with nitrite. This result, too, supports the cyclic structure of plastein.

(5) Plastein is formed in the pepsin hydrolysates of all proteins examined which contain abundantly amino-dicarboxylic acids. Gliadine, which contains 25·5 per cent of total nitrogen as amino-dicarboxylic acid-nitrogen, yields under the same conditions more plastein than does zein containing 18·8 per cent amino-dicarboxylic acid-nitrogen. On the other hand, amino-nitrogen did not decrease and plastein could not be obtained with papain nor with pepsin, in a papain hydrolysate of gelatine, although plastein is precipitated from the papain hydrolysate of zein with both enzymes. The results so far seem to indicate that the acid groups in the peptides are indispensable for the formation of plastein. In a mixture containing glycyl-glycine, glycyl-*l*-leucine, *l*-leucyl-*l*-tyrosine, *l*-leucyl-glycyl-glycine, *dl*-alanyl-glycine, chloracetyl-*l*-tyrosine and hippuryl-glycine, amino-nitrogen was not lowered by pepsin action at *p*H 4, nor was plastein precipitated.

(6) In the trypsin hydrolysates of zein and casein, pepsin produced at *p*H 4 only 1–1·5 per cent plastein of the weight of protein used. In corresponding circumstances, ten to fifteen times more plastein was obtained from pepsin hydrolysates. Since pepsin and trypsin break the peptide bonds of protein at different points, it probably explains the difference. In the pepsin hydrolysis of zein, the peptide chain seems to break at the point nearest glutamic acid[2].

(7) Plasteins are slowly hydrolysed in hydrochloric acid at *p*H 1·5 at the opening of the ring. The reaction takes place much more rapidly under the action of pepsin in the same conditions. Acid hydrolysis (*p*H 1·5 and 37° C.) without pepsin brought 67 per cent of the plastein into solution in 33–55 days. On the basis of the amino-groups set free the average molecular weight of cyclopeptides would be the same as that of tetrapentapeptides. In the soluble and insoluble fraction the amount of amino-dicarboxylic acids seems to be practically the same, which supports the idea of each cyclopeptide molecule having one amino-dicarboxylic acid residue. On the contrary, proline is accumulated in the insoluble fraction. The soluble fraction, again, contains considerably more basic acids as well as acids of the group alanine + valine + leucine + *iso*leucine + phenylalanine + methionine than does the insoluble fraction.

The elementary composition of zein plastein (water and ash-free material) was as follows: C = 54·3, H = 7·6, N = 12·9 (calculated values for cyclic peptides: C = 54·1, H = 7·1, N = 13·8). Nitrogen of the amino-acids hitherto estimated in zein accounts for 94 per cent of the total nitrogen. The rest of the nitrogen is still of unknown nature. The calculated values are therefore only approximate.

We regard the present results as confirming the concept of the cyclic structure of plasteins. A detailed account of our work and further developments will be published in *Acta Chemica Scandinavica*.

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Jan. 27.

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[2] Laine, *Ann. Acad. Sci. Fenn.*, Ser. A. II, Chem. No. 11 (1944).

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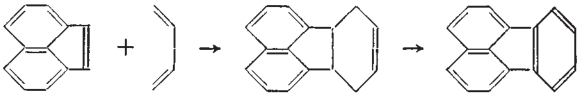
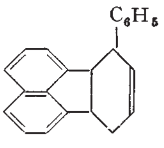
A Synthesis of Fluoranthene Derivatives

IN a recent investigation[1], the theory has been put forward that the formation of aromatic hydrocarbons in the high-temperature cracking of petroleum or petroleum fractions is due to diene syntheses between butadiene, which is one of the primary cracking products, and olefinic hydrocarbons. It occurred to us that fluoranthene (I), which is a characteristic product of this aromatizing cracking, may be formed from acenaphthylene and butadiene by the following reaction:



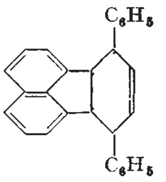
I

It has, indeed, been found that acenaphthylene reacts easily at 160–200° with dienes to give hydrogenated substituted fluoranthene derivatives: from 1-phenyl-butadiene and 1·4-diphenyl-butadiene, for example, 10-phenyl- and 10 : 13-diphenyl-9 : 10 : 13 : 14-tetrahydro-fluoranthene (II, III) have been obtained.



C_6H_5

II

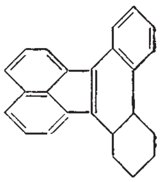


C_6H_5

C_6H_5

III

IV



V

Compound (II) had m.p. 156°, after recrystallization from alcohol (calc. for $C_{22}H_{18}$: C, 93·6; H, 6·4; found: C, 93·6; H, 6·4), and (III) had m.p. 202°, after recrystallization from chlorobenzene (calc. for $C_{28}H_{22}$: C, 93·9; H, 6·1; found: C, 93·6; H, 6·1).

With dicyclohexenyl (IV) the condensation seems to be accompanied by partial dehydrogenation and the analysis of the product corresponded to formula (V), of a 10 : 11-benzo-12 : 13-tetramethyleno-12 : 13-dihydro-fluoranthene[2]; it crystallized from a mixture of chlorobenzene and butyl acetate as a white, crystalline powder (calc. for $C_{24}H_{18}$: C, 94·1; H, 5·9; found: C, 93·9; H, 5·7).

It is interesting to note that sorbic acid behaves also as a diene[3]; in the course of the condensation with acenaphthylene, however, the carboxyl group is split off.

Acenaphthylene behaves, therefore, towards dienes like indene[4] and certain styrene derivatives[5]. This is in keeping with the fact that it contains an evidently very reactive double bond which makes the hydrocarbon also prone to polymerization and co-polymerization reactions[6,7].

A detailed description of the experiments will follow when the obvious possibilities of extension of this reaction will have been explored. It becomes possible to determine the position of substituents entering the fluoranthene molecule[8], from the location of substituents in the acenaphthene molecule, the reactions of which have been thoroughly investigated[9].

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[2] Such dehydrogenation has also been observed in the reaction of acenaphthylene and tetracyclone (Dilthey, Henkels and Schaefer, *Ber.*, **71**, 974 (1938)).

[3] This has been observed before in some isolated instances: Diels and Alder, *Liebigs Ann.*, **470**, 91 (1929). Farmer and Warren, *J. Chem. Soc.*, 906 (1929). Wagner-Jauregg and Helmert, *Ber.*, **71**, 2535 (1938). Wicks, Daly and Lack, *J. Org. Chem.*, **12**, 713 (1947), who also observed decarboxylation in the course of the reaction.

[4] Alder and Rickert, *Ber.*, **71**, 379 (1938). See Bergmann, E., and Bergmann, F., *J. Amer. Chem. Soc.*, **60**, 1805 (1938).

[5] Hudson and Robinson, *J. Chem. Soc.*, 715 (1941). Tamayo, *Chem. Abs.*, **41**, 4468, 6539, 6840 (1947).

[6] See, also, for references, Flowers and Miller, *J. Amer. Chem. Soc.*, **69**, 1388 (1947).

[7] Acenaphthylene shows dienophilic properties also towards tetracyclone and acecyclone: Dilthey and co-workers (ref. 2).

[8] See v. Braun and co-workers, *Ber.*, **63**, 2608 (1930); **67**, 4051 (1934); *Liebigs Ann.*, **488**, 111 (1931); **496**, 170 (1932). Tobler *et al.*, *Helv. chim. Acta*, **24**, 100 E (1941).

[9] It is substituted in 5-position (see, for example, Fleischer and Wolff, *Ber.*, **53**, 925 (1920). Dziewonski and Spirer, *Bl. Acad. Polon.*, A, 232 (1931). Liebermann and Zsuffa, *Ber.*, **44**, 207 (1911); but sulphonation at 100° attacks the 3-position (Dziewonski *et al.*, *Chem. Zentralbl.*, **97**, II, 2816 (1926); Dziewonski and Stolyhwo, *Ber.*, **57**, 1531 (1924); Morgan and Yarsley, *J. Soc. Chem. Ind.*, **44**, 513T (1925)).

Chemical Mechanism of Permanent Set

THE permanent set which strained wool fibres acquire in steam or boiling water is believed to be due to two consecutive intramolecular reactions, namely, hydrolysis of the disulphide bonds to give sulphenic acid and mercapto side-chains, followed by condensation of the sulphenic acid, or the aldehyde to which it gives rise on decomposition, with the basic side-chains of lysine and arginine[1]. Disulphide bond breakdown promotes relaxation, and the relaxed structure is stabilized by the new cross-linkages. The main evidence that the basic side-chains play an essential part in the linkage-rebuilding reaction is the failure of deaminated fibres to acquire a permanent set in steam. It seemed desirable that further evidence should be obtained because of recent suggestions[2] that the breakdown and re-formation of hydrogen bonds between the peptide chains may be sufficient to impart a permanent set to strained fibres. The setting power of wool treated with 2 : 4-dinitrofluorobenzene has therefore been examined.

Purified Lincoln root wool was treated with 2 : 4-dinitrofluorobenzene according to Sanger's procedure[3]. The wool (0·2 gm.) was first wetted out with a solution of sodium bicarbonate (0·2 gm.) in water (5·0 ml.). After adding a solution of 2 : 4-dinitrofluorobenzene (0·2 ml.) in ethanol (10 ml.), the wool was heated in the reagent for 23 hours at 40° C., the resulting gain in weight being 9·4 per cent. For reference purposes, a further sample of wool was treated with all the reagents except 2 : 4-dinitrofluorobenzene for 23 hours at 40° C. The setting power of these wools was then compared with that of untreated wool.

Each fibre was stretched 40 per cent in distilled water and set by immersion in a boiling 2 per cent solution of borax for 30 minutes. To determine the extent and permanence of the set, the fibre was then released in boiling water and its length redetermined at intervals. A summary of the results is given in the accompanying table, each value being the mean of ten observations on different fibres.

Wool	Percentage set retained after release in boiling water for 0 min.	2 min.	15 min.	60 min.
Untreated	40·0	26·1	25·3	24·4
Buffer-treated	40·0	24·0	23·2	21·0
Treated with 2 : 4-dinitrofluorobenzene	40·0	16·9	15·3	11·8

Since the setting power of wool is reduced to such a striking extent by treatment with 2 : 4-dinitrofluorobenzene, it seems reasonable to conclude, in accordance with earlier evidence, that the free amino-groups of wool play an essential part in the cross-linking reaction which is responsible for permanent set.

We are indebted to Mr. W. R. Middlebrook for the preparation of the wools used in this investigation.

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[2] Rudall, "Fibrous Proteins", 15 (Society of Dyers and Colourists, 1946). Phillips, *ibid.*, 39.

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Energy of the Central C–C Bond in Diphenyl

THE value of the energy of the central C—C bond in diphenyl (that is, the heat of dissociation of the molecule into two radicals (or atoms) formed by the fission of this bond) is of considerable interest. The difference between the energy of this bond and the energy involved in the C—C bond of ethane provides a measure of conjugation which was generally considered as 6–8 kcal. only[1]. We use the following two thermochemical equations for the calculation of the energy of the central C—C bond in diphenyl:

$$\Delta H_f(C_6H_5.C_6H_5) = 2\Delta H_f(C_6H_5) - D(C—C);$$

$$2\Delta H_f(C_6H_6) = 2\Delta H_f(C_6H_5) + 2\Delta H_f(H) - 2D(C—H).$$

The heats of formation of diphenyl and benzene were estimated by Huffman[2] as 20·8 kcal./mole for solid diphenyl and 11·6 kcal./mole for liquid benzene. The heat of sublimation of diphenyl is 16·4 kcal./mole[3], that of vaporization of benzene 8·1 kcal./mole. For the C—H bond energy in benzene we accept the suggested value of 106 kcal.[4], which seems to be very plausible. Thus we obtain for the central C—C bond energy in diphenyl a value of 110 kcal. Its strengthening as compared to the C—C bond in ethane is 25 kcal., which shows how considerable is the contribution of the conjugation to the bond energy. This strengthening effect makes it possible to predict the length of the central C—C bond in diphenyl as 1·43–1·45 A., using the relationship between the bond energy and bond length.

There are two experimental studies dealing with the length of this bond. Dhar used the rotating crystal X-ray technique[5]; his value is 1·48 A., the estimated accuracy being about 10 per cent. Karle and Brockway[6] used an electron diffraction method. Assuming that both phenyl rings are regular hexagons having sides of 1·39 A., they find for the central C—C bond a length of 1·54 A.; if they assume the hexagons