510. *Cyclic Conjugated Polyenes. Part III. Attempts to Prepare Heptalene by Dehydrogenation and Dehydrobromination Reactions.*

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Catalytic dehydrogenation of *ethyl* bicyclo[5 : 5 : 0]*dodeca*-2 : 4 : 7(1)-*triene*-x-*carboxylate* (III) in the liquid phase yielded dimethylnaphthalenes, whilst in the vapour phase both it and the *methyl* bicyclo[5 : 5 : 0]*dodeca*-2 : 4 : 7(1) : 11-*tetraene*-x-*carboxylate* (cf. X) yielded in addition traces of deep-blue dehydrogenation products. These have not been identified, but they so resemble azulenes in spectral characteristics that the possibility of their being heptalenes is small. Dehydrogenation of *ethyl* bicyclo[5 : 4 : 0]*undeca*-2 : 4 : 7(1)*trienecarboxylate* (V) leads to similar ready contraction of the 7-ring to yield a mixture of methylnaphthalenes. Bromination of the above-mentioned methyl ester with *N*-bromosuccinimide, followed by dehydrobromination, did not yield a product with the characteristics expected of a heptalene derivative.

The difficulties experienced in these attempts to synthesise heptalenes suggest that this structure (I) is not easily capable of synthesis and is therefore unlikely to be very stable or aromatic in type.

IN view of the production of azulenes by dehydrogenation of substances containing the *bicyclo*-[5 : 3 : 0]decane ring system, a synthesis of heptalene (I) has been sought in the similar dehydro-genation of *bicyclo*[5 : 5 : 0]dodecane derivatives prepared by the interaction of ethyl diazoacetate and 1 : 2-benz*cyclo*heptenes. The product from ethyl diazoacetate and 1 : 2-benz*cyclo*heptene (II) itself absorbed 3 moles of hydrogen in the presence of a colloidal platinum catalyst and is therefore formulated as the expected ethyl *bicyclo*[5 : 5 : 0]dodeca-2 : 4 : 7(1)-trienecarboxylate (III), this rather than a norcaradiene structure such as (IV) being supported by the resemblance of its absorption spectrum (Fig. 1) to that of ethyl *cyclo*heptatrienecarboxylate. (III) did not give the distinctive colour reaction with sulphuric acid characteristic of many structures of type (IV). The product of interaction of tetrahydronaphthalene with ethyl diazoacetate possessed similar properties and thus probably had a similar structure, *e.g.*, (V; R = Et).

No identifiable product resulted from dehydrogenation of (III) in the liquid phase, but in the vapour phase with palladium–charcoal the main product isolated was a colourless hydrocarbon

which gave a crystalline picrate with the composition of a dimethylnaphthalene picrate and had an absorption spectrum almost identical with that of 2 : 7-dimethylnaphthalene (cf. Laszlo, *J. pr. Chem.*, 1925, **117**, 401). A similar easy isomerisation of the *cyclo*heptene to a benzenoid ring system was observed on dehydrogenation, under similar conditions, of bicyclo-[5 : 4 : 0]-*undecatrienecarboxylic acid* derived from (V). This acid yielded a 2 : 1 mixture of 1- and 2-methylnaphthalene.

FIG. 1.
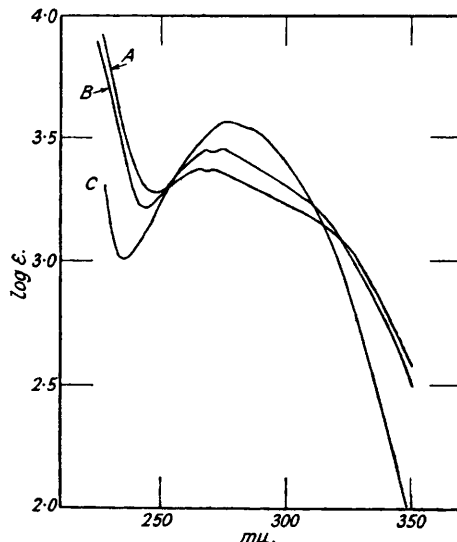
A. *Condensation product* (V) *of* 1 : 2-benzcycloheptene *with ethyl diazoacetate.*
B. *Condensation product* (VII) *of tetrahydronaphthalene with ethyl diazoacetate.*
C. *Ethyl* cyclo*heptatrienecarboxylate.*

These facts made it clear that the formation of heptalene was to be sought under milder conditions of reaction, and attention was therefore directed to vapour-phase dehydrogenation under conditions such that the initial products were more quickly removed from the sphere of reaction (cf. Nunn and Rapson, this vol., p. 829). The product then obtained from ethyl


(I.)   (II.)   (III.)   (IV.)   (V.)
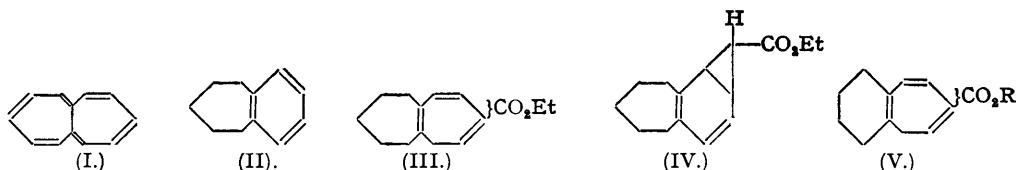
bicyclo[5 : 5 : 0]dodecatrienecarboxylate was a deep-blue oil, which was separated by distillation into a deep-blue hydrocarbon fraction, b. p. 100—120°/15 mm., and deep-bluish-violet ester fraction, b. p. 140—170°/15 mm. The hydrocarbon was treated in light petroleum solution with 85% phosphoric acid, and an azulene-like material liberated from the acid layer by the addition of water as an intense-ultramarine-coloured oil. The absorption spectrum of this oil in the visible region was very similar (Fig. 2) to that of 2-ethylazulene (Wagner-Jauregg *et al.*, *Ber.*, 1941, **74**, 1522) which shows distinctive absorption maxima at 686·5, 623, 579·5, and 570·5 mμ. and weak maxima at 660, 645·5, 634, 601, 589·5, and 586 mμ. The hydrocarbons which were not soluble in 85% phosphoric acid yielded a small quantity of a picrate from which a product similar to the dimethylnaphthalene mixture described above was isolated.

The ester fraction similarly yielded a trace of azulene-like material and a colourless fraction which appeared to be largely unchanged material. As in the case of the hydrocarbon fraction, it was not possible to obtain a crystalline derivative of the azulene-like portion, but its absorption spectrum in the visible region (Fig. 2) was generally very similar to that recorded by Wagner-Jauregg *et al.* (*loc. cit.*) for ethyl 2-ethylazulene-6-carboxylate and also to that of ethyl azulenecarboxylate.

Although the evidence is thus negative, it seems clear that the heptalene structure is not characterised by a stability sufficient to enable it to be produced in workable yield, if at all, by dehydrogenation at elevated temperatures of bicyclo[5 : 5 : 0]dodecane derivatives. Under more severe conditions this system rearranges to yield dimethylnaphthalenes and intermediate products, whilst under milder conditions traces of deep-blue reaction products are formed, which are more likely to be azulenes, formed by rearrangement reactions, than heptalene derivatives.

Fig. 2.
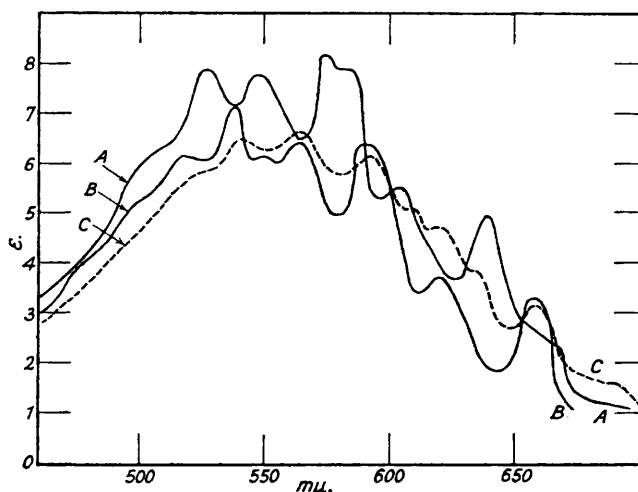
A. *Ethyl azulenecarboxylate.*
B. *Blue hydrocarbon from the dehydrogenation of* (V).
C. *Blue ester from the dehydrogenation of* (V).

Although this failure to prepare heptalene derivatives by dehydrogenation does not prove that this system is not capable of existence, it does suggest that it is not as stable as might be expected on theoretical grounds and that reactions milder than catalytic dehydrogenation should be employed in its synthesis. An attempt has therefore been made to synthesise heptalenes in the following manner :

(VI.)   (VII.)   (VIII.)

(IX.)   (X.)   (XI.)   (XII.)
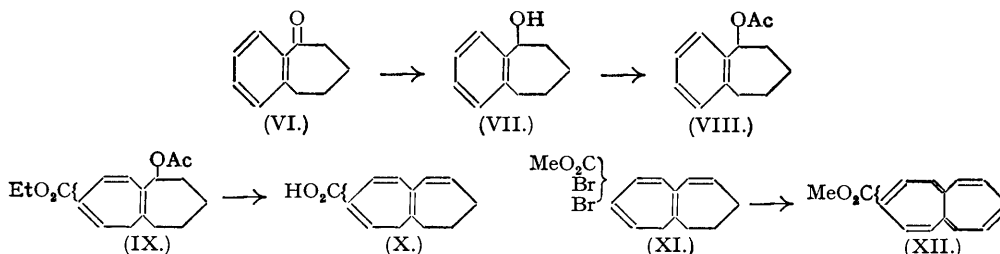
2 : 3-*Benz*cyclohept-2-en-1-yl acetate (VIII) was prepared from 2 : 3-benz*cyclo*hept-2-en-1-one (VI) by reducing it to 2 : 3-benzcyclo*hept-2-en*-1-ol (VII) with sodium and alcohol and treating this with acetic anhydride. (VIII) was treated with ethyl diazoacetate in the usual way and yielded a high-boiling product which was probably a mixture of isomeric ethyl acetoxy*bicyclo*-[5 : 5 : 0]dodecatrienecarboxylates (IX), since on hydrolysis and dehydration of the resulting hydroxy-acid mixture (A) an acid with the properties expected of a bicyclo[5 : 5 : 0]*dode-catetraenecarboxylic acid* (X) was obtained. In order to show that this acid had a bicyclo[5 : 5 : 0]-dodecane and not a benzenoid structure, its *methyl* ester was hydrogenated in the presence of a mild palladium–calcium carbonate catalyst, whereupon it quickly absorbed hydrogen equivalent to two double bonds; this precludes the presence of a benzenoid nucleus in the molecule. Under similar conditions ethyl bicyclo[5 : 5 : 0]dodecatrienecarboxylate (III) absorbed hydrogen equivalent to one double bond to yield products showing almost identical light-absorption characteristics. bicyclo[5 : 4 : 0]Undecatrienecarboxylic acid also absorbed but one mole of

hydrogen in the presence of palladium–calcium carbonate. It is suggested that in each of these cases two double bonds escape attack, the one through its position at the site of ring fusion and the other because of conjugation with the carboxyl group (cf. Farmer and Galley, *J.*, 1933, 687), as exemplified in structure (XIII).

A secondary product in the dehydration of the hydroxy-acid mixture (*A*) was a hydrocarbon which closely resembling 1 : 2-*benz*cyclohepta-1 : 3-*diene* (XIV) (see Table) which was prepared for comparison by dehydration of (VII). On the basis of this resemblance and of analysis, it is formulated as a mixture of *methyl*-1 : 2-*benz*cyclohepta-1 : 3-*dienes* (XV), probably formed by rearrangement of the *cyclo*heptatriene ring during the dehydration.

(XIII.)   (XIV.)   (XV.)
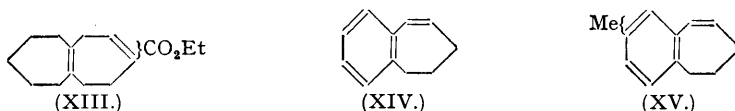
The methyl ester of (X) behaved exactly like (V) on dehydrogenation. It was therefore treated with 2 mols. of *N*-bromosuccinimide, bromine equivalent to 1·8 bromine atoms being absorbed. Attempts to purify the products for analysis by distillation failed because of decomposition. Alcoholic silver nitrate solution removed almost all the bromine, indicating that it was held as " allyl " bromide and not as " vinyl " bromide.

TABLE.

	B. p.	$n_D^{19.5}$.	$\varepsilon_{max.}$.	$m\mu$.
(XIV)	108—110°/18 mm.	1·5873	15,600	254
(XV) (?)	*ca.* 100°/17 mm.	1·5869	13,400	251—257

The dehydrobromination of the bromide was carried out under varying conditions with different dehydrobrominating agents, but all the products absorbed ultra-violet light much less strongly than did the starting material; thus rearrangement to more weakly absorbing benzenoid structures had probably taken place. As the tetraene ester is fairly stable, it must be concluded that the introduction of two more double bonds into the molecule produces considerable strain which favours rearrangement to a more stable structure.

It is concluded from these observations that the heptalene structure is not one easily susceptible of synthesis and this fact argues strongly against the possibility of its being very stable or aromatic in type.

EXPERIMENTAL.

M. p. are uncorrected.

bicyclo[5 : 5 : 0]*Dodeca*-2 : 4 : 7(1)-*triene-x-carboxylic Acid.*—1 : 2-Benz*cyclo*heptene (56 g.; Plattner, *Helv. Chim. Acta*, 1944, **27**, 174) was treated dropwise with ethyl diazoacetate (6 g. of 85%) at 130—135° during 2 hours, and the temperature then raised slowly during a further 2 hours to 165°. After being cooled to 130°, the mixture was treated with a further 6 g. of ethyl diazoacetate and the heating repeated as above. Distillation of the reaction mixture gave recovered 1 : 2-benz*cyclo*heptene (52 g.), b. p. 100—105°/15 mm., and a fraction (9 g.), b. p. 120—200°/15 mm. The recovered hydrocarbon was retreated as described above and, after treatment of the material ten times in this manner, the combined products were redistilled to yield recovered 1 : 2-benz*cyclo*heptene (15 g.) and a crude ester fraction (16 g.), b. p. 160—190°/13 mm., as a pale-yellow mobile liquid which failed to give the characteristic norcaradiene colour reaction with concentrated sulphuric acid. Since it could not be purified by fractional distillation, it was hydrolysed to facilitate removal of nitrogenous impurities.

The crude ester (8·0 g.) was heated under reflux for 8 hours with a solution of potassium hydroxide (4 g.) in water (4 c.c.) and alcohol (20 c.c.). The alcohol was then distilled off under reduced pressure, water added, and the solution extracted with ether. After acidification of the aqueous layer, the liberated acid was taken up in ether, and the ethereal layer well washed with water to free it from water-soluble acids, and dried (Na₂SO₄). After removal of the ether the *acid* (3·3 g.) distilled as a highly viscous oil, b. p. 145—155°/0·4 mm. (Found : C, 76·4 ; H, 7·4. $C_{13}H_{16}O_2$ requires C, 76·5 ; H, 7·8%).

Hydrogenation of bicyclo[5 : 5 : 0]*Dodecatrienecarboxylic Acid.*—(*a*) In the presence of palladium–calcium carbonate at atmospheric pressure, absorption of hydrogen was equivalent to only 0·9 mol.

(*b*) In the presence of colloidal palladium at atmospheric pressure, hydrogen equivalent to 1·9 double bonds was absorbed, and the product of reaction was a highly viscous, almost colourless oil, which slowly reduced potassium permanganate in acetone or aqueous acid solution. This was indicative of the presence of a third double bond, and the use of a more active catalyst was explored.

(*c*) In the presence of a colloidal platinum catalyst at atmospheric pressure, hydrogen equivalent to 3·07 double bonds was absorbed ; the product, *bicyclo*[5 : 5 : 0]*dodecanecarboxylic acid*, was a pale yellow oil which did not reduce potassium permanganate solution.

Ethyl bicyclo[5 : 5 : 0]*Dodeca*-2 : 4 : 7(1)-*trienecarboxylate.*—Esterification of the acid (2 g.) with alcohol (6 c.c.) and concentrated sulphuric acid (0·6 c.c.) yielded this ester (1·3 g.) as a pale yellow viscous oil, b. p. 117—180°/15 mm. Its absorption spectrum is recorded in Fig. 1.

Dehydrogenation of bicyclo[5 : 5 : 0]*Dodecatrienecarboxylic Acid and the Ethyl Ester.*—(a) *Experiments in the liquid phase.* Distillation of the acid (1 g.) from palladium–charcoal (0·2 g.) in the manner recommended by Plattner and Wyss (*Helv. Chim. Acta*, 1940, **23**, 907) caused considerable charring, and only one drop of a low-boiling mobile greenish oil was obtained. The use of sulphur to effect dehydrogenation was also unsuccessful.

(b) *Experiments in the vapour phase.* (i) (cf. Linstead, *J.*, 1937, 1146). The ester was delivered slowly into a catalyst chamber at a rate of 0·005 c.c. per minute through a fine capillary tube. The catalyst tube (7·5 cm. long, 1·5 cm. in diameter) was packed with a mixture of 30% palladium–charcoal (0·78 g.), prepared according to the directions of Linstead (*loc. cit.*), and 5% palladium–asbestos (0·7 g.), and was heated in a closely-fitting solid copper block made in two halves. The outlet from the receiver was connected to a Dumas nitrometer where the gas evolved was collected and measured over 50% potassium hydroxide solution. The optimum temperature for dehydrogenation was found to be 350—360°. At 310°, evolution of hydrogen was very slow. This apparatus gave good yields of ethyl azulene-carboxylate from ethyl bicyclo[5 : 4 : 0]dodecatrienecarboxylate. Under the above conditions the ester (2·5 g.) yielded a colourless mobile liquid distillate (0·5 c.c.) with the evolution of gas equivalent to *ca.* four mols. per mol. of ester. The distillate was heated under reflux with alcoholic alkali for 1 hour, and one drop of acidic product separated. The bulk of the material (0·36 g.), which was neutral, was treated with picric acid (0·18 g.) in alcohol (3·7 c.c.). A picrate separated, after warming, as orange needles, which were recrystallised twice from alcohol and then had m. p. 121—122° (mixed m. p. with picric acid, *ca.* 105°) (Found : C, 55·8; H, 3·9. Calc. for $C_{18}H_{15}O_7N_3$: C, 56·1; H, 3·9%). The once-crystallised material (0·05 g.; m. p. 120—122°) was freed from picric acid by shaking an ethereal solution of it with dilute sodium hydroxide solution. Removal of the ether left one drop of a colourless mobile oil, which was used for the determination of the absorption spectrum which was characteristically that of an alkylated naphthalene (cf. Laszlo, *loc. cit.*). This product was thus almost certainly a mixture of dimethylnaphthalenes.

(ii) Dehydrogenations were therefore next conducted in an apparatus (see Part I, *loc. cit.*) designed to give the briefest possible period of contact. With a rate of 0·18 c.c. per minute, the distillate (2·0 g.) was deep blue in colour. It was redistilled, the following fractions being collected : (1) b. p. 110—120°/15 mm. (0·15 g., deep blue); (2) b. p. 120—140°/15 mm. (0·03 g., deep blue); (3) b. p. 140—170°/15 mm. (0·70 g., intense violet-blue); and (4) b. p. 170—175°/15 mm. (0·30 g., greenish).

Fraction (1) was dissolved in light petroleum and extracted with ice-cold 85% phosphoric acid, the red phosphoric acid extracts were washed with light petroleum, and the azulene-like hydrocarbon was regenerated by pouring into a vigorously stirred mixture of ether, ice, and water. The ethereal layer was then washed with dilute alkali and water, dried, and evaporated in a current of carbon dioxide. The residue was an intensely ultramarine-coloured oil (*ca.* 5 mg.). It was not possible to obtain a crystalline derivative; the absorption spectrum of this material in the visible region was measured directly and is recorded in Fig. 2.

Fraction (3) was separated, in the same way as fraction (1), into a deep-blue part (0·03 g.), soluble in 85% phosphoric acid, and a phosphoric-acid-insoluble part. The deep-blue oil did not yield a picrate or 2 : 4 : 6-trinitrotoluene complex, but its ester function was clear from its reaction with alkali. Its absorption spectrum in the visible region is also recorded in Fig. 2.

The phosphoric-acid-insoluble products (5 g.) from 3 dehydrogenations were hydrolysed with 10% aqueous potassium hydroxide. The neutral products (0·52 g.) yielded with picric acid (0·25 g.) in alcohol (5 c.c.) the same picrate (0·11 g., m. p. 120—121°) as was obtained in previous dehydrogenations. The material which did not react with picric acid was recovered, and found to have an absorption spectrum very similar to that of 1 : 2-benz*cyclo*heptene. It is possible, therefore, that this material contained partial dehydrogenation products such as methyl-1 : 2-benz*cyclo*heptenes.

bicyclo[5 : 4 : 0]*Undeca*-2 : 4 : 7(1)-*triene-x-carboxylic Acid.*—To tetrahydronaphthalene (198 g.) heated to 140—150° in an oil-bath ethyl diazoacetate (56·4 g.) was added dropwise, with constant stirring, during 8 hours. The mixture was then heated for a further hour to complete the reaction, the excess of tetralin hydronaphthalene was distilled off under reduced pressure, and a crude reaction product, b. p. 130—200°/20 mm., collected. Several unsuccessful attempts were made to purify this material by fractional distillation. The crude condensation product (86 g.) was therefore added to 50% aqueous potassium hydroxide (80 c.c.) and ethyl alcohol (200 c.c.) and the whole heated under reflux for 12 hours. After cooling the liquid was decanted from a crystalline deposit of potassium maleate and steam-distilled until free from alcohol. The residue was extracted with ether, the aqueous layer was acidified and extracted with ether, and the ethereal extracts were dried (Na₂SO₄) and evaporated. On distillation of the residue *in vacuo*, there was obtained a sticky, pale yellow oil (40 g.), b. p. 168—178°/2 mm. Redistillation yielded the pure *acid* (31·1 g.), b. p. 161—164°/1·5 mm., which did not crystallise (Found : C, 77·0; H, 8·3; equiv., 190·7. $C_{12}H_{14}O_2$ requires C, 77·1; H, 8·2%; equiv., 190·2).

The pure acid (20 g.; b. p. 161—164°/1·5 mm.) was dissolved in absolute alcohol (60 c.c.), concentrated sulphuric acid (6 c.c.) added, and the mixture boiled under reflux for 5 hours. Most of the alcohol was then distilled off, water was added, and the ester taken up in ether. After being washed with sodium carbonate solution and water, the ethereal extracts were dried and evaporated. On distillation of the residue *in vacuo*, the *ester* (16 g.) b. p. 175—178°/20 mm., was obtained (Found : C, 77·0; H, 8·3. $C_{14}H_{18}O_2$ requires C, 77·1; H, 8·2%). The absorption spectrum of this substance is recorded in Fig. 1.

The pure acid (10 g.) was shaken with phosphorus trichloride (3·6 g.) for 1 hour and then allowed to stand until the two layers had separated completely. The mixture was cooled in a freezing mixture and after a short time the acid chloride was decanted from the viscous phosphoric acid and was added dropwise to concentrated ammonia solution (50 c.c.) with shaking. A curdy yellow mass, changing to a white one, was formed. It was taken up in ether and washed with 2% sodium hydroxide solution. After removal of the ether, a resinous mass remained which was crystallised with difficulty from 80% alcohol. After five crystallisations a small quantity of a pure *amide* (0·1 g.)., m. p. 119·5—121°, was obtained (Found : C, 76·2; H, 7·9. $C_{12}H_{15}ON$ requires C, 75·9; H, 7·8%).

Hydrogenation of bicyclo[5 : 4 : 0]*Undecatrienecarboxylic Acid.*—In the presence of palladium–

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calcium carbonate at atmospheric pressure, hydrogen equivalent to 0·9 double bond was absorbed, and the product was an almost colourless, glutinous oil, b. p. 155—160°/1 mm. In the presence of colloidal platinum, hydrogen equivalent to 2·94 double bonds was absorbed.

Dehydrogenation of bicyclo[5 : 4 : 0]*Undecatrienecarboxylic Acid.*—The acid (16·5 g.) was heated with 20% palladium–charcoal in a long-necked flask in a current of air-free carbon dioxide. The gases evolved in the reaction were collected in a Dumas nitrometer. Hydrogen evolution began at 210°, became vigorous at 270°, and ceased after 2 hours when only half the expected hydrogen had been evolved. The reaction products were then taken up in ether, washed with alkali, and dried, and the ether evaporated off. On distillation of the residue there was obtained a distillate (7 g.), b. p. 113—133°/20 mm., which yielded a colourless mobile oil, b. p. 114—122°/19 mm., on redistillation. This oil (4·72 g.) with picric acid (5·7 g.) in alcohol (30 c.c.) gave, on cooling, pale orange needles (6·02 g.), m. p. 120—123°. These crystals were recrystallised from alcohol (40 c.c.) to yield a picrate (3·48 g.), m. p. 123—124° (Found : C, 54·7; H, 3·4. Calc. for $C_{17}H_{13}O_7N_3$: C, 55·0; H, 3·5%), undepressed by a mixture of 1- (65 parts) and 2-methyl-naphthalene picrate (35 parts). On regeneration from the picrate, the hydrocarbon gave an absorption spectrum closely similar to that of 1-methylnaphthalene.

2 : 3-Benzcycloheptenol.—Sodium (30 g.) was added in small pieces during 1 hour to a boiling solution of 2 : 3-benzcycloheptenone (32 g.) in absolute alcohol (320 c.c.). When all the sodium was dissolved, the mixture was poured into water and the crystalline *alcohol* filtered off. A further quantity of the alcohol was obtained by extracting the filtrate with ether, and the combined materials were then crystallised from light petroleum (b. p. 35—50°) and yielded the almost pure alcohol, m. p. 100° (23 g.). The mother-liquors were evaporated to dryness and distilled, the fraction, b. p. 140—150°/16 mm., being retained. It was crystallised from light petroleum and yielded a further quantity (3 g.) of the alcohol. The alcohol sublimed in long colourless needles, m. p. 101° (Found : C, 81·49; H, 8·7. $C_{11}H_{14}O_2$ requires C, 81·45; H, 8·7%).

2 : 3-Benzcycloheptenyl Acetate.—The once-crystallised 2 : 3-benzcycloheptenol (54 g.) was mixed with acetic anhydride (33 c.c., 10% excess) and slowly heated to 120° in an oil-bath during 6 hours. The mixture was then poured into water, and the *ester* taken up in ether. The ethereal layer was shaken with sodium carbonate solution until free from acetic anhydride and acetic acid, washed with water, and dried (Na_2SO_4). After removal of the ether the residue was distilled, the fraction, b. p. 147—148°/13 mm. (63·7 g., 94%), being collected. After cooling the ester set to a solid mass which was recrystallised from light petroleum to yield crystals, m. p. 37° (Found : C, 76·4; H, 8·0. $C_{13}H_{16}O_2$ requires C, 76·4; H, 7·9%).

Ethyl Acetoxy bicyclo[5 : 5 : 0]*dodecatrienecarboxylate.*—2 : 3-Benzcycloheptenyl acetate (62 g.) in a three-necked flask (250-c.c. capacity) immersed in an oil-bath at 135—140° and equipped with a stirrer, dropping funnel, and air condenser was treated dropwise with 90% ethyl diazoacetate (12 c.c.) during 5 hours. The temperature was then slowly raised to 160° during 3 hours. The product was distilled and the low-boiling fraction, b. p. 105—130°/1 mm., which was mainly unchanged acetate, re-treated with ethyl diazoacetate. The combined high-boiling products (48 c.c.; b. p. 120—170°/0·4 mm.) from four such successive condensations were redistilled at 0·5 mm., and fractions, b. p. 100—145° (pale yellow mobile oil; 5·0 g.) and 145—185° (pale orange viscous oil; 19·0 g.), were collected. As it was impossible to purify fraction (ii) by fractionation it (3 g.) was directly hydrolysed by boiling under reflux with potassium hydroxide (3 g.) in water (100 c.c.) until dissolution was complete (4 hours). The acid was recovered in the usual manner and distilled at 150—200°/0·2 mm. Carbon and hydrogen contents indicate that it is a mixture of bicyclo[5 : 5 : 0]dodecatetraenecarboxylic acid and some hydroxybicyclo-[5 : 5 : 0]dodecatrienecarboxylic acid (Found : C, 75·3; H, 7·2. Calc. for $C_{13}H_{14}O_2$: C, 77·2; H, 6·9. Calc. for $C_{13}H_{16}O_3$: C, 70·9; H, 7·3%). Use of concentrated alcoholic potassium hydroxide gave similar results.

bicyclo[5 : 5 : 0]*Dodecatetraenecarboxylic Acid.*—The mixed acids (b. p. 160—200°/0·4 mm., 6·2 g.) obtained by hydrolysis of the crude acetoxy-ester were heated to 160° *in vacuo* with finely-ground fused potassium hydrogen sulphate (14·0 g.) for ½ hour. After cooling, the material was mixed with water and ether. The ethereal layer (*A*) was shaken with 5% sodium hydroxide solution, and this aqueous layer twice washed with ether to remove neutral decarboxylation products. The original aqueous layer, after acidification, was extracted with ether, and this extract (*B*) washed with water and dried (Na_2SO_4). The ether was removed from (*B*), and the *acid* (4·06 g.) distilled, b. p. 150—160°/0·4 mm., as a viscous pale yellow oil (Found : C, 76·7; H, 6·7. $C_{13}H_{14}O_2$ requires C, 77·2; H, 6·9).

Methyl-1 : 2-benzcyclohepta-1 : 3-diene.—The ethereal extract (*A*) which contained the neutral material was dried (Na_2SO_4), and the ether distilled off. A mobile oil with a pleasant petrol-like odour remained. It was distilled into 2 fractions at 17 mm. pressure : b. p. 90—100° (0·5 g.; colourless mobile oil) and b. p. 200—220° (0·2 g., pale yellow viscous oil). The former was redistilled and the *diene* boiling at about 100° collected (the quantity was too small to obtain an acurate boiling point) (Found : C, 90·9; H, 9·0. $C_{12}H_{14}$ requires C, 81·1; H, 8·9%), $n_D^{19.5}$ 1·5869, $\varepsilon_{max.}$ 13,400 at 251—257 mμ.

1 : 2-Benzcyclohepta-1 : 3-diene.—Pure 1 : 2-benzcyclohepten-3-ol (2·21 g.) was heated with finely ground potassium hydrogen sulphate (4·0 g.) *in vacuo* at 160° for 1 hour. The hydrocarbon (1·6 g.) was then extracted with ether and distilled at 10 mm. to yield fractions, (i) b. p. 80—85° (0·8 g.), and (ii) b. p. 140—150° (0·6 g.). Fraction (i) was redistilled, the diene, b. p. 108—110°/18 mm., being collected as a colourless mobile oil with a pleasant petrol-like odour (Found : C, 91·5; H, 8·5. Calc. for $C_{11}H_{12}$: C, 91·7; H, 8·3%, $n_D^{19.5}$ 1·5873, $\varepsilon_{max.}$ 15,600 at 254 mμ. (cf. Kipping and Hunter, *J.*, 1903, **83**, 246).

Methyl bicyclo[5 : 5 : 0]*Dodecatetraenecarboxylate.*—The pure distilled acid (3·18 g.) was heated under reflux in absolute methyl alcohol (15 c.c.) containing concentrated sulphuric acid (1·5 c.c.) for 2 hours, poured into water, and worked up in the usual manner. The ester (3·28 g.) was distilled, and the fraction, b. p. 95°/0·01 mm., collected as a pale yellow oil (Found : C, 77·4; H, 7·6. Calc. for $C_{14}H_{16}O_2$: C, 77·7; H, 7·5%), n_D^{18} 1·5682, $\varepsilon_{max.}$ 11,450 at 245 mμ., $\varepsilon_{inflex.}$ 1130 at 320 mμ.

When the ester was hydrogenated in the presence of palladium–calcium, hydrogen equivalent to 1·8 double bonds was absorbed. The hydrogenated ester was recovered by filtering off the catalyst and distilling off the alcohol. The oily residue was distilled at 0·1 mm. and the fraction, b. p. 95°, reserved for study of the absorption spectrum; it showed a continuous absorption of light throughout the

spectrum, which was almost identical with that found for the hydrogenation product of ethyl *bicyclo*[5 : 5 : 0]dodecatrienecarboxylate.

Bromination and Subsequent Dehydrobromination of Methyl bicyclo[5 : 5 : 0]*Dodecatetraenecarboxylate.*—*N*-Bromosuccinimide (1·67 g., 2 mols.) was added to pure methyl *bicyclo*[5 : 5 : 0]dodecatetraene-carboxylate (1 g.) in dry carbon tetrachloride (4 c.c.). Freshly prepared benzoyl peroxide (0·05 g. ; no reaction took place in the absence of this catalyst) was then added and the mixture heated under reflux. Reaction quickly set in, as was shown by the tendency of the insoluble material to float on the surface of the carbon tetrachloride. After 2 hours a test portion of the solid was acidified with dilute acid, and a drop of potassium iodide added. Only a pale yellow colour was produced, indicating that the reaction was almost complete. The mixture was then cooled, and the succinimide filtered off and dried (0·90 g. ; theoretical quantity, 0·93 g.). The filtered carbon tetrachloride solution, evaporated to dryness left a dark brown viscous mass. An attempt to obtain pure material by distillation proved unsuccessful as the material readily decomposed into a charred mass. A drop of the material, treated with alcoholic silver nitrate solution, instantaneously yielded a yellow precipitate of silver bromide, thus demonstrating that the bromine was held in an allylic position in the molecule. A portion of the bromo-derivative was heated with a molecular quantity of diethylaniline for 1 hour at 100°, but, after working up, the product still gave a precipitate with alcoholic silver nitrate ; the bromine was completely removed only after 4 hours on a steam-bath.

The material was then mixed with ether and extracted with dilute acid. The ethereal layer was washed with water and finally dried (Na_2SO_4). Removal of the ether and distillation gave viscous oils, (i) b. p. 100—110°/0·1 mm. (pale yellow, 0·1 g.), and (ii) b. p. 110—130°/0·1 mm. (0·1 g.). Fraction (i) gave a negative test with alcoholic silver nitrate and contained only 0·86% of bromine, showing that only a negligible quantity of the bromine was held as vinyl bromide. Fraction (i) showed two absorption maxima : $\varepsilon_{max.}$ 7560 at 241 mμ. and $\varepsilon_{max.}$ 7560 at 256 mμ. Fraction (ii) showed $\varepsilon_{max.}$ 7000 at 245 mμ. and $\varepsilon_{max.}$ 7130 at 256 mμ. Thus both fractions had an absorption *less* than that of methyl *bicyclo*[5 : 5 : 0]-dodecatetraenecarboxylate.

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