798. *Attempts to prepare New Aromatic Systems. Part V.*[1] *Benzopentalene* (cyclo*Pent*[a]*indene*).

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Further study of fluorosulphonic acid as a cyclodehydrating agent has shown that it is most active when it contains sulphur trioxide, and this has led to an improvement in the preparation of the diketone (III) from the acid (II). The action of phosphorus pentachloride on this ketone gave the dichlorodiene (V). Attempts to convert the dichlorodiene (V), or the diphenyldiene (IV), into the corresponding disubstituted benzopentalenes were unsuccessful.

RECORDED experiments in this series of papers directed towards the synthesis of benzopentalene (*cyclo*pent[*a*]indene) (I), or simple derivatives thereof, have led to the preparation, amongst other compounds, of 3 : 4 : 5 : 6 : 7 : 8-hexahydro-3 : 6-dioxobenzopentalene (III) and of 4 : 5-dihydro-3 : 6-diphenylbenzopentalene (IV).[1] Further work on compounds (III) and (IV) is now recorded.

The yields of the diketone (III) obtained by cyclisation of 3-oxo-2-phenyl*cyclo*pentane-1-carboxylic acid (II) with technical fluorosulphonic acid [1,2] were found to be very variable. The effectiveness of fluorosulphonic acid has now been found to be due in part to the fact that the commercial acid contains varying amounts of free sulphur trioxide, the optimum amount being about 2·5% (w/v). The cyclisation proceeds best in carbon disulphide solution.

The preparation of 4 : 5-dihydro-3 : 6-diphenylbenzopentalene (IV) from the diketone (III) has been improved, and attempts have been made to dehydrogenate it to 3 : 6-diphenylbenzopentalene. These included catalytic and transfer dehydrogenation,[3] and heating with chloranil, dehydroindigo, ethylene–platinous chloride, lead tetra-acetate, selenium dioxide, or sulphuryl chloride. Direct bromination of (IV) gave a trace of a monobromo-compound, probably 4(or 5)-bromo-4 : 5-dihydro-3 : 6-diphenylbenzopentalene. Reaction of (IV) with *N*-bromosuccinimide followed by treatment with *NN*-dimethylaniline gave a dimeric halogen-free compound whose ultraviolet and visible absorption spectra are very similar to those of the starting material (see Table) and suggest that the product is di[4 : 5-dihydro-3 : 6-diphenylbenzopentalene-4(or 5)-yl].

Reaction of phosphorus pentachloride with the diketone (III) in benzene solution gave a yellow product, $C_{12}H_8Cl_2$, which from its method of formation and colour would be expected to be the most stable of the eleven theoretically possible isomeric 3 : 6-dichlorodihydrobenzopentalenes, namely, 3 : 6-dichloro-4 : 5-dihydrobenzopentalene (V), a compound which is in effect a benzofulvene. This expectation is very strongly supported by the fact that the dichloro-compound shows principal ultraviolet absorption maxima at

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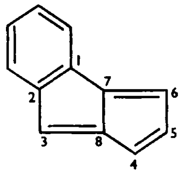
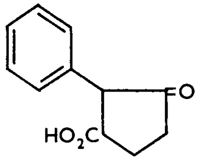
[1] Part IV, Baker, Glockling, and McOmie, *J.*, 1951, 3357.
[2] Baker, Coates, and Glockling, *J.*, 1951, 1376.
[3] Blood and Linstead, *J.*, 1952, 2255.

263·5 ($\log_{10} \varepsilon$ 4·42) and 302·2 mμ ($\log_{10} \varepsilon$ 3·69), corresponding very closely to the recorded maxima for the 6 : 6-dimethyl-2 : 3-benzofulvene (VI) at 261 ($\log_{10} \varepsilon$ 4·41) and 308 mμ ($\log_{10} \varepsilon$ 3·80).[4] All the other isomers would be expected to absorb at appreciably shorter wavelengths. The possibility that the 7 : 8-bond has broken, to give 2 : 5-dichlorobenzo*cyclo*octatetraene, is excluded by the fact that the infrared spectrum of the dichloro-compound, determined in carbon tetrachloride, showed strong bands at 2846 and 2925 cm.$^{-1}$, corresponding to those expected[5] for saturated methylene groups, *i.e.*, 2853 and 2926 ± 10 cm.$^{-1}$.



(I)



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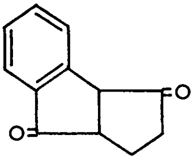

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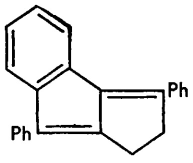

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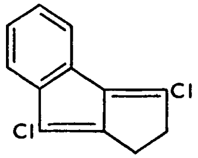

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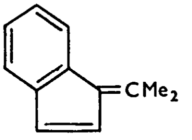
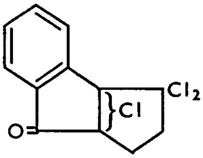
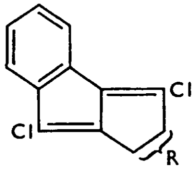


(VI)



(VII)



(VIII)

When the diketone (III) and phosphorus pentachloride were allowed to react under more vigorous conditions and the product was boiled with ethanolic potassium acetate, two products were isolated, a trichloro-compound, $C_{12}H_9OCl_3$, and a high-melting, apparently dimeric substance, $C_{24}H_{14-16}Cl_2$, of unestablished structure. The trichloro-compound shows infrared absorption bands of medium intensity at 1585 and 1600 and a strong band at 1721 cm.$^{-1}$, showing the presence of a carbonyl group adjacent to the benzene ring,[5] and it is therefore probably 6 : 6 : 7(or 8)-trichloro-3 : 4 : 5 : 6 : 7 : 8-hexahydro-3-oxobenzopentalene (VII).

Ultraviolet absorption spectra.

Compound	Solvent	λ (mμ)	$\log_{10} \varepsilon_{\text{max.}}$	λ (mμ)	$\log_{10} \varepsilon_{\text{max.}}$
Diphenyl-diene (IV)	EtOH	226	4·44	328·5	4·26
		291·5	4·38	410	3·71
Diphenyl-diene dimeride	Bu^{n}OH	292	4·76	330	4·62
				420	4·19
Dichloro-diene (V)	EtOH	232	4·05	291	3·69
		240·5	4·10	302·5	3·69
		263·5	4·42	314·5	3·56
		270	4·37	362	3·45
Methoxydichloro-diene (VIII; R = OMe)	EtOH	234	4·22	309	3·85
		241·5	4·29	321	3·77
		266	4·43	352	3·48
Acetoxydichloro-diene (VIII; R = OAc)	EtOH	232·5	4·20	303	3·84
		240·5	4·29	314·5	3·73
		263·5	4·57	360	3·46
		292·5	3·80		
Dichloro-compound $C_{24}H_{14\text{ or }16}Cl_2$	EtOH	258	4·54	325	3·91
		300	4·00	382	3·58
		312	3·98		

The dichloro-compound (V) is a promising intermediate for the synthesis of 3 : 6-dichlorobenzopentalene. Treatment with *N*-bromosuccinimide, followed by recrystallisation

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[4] Pullman, *Bull. Soc. chim. France*, 1951, **18**, 702.

[5] Bellamy, " The Infra-Red Spectra of Complex Molecules," Methuen, London, 1954.

of the product from methanol, gave a bromine-free methoxy-compound (VIII; R = OMe) whose light absorption (see Table) resembled that of the starting material. This substance probably arises by bromination at one of the two allylic positions 4 and 5, followed by replacement of the reactive bromine atom by a methoxyl group through interaction with the solvent. Attempts to isolate this intermediate bromo-compound (VIII; R = Br) were unsuccessful. Treatment of the crude product with potassium acetate yielded 4(or 5)-acetoxy-3 : 6-dichloro-4 : 5-dihydrobenzopentalene (VIII; R = OAc), a remarkably stable compound which could not be made to lose acetic acid. Attempts to prepare the related compounds (VIII; R = O·CMe$_3$) and (VIII; R = O·SO$_2$·C$_6$H$_4$Me-*p*) were unsuccessful.

Benzopentalene (I) shows little if any tendency towards formation, and we conclude that it is probably not a stable, aromatic structure (cf. refs. 3 and 6 and the following paper).

EXPERIMENTAL

3 : 4 : 5 : 6 : 7 : 8-*Hexahydro*-3 : 6-*dioxobenzopentalene* (III) (with J. HANCOCK).—Commercial fluorosulphonic acid was distilled, and the fraction of b. p. 162° shaken with a little water to hydrolyse any sulphur trioxide (fluorosulphonic acid is hydrolysed only slowly), and redistilled. The optimum conditions for cyclisation were as follows. To a rapidly stirred suspension of dried 3-oxo-2-phenyl*cyclo*pentane-1-carboxylic acid (II) (15 g.) in boiling carbon disulphide (75 ml.) was added fluorosulphonic acid [45 ml., containing 2·5% (w/v) of sulphur trioxide] as quickly as the vigorous reaction permitted. Heating was continued for 20 min., and the mixture was allowed to cool (rapid stirring). The solution was cautiously poured on crushed ice and extracted with ether (250 and 2 × 100 ml.). The combined extracts were washed with saturated potassium hydrogen carbonate solution, and yielded the diketone (III) (10 g., 73%), m. p. 86—88°. The potassium hydrogen carbonate solution yielded some keto-acid (*ca.* 1 g.).

The diketone gave an orange *bis*-2 : 4-*dinitrophenylhydrazone* which, crystallised from acetic acid, had m. p. 277° (decomp.) (Found: C, 52·5; H, 3·3; N, 20·3. $C_{24}H_{18}O_8N_8$ requires C, 52·7; H, 3·3; N, 20·5%). The *piperonylidene derivative* of the diketone, purified by chromatography on alumina and by crystallisation from benzene–ethanol, formed yellow prisms, m. p. 181—182° (Found: C, 75·4; H, 4·3; $C_{20}H_{14}O_4$ requires C, 75·5; H, 4·4%).

5 : 5 : 7 : 8(?)-*Tetrabromo*-3 : 4 : 5 : 6 : 7 : 8-*hexahydro*-3 : 6-*dioxobenzopentalene*.—A mixture of the diketone (III) (0·25 g.) and bromine (0·10 g.) in chloroform (10 ml.) was heated under reflux for 3 hr. After removal of solvent, the *product* was twice recrystallised from methanol, giving plates, m. p. 147—148° (Found: C, 28·5; H, 1·3; Br, 63·8. $C_{12}H_6O_2Br_4$ requires C, 28·7; H, 1·2; Br, 63·7%).

4 : 5-*Dihydro*-3 : 6-*diphenylbenzopentalene* (IV).—The yield of the diphenyl compound (IV) from the diketone (III)[1] was raised from 52 to 74% by using an excess (3·2 mols.) of phenylmagnesium bromide. The intermediate dihydroxy-diphenyl compound (1·0 g.) was heated with acetyl chloride (1·0 ml.) in pyridine (10 ml.) at 120° (oil-bath temp.) for 1 hr., and, after cooling to 50°, the mixture was added to 5N-hydrochloric acid (50 ml.), and the solid collected. Sublimation at 180°/0·5 mm. gave the compound (IV) (0·85 g., 95%), m. p. 180°.

Bromination of 4 : 5-*Dihydro*-3 : 6-*diphenylbenzopentalene* (IV).—(*a*) Bromine (0·16 g.) in chloroform (10 ml.) was added to the diphenyl compound (IV) (0·1 g.) in chloroform (10 ml.), and the mixture was heated till evolution of hydrogen bromide ceased. The solvent was replaced by benzene, then by ethanol, giving a small amount of dark brown crystals of 4(or 5)-*bromo*-4 : 5-*dihydro*-3 : 6-*diphenylbenzopentalene*, m. p. 208—210° (decomp.) (Found: Br, 20·7. $C_{24}H_{17}Br$ requires Br, 20·7%).

(*b*) The diphenyl compound (IV) (0·4 g.) was heated with *N*-bromosuccinimide (0·24 g.) and barium carbonate (0·6 g.) in carbon tetrachloride for 1 hr., and cooled. The filtrate was heated on a steam-bath with *NN*-dimethylaniline (10 ml.) for 1½ hr., pyridine (5 ml.) was added, and heating continued for ½ hr. The product was dissolved in benzene (100 ml.) and washed with 5N-hydrochloric acid (2 × 50 ml.) and with water. After removal of the solvent, the residue (0·12 g.)

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[6] Baker and McOmie, in " Progress in Organic Chemistry," ed. J. W. Cook, Butterworths, London, 1955, Vol. III, Chapter 2, pp. 44—80; Baker, in " Perspectives in Organic Chemistry," ed. Sir A. Todd, Interscience, New York, 1956, pp. 28—67.

was washed with acetone and then crystallised from benzene, giving *di-*[4 : 5-*dihydro*-3 : 6-*diphenylbenzopentalene*-4(*or* 5)-*yl*] as orange-brown needles, m. p. 277° (decomp.) (Found: C, 94·6; H, 5·3; *M*, ebullioscopic in benzene, 584. $C_{48}H_{34}$ requires C, 94·4; H, 5·6%; *M*, 610).

The compound did not form a picrate or a 2 : 4 : 7-trinitrofluorenone complex. It gave a blue-black colour with warm concentrated sulphuric acid.

Reaction of the Diketone (III) *with Phosphorus Pentachloride*.—(*a*) 3 : 6-*Dichloro*-4 : 5-*dihydrobenzopentalene* (V). The diketone (III) (4 g.) in dry benzene (40 ml.) was added to phosphorus pentachloride (10·8 g.) in dry benzene (80 ml.). After 5 hr., the solution was heated for ½ hr., and poured on ice. The benzene layer was washed with sodium hydrogen carbonate solution and with water, dried, and distilled, giving a yellow oil (2·8 g.), b. p. 125—135°/0·5 mm., which solidified. Crystallisation from methanol and then from light petroleum (b. p. 60—80°), followed by sublimation *in vacuo*, gave 3 : 6-*dichloro*-4 : 5-*dihydrobenzopentalene* (V) as yellow needles, m. p. 117—117·5° (Found: C, 64·2; H, 3·5; Cl, 31·4. $C_{12}H_8Cl_2$ requires C, 64·6; H, 3·6; Cl, 31·8%).

(*b*) *Isolation of compounds* $C_{12}H_9OCl_3$ (VII) *and* $C_{24}H_{14\,\mathrm{or}\,16}Cl_2$. The diketone (III) (4 g.) and phosphorus pentachloride (10·8 g.) in benzene (120 ml.) were boiled for 3 hr. and worked up as before. The product was boiled with potassium acetate (1·0 g.) in ethanol, filtered, distilled (b. p. 122—130°/0·3 mm.), and crystallised from methanol, yielding the dichloro-compound (V) (0·22 g.) and 6 : 6 : 7(*or* 8)-*trichloro*-3 : 4 : 5 : 6 : 7 : 8-*hexahydro*-3-*oxobenzopentalene* (VII) (0·42 g.), m. p. 108—109° (Found : C, 52·1; H, 3·3; Cl, 38·7. $C_{12}H_9OCl_3$ requires C, 52·3; H, 3·3; Cl, 38·7%).

A closely similar experiment carried out in more concentrated solutions gave a substance which separated from light petroleum (b. p. 60—80°) in yellow needles, m. p. 241—242° (decomp. (Found: C, 77·2; H, 4·1; Cl, 18·8. Calc. for $C_{24}H_{14}Cl_2$: C, 77·4; H, 3·8; Cl, 19·1. Calc. for $C_{24}H_{16}Cl_2$: C, 76·8; H, 4·3; Cl, 18·9%).

Reaction of 3 : 6-*Dichloro*-4 : 5-*dihydrobenzopentalene* (V) *with* N-*Bromosuccinimide*.—(*a*) The dichloro-compound (V) (0·3 g.), *N*-bromosuccinimide (0·25 g.), and benzoyl peroxide (0·01 g.) in carbon tetrachloride (20 ml.) were heated under reflux for 4 hr. The filtered solution was washed with 2N-sodium hydroxide and then with water. After drying, and removal of the solvent, the residual oil was purified by crystallisation from methanol before and after sublimation (70—80°/0·1 mm.), giving 3 : 6-*dichloro*-4 : 5-*dihydro*-4(*or* 5)-*methoxybenzopentalene* (VIII; R = OMe) as yellow needles, m. p. 96° (Found: C, 61·6; H, 3·8; Cl, 28·0. $C_{13}H_{10}OCl_2$ requires C, 61·7; H, 4·0; Cl, 28·0%).

(*b*) The dichloro-compound (V) (0·25 g.), *N*-bromosuccinimide (0·21 g.), and benzoyl peroxide (0·01 g.) in carbon tetrachloride (15 ml.) were heated under reflux for 1 hr. The solvent was removed from the filtered solution. and the residual oil was boiled for a few minutes with potassium acetate (0·1 g.) in acetic acid (20 ml.). After being kept for 4 hr., the solution was concentrated under reduced pressure, decanted from solid, and poured into water. Extraction with ether gave a solid which was crystallised from methanol, then sublimed (110°/0·5 mm.; 0·05 g. of yellow crystals, m. p. 110—114°), and recrystallised from methanol giving 4(*or* 5)-*acetoxy*-3 : 6-*dichloro*-4 : 5-*dihydrobenzopentalene*, m. p. 117—118° (Found: C, 59·4; H, 3·6. $C_{14}H_{10}O_2Cl_2$ requires C, 59·8; H, 3·6%). The compound sublimed very slowly at 100° under atmospheric pressure and very little decomposition occurred when the vapour was passed at a pressure of 4×10^{-3} mm. through a tube heated to *ca.* 500°. Owing to its volatility and hence brief preheating, it is probable that the vapour temperature was considerably less than 500°. The compound decomposed when heated above its m. p. with anhydrous potassium carbonate.

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