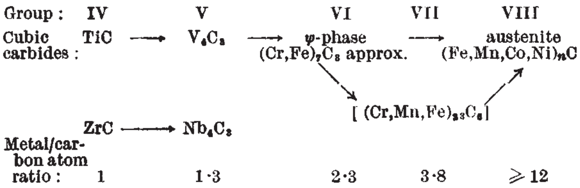
the cubic carbide, yet richer in carbon than Me_7C_3, such as Me_2C.) To differentiate the carbide from austenite it will here be referred to as 'ψ'.

From the point of view of structure chemistry, the present carbide may be shown to fall naturally into place. Petch[2] has shown that in austenite the carbon atoms occupy the octahedral positions; but, even for maximum saturation, only one among twelve of these sites is filled. On the other hand, within the group of carbides of NaCl type of structure, carbon atoms begin to be omitted from the ideal *Me*C lattice in a manner complementary to the austenite solid solutions, as becomes apparent when arranged according to the periodic table:



In this series, chromium and manganese occupy transitional positions; of their carbides, one simulates the cubic, one the hexagonal, and one the orthorhombic symmetry of those of the surrounding elements (V_4C_3, Mo_2C and Fe_3C respectively). But $(Cr,Mn,Fe)_{23}C_6$, though belonging to the cubic class, does not actually adopt the NaCl structure, having a complex unit cell with 116 atoms. The ψ-phase thus bridges a gap between austenite and the rock-salt type of carbides, being isomorphous to both and consistently falling into the above sequence of metal/carbon ratios. In this light, austenite may, incidentally, be itself regarded as a 'carbide', being the ultimate member of the cubic group.

The substitution in ψ of chromium by manganese, to give an analogue to ψ in plain manganese steels, is highly probable, though its existence has not, to my knowledge, been reported and may well in the past have been obscured by the predominant austenite.

The following implications of the ψ-carbide are suggested.

(1) Its existence imposes caution in interpreting an apparent austenite as such, when occurring in a ferrite or martensite matrix. Spacing measurements or the microscope will not necessarily decide between austenite and ψ. In high-speed steels, for example, the 'persistent' portion of retained austenite which only repeated tempering can destroy is quite liable to involve carbon-enriched ψ, or a solid solution of its type.

(2) The carbide can be produced in chromium-bearing tool or magnet steels, where, in view of its structure and composition, it would tend to induce physical properties compromising between a hard carbide and the more ductile austenite.

(3) Being stable only at high temperatures (though metastable at lower ones) and tending to transform into either trigonal $(Cr,Fe)_7C_3$, $(Cr,Fe)_{23}C_6$ or cementite, or assemblies thereof, the carbide holds promise of showing precipitation hardening effects, that is, by one carbide nucleating within another.

(4) Since the lattice dimensions are favourable to the formation of high-temperature solid solutions with austenite in chromium–nickel heat-resisting and stainless steels (but only for certain composition ranges), its tendency to segregate from the matrix and at the same time itself to decompose is likely to influence creep-resistance and high-temperature strength. X-ray analysis conducted in these laboratories on heat-resisting steels actually reveals sequences of ostensible 'austenites' of varying lattice parameter, some of which probably represent ψ-phases intermediate in composition to the austenite base and the co-existing close-packed cubic TiC type carbides.

(5) Prepared synthetically, ψ is a carbide of possible interest in sintered hard-metal materials, particularly being isomorphous with titanium carbide as well as with metallic cobalt and, on structural grounds, probably also intersoluble with tungsten carbide.

An account of the work on carbides in steels, of which this forms part, will be published elsewhere. I wish to thank Mr. D. A. Oliver, director of research, B.S.A. Group of Companies, for his interest and encouragement, and Mr. E. Harpham for the carbide extractions.

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[1] Westgren, A., *Nature*, **133**, 480 (1933). *Jernkont. Ann.*, **117**, 501 (1933); **119**, 231 (1935).

[2] Petch, N., *J. Iron and Steel Inst.*, **145**, 111 (1942).

Photochemical Action of Ethylorthoformate

Ciamician and Silber[1] showed that when an ethyl alcohol solution of benzophenone is exposed to sunlight, the alcohol is oxidized to aldehyde and the ketone reduced to benzpinacol; in the place of ethyl alcohol, *iso*propyl alcohol has frequently been used[2].

$$2\,Ph_2C:O + CHMe_2OH \xrightarrow{\text{sunlight}} Ph_2COH.COHPh_2 + Me_2CO.$$

A large number of benzophenone derivatives react in the presence of alcohols as above[3].

In a number of cases, pinacols have frequently been obtained from diaryl ketones, as by-products, when the ketones were treated with aromatic hydrocarbons, for example, toluene[4], or ether, *iso*-amylether, acetal and dimethylether of glycerol[5], or with esters, such as ethyl acetate, ethyl malonate[5], or acids, for example, phenylacetic acid[6]. The action of aliphatic alcohols on quinones, for example, *p*-benzoquinone in sunlight, yields hydroquinone[7]. Benzil, in absolute ethyl alcohol, forms benzilbenzoin[8].

Recently, I have found that on exposure to sunlight of benzophenone, *p,p'*-ditolylketone, *p,p'*-dimethoxybenzophenone and *p,p'*-dichlorobenzophenone with ethylorthoformate in sealed 'Pyrex'-glass tubes, the corresponding pinacols, namely, benzpinacol, 4 : 4′ : 4″ : 4‴-tetramethyl-, 4 : 4′ : 4″ : 4‴-tetramethoxy- and 4 : 4′ : 4″ : 4‴-tetrachlorobenzpinacol were obtained; deoxybenzoin gave a deoxybenzoin-pinacol, whereas benzil yielded benzilbenzoin. On the other hand, the action of ethylorthoformate on *p*-benzoquinone, toluquinone, chloranil and phenanthraquinone, yielded hydroquinone, toluhydroquinone, tetrachlorohydroquinone and 9 : 10-dihydroxyphenanthrene respectively. Identification of the photo-products was carried out by melting point and mixed melting point determination with authentic specimens. In all these experiments, the fate of ethylorthoformate has not yet been investigated. Control experiments in the dark, but otherwise under identical conditions, showed no reaction.

The application of ethylorthoformate as a photochemical reducing agent in sunlight is still under investigation.

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[1] *Ber.*, **33**, 2911 (1900).

[2] Cohen, *Rec. trav. chim.*, **39**, 243 (1920).

[3] Comp. Migita, *Bull. Chem. Soc. Japan*, **7**, 334 (1932). Schönberg and Mustafa, *J. Chem. Soc.*, 67 (1944). Bachmann, *J. Amer. Chem. Soc.*, **55**, 391 (1933).

[4] Comp. Ciamician and Silber, *Ber.*, **43**, 1536 (1910).

[5] Ciamician and Silber, *Ber.*, **44**, 1280 (1911). Paterno and Chieffi, *Gazz. Chim. Ital.*, **40**, ii, 321 (1910).

[6] De Fazi, *Atti Accad. Lincei*, **6**, 266 (1925); *Gazz. Chim. Ital.*, **57**, 551 (1927).

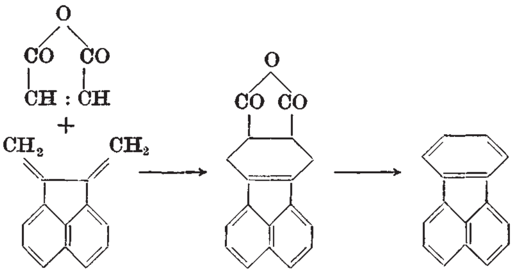
[7] Comp. Klinger, *Ber.*, **19**, 1864 (1886). Ciamician and Silber, *Ber.*, **34**, 1530 (1901).

[8] Benrath, *J. prakt. Chem.*, **73**, 383 (1906).

Fluoranthene Syntheses

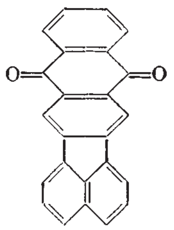
THE recent communication by Bergmann[1] on the formation of fluoranthene from acenaphthylene and butadiene prompts us to report briefly two somewhat similar syntheses of the hydrocarbon which have been developed in our laboratories.

trans-9 : 10-Dimethylacenaphthene-9 : 10-diol[2] when heated with acetic anhydride and maleic anhydride readily gives 10 : 11 : 12 : 13-tetrahydrofluoranthene-11 : 12-dicarboxylic acid anhydride (II), presumably by formation of the intermediate 9 : 10-dimethyleneacenaphthene (I) [3]. Dehydrogenation and decarboxylation of the product yield fluoranthene (III).

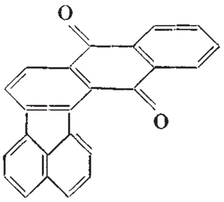


I II III

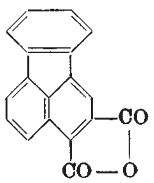
It is obvious that, by the use of substituted acenaphthenes or acenaphthenediols and replacement of the maleic anhydride by other ethylenic components, substituted fluoranthenes of known structure can be obtained. For example, substitution of maleic anhydride by α-naphthoquinone in the above reaction gives a quinone, melting point higher than 300°, which must have structure IV. The compound prepared by another method and regarded as having this structure[4] must be the isomeric quinone with formula V.



IV



V



VI

9-Methylfluorenol is known to undergo dehydration to the unstable 9-methylenefluorene[5]. By heating the carbinol with acetic anhydride and maleic anhydride, the intermediate methylene compound gives fluoranthene-3 : 4-dicarboxylic acid anhydride (VI), one of the nuclear double bonds being sufficiently reactive to participate in the Diels – Alder reaction. Decarboxylation gives fluoranthene (III). The reaction does not take place so readily as in the first method, but the structures of the products are unambiguously established.

Details of these and related experiments will be published elsewhere.

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[1] *Nature*, **161**, 889 (1948).

[2] Criegee, R., Kraft, L., and Rank, B., *Annalen*, **507**, 159 (1933).

[3] Cf. Maxim, N., *Bull. Soc. Chim.*, **45**, 1137 (1929).

[4] v. Braun and Manz, *Annalen*, **496**, 170 (1932).

[5] Wieland, Reindel and Ferrer, *Ber.*, **55**, 3313 (1922).

Sulphur-containing Steroid Derivatives

PREVIOUS communications[1,2] have recorded the synthesis of antibacterial compounds derived from bile acids and sterols which contained basic groups, such as the amino-, amidino- and guanido-groups. In general, these derivatives were bacteriostatic for Gram-positive bacteria, but had little activity against Gram-negative organisms. Whereas surface tension measurements seemed to reveal a relationship between the bacteriostatic and surface activities of the bile acids and their anionic derivatives[3], no such relationship was apparent in the properties of a series of the basic steroid compounds[4]. In an extension of these studies, we have synthesized and investigated several water-soluble, sulphur-containing, steroid derivatives.

A series of mercaptals has been obtained by the condensation of thioglycollic acid with various keto-derivatives of steroids, a reaction which occurs without a catalyst and appears to be specific for a keto group at position 3. For example, 3 : 7 : 12-triketocholanic acid yielded 3 : 3-di-(carboxymethylmercapto)-7 : 12-diketocholanic acid, m.p. 203°, $[\alpha]_D^{24^\circ} + 55\cdot0^\circ$; (trimethyl ester: m.p. 78°, $[\alpha]_D^{17\cdot5^\circ} + 51\cdot3^\circ$); 3-keto-7 : 12-dihydroxycholanic acid gave 3 : 3-di-(carboxymethylmercapto) - 7 : 12-dihydroxycholanic acid, m.p. 141°, $[\alpha]_D^{20^\circ} + 35\cdot7^\circ$; and Δ^4-cholesten-3-one afforded 3 : 3-di-(carboxymethylmercapto)-Δ^4-cholestene, m.p. 122–124°, $[\alpha]_D^{19^\circ} + 108^\circ$. 3 : 3-Dithiophenyl-7 : 12-diketocholanic acid was derived from the condensation of thiophenol with 3 : 7 : 12-triketocholanic acid by a modification of the method of Mylius[5]. In a similar manner, 3 : 3-di(N-acetyl-*p*-aminothiophenyl)-7 : 12-diketocholanic acid : m.p. 165°, $[\alpha]_D^{18^\circ} + 13\cdot0^\circ$, was obtained by the condensation of N-acetyl-*p*-aminothiophenol with 3 : 7 : 12-triketocholanic acid. The monobasic, sulphur-containing acid, 3-carboxymethylmercapto-Δ^5-cholestene, m.p. 145°, $[\alpha]_D^{21^\circ} - 34\cdot2^\circ$, was obtained by the reaction of thiocholesterol with monochloroacetic acid.

Treatment of the sodio-derivative of thiocholesterol with methyl iodide afforded the methyl thioether, m.p. 141°, $[\alpha]_D^{18^\circ} - 24\cdot6^\circ$, which gave, upon further treatment with methyl iodide, Δ^5-cholestene-3-