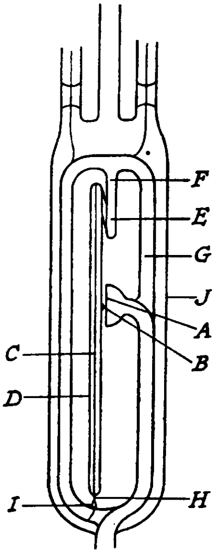
NOTES.

717. *A New All-glass Membrane Manometer.*

By A. Kabesh and R. S. Nyholm.

In pressure measurements involving substances which are capable of attacking mercury all-glass manometers have proved to be of great value. They may be used as direct-reading instruments after being calibrated, but as a rule they are employed as null instruments. The gauge which changes its shape when pressure is applied inside or outside indicates a balance between the pressure to be measured, *e.g.* of the corrosive gas, and an adjustable known pressure usually measured by a mercury manometer. In both methods for using the gauge the deformation is suitably magnified and followed by a convenient apparatus. Several manometers of this type are described in the literature, a summary of which is given by Partington ("An Advanced Treatise on Physical Chemistry," Longmans, Green and Co., 1950, Vol. I, p. 656). Our experience in the use of manometers over a fairly wide range of temperature, involving successive heating and cooling of the gauge, has shown that many of these devices are unsatisfactory. The chief difficulty lies in the magnification system which is frequently affected by variation in temperature. Furthermore, whilst most gauges are sensitive and reliable when used at a fixed temperature or over a small range in temperature, the zero setting of the gauge is usually found to be subject to large and inconsistent changes with change in temperature. By zero setting is meant the small positive pressure applied on the diaphragm to make or break an electrical circuit.

Some experimenters have tried to overcome this difficulty by keeping the dead space at the head of the gauge as small as possible and at the same time keeping the head separately heated to a constant temperature. Others have tried to calibrate the gauge before using it. The first method has the disadvantage that there is a temperature gradient between one end of the reaction vessel and the other. We have found the second method unsuitable because successive heating and cooling of the gauge gave inconsistent zero readings. These difficulties called for the construction of a gauge which should conform to the following requirements: (*a*) the gauge must be sensitive to at least 0·1 mm. Hg, and at the same time be rigid enough to withstand fairly large pressure differences without breaking; (*b*) the adjustment of the contact points should be fairly simple; (*c*) the zero setting of the gauge should be reproducible.



The Apparatus.—The gauge shown in the figure substantially fulfils the requirements detailed above. The actual dimensions of an instrument of this type depend upon the circumstances for which it is required; in our own case the dimensions are given below. The membrane *A* (1·5—2·0 cm. in diameter) was made as thin as possible, consistent with the necessary mechanical strength; the thickness was not measured. Several membranes were blown and a suitable one chosen from these. The head of the gauge was bent so that the membrane *A* was in a vertical position, and a glass rod *G* was sealed to it to act as a supporting frame. The lever *D*, 10 cm. long, was made by sealing a platinum wire *C*, 0·45 mm. in diameter, in a glass capillary tube 3 mm. in external diameter. One end of the lever was sealed to a glass spiral *E* consisting of 2 turns, of approximately 2·5 cm. diameter, of glass rod, 0·3 cm. in diameter; the spiral was then sealed to the frame at *F*. Meanwhile, the glass pip *B* was made to rest with slight pressure on the membrane at the point of maximum tilting. According to Frank and Bromeser's theory for the bending of a plate of this type (*Sitzungsber. Ges. Morphol. Physiol.*, 1912, **28**, 45) the point of maximum tilting occurs at a point $r/\sqrt{3}$ from the centre. The platinum tip *H*, which was left uncovered at the end of the lever, should be only just making contact with the platinum stirrup *I*, sealed to the frame. The adjustment of the contact points was then completed before sealing the assembly in the outer jacket *J*. Once this adjustment has been made the apparatus should need no further attention. It is advisable to have the lever in a vertical position parallel to the plane of the membrane, thus reducing the effect of gravity.

In this gauge an attempt has been made to eliminate the usual factors which normally result in an irregular variation of the zero setting, but it is obvious that nothing can be done to change the inherent properties of the glass itself. The variation of the zero setting with temperature is linear and is affected by both the diameter and the thickness of the diaphragm. Other things being equal, the zero setting was found to increase with increasing temperature, possibly owing to the variation of the modulus of elasticity of glass with temperature. It is of interest to note that a gauge of this type, but made of silica, showed a decrease in zero setting with increasing temperature. Silica, unlike most elastic solids, shows an increase in its modulus of elasticity with increase of temperature.

This gauge has been used successfully in the measurement of the vapour pressures of the stannic halides over the temperature range from room temperatures to about 340° (see *J.*, 1951, 3245).

The authors are indebted to Mr. Sharaf El-Din and Mr. J. Frost for technical assistance in the development of this manometer.

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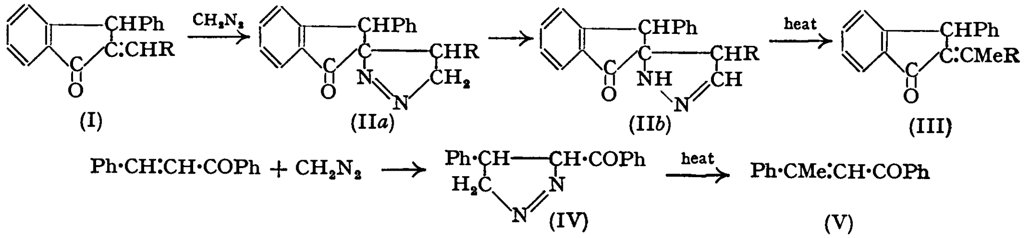
718. *Action of Diazomethane on 2-Arylidene-3-phenylindan-1-ones.*

By Ahmed Mustafa and Mustafa Kamal Hilmy.

In continuation of investigations on the action of diazomethane on aromatic compounds (Schönberg and Mustafa, *J.*, 1946, 746; 1948, 605; Schönberg, Mustafa, and Hilmy, *J.*, 1947, 1045; Mustafa, *J.*, 1949, 234), the behaviour of the 2-arylidene-3-phenylindan-1-ones listed in Table I towards diazomethane in ether–methanol has been studied. In all cases the coloured starting materials (I) were transformed into colourless or almost colourless substances (II*a* or *b*) containing active hydrogen. Structure (II*b*) is preferred, and (II*a*) is regarded as an intermediate product. These products were decomposed by heat to the alkylated ethylenes (III) [cf. the thermal decomposition of 3-benzoyl-4-phenyl-Δ^1-pyrazoline (IV) obtained by the action of ethereal diazomethane on benzylideneacetophenone], which yielded the dypnone (V) (Smith and Pings, *J. Org. Chem.*, 1937, **2**, 23; Smith and Howard, *J. Amer. Chem. Soc.*, 1943, **65**, 159).



When (III; R = C_6H_4·OMe-*p*) is treated with alcoholic hydrochloric acid or (15%) potassium hydroxide, it yielded *p*-methoxyacetophenone and 3-phenylidan-1-one, which were identified as the corresponding 2 : 4-dinitrophenylhydrazones (cf. the hydrolysis of 2-hydroxymethylene-3-phenylindan-1-one with 2% potassium hydroxide; Johnson and Shelberg, *J. Amer. Chem. Soc.*, 1945, **67**, 1758). The action of hydroxylamine hydrochloride in the presence of aqueous sodium hydroxide on (III; R = C_6H_4·OMe-*p*) or (I; R = C_6H_4·OMe-*p*) gave, as expected, 3-phenylidan-1-one oxime.

Experimental.—Substituted 2-Arylidene-3-phenylindan-1-ones (I).—3-Phenylindan-1-one (0·1 mol.) (Pfeiffer and de Waal, *Annalen*, 1935, **520**, 185) and the appropriate aldehyde (0·1 mol.) in ethyl alcohol (15 c.c.) were treated with 10% aqueous sodium hydroxide (1·5 c.c.), whereupon the 2-arylidene derivative separated quickly. It was filtered off, washed with water, and recrystallised from benzene. The yellow *2-arylidene* compounds listed in Table I were thus prepared; all gave yellow or orange solutions in cold concentrated sulphuric acid.

Table I.

Substituted 2-arylidene-3-phenylindan-1-ones (I).

				Found, %		Reqd., %	
Aryl =	M. p.	Yield, %	Formula	C	H	C	H
Phenyl [a]	158°	85%	$C_{22}H_{16}O$	89·2	5·4	89·2	5·4
o-C_6H_4·OMe	199	70%	$C_{23}H_{18}O_2$	84·6	5·5	84·7	5·5
p-C_6H_4·OMe [a]	174	82%	$C_{23}H_{18}O_2$	84·5	5·3	84·7	5·5
p-C_6H_4Me	220	80%	$C_{23}H_{18}O$	89·2	5·7	89·0	5·8
m-C_6H_4·NO_2	194	36%	$C_{22}H_{15}O_3N$ [b]	77·2	4·0	77·4	4·4
o-C_6H_4Cl	140	62%	$C_{22}H_{15}OCl$ [c]	80·0	4·5	79·9	4·5
2-Furyl	160	45%	$C_{20}H_{14}O_2$	84·0	4·7	83·9	4·9

[a] Pfeiffer and de Waal, *loc. cit.*

[b] Found : N, 4·0. Reqd. : N, 4·1%.

[c] Found : Cl, 10·5. Reqd. : 10·7%.

Action of Diazomethane on 2-Arylidene-3-phenylindan-1-ones. 2-*p*-Methoxybenzylidene-3-phenylindan-1-one (I; R = C_6H_4·OMe-*p*) (1 g.) (Pfeiffer and de Waal, *loc. cit.*) in cold methyl alcohol (1 c.c.) was treated with an excess of cold, ethereal diazomethane solution [from nitrosomethylurea (8 g.)], and the mixture left at 0° for 72 hours, during which fresh amounts of etheral diazomethane solution were added. The ether was then evaporated off and the resulting colourless crystals were collected, washed with light petroleum (b. p. 40—60°), and crystallised from benzene–light petroleum (b. p. 40—60°) with decomposition. *3-Phenylindan-1-one-*2-spiro-2′-(4′-p-*methoxyphenyl-*Δ^1-*pyrazoline*) (II; R = C_6H_4·OMe-*p*), m. p. 124°, is easily soluble in benzene or hot ethyl alcohol, but difficultly soluble in light petroleum (b. p. 50—60°) (Found : C, 78·1; H, 5·2; N, 7·5. $C_{24}H_{20}O_2N_2$ requires C, 78·2; H, 5·4;

N, 7·6%). The *pyrazoline* derivatives listed in Table II were similarly prepared; they were crystallised from benzene–light petroleum, and in cold concentrated sulphuric acid gave yellow or orange solutions with much decomposition.

TABLE II.

Substituted pyrazoline derivatives (II).

R	M. p.[a] (decomp.)	Formula	Found, % C	H	N	Required, % C	H	N
Ph	120—122°	$C_{23}H_{18}ON_2$	81·5	5·3	7·9	81·6	5·3	8·3
o-C_6H_4·OMe	118	$C_{24}H_{20}O_2N_2$ [a]	78·1	5·6	7·2	78·2	5·4	7·6
p-C_6H_4·OMe	124	$C_{24}H_{20}O_2N_2$	78·0	5·2	7·5	78·2	5·4	7·6
p-C_6H_4Me	133—134	$C_{24}H_{20}ON_2$	81·7	5·7	7·9	81·8	5·7	7·95
m-C_6H_4·NO_2	136	$C_{23}H_{17}O_3N_3$	71·8	4·3	10·8	72·1	4·4	10·97
o-C_6H_4Cl	125	$C_{23}H_{17}ON_2Cl$ [b]	74·0	4·6	7·3	74·1	4·6	7·5
Furyl	128	$C_{21}H_{16}O_2N_2$	76·5	4·5	8·2	76·8	4·8	8·5

[a] Found: Active H, 0·26. Reqd.: Active H, 0·27%. [b] Found: Cl, 9·3. Reqd.: Cl, 9·5%. The compounds were recrystallised from benzene–light petroleum (b. p. 40—60°). In cold, concentrated sulphuric acid, they give yellow to orange solutions with strong decomposition.

Thermal Decomposition of the Pyrazoline Derivatives (II).—(*a*) The spiran (II; R = C_6H_4·OMe-*p*) was heated at 200° (bath-temp.) in a stream of dry carbon dioxide for 0·5 hour. The product, after cooling, was extracted several times with ligroin (b. p. 60—80°); the extracts were evaporated slowly and the resulting yellow crystals of 2-(p-*methoxy-a-methylbenzylidene*)-3-*phenylindan*-1-*one* (m. p. 145°) were filtered off and recrystallised from ethyl alcohol (Found: C, 84·4; H, 5·6. $C_{24}H_{20}O_2$ requires C, 84·7; H, 5·9%). The compound is easily soluble in benzene, but difficulty soluble in light petroleum (b. p. 30—50°) and gives an orange solution with concentrated sulphuric acid.

(*b*) The *o*-methylphenyl isomer (II) was heated at 180° (bath-temp.) for 15 minutes. The o-*methoxybenzylidene* compound (III) formed pale yellow crystals (from ethyl alcohol), m. p. 158—159° (Found: C, 84·5; H, 5·8. $C_{24}H_{20}O_2$ requires C, 84·7; H, 5·9%). It is easily soluble in benzene or acetic acid but difficultly soluble in light petroleum (b. p. 40—60°), and gives a yellowish-orange colour with sulphuric acid.

(*c*) The p-*methylbenzylidene* derivative (III), obtained at 220° (0·5 hour), forms in yellow crystals, m. p. 145—146°, from ethyl alcohol (Found: C, 88·6; H, 6·3. $C_{24}H_{20}O$ requires C, 88·9; H, 6·2%). It gives a yellow solution with sulphuric acid and is easily soluble in benzene or chloroform.

Behaviour of the Olefin (III; R = C_6H_4·OMe-*p*) *towards* (a) *alcoholic hydrochloric acid, and* (b) *alcoholic potassium hydroxide*.—(*a*) The olefin (III; R = C_6H_4·OMe-*p*) was heated under reflux with alcoholic hydrochloric acid [ethyl alcohol (10 c.c.); hydrochloric acid (*d* 1·18) (5 c.c.)] for 3 hours, during which fresh amounts of the acid (about 5 c.c.) were added. On cooling, the reaction mixture was poured into water, extracted with ether, washed with dilute aqueous sodium carbonate and then water, and dried (Na_2SO_4), and the ether evaporated off. The oily residue was washed several times with cold light petroleum (b. p. <40°); some material (*A*) was insoluble. The light petroleum solution was evaporated; the solution of the oily residue in acetic acid was treated with 2 : 4-dinitrophenylhydrazine in acetic acid, and the reaction mixture refluxed for 10 minutes. On concentration and cooling, orange-red crystals of *p*-methoxyacetophenone 2 : 4-dinitrophenyl hydrazone separated, which after recrystallisation from acetic acid had m. p. and mixed m. p. 220°. The insoluble material (*A*) gave similarly 3-phenylindane-1-one hydrazone, orange-red crystals (from acetic acid), m. p. 218° (m. p. and mixed m. p. with an authentic specimen) (Found: C, 64·6; H, 4·1; N, 14·3. $C_{21}H_{16}O_4N_4$ requires C, 64·9; H, 4·1; N, 14·4%).

(*b*) A solution of the olefin (0·5 g.) in ethyl alcohol (10 c.c.) and 15% alcoholic potassium hydroxide (5 c.c.) were refluxed for 3 hours. The reaction mixture was poured into water and worked up as above, giving the same products.

Similarly, the *p*-methylbenzylidine compound (III; R = C_6H_4·Me-*p*) and alcoholic potassium hydroxide led to *p*-methylacetophenone and 3-phenylindan-1-one, which were identified as the corresponding 2 : 4-dinitrophenylhydrazones (m. p. and mixed m. p.).

Action of Hydroxylamine Hydrochloride on 2-*p*-*Methoxybenzylidene*-3-*phenylindane*-1-*one*.—The compound (I; R = C_6H_4·OMe-*p*) (0·3 g.) and hydroxylamine hydrochloride (0·4 g.) in ethyl alcohol (10 c.c.) and alcoholic potassium hydroxide [potassium hydroxide (0·7 g.); water (0·5 c.c.); ethyl alcohol (5 c.c.)] were refluxed for 3 hours (water-bath). The reaction mixture was poured into acidified ice-cold water, extracted with ether, washed with water, dried (Na_2SO_4), and evaporated. The colourless crystals of 3-phenylindan-1-one oxime that separated were recrystallised from ethyl alcohol, and had m. p. and mixed m. p. 143° (Found: C, 80·5; H, 5·7; N, 6·4. Calc. for $C_{15}H_{13}ON$: C, 80·7; H, 5·8; N, 6·3%) (Liebermann and Hartmann, Ber., 1892, **25**, 2124, gave m. p. 141°).

The analogues (I; R = C_6H_4·OMe-*o* and C_6H_4Me-*p*), and the compounds (III; R = C_6H_4·OMe-*o* and -*p*, and C_6H_4Me-*p*) behaved similarly.

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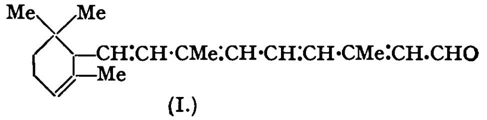
719. *Isomers of Retinene 2 : 4-Dinitrophenylhydrazone.*

By Marc Julia and B. C. L. Weedon.

Recently Braude and Forbes (*J.*, 1951, 1762) reported the oxidation of vitamin A by 2 : 4-dinitrophenylhydrazine in acid solution to an aldehyde which was isolated as its 2 : 4-dinitrophenylhydrazone. This derivative, m. p. 204°, was isomeric with that, m. p. 208°, prepared directly from retinene (vitamin-A aldehyde), and exhibited maximum light absorption at a wave-length (4220 Å) considerably shorter than that (4420 Å) of the authentic derivative. Braude and Forbes suggested that the lower-melting derivative may be either a geometrical isomer of retinene 2 : 4-dinitrophenylhydrazone, or a derivative of an isomer (I) of retinene, formed during the oxidation reaction by migration of the cyclic double bond out of conjugation with the polyene side chain. In view of this publication it seems of interest to record that a derivative, which is believed to be identical with that of Braude and Forbes, was synthesised in the following manner.



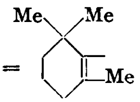
(I.)

(III.) $R_{\beta}\cdot CH_2\cdot CH{:}CMe\cdot CHO$ $HC{⋮}C\cdot CMe(OH)\cdot CH{:}CHCl$ (II.)

$R_{\beta}\cdot CH_2\cdot CH{:}CMe\cdot CH(OH)\cdot C{⋮}C\cdot CMe(OH)\cdot CH{:}CHCl$ (IV.)

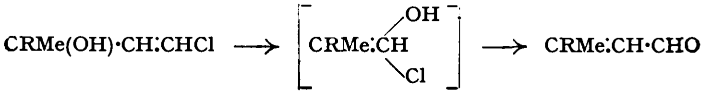
$R_{\beta}\cdot CH_2\cdot CH{:}CMe\cdot CH(OH)\cdot CH{:}CH\cdot CMe(OH)\cdot CH{:}CHCl$ (V.)

R_{β} =



Reaction of the Grignard complex from 1-chloro-3-methylpent-1-en-4-yn-3-ol (II) with the C_{14} aldehyde (III) yielded the crystalline glycol (IV). Partial hydrogenation of the latter and treatment of the resulting crude ethylenic glycol (V) with methanolic 2 : 4-dinitrophenylhydrazine sulphate (Brady's reagent) led to a 2 : 4-dinitrophenylhydrazone, m. p. 203° ($\lambda_{max.}$ 4190 Å). No depression in melting point was observed on admixture of this derivative with that prepared by Braude and Forbes, but the melting points of both were depressed on admixture with an authentic specimen of retinene 2 : 4-dinitrophenylhydrazone.

The formation of derivatives of αβ-unsaturated aldehydes (VI) has also been observed on addition of Brady's reagent to chlorovinylcarbinols (VII), where R is alkyl, aryl, acetylenyl, or vinyl (cf. Julia, *Ann. Chim.*, 1950, 5, 595). With the exception of (VII; R = $CH_2{:}CH$),

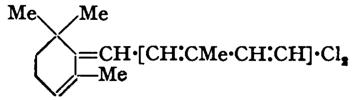


$$\mathrm{CRMe(OH)\cdot CH{:}CHCl} \longrightarrow \left[\mathrm{CRMe{:}C}\overset{\mathrm{OH}}{\underset{\mathrm{Cl}}{\mathrm{H}}}\right]^{-} \longrightarrow \mathrm{CRMe{:}CH\cdot CHO}$$

(VII.) (VI.)

$CH_2(OH)\cdot CH{:}CMe\cdot CH{:}CHCl$

(VIII.)



(IX.)

$R_{\beta}\cdot CH_2\cdot CH(OMe)\cdot CMe{:}CH\cdot C{⋮}C\cdot CMe{:}CH\cdot CHO$ (X.)

these alcohols yield the aldehydes (VI) themselves on treatment with mineral acids (*idem, loc. cit.*; Jones and Weedon, *J.*, 1946, 937). The carbinol (VII; R = $CH_2{:}CH$) under similar conditions gives the isomer (VIII) and not the aldehyde (VI; R = $CH_2{:}CH$), the derivative of which is obtained by the action of Brady's reagent (Julia, *loc. cit.*).

Attempts to convert the glycol (V) into retinene, or its isomer (I), were unsuccessful. Treatment of (V) with a solution of iodine in toluene gave a halogen compound which did not react with carbonyl reagents but exhibited light-absorption properties similar to those of anhydrovitamin A. By analogy with the structure proposed for the latter (Meunier, Doulou, and Vinet, *Compt. rend.*, 1943, 216, 907) the product is tentatively formulated as (IX).

EXPERIMENTAL.

A solution of 1-chloro-3-methylpent-1-en-4-yn-3-ol (20 g.) (Jones and Weedon, *J.*, 1946, 937) in ether (70 c.c.) was added dropwise to a stirred solution of ethylmagnesium bromide (from 7·1 g. of magnesium) in ether (200 c.c.). The mixture was heated under reflux for 5 hours and then cooled. A solution of 2-methyl-4-(2 : 6 : 6-trimethyl*cyclo*hex-1-enyl)but-2-en-1-al (14 g.) (Cheeseman, Heilbron, Jones, Sondheimer, and Weedon, *J.*, 1949, 1516) in ether (50 c.c.) was added dropwise and the mixture was heated under reflux for 5·5 hours and then again cooled. The complex was decomposed by the addition of a saturated aqueous solution of ammonium chloride, and the ethereal layer was then separated, washed with water, dried, and evaporated, the residue being heated at 100°/0·01 mm. whereupon the excess of 1-chloro-3-methylpent-1-en-4-yn-3-ol (10·5 g.) was recovered. A solution of the residual oil (17·4 g.) in light petroleum (b. p. 40—60°; 150 c.c.) was cooled to 0° whereupon a solid (13·7 g.) separated. Recrystallisation from light petroleum (b. p. 60—80°) gave 1-*chloro*-3 : 7-*dimethyl*-9-(2 : 6 : 6-*trimethyl*cyclo*hex*-1-*enyl*)*nona*-1 : 7-*dien*-4-*yne*-3 : 6-*diol* (IV) as needles (9·0 g.), m. p. 121—122° (Found : C, 71·1; H, 8·75. $C_{20}H_{29}O_2Cl$ requires C, 71·3; H, 8·7%). The glycol exhibited no light absorption maximum in the region 2000—4000 Å.

In some experiments it was found advantageous to purify the crude glycol by extracting it with aqueous methanol (80%) from its solution in light petroleum (b. p. 40—60°). Dilution of the pale yellow methanolic extracts with water precipitated the glycol which was then extracted with light petroleum. The extract was dried and cooled whereupon the glycol readily crystallised.

This glycol (0·3 g.) was dissolved in Brady's reagent [from 2 : 4-dinitrophenylhydrazine (0·75 g.), concentrated sulphuric acid (0·8 g.), and methanol (7 c.c.)], and the mixture was kept for 24 hours at 20° during which time a red solid separated. The mixture was cooled to 0°, and the solid filtered off; recrystallisation from light petroleum (b. p. 60—80°) gave a 2 : 4-*dinitrophenylhydrazone* (0·2 g.) as red needles, m. p. 115—117°. This, in view of its mode of formation and light-absorption properties, is formulated as a derivative of the aldehyde (X) (Found : N, 11·6. $C_{27}H_{34}O_5N_4$ requires N, 11·35%). Light absorption in chloroform (main band only) : maximum, 3970 Å; ε = 45,000. The 2 : 4-dinitrophenylhydrazone of (VII; R = $CH_2{:}CH{\cdot}C{\vdots}C$) exhibits maximum light absorption in chloroform at 3900 Å (ε = 40,000) (Jones and Weedon, *loc. cit.*).

A solution of the acetylenic glycol (1·0 g.) in ethyl acetate (10 c.c.) was shaken in an atmosphere of hydrogen in the presence of a palladium–calcium carbonate catalyst (0·1 g.; 2% Pd) until 70 c.c. of hydrogen had been absorbed. The reaction was then interrupted, the catalyst filtered off, and the solvent evaporated at 20° under reduced pressure, giving the impure glycol (V) as a viscous oil, n_D^{21} 1·5120. Light absorption in alcohol : maximum, 2410 Å; $E^{1\%}_{1\,\mathrm{cm.}}$ = 180.

The crude product was treated at 20° with Brady's reagent [from 2 : 4-dinitrophenylhydrazine (1·5 g.), concentrated sulphuric acid (1·0 g.), and methanol (10 c.c.)]. The mixture was kept for 2 hours at 0° and the solid (1·15 g.) which separated was removed. This was purified by chomatographic adsorption from benzene solution on a column of partly deactivated alumina and the main, deep red band was eluted with acetone. Evaportion of the solvent under reduced pressure gave a dark red oil (800 mg.), of which an acetone solution was kept at 0°. The crystals (300 mg.) which separated had m. p. 195—197°; light absorption in chloroform (main band only) : maximum, 4350 Å; $E^{1\%}_{1\,\mathrm{cm.}}$ = 850. Further recrystallisation from the same solvent gave the derivative, m. p. 203° (Found : N, 11·8. Calc. for $C_{26}H_{32}O_4N_4$, N, 12·1%). Light absorption in chloroform (main band only) : 4190 Å; ε = 42,000. The m. p. was undepressed on admixture with the derivative prepared from vitamin A by Braude and Forbes (*loc. cit.*), who give m. p. 204° and light absorption in chloroform (main band only) : maximum, 4220 Å; ε = 42,000. An authentic specimen of retinene 2 : 4-dinitrophenylhydrazone had m. p. 208° and exhibited maximum light absorption in chloroform at 4450 Å; ε = 60,000 (Ball, Goodwin, and Morton, *Biochem. J.*, 1948, **42**, 516, give m. p. 208°, maximum at 4420 Å; ε = 54,000).

A solution of the crude glycol (V) (200 mg.), prepared in the manner described above, in toluene (10 c.c.) was heated in an atmosphere of nitrogen on a steam-bath. A solution of iodine (15 mg.) in toluene (3 c.c.) was added in three portions at 5-minute intervals. The solution was then cooled, washed with aqueous sodium thiosulphate solution (2% wt./vol.), and dried and the solvent evaporated under reduced pressure. The residue was dissolved in light petroleum (b. p. 40—60°), and the solution poured on to a column of partially deactivated alumina. The chromatogram was developed with the same solvent and the single broad yellow band was eluted. Evaporation of the solvent gave a yellow oil (120 mg.) which gave a positive Lassaigne test for halogen. Light absorption in *cyclo*hexane : maxima, 3530, 3730, and 3940 Å; $E^{1\%}_{1\,\mathrm{cm.}}$ = 1040, 1300, and 1100, respectively. Anhydrovitamin A, m. p. 77—78°, exhibits light absorption in *cyclo*hexane : maxima, 3510, 3710, and 3920 Å; $E^{1\%}_{1\,\mathrm{cm.}}$ = 2500, 3650, and 3180, respectively (Shanz, Cawley, and Embree, *J. Amer. Chem. Soc.*, 1943, **65**, 901).

The authors thank Professors Sir Ian Heilbron and E. R. H. Jones for their interest in this work, Professor R. A. Morton for kindly supplying a sample of retinene, the British Council for a Scholarship (to M. J.), Dr. E. A. Braude for the light-absorption data, and Mr. W. F. Forbes for the mixed melting-point determinations.

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720. 4 : 5-*Dichloro*-o-*phenylenediamine.*

By W. DAVIS and W. C. J. ROSS.

4 : 5-DICHLORO-*o*-PHENYLENEDIAMINE has been examined as an antimetabolite of 4 : 5-dimethyl-*o*-phenylenediamine which is recognised as a probable precursor of riboflavin and vitamin B_{12} (Woolley, *J. Exp. Med.*, 1951, **93**, 13). Woolley has shown that the dichloro-diamine retards the growth of organisms which do not exhibit a nutritional need for these vitamins : the compound has now been prepared for test as a tumour-growth inhibitor.

Nietzki and Konwaldt (*Ber.*, 1904, **37**, 3892) reduced 1 : 2-dichloro-4 : 5-dinitrobenzene by an unspecified method and showed that the product was an *o*-diamine by preparing a quinoxaline derivative by reaction with benzil—neither the diamine nor the derivative was characterised. Hartley and Cohen (*J.*, 1904, **85**, 865) also obtained a crude form of the diamine. Woolley (*loc. cit.*) prepared the diamine by the reduction of 1 : 2-dichloro-4 : 5-dinitrobenzene or 4 : 5-dichloro-2-nitroaniline, using tin and hydrochloric acid. It has now been found that 4 : 5-dichloro-*o*-phenylenediamine may be more conveniently prepared, in a purer form, by catalytic reduction of these nitro-compounds. The diamine has been characterised by the preparation of a mono- and a di-hydrochloride and a dibenzoate and also by conversion into 6 : 7-dichloro-2 : 3-diphenylquinoxaline and 11 : 12-dichlorophenanthrazine.

Experimental.—4 : 5-*Dichloro*-o-*phenylenediamine.* A solution of 1 : 2-dichloro-4 : 5-dinitrobenzene (1 g.; Kuhn, Weygand, and Moller, *Ber.*, 1943, **76**, 1044) or 4 : 5-dichloro-2-nitroaniline (1 g.; Nietzki and Konwaldt, *loc. cit.*) in ethanol (70 ml.) containing Raney nickel (1 g.) was shaken in an atmosphere of hydrogen. The theoretical volume of hydrogen was taken up in 15 minutes. The residue obtained after evaporation of the filtered solution under reduced pressure was crystallised from benzene and then from benzene–light petroleum (b. p. 40—60°). The diamine formed colourless, flattened needles, m. p. 163° (Found : C, 41·0; H, 3·0. Calc. for $C_6H_6N_2Cl_2$: C, 40·8; H, 3·4%). Woolley (*loc. cit.*) obtained white or pink crystals which melted at 160° after sintering at 130°.

A stream of dry hydrogen chloride was passed into a solution of the diamine (100 mg.) in dry ether (10 ml.) until precipitation was complete. The product formed colourless plates from alcohol–ether and when sublimed at 100°/0·2 mm. afforded the *monohydrochloride* which decomposed when heated to 200—220° in sealed capillaries (Found : Cl^-, 16·6. $C_6H_6N_2Cl_2,HCl$ requires Cl^-, 16·6%).

Hydrogen chloride was passed into a solution of the diamine (100 mg.) in concentrated hydrochloric acid (7 ml.), and the precipitated dihydrochloride was collected, washed with a little concentrated acid, and dried in a vacuum-desiccator. The colourless plates decomposed at 205—220° when heated in sealed capillaries (Found : Cl^-, 28·0. Calc. for $C_6H_6N_2Cl_2,2HCl$: Cl^-, 28·4%). Woolley (*loc. cit.*) obtained white needles which were transformed into plates at 155° and melted with decomposition at 193°.

A suspension of the diamine (60 mg.) in potassium hydroxide solution (20 ml.; 5%) was shaken with benzoyl chloride (0·5 ml.). Slow cooling of an ethanol solution of the product afforded the *dibenzoate* as fine, colourless needles; more rapid cooling produced prisms; both forms had m. p. 257° (Found : C, 62·6; H, 3·8. $C_{20}H_{14}O_2N_2Cl_2$ requires C, 62·4; H, 3·7%).

A solution of the diamine (53 mg.) and benzil (64 mg.) in ethanol (4 ml.) was heated on a steam-bath for 1 hour. Careful addition of water caused the product to crystallise. After recrystallisation from aqueous ethanol the *quinoxaline* formed fine, colourless needles, m. p. 153° (Found : C, 68·6; H, 3·6. $C_{20}H_{12}N_2Cl_2$ requires C, 68·5; H, 3·4%).

Addition of a solution of the diamine (32 mg.), in ethanol (2 ml.), to phenanthraquinone (42 mg.), dissolved in warm acetic acid (3 ml.), caused immediate formation of a flocculent yellow precipitate. 11 : 12-*Dichlorophenanthrazine* forms long yellow needles, m. p. 264°, from acetic acid (Found : C, 69·1; H, 2·6. $C_{20}H_{10}N_2Cl_2$ requires C, 68·8; H, 2·9%).

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721. *Aromatic Hydrocarbons. Part LXII.**
1 : 2-3 : 4-9 : 10-*Tribenzopyrene.*

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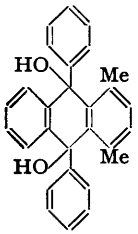
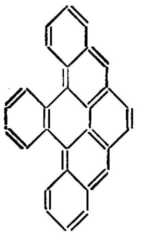
1 : 2-3 : 4-9 : 10-TRIBENZOPYRENE (II) was obtained from 9 : 10-dihydro-9 : 10-dihydroxy-1 : 4-dimethyl-9 : 10-diphenylanthracene (I) by the action of copper powder at *ca.* 400°.

(I)





(II)

Experimental.—M. p.s are uncorrected and were taken in evacuated capillaries. Microanalyses were done by Drs. Weiler and Strauss, Oxford.

9 : 10-*Dihydro*-9 : 10-*dihydroxy*-1 : 4-*dimethyl*-9 : 10-*diphenylanthracene.* The Grignard reaction, following Scholl and Meyer (*Annalen*, 1934, **512**, 112), gave a 39% yield of this diol as colourless needles (m. p. 219—220°; lit., m. p. 221—222°). Use of phenyl-lithium gives a higher-melting isomer. To a solution of phenyl-lithium from lithium chips (2·7 g.) in ether (100 c.c.) and bromobenzene (32 g.) in ether (100 c.c.), 1 : 4-dimethylanthraquinone (20 g.) was added in portions, and the solution was refluxed for 30 minutes. After decomposition of the mixture, the ether was distilled off and the residue extracted with alkaline dithionite (hydrosulphite). The yield of product was 28 g. and the m. p. 215—245° (decomp.). Extraction with boiling alcohol (150 c.c.) left a residue (17·5 g.) of m. p. 254—258°, raised by further extraction with benzene to 259—262°. Crystallisation from xylene lowered the m. p. to 213—215°. The diol, m. p. 259—262°, and the diol, m. p. 221°, both gave only 1 : 4-dimethyl-9 : 10-diphenylanthracene (Dufraisse and Horclois, *Bull. Soc. chim.*, 1936, **3**, 1900) on reduction with potassium iodide and sodium hypophosphite in acetic acid.

1 : 2-3 : 4-9 : 10-*Tribenzopyrene.*—The diol, m. p. 221° (2 g.), and copper powder (0·2 g.) were heated at 400° in carbon dioxide for 3 hours. Extraction with benzene, concentration, and dilution with light petroleum yielded a gum which was removed. Concentration of the mother-liquor to a very small volume and cooling gave an orange-yellow powder, which on recrystallisation from very little benzene yielded 25 mg. of 1 : 2-3 : 4-9 : 10-*tribenzopyrene*, m. p. 236—238°. Similar treatment of the diol, m. p. 254—258 (10 g.), followed by distillation (320°/2 mm.), gave small orange plates, m. p. 238° (175 mg.), from benzene (Found : C, 94·7; H, 4·6. $C_{28}H_{16}$ requires C, 95·4; H, 4·6%). The hydrocarbon showed a green fluorescence in organic solvents and gave a green solution in sulphuric acid, becoming brown on storage.

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