stereochemistry of various sulphur compounds and in 1900 was able to announce the resolution of an asymmetric sulphonium salt. Aware that Pope and Peachey were working along similar lines Smiles, with characteristic generosity, withheld his paper on this subject until they also had submitted their results for publication. The two papers, therefore, appeared in this *Journal* almost side by side.

In 1901 he was awarded the D.Sc. degree for a thesis which embodied this and other work.

About this time, having been granted an 1851 Exhibition, Smiles went, on the advice of Sir William Ramsay, to study for one year with Professor Knorr at Jena, then for a year in Paris under Professor Moissan with whom he published three papers on silicon and silicon hydrides.

At the end of 1902 Smiles returned to University College as assistant under Professor Collie in the newly formed department of organic chemistry, and in the following years he worked enthusiastically both at his teaching and his research, the title of Assistant Professor being conferred on him in 1911. It was during this period also that his book on " The Relations between Chemical Constitution and some Physical Properties " was published as one of the volumes in Sir William Ramsay's series of Text Books on Physical Chemistry.

In 1919 Smiles was appointed Professor of Organic Chemistry at Armstrong College, Newcastle-on-Tyne, but returned to London the following year as Daniell Professor of Chemistry at King's College, a position which he held until his retirement in 1938.

In July of the same year, 1920, he married Minnie Patterson, who survives him. She was the youngest daughter of the late G. N. Patterson of Newcastle-on-Tyne, owner of the Northern Steamship Company.

During his tenure of the Chair at King's College Professor and Mrs. Smiles lived at Tunbridge Wells. After his retirement he lived throughout the second World War in Inverness and only returned to Tunbridge Wells a short time before his death.

The work of Smiles, which is contained in some 120 scientific papers,* extended our knowledge of almost every class of sulphur compound.

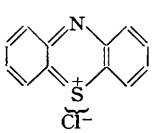
Sulphonium salts

His first important achievement was the resolution into its optical antipodes of the sulphonium salt $Ph{\cdot}CO{\cdot}CH_2{\cdot}SMeEt^+\}\ X^-$, showing that a sulphur atom could function as a centre of dissymmetry in an optically active compound.

A few years later, as a result of a study of the formation of sulphinic acids and sulphoxides, the first triarylsulphonium salts were isolated. He showed that the condensation of thionyl chloride with benzene, and its simple derivatives such as phenetole, involved a sequence of reactions such as :

$$C_6H_5{\cdot}OEt \longrightarrow EtO{\cdot}C_6H_4{\cdot}SOCl \longrightarrow SO(C_6H_4{\cdot}OEt)_2 \longrightarrow [^+S(C_6H_4{\cdot}OEt)_3]Cl^-$$

With benzene the sulphinic acid was isolated and further condensation did not occur; in other cases the products of all three stages of the process were obtained. In this connection the production of a sulphinic acid by the action of sulphur dioxide and aluminium chloride on an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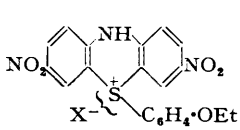
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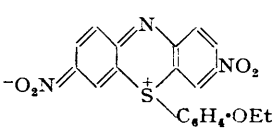
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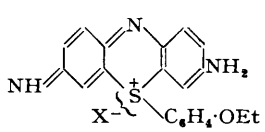
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aromatic compound was also described in a note which anticipated the well-known communication of the same result by Knoevenagel and Kenner in 1908. With selenium dioxide a similar

* For a complete bibliography see *Obit. Not. Roy. Soc.*, 1953, **8**, 583.

reaction occurred with phenolic ethers, and by further condensation the stable triarylselenonium salts resulted.

The last stage in this formation of sulphonium (and selenonium) salts was a condensation of a sulphoxide with the aromatic nucleus. This process was also separately investigated as applied to sulphoxides derived from thiodiphenylamine (dibenzothiazine). Its sulphoxide gave with hydrochloric acid a dark brown azothionium salt (I). The corresponding dinitro-sulphoxide condensed readily with phenetole in presence of sulphuric acid to give a green sulphate of the structure (II), and a number of related compounds were studied, including the thetine (III) and the deep blue dye (IV) obtained by reduction.

Sulphenic acids, thiaxanthones, and thionaphthens

As early as 1910 Smiles put forward the view that disulphides in presence of sulphuric acid undergo reversible hydrolysis :

$$Ar{\cdot}S{\cdot}S{\cdot}Ar + H_2O \rightleftharpoons Ar{\cdot}S{\cdot}OH + Ar{\cdot}SH$$

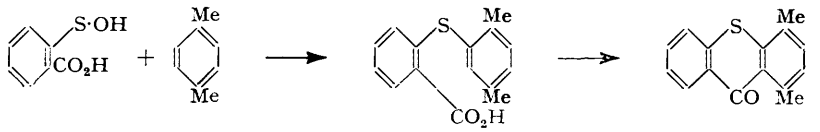
and that this hydrolysis is promoted by higher temperatures and also by the addition of aromatic compounds, which condense with the highly reactive sulphenic acid Ar·S·OH :

$$Ar{\cdot}S{\cdot}OH + Ar'H \longrightarrow Ar{\cdot}S{\cdot}Ar' + H_2O$$

Sulphenic acids were at the time hypothetical, but the sulphenyl chlorides Ar·SCl were known and a true sulphenic acid of anthraquinone was in fact subsequently isolated by Fries (in 1912).

This view explained the high yields obtained by the reaction of the disulphide with an aromatic compound in presence of sulphuric acid, since the removal of the sulphenic acid in the condensation left the thiol Ar·SH in solution, which was at once reoxidised to the disulphide by the sulphuric acid. In this way the whole of the original disulphide could ultimately be brought into reaction. It also made clear the mechanism of Fries and Volk's conversion of diphenyl disulphide into thianthren by sulphuric acid, which was evidently a double condensation of the same kind :

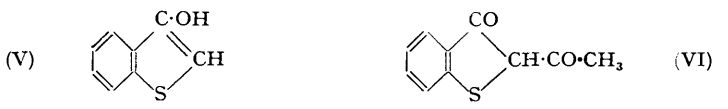
This method of introducing an arylthio-group was exploited by Smiles in various directions. Starting with 2 : 2′-dicarboxydiphenyl disulphide $(HO_2C{\cdot}C_6H_4{\cdot}S{\cdot})_2$, it afforded a most convenient method for the synthesis of thiaxanthone and its derivatives. For example, with *p*-xylene and sulphuric acid it furnished the dimethylthiaxanthone :



and this reaction was extensively applied.

A general study was made of the hydroxy- and methoxy-thiaxanthones which revealed some interesting cases of salt formation and the anomalous behaviour of those thiaxanthones having a hydroxyl group in position 1 (*ortho* to the keto-group).

A similar reaction was found to occur with the reactive methylene group of keto-enolic substances such as β-diketones. *o*-Mercaptobenzoic acid condensed in sulphuric acid with malonic acid, acetylacetone, or ethyl acetoacetate to give 3-hydroxythionaphthen (V) in good



yield, which was readily oxidised to thioindigo. By careful control of the reaction with acetylacetone it was found possible to isolate the intermediate ketone (VI).

The "disulphoxides"

The compounds obtained by gentle oxidation of disulphides had been known as "disulphoxides" and were usually written as R·SO·SO·R, the alternative structure of thiolsulphonic esters, R·SO_2·S·R having been proposed, but generally abandoned, because they appeared to resemble sulphoxides very closely both in their manner of formation and in their ease of reduction. They are produced from the disulphides by oxidation with hydrogen peroxide, a reagent which Smiles himself had shown to be most useful for converting sulphides into sulphoxides; and they are readily reduced by hydrogen iodide or even by hydrogen bromide—again in the manner of sulphoxides.

Smiles, however, marshalled overwhelming evidence in favour of the unsymmetrical thiolsulphonic ester structure. The results of various methods of reduction could only be accepted as evidence for the disulphoxide structure if the reduction took place without any rupture between the two sulphur atoms, but experiment showed that rupture did in fact occur. For instance, the reduction by hydrogen iodide of a "disulphoxide" of the structure Ar·SO_2·S·Ar′ with two different aromatic radicals gave good yields of the simple disulphide Ar·S·S·Ar, so that the process must clearly have involved a division of the original molecule into Ar·SO_2H and Ar′·SH, the sulphinic acid Ar·SO_2H being known to be very readily reduced to Ar·SH or its disulphide. Similarly, when the reduction of the simple "disulphoxide" Ar·SO_2·S·Ar was effected by means of another thiol Ar′·SH, the sulphinic acid Ar·SO_2H and not Ar′·SO_2H was always found in the products.

A number of "disulphoxides" were synthesised by condensing a chloro-thiol with the silver salt of a sulphinic acid, *e.g.*:

$$NO_2\cdot C_6H_4\cdot SCl + AgO_2S\cdot C_6H_3Cl_2 \longrightarrow AgCl + NO_2\cdot C_6H_4\cdot S\cdot SO_2\cdot C_6H_3Cl_2$$

and in this way the two isomeric "disulphoxides" Ar·S·SO_2·Ar′ and Ar′·S·SO_2·Ar were obtained as stable distinct substances.

It had been reported that the arylsulphonation of a thiol did not produce the "disulphoxide" as it should do according to the unsymmetrical formula, but Smiles showed that this direct formation of R·S·SO_2·R′ was successful when the thiol R·SH was added to a large excess of the heated sulphonyl chloride R′·SO_2Cl.

One reaction of the "disulphoxides" was also shown to be of considerable synthetic value as it afforded another method of inserting the arylthio-group into other molecules, namely, that with substances containing a reactive CH_2 group:

$$R\cdot SO_2\cdot S\cdot R' + NaCHX_2 \longrightarrow R\cdot SO_2Na + R'S\cdot CHX_2$$

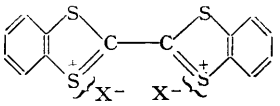
where X is one of the usual activating groups such as CN, CO_2R, or COMe. In this way two arylthio-groups could be inserted in, for example, phenylacetonitrile, phenylacetic ester, or deoxybenzoin, and the reaction could also be applied to phenols, one or more arylthio-groups being introduced into the nucleus of α- and β-naphthol, resorcinol, and phloroglucinol.

Heterocyclic compounds

In addition to his numerous syntheses of thiaxanthones and of thionaphthen derivatives Smiles made many other experiments on the formation of heterocyclic compounds with sulphur in the ring. The dibenzo- and dinaphtho-thioxins are referred to below in connection with the two sulphides of β-naphthol. Several heterocyclic types were also examined in which there are two sulphur atoms in rings of various sizes.

o-Dimercaptobenzene reacted with aldehydes and ketones to yield benzodithioles such as $C_6H_4\langle{}^{S}_{S}\rangle CMe_2$ from acetone. The phenylbenzodithiole from benzaldehyde was oxidised by nitric acid to a bright yellow benzodithiylium salt $C_6H_4\langle{}^{S}_{S}\rangle{}^{+}CPh$, NO_3^-, and when the dimercaptobenzene was condensed with oxalyl chloride it gave a colourless pseudo-base leading to the purple dithiylium salt (VII). The reaction of the thiosulphonic ester Ar·SO_2·SR to introduce the RS-group was applied to the production of other cyclic systems. Ethylene- and trimethylene-

bisthiosulphonic esters condensed easily with ethyl malonate or deoxybenzoin to give derivatives of 1 : 3-dithiolan and 1 : 3-dithian such as (VIII) and (IX) :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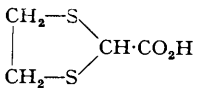
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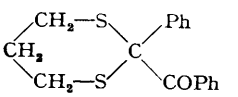
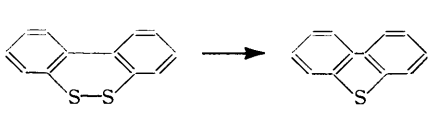
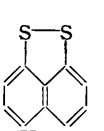
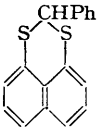

(IX)

An examination of the gentle oxidation of the dimercaptodiphenyls showed that whereas the products from the 3 : 3′- and 4 : 4′-isomerides were polymeric disulphides of high molecular weight, that from the 2 : 2′-dithiol was the crystalline monomeric cyclic disulphide (X), converted by hot copper into dibenzothiophen (XI). By condensation with aldehydes and ketones


(X) (XI) (XII)

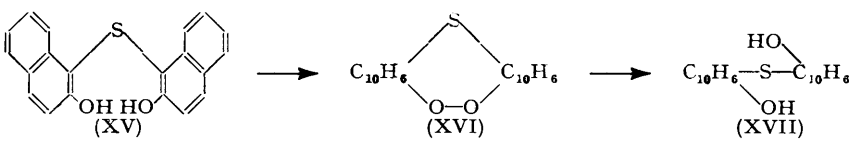

(XIII)


(XIV)

the 2 : 2′-dimercaptodiphenyl also gave cyclic products having a seven-membered ring such as (XII). Analogous products were also synthesised from 2 : 2′-dimercapto-1 : 1′-dinaphthyl. Finally the mild oxidation of 1 : 8-dimercaptonaphthalene yielded the crystalline cyclic 1 : 8-disulphide (XIII), and by condensation with benzaldehyde the same dithiol yielded the cyclic disulphide (XIV).

The two sulphides of β-naphthol

A problem which early attracted Smiles's attention was that of the nature of the two sulphides derived from β-naphthol described by Henriques in 1894. Gentle alkaline oxidation of the α-sulphide from β-naphthol had yielded a stable scarlet " dehydro-β-naphthol sulphide," and this on acid reduction was converted into a distinct substance (the so-called " *iso*-β-naphthol sulphide ") isomeric with the first. Henriques regarded the dehydro-compound as a peroxide (XVI) and represented the two sulphides as stereoisomers (XV) and (XVII) arising from some sort of fixed position of the two nuclei :

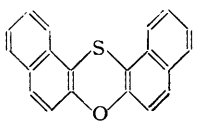

(XV) (XVI) (XVII)

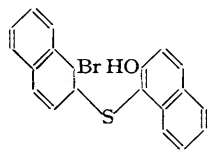
The action of hot alkali on (XVII) converted it into the original sulphide (XV). Smiles began the study of these substances in 1911 and during the next twenty years he and his students published some twenty papers on this problem and its ramifications. In the course of this work he incidentally developed general methods for synthesis of naphthothioxins, discovered an interesting group of covalent alkali derivatives, and finally elucidated an intramolecular rearrangement which led to the detailed study of a large group of similar isomeric changes.

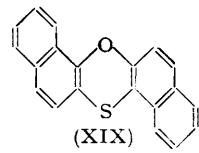
From the first Smiles was inclined to doubt the supposed stereoisomeric relation of the two sulphides (XV) and (XVII). Moreover, a close examination of the dehydro-compound (XVI) showed that it resembled β-naphthaquinone, reacted readily with phenylhydrazine, and was probably of quinonoid structure.

A careful study was made of the action of a variety of reagents on the two isomerides and on the dehydro-compound, from which it became clear that the chemical behaviour of the isomerides was quite distinct and their products different. For example, the sulphide (XV) on bromination gave 1 : 6-dibromo-β-naphthol, the sulphur being eliminated, whereas the " *iso*-sulphide " (XVII) gave a tribromo-derivative without loss of sulphur. Again. dehydration of (XV) readily produced the dinaphthothioxin (XVIII) whereas (XVII) under similar conditions yielded a similar but distinct *iso*dinaphthothioxin. The action of acetyl chloride on the dehydro-compound (XVI) gave a chloro- and a dichloro-dinaphthothioxin but these were found to be distinct from the chloro-derivatives of (XVIII), and when acetyl iodide was used in place of acetyl chloride the product was an unhalogenated dinaphthothioxin which was the same *iso*-

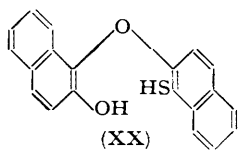
dinaphthothioxin as that obtained by dehydration of (XVII). There are several possible isomerides of dinaphthothioxin. Methods of synthesis of these thioxins were explored and the structure of this *iso*dinaphthothioxin finally shown to be (XIX) by its formation from a known bromohydroxydinaphthyl sulphide :

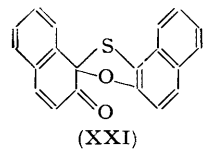

(XVIII)



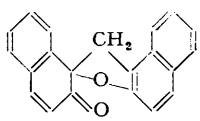

(XIX)

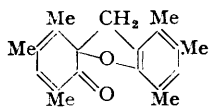
The " *iso*-sulphide " readily gave lead and zinc salts and was oxidised by iodine to a disulphide. This indicated that it was not a sulphide but a thiol, and in view of its ready dehydration to the *iso*dinaphthothioxin (XIX) it was formulated as (XX)–(XVII). Confirmation of this view was obtained by oxidising the *S*-methyl derivative to the sulphone, which on reduction

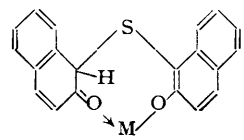

(XX)


(XXI)

lost the sulphur group and yielded, as expected, 2-hydroxydinaphthyl ether. The scarlet dehydro-compound, which yielded (XX) by acid reduction, was reduced in alkaline solution to the original sulphide (XV) and so was explained as a cyclic quinole of the structure (XXI)–(XVI), similar dehydrophenols having been reported by Pummerer in 1914.


(XXII)


(XXIII)


(XXIV)

It was found that 2 : 2′-dihydroxydi-1-naphthyl sulphone gave a similar dehydro-compound, reducible to an " *iso*-sulphone," which proved to be in fact a sulphinic acid, and this was similarly reconverted into the original sulphone by alkali.

Examination of related substances showed that in addition to the original sulphide and its sulphone, the corresponding selenide and the dinaphthylmethane (CH_2 in place of S) also gave analogous dehydro-compounds, but, when benzene analogues were tested, only those with a methyl group in position 6 (in the second *ortho* position to S or CH_2) yielded dehydro-compounds, for example (XXII) and (XXIII). The formation of a stable dehydro-compound thus always depended on there being a substituent in position 6—either the 5 : 6-benzo-group in the naphthyl derivatives or a 6-methyl group in a benzene nucleus.

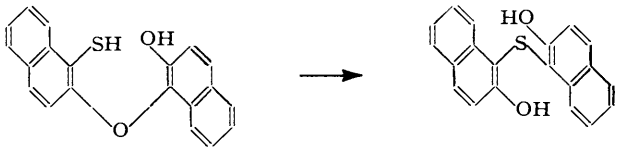
At the same time it had been observed that the sulphide (XV) formed stable mono-sodium, -potassium, -rubidium, and -lithium compounds with 2 or 4 mols. of water, soluble in ether, chloroform, and benzene, which were clearly covalent compounds of the type described by Sidgwick and Brewer in 1925. The corresponding selenide and dinaphthylmethane showed the same behaviour, but not the monomethyl ethers of these compounds. They were therefore formulated as (XXIV) derived from the ketonic form of the naphthol. This involves a large chelate ring which must necessarily be puckered.

When evidence of similar behaviour among analogous benzene derivatives was sought it was found that such covalent alkaline compounds were obtained only in those cases where formation of a stable dehydro-compound had been observed. The necessary condition once again was a substituent in position 6.

Smiles regarded the action of the 6-methyl group in these compounds as being of a polar nature, which, by rendering the adjacent carbon atom more negative, tended to stabilize the ketonic form of the phenol and so to facilitate the formation of both the dehydro-compound and the covalent alkaline derivative.

The conversion of the " *iso*sulphide " into the original sulphide by warm alkali was recognized

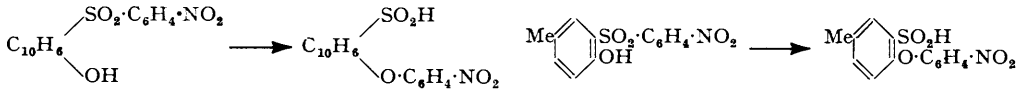
as an intramolecular transformation which was actually a displacement of the ether group by the thiol group (in its ionized form) facilitated by the convenient positions of the groups in space thus :



The dehydro-compound was seen to be closely related to the transitory intermediate phase of the molecule during this rearrangement.

The Smiles rearrangement

A closer examination of this isomeric change led to the study of a whole class of such transformations involving the intramolecular migration of an aromatic radical which came to be known as " Smiles rearrangements." The following two instances are typical :



The change is truly intramolecular and there is an essential steric requirement that the substituents concerned must be in such positions as to give a transitory intermediate having a five-atom (or in a few cases a six-atom) ring : thus the isomeride having the hydroxyl group *para* instead of *ortho* to the sulphone group resists any such change. Since the rearrangement is promoted by alkali it probably takes place in the ion.

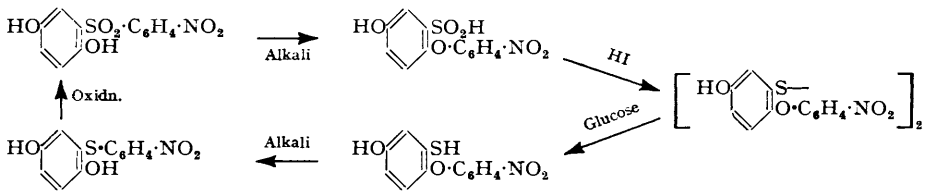
These changes may be represented in the following general form :

In the original transformation of the dihydroxydinaphthyl sulphides X is O and YH is SH, but for most of the changes studied X was SO_2, SO, or S while YH was NHAc, NH_2, or OH.

Apart from the all-important steric consideration, the factors which determine the ease of rearrangement are : (*a*) the positive character of the carbon atom in ring B at which the reaction occurs; (*b*) the positive character of X or, more precisely, the relative positivity of X in comparison with YH or Y^-; (*c*) the tendency of YH to lose a proton to the medium; and (*d*) the capacity of Y to meet the electron demand, *i.e.*, to act as an electron donor.

The factor (*a*) is affected by substitution in nucleus B, and various comparative experiments, some of which were quantitative measurements by a colorimetric method, showed that substituents in B caused the speed of the isomeric change to diminish in the following order : 2 : 4-dinitro > 2-nitro-4-chloro > 2-nitro > 4-nitro > 4-methanesulphonyl.

The effect of condition (*b*) is illustrated by the rearrangement of compounds in which YH = NHAc when X was SO_2, SO, or S, whereas when YH was aliphatic hydroxyl (nucleus A replaced by C_2H_4) X could be SO_2 or SO but not S, and when YH was phenolic hydroxyl the change took place only when X was SO_2. The action of a change in the character of X was elegantly illustrated in a number of instances of which one is shown diagrammatically in the following scheme. The rearrangement proceeds in opposite directions when X is SO_2 or S respectively and so leads to a cyclic process :



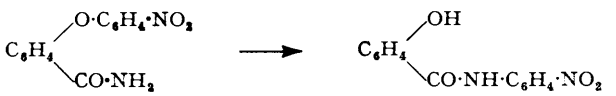
As regards factor (*c*) an increased alkalinity does, in general, accelerate the change and, further, in alcoholic solvents the speed of rearrangement increases in the order NaOH < NaOMe < NaOEt < $NaOPr^i$, this being the familiar order of proton acceptance.

Condition (*d*) causes the ease of rearrangement to decrease when YH is varied in the following series: NHAc>OH (aliphatic)>NH_2>OH (phenolic)>SH. Moreover, when YH is phenolic hydroxyl, the change is influenced by substituents in nucleus A, which modify the activity of the hydroxyl group. Consequently speeds of rearrangement diminish for the following substituents in the order: 5 : 6-C_6H_4>3 : 5-dimethyl>5-methyl; and 5-$\bar{O}$–>5-OMe>4-$\bar{O}$–.

The factors (*c*) and (*d*) must often be considered together. When YH is of the substituted amino-type the donor capacity (*d*) must fall in the order NHMe>NH_2>NHAc>NH·CO·C_6H_4·NO_2>NH·SO_2·Ph, but at the same time the tendency (*c*) to lose a proton must be in the reverse order. For the sulphones (X = SO_2) with these various substituents YH, it was found that they all underwent rearrangement, but the first and the last member of the series did so only with difficulty, and there was a maximum speed of rearrangement in the middle of the series, arising from the simultaneous and the opposed operation of factors (*c*) and (*d*). Similarly in the corresponding series of sulphides (X = S) it was only the acetamido- and 2-nitrobenzamido-derivatives which rearranged in hot alkali. One interesting feature of these isomeric changes, for which no simple explanation is apparent, is that the speed of the rearrangement was in all cases very much faster when there was a methyl group in position 6, that is to say, with those structures which had already been found to permit the formation of a stable dehydro-compound and of a covalent alkali derivative.

This type of rearrangement was finally extended to substances not including a sulphur atom, for example, the aryl salicylates:

and the *o*-carbamyl derivatives of diphenyl ether:



During the first World War Smiles acted as chemist to the Small Arms Ammunition Committee of the Ministry of Munitions and carried out work on tracer bullets. For these services he received the O.B.E. in 1918.

He was made a Fellow of University College in 1912 and of King's College in 1933 and was elected a Fellow of the Royal Society in 1918.

A life-long Fellow of the Chemical Society, he served as Honorary Secretary from 1912 to 1920 and as a Vice-President for 1920 to 1923. He became a Fellow of the Royal Institute of Chemistry in 1916 and subsequently held office as Examiner in General Chemistry, 1920—1924, and as a member of Council, in 1932—1935 and 1936—1939.

The University of Belfast conferred on him the honorary degree of D.Sc.

The department of Chemistry at King's College flourished and expanded under Smiles's genial guidance. In spite of difficulties an adjacent building was secured and used to provide a considerable addition to the laboratory accommodation for research.

Smiles was an enthusiastic and inspiring leader of his research students and although he was keenly critical in scientific matters he was most kindly and tolerant in his attitude to them personally. If an experiment failed he would never blame the worker who might have been thought responsible for the failure. He would often chat with them of everyday affairs, games, or holidays. He enjoyed motoring, was a keen photographer, and a first-class tennis player.

Always most conscientious in the discharge of his teaching duties he maintained the excellent tradition of himself lecturing on inorganic chemistry to the 1st-year students. Loyally supported by his colleague Professor A. J. Allmand he regarded the needs of his students as the first responsibility of the department and he was ready to go to any amount of trouble to help them in their choice of employment or in their subsequent careers.

Among those who gained their first experience of research in collaboration with Smiles there are a number who have since distinguished themselves in academic or industrial chemistry, including T. P. Hilditch, E. de B. Barnett, H. T. Clarke, O. L. Brady, T. J. Nolan, and L. G. Brooker.

At the time of his retirement he wrote as follows:

" All those engaged in an experimental science who take up an academic career soon find

that there are two main aspects of their work : that of teaching and training of students to fit themselves for their careers, and the advancement of science by research. These duties are by no means incompatible, but I have found one of my most difficult tasks to be the maintaining of what appeared to be the proper balance between them.

" I must confess that, as with many of us, in my younger days the prosecution of research seemed to me to be by far the more important and interesting, but as years passed and I gained experience of life the situation gradually became altered, until in the last ten years or so the training of the student has seemed the more important, and indeed, sometimes research appeared to be a means to that end."

Nevertheless, the scientific standard of research in his department was in fact always maintained at a high level.

The affection and esteem in which Smiles was held by his old students and colleagues were well expressed by the inscription in the watch which they presented to him at the farewell dinner in 1938 : Samuel Smiles, Teacher and Friend.

I am glad to acknowledge the help I have received in writing this notice from several of those who worked with him at King's College, and particularly Dr. R. Child and Dr. J. A. C. McClelland.

G. M. Bennett.