

g.) and benzene (100 c.c.) were heated under reflux while phosphoric oxide (10 g.) was added in small portions during 3 hrs. The mixture was decomposed with water (200 c.c.), and the whole basified (sodium hydroxide) and extracted with ether (extract *A*). The aqueous solution was acidified and extracted again with ether (extract *B*). Extract *A* was washed with water, dried, and the ether removed. The residue, recrystallised several times from dilute alcohol, gave needles (0.18 g.), m. p. 174° (Found : C, 75.9; H, 5.65. $C_{17}H_{14}O_2$ requires C, 76.1; H, 6.0%). Extract *B* similarly gave 0.049 g. of leaflets from dilute alcohol, m. p. 147° (compound *H*).

(2) The cyclohexanone (5 g.) was dissolved in chloroform (40 c.c.), and phosphorus oxychloride (6 c.c.) added. The whole was kept overnight, shaken with water, and then with sodium carbonate solution. The chloroform layer was filtered and dried, the chloroform removed, and the residue (*ca.* 1 g.) dissolved in a little alcohol. The crystals deposited on standing were recrystallised from dilute alcohol, affording needles (0.2 g.), m. p. and mixed m. p. with the above 174°.

The above compound, m. p. 174° (0.05 g.), was heated at 290—300° with selenium (0.1 g.). The sublimate (*ca.* 0.03 g.), resublimed in a vacuum, had m. p. and mixed m. p. with phenanthrene, 99°; picrate (from alcohol), m. p. 141°.

3-Acetoxy-2-methoxyphenanthrene (VII; R = Ac).—(1) The above dihydro-compound (0.1 g.) was mixed with palladium-black (0.1 g.) and heated at 210—220° until no further change was visible. Alcohol (2 c.c.), was added, the whole warmed and filtered, the filtrate concentrated to 0.3 c.c., and hot water (1 c.c.) added. The crystals which separated on cooling, recrystallised from dilute alcohol, formed needles (0.02 g.), m. p. 144°.

(2) The dihydro-compound (0.3 g.) was heated under reflux for 5 hrs. with maleic acid (0.8 g.), palladium-black (0.25 g.), and water (6 c.c.), diluted with alcohol (12 c.c.), filtered hot, and the filtrate evaporated to dryness. The residue was warmed and stirred with sodium carbonate solution (12 c.c.) and extracted several times with ether, the extract dried, and the ether removed. The residue recrystallised from alcohol in stout, colourless needles (0.2 g.), m. p. 144° (Gilman and Cook, *loc. cit.*, give 146—147°) (Found : C, 74.6; H, 5.6. Calc. for $C_{17}H_{14}O_2$: C, 74.9; H, 5.3%).

3-Hydroxy-2-methoxyphenanthrene. (1) The above acetoxy-compound (0.16 g.) was heated for 2 hrs. with sodium hydroxide solution (8%, 3 c.c.), and the solution acidified, allowed to cool, and filtered. The precipitate recrystallised from dilute alcohol in short needles (0.11 g.), m. p. 143° (Gilman and Cook, *loc. cit.*, give 145—146°) (Found : C, 80.3; H, 5.6. Calc. for $C_{15}H_{12}O_2$: C, 80.5; H, 5.35%).

(2) Compound *H* (above) (0.03 g.) was refluxed for 4 hrs. with maleic acid (0.1 g.), palladium-black (0.05 g.), and water (1.2 c.c.), and the product worked up as above; it gave 0.01 g. of needles, m. p. and mixed m. p. with the above, 143°.

2 : 3-Dimethoxyphenanthrene. The above hydroxy-compound (0.1 g.) was dissolved in sodium hydroxide solution (3 c.c., 2%), and the solution heated on the water-bath. Methyl sulphate (0.1 c.c.) was added with stirring, and after 0.25 hr., sodium hydroxide solution (3 c.c., 4%) was added, and the whole heated for a further 0.25 hr. The reaction mixture when cold was extracted with ether, and the extract dried. The ether was removed, and the residue recrystallised from dilute alcohol in leaflets (0.08 g.), m. p. 130—131° (Pschorr and Buckow, *loc. cit.*, and Pschorr, *Annalen*, 1912, **391**, 39, give m. p. 131°) (Found : C, 80.5; H, 5.7. Calc. for $C_{15}H_{14}O_2$: C, 80.7; H, 5.9%). The picrate separated in yellow needles, m. p. 125—126° (Pschorr, *loc. cit.*, gives 127°).

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NOTES.

Derivatives of Indene and of Butyric Acid. By J. S. H. DAVIES and D. S. MORRIS.

THE work of various authors (*Chem. Reviews*, 1945, **37**, 481) has shown that certain derivatives of 6-hydroxy-2-*p*-hydroxyphenylindene and of 6-hydroxy-2-*p*-hydroxyphenyl-3 : 4-dihydronaphthalene possess oestrogenic activity. Our programme to extend the work of these authors, although well advanced, was anticipated by the publication of Silverman and Bogert (*J. Org. Chem.*, 1946, **11**, 34).

The present note deals with two similar indenenes, not previously described, and also with unsuccessful attempts to prepare $\alpha\gamma$ -diphenylbutyric acid and $\alpha\gamma$ -di-*p*-methoxyphenylbutyric acid from ethyl $\alpha\gamma$ -diphenylacetoacetate and its di-*p*-methoxy-derivative respectively, as intermediates in an alternative route to 2-phenyltetralone and 7-methoxy-2-*p*-methoxyphenyltetralone.

6-Methoxy-2-*p*-methoxyphenylindene.—The 6-methoxy-2-*p*-methoxyphenylindanone required was prepared by the route independently used by Silverman and Bogert (*loc. cit.*). The indanone (1 g.) was hydrogenated at ordinary temperature and pressure in ethyl alcohol in presence of Raney nickel (2 g.). The residue obtained after filtration and removal of solvent was stirred with concentrated sulphuric acid (1 drop), warmed for a few minutes on the water-bath, and extracted with benzene. The indene formed small needles, m. p. 194° from alcohol (Found : C, 80.2; H, 6.2. $C_{17}H_{16}O_2$ requires C, 81.0; H, 6.3%).

6-Methoxy-2 : 3-di-*p*-methoxyphenylindene.—The above indanone (1.5 g.) in toluene (14 c.c.) was added to the Grignard reagent prepared from *p*-anisyl bromide (2.1 g.), magnesium (0.27 g.), and ether (28 c.c.). After the ether had been removed, the toluene solution boiled for 1 hour, and the complex decomposed, the residue from the toluene was dissolved in a mixture of light petroleum (b. p. 40—60°) and benzene (1 : 1 by vol.) and chromatographed (alumina). Pure 6-methoxy-2 : 3-di-*p*-methoxyphenylindene (0.7 g.) was obtained as small needles, m. p. 129—130° (Found : C, 80.0; H, 6.4. $C_{24}H_{22}O_2$ requires C, 80.4; H, 6.1%).

β -Hydroxy- $\alpha\gamma$ -diphenylbutyric Acid.—Ethyl $\alpha\gamma$ -diphenylacetoacetate (28.2 g.), prepared by the

method of Conant and Blatt (*J. Amer. Chem. Soc.*, 1929, **51**, 1227), was hydrogenated in ethyl alcohol at atmospheric pressure and a maximum temperature of 50–60° in presence of Raney nickel; only one molecular proportion of hydrogen was absorbed. Removal of the catalyst and solvent, followed by hydrolysis of the residue by refluxing it for 4 hours with potassium hydroxide (6.5 g.) in 50% aqueous alcohol, furnished a mixture of a neutral substance (3.8 g.), believed to be phenylethyl alcohol, and β -hydroxy- α -diphenylbutyric acid (13.5 g.) which formed needles, m. p. 210°, from aqueous methyl alcohol (Found: C, 75.1; H, 6.6; equiv., 254. $C_{16}H_{16}O_3$ requires C, 75.0; H, 6.3%; equiv., 256).

The application of Rosenmund's procedure (*Ber.*, 1942, **75**, 1850) to ethyl α -diphenylacetate (1 g.) using palladised barium sulphate (1 g.) in acetic acid (100 c.c.) containing perchloric acid (1 drop) in order to effect further reduction was unsuccessful, the products isolated after hydrolysis being β -hydroxy- α -diphenylbutyric acid (0.3 g.), phenylacetic acid (0.7 g.), and a neutral substance, probably phenylethyl alcohol. The hydrogenation of sodium β -hydroxy- α -diphenylbutyrate in water with copper chromite at 200° and 160 atmospheres gave likewise an acidic product consisting almost entirely of phenylacetic acid.

Ethyl ester. The β -hydroxy-acid (10.5 g.) was refluxed for 4 hours in ethyl alcohol saturated with dry hydrogen chloride. The ester was obtained as an oil (9.5 g.), b. p. 158–160°/1 mm., which slowly solidified and melted at 61–62° (Found: C, 76.3; H, 7.3. $C_{18}H_{20}O_3$ requires C, 76.1; H, 7.0%).

All attempts to dehydrate the acid or ester, which included the phosphoric oxide method of Kon and Nargund (*J.*, 1932, 2461) and the xanthate method (Kon and Narracott, *J.*, 1938, 672), were unsuccessful.

*Ethyl α -Di-*p*-methoxyphenylacetate.*—Following the method of Conant and Blatt (*loc. cit.*) ethyl *p*-methoxyphenylacetate (114 g.) in ether (100 c.c.) was slowly added to a stirred, cold solution of isopropylmagnesium bromide, prepared from isopropyl bromide (123 g.), magnesium (24.3 g.), and ether (200 c.c.). The mixture was stirred at room temperature for 1 hour, refluxed for 4 hours, and left overnight. Propane was evolved during the reaction. After processing, the oil was distilled and the fraction, b. p. 140–150°/0.0001 mm. (56 g.), was collected. This fraction solidified on standing and was crystallised from alcohol to yield the ester as pale yellow needles, m. p. 61–62° (Found: C, 70.4; H, 6.4. $C_{20}H_{22}O_5$ requires C, 70.2; H, 6.4%).

*β -Hydroxy- α -di-*p*-methoxyphenylbutyric Acid.*—The above ester (4.5 g.) in ethyl alcohol (200 c.c.) was hydrogenated at ordinary temperature and pressure in the presence of Raney nickel (2 g.); only one molecular proportion of hydrogen was absorbed. Removal of the catalyst and solvent gave the crude ester as an oil (4.5 g.). The oil (1 g.) was shaken for 6 hours at room temperature with aqueous sodium hydroxide (20 c.c., 2N) and ethyl alcohol (10 c.c.). The acid (0.4 g.) was obtained as small needles, m. p. 135–136° raised to 138° after crystallisation from benzene-light petroleum (b. p. 40–60°) (Found: C, 68.3; H, 6.6. $C_{18}H_{20}O_5$ requires C, 68.4; H, 6.3%).—BRITISH SCHERING RESEARCH INSTITUTE, BROOK LANE, ALDERLEY EDGE, CHESHIRE. [Received, January 21st, 1947.]

Compounds Related to 2:3-Dimethylpyridine. By AHMED MUSTAFA and MUSTAFA KAMAL HILMY.

(I) *Action of Aromatic Aldehydes on 2:3-Dimethylpyridine*—(a) *In presence of acetic anhydride.* The following stilbazoles were prepared by refluxing the appropriate benzaldehyde (1 mol.) with 2:3-dimethylpyridine (1 mol.) and acetic anhydride (6 mols.) for 30 hours, followed by steam distillation (cf. Shaw and Wagstaff, *J.*, 1933, 77). 3-Methyl-2-stilbazole, obtained as colourless crystals from light petroleum (b. p. 30–50°), m. p. 55° (Found: C, 85.8; H, 6.5; N, 7.1. $C_{14}H_{13}N$ requires C, 86.2; H, 6.6; N, 7.2%), was easily soluble in benzene, alcohol, and hot light petroleum (b. p. 50–70°); picrate, yellow needles, m. p. 198° from alcohol. Its 2'-nitro-derivative, pale yellow needles from light petroleum (b. p. 50–80°), m. p. 105° (Found: C, 69.9; H, 5.0; N, 11.7. $C_{14}H_{13}O_2N_2$ requires C, 70.0; H, 5.0; N, 11.7%), was easily soluble in ether and hot ethyl alcohol; picrate, yellow crystals, m. p. 190–191° from alcohol. Its 3'-nitro-derivative, yellow crystals from ethyl alcohol, m. p. 124° (Found: C, 69.7; H, 5.0; N, 11.7%), was difficultly soluble in cold benzene or cold ethyl alcohol; picrate, yellow crystals, m. p. 208–209° from alcohol; and the 4'-nitro-derivative, yellow crystals from alcohol, m. p. 145° (Found: C, 69.7; H, 4.9; N, 11.8%), was soluble in hot ethyl alcohol and hot benzene; picrate, yellow crystals, m. p. 198–199°, from alcohol.

(b) *In presence of water.* The following alkenes were prepared by heating the aromatic aldehyde and 2:3-dimethylpyridine (1 mol. each) with water (4 mols.) in a sealed tube for 10 hours at 170°. The mixtures were not homogeneous at room temperature. The products were treated as in the preparation of the corresponding stilbazoles (Shaw and Wagstaff, *loc. cit.*). They crystallised as pale yellow crystals from ethyl alcohol. 2'-Nitro-3-methyl-2-stilbazolealkene, m. p. 105° (Found: C, 65.1; H, 5.1; N, 10.5. $C_{14}H_{14}O_2N_2$ requires C, 65.1; H, 5.4; N, 10.9%); 3'-nitro-analogue, m. p. 131° (Found: C, 65.0; H, 5.3; N, 11.1%); 4'-nitro-isomer, m. p. 125–126° (Found: C, 65.1; H, 5.4; N, 10.6%).

The above three alkenes (1 mol. each), boiled with acetic anhydride (4 mols.) for 2 hours, afforded the corresponding stilbazoles (mixed m. p.) in almost pure condition.

(II) *Action of Aromatic Aldehydes on 2:3-Dimethylpyridine Methiodide.*—Solutions of equimolecular amounts of the reagents in a minimum of absolute ethyl alcohol, treated with a few drops of piperidine and then set aside at room temperature for some time, deposited crystals of the condensation product; when this was heated at about 250° under reduced pressure, the corresponding stilbazole distilled over (cf. Koelsch, *J. Amer. Chem. Soc.*, 1944, **66**, 2166).

2:3-Dimethylpyridine methiodide, colourless crystals from absolute ethyl alcohol, m. p. 205° (Found: C, 39.0; H, 5.0; N, 5.6; I, 51.1. $C_8H_{12}NI$ requires C, 38.5; H, 4.8; N, 5.6; I, 51.0%), easily soluble in cold water and soluble in ether, afforded 4'-methoxy-2-methyl-2-stilbazole methiodide, yellow needles from water, m. p. 234° (decomp.; orange melt) (Found: C, 52.4; H, 4.9; N, 3.7; I, 34.2. $C_{16}H_{18}ONI$ requires C, 52.3; H, 4.9; N, 3.8; I, 34.6%), readily soluble in hot water and practically insoluble in benzene and light petroleum (b. p. 30–50°). The corresponding stilbazole formed almost colourless crystals from light petroleum (b. p. 50–70°), m. p. 88° (Found: C, 79.7; H, 6.7; N, 6.2. $C_{15}H_{15}ON$

requires C, 80.0; H, 6.6; N, 6.2%); it was soluble in ethyl alcohol; picrate, yellow crystals, m. p. 196—197° from ethyl alcohol.

2'-Methoxy-3-methyl-2-stilbazole methiodide formed yellow crystals from water, m. p. 205° (decomp.) (Found: C, 52.3; H, 4.8; N, 3.7; I, 35.0%), and the stilbazole separated in colourless crystals from light petroleum (b. p. 30—50°), m. p. 60° (Found: C, 79.6; H, 6.5; N, 5.9%); picrate, yellow crystals from alcohol, m. p. 208—209°.

3'-Nitro-3-methyl-2-stilbazole methiodide, pale yellow crystals from water, m. p. 245° (decomp.) (Found: C, 44.9; H, 4.4; N, 6.7; I, 32.1. $C_{15}H_{15}O_2N_2I \cdot H_2O$ requires C, 45.0; H, 4.3; N, 7.0; I, 31.7%), difficultly soluble in cold ethyl alcohol and light petroleum (b. p. 30—50°), afforded the stilbazole as yellow crystals from light petroleum (b. p. 90—100°), m. p. 124° (Found: C, 69.5; H, 5.2; N, 11.6%), identical (mixed m. p.) with the specimen described in (I).

3-Methylpiperolidine-2-picoline methiodide, yellow crystals from hot water, m. p. 260° (Found: C, 50.4; H, 4.5; N, 3.7; I, 33.0. $C_{16}H_{16}O_2NI$ requires C, 50.4; H, 4.2; N, 3.7; I, 33.3%), almost insoluble in light petroleum (b. p. 50—70°), afforded the base as almost colourless crystals from light petroleum (b. p. 90—100°), m. p. 117° (Found: C, 75.0; H, 5.4; N, 6.1. $C_{15}H_{15}O_2N$ requires C, 75.3; H, 5.4; N, 5.9%), soluble in hot ethyl alcohol or benzene; picrate, yellow crystals, m. p. 219° (decomp.), from ethyl alcohol.

4'-Dimethylamino-3-methyl-2-stilbazole methiodide, reddish silky crystals from hot water, m. p. 255° (decomp.) (Found: N, 6.9; I, 33.0. $C_{17}H_{21}N_2I$ requires N, 7.4; I, 33.4%), almost insoluble in cold water and in light petroleum (b. p. 30—50°), afforded the stilbazole as golden-yellow needles from ethyl alcohol, m. p. 93° (yellow-brown melt) (Found: C, 80.5; H, 7.5. $C_{16}H_{18}N_2$ requires C, 80.7; H, 7.5%), soluble in benzene and hot light petroleum (b. p. 80—90°); picrate, brick red crystals, m. p. 202° (red melt) from ethyl alcohol.

(III) Action of Alcoholic Potassium Hydroxide on Stilbazoles.—4'-Nitro-3-methyl-2-stilbazole (1 g.) and ethyl alcoholic potassium hydroxide (15%; 10 c.c.) were heated at 100° for 15 minutes; the crystals which separated were filtered off, washed with water, and crystallised from benzene, forming golden-yellow crystals, m. p. 220° (red melt) (Found: C, 78.2; H, 5.6; N, 13.3. $C_{22}H_{24}ON_4$ requires C, 77.8; H, 5.5; N, 13.0%). 4'-Azoxy-3-methyl-2-stilbazole was difficultly soluble in ethyl alcohol and gave a deep red colour with concentrated sulphuric acid. Similarly, the 3'-azoxy-compound was obtained as brown crystals from benzene, m. p. 157° (Found: C, 78.2; H, 5.3; N, 12.9%), difficultly soluble in cold ethyl alcohol and giving a red colour with sulphuric acid; and the 2'-azoxy-isomer formed pale yellow crystals, from benzene, m. p. 174° (Found: C, 78.3; H, 5.6; N, 12.7%), difficultly soluble in ethyl alcohol and giving an orange-red colour with sulphuric acid.—FOUAD I UNIVERSITY, FACULTY OF SCIENCE, ABBASSIA-CAIRO, EGYPT. [Received, January 27th, 1947.]

The Infra-red Spectrum of Vulcanised Rubber and the Chemical Reaction Between Rubber and Sulphur.

By N. SHEPPARD and G. B. B. M. SUTHERLAND.

IN an earlier paper (*Trans. Faraday Soc.*, 1945, **41**, 261) we described an infra-red spectroscopic investigation of the vulcanisation of rubber, and drew attention to a band at 10.4μ (960 cm^{-1}) which appeared in the spectrum of both straight and accelerated vulcanisation. We have further investigated this phenomenon and find that the intensity of this band correlates well with the amount of sulphur chemically incorporated, but not with the degree of vulcanisation as reflected in the physical properties of the finished product.

We were unable to explain this band in a convincing manner in terms of C-S linkages, but more recently have found a band in the same position (10.4μ), and another at 11.2μ (890 cm^{-1}) in certain thermally degraded rubbers. Since in this case the two new bands are obviously due respectively to the development of new CHR:CHR' and CRR':CH₂ groups, it seemed probable that the 10.4μ band in vulcanised rubber might also be caused by new groupings of the former type. An investigation of the spectrum of an ebonite (in which the rubber-sulphur reaction has been carried to an extreme) gave confirmation of this idea. In this spectrum, absorptions in the region of 6μ showed that a considerable number of double bonds remained, but the characteristic absorption at 12.0μ arising from CRR':CHR' groups in rubber had largely disappeared. On the other hand the band at 10.4μ (although now shifted to slightly longer wave-lengths) had greatly increased in intensity.

These facts find a convincing explanation in the hypothesis that the reaction between rubber and sulphur causes at some stage a shift in the position of the double bond of type —CMe:CH— in the rubber chain, giving rise to a group of the type CHR:CHR'. Further confirmation of this comes from the studies of Farmer and Shipley (this vol. p. 1519) on the reaction between sulphur and the diolefins, geraniolene and dihydromyrcene. The available data on the structures of these reaction products have led these authors to conclude that α -methylene initiation of the sulphuration reaction occurs to an important extent.

They envisage attack of the — $\overset{1}{\text{C}}\text{H}_2\text{C}(\overset{2}{\text{C}}\text{Me})\overset{3}{\text{C}}\text{H}\overset{4}{\text{C}}\text{H}_2$ — group which is common to rubber and the diolefins at positions (1) or (4) with the initial removal of a hydrogen atom from the α -methylene carbon atoms. The radical formed by removal of a hydrogen atom from (1) could by resonance cause the double bond to move to the left. In this new position the double bond would still be of type CRR':CHR' and would be expected to absorb at the usual 12.0μ position. However, removal of the hydrogen atom from (4) would give rise to a radical which could move the double bond to the right and thus give rise to CHR:CHR' groups, and hence to a band at 10.4μ in the final product.

The work described above on the vulcanisation and degradation of rubber will be published in more detail later. We should like to express our thanks to Dr. E. H. Farmer and Dr. R. F. Naylor for helpful discussions on the above points.—THE LABORATORY OF COLLOID SCIENCE, CAMBRIDGE. [Received, March 24th, 1947.]