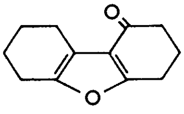
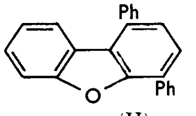
1011. *Derivatives of Dibenzofuran and Dibenzothiophen. Part III.*[1] *Condensation of 4-Phenylcyclohexane-1,3-dione with 2-Chlorocyclohexanone.*

By E. B. McCall, A. J. Neale, and T. J. Rawlings.

The condensation of cyclohexane-1,3-dione with 2-chlorocyclohexanone, an elaboration of the Feist–Benary furan synthesis,[2] has been shown [3] to be a useful route to 1,2,3,4,6,7,8,9-octahydro-1-oxodibenzofuran (I) and to the 1-methyl [3] and 1-phenyl [4] derivatives of dibenzofuran. As a possible route to 1,4-diphenyldibenzofuran (II), we have attempted to extend the scope of the condensation by using 4-phenylcyclohexane-1,3-dione (III) and 2-chlorocyclohexanone. The reaction yields a mixture of the two ketones, (IV) and (V), from which the former was isolated and characterised by conversion into 4-phenyldibenzofuran.[3] Conventional methods convert the ketone (IV) into 1,4-diphenyldibenzofuran (II), and the mixture of ketones into a mixture from which both 1,4- (II) and 1,2-diphenyldibenzofuran (VI) have been isolated.



(I)



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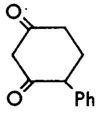

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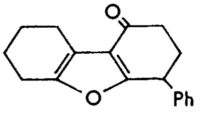
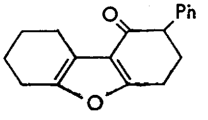
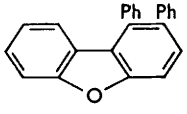


(IV)



(V)



(VI)

Experimental.—1,2,3,4,6,7,8,9-*Octahydro*-1-*oxo*-4-*phenyldibenzofuran* (IV). 2-Chlorocyclohexanone (18·8 g., 0·142 mole) in methanol (100 ml.) was added to 4-phenylcyclohexane-1,3-dione [5] (24·5 g., 0·131 mole) and potassium hydroxide (7·35 g., 0·131 mole) in water, and the mixture was refluxed for 3 hr. Precipitated potassium chloride and the excess of methanol were removed and subsequent treatment with 2N-sodium hydroxide (100 ml.) gave a sticky yellow solid which was filtered off, washed with water, and dried. Distillation gave the mixture of ketones (M) (20·6 g., 59%) as a pale yellow oil, b. p. 220—226°/4 mm., m. p. 80—83°. Three crystallisations from ethanol gave the *ketone* (IV) as colourless needles (6 g.), m. p. 117·5—118·5° (Found: C, 81·35; H, 6·8. $C_{18}H_{18}O_2$ requires C, 81·1; H, 6·8%) [2,4-*dinitrophenylhydrazone*, m. p. 250—251·5° (Found: C, 64·2; H, 5·1; N, 12·95. $C_{24}H_{22}N_4O_5$ requires C, 64·6; H, 4·9; N, 12·55%)]. This product (1 g.) was reduced by the Huang-Minlon procedure (190—200° for 4 hr.) to a brown oil which on dehydrogenation with 5% palladium–charcoal gave an oil having an infrared spectrum identical with that of 4-phenyldibenzofuran.[4]

1,4-*Diphenyldibenzofuran* (II). The ketone (IV) (3 g., 0·011 mole) was refluxed with phenylmagnesium bromide (from 0·033 mole of bromobenzene and 0·034 g.-atom of magnesium) in tetrahydrofuran for 4 hr. and after the standard isolation gave a pale yellow oil (4·3 g.) which was heated with 5% palladium–charcoal (1·2 g.) for 5 hr. at 310°. Extraction of the catalyst with benzene gave a waxy solid, m. p. 95—105° (3·7 g.), and crystallisation from light petroleum (b. p. 60—80°) gave 1,4-*diphenyldibenzofuran*, m. p. 110—111° (Found: C, 89·8; H, 5·1%; *M*, 307. $C_{24}H_{16}O$ requires C, 90·0; H, 5·0%; *M*, 320) [2,4,7-*trinitrofluorenone derivative*, m. p. 165—166° (Found: C, 70·1; H, 3·6; N, 6·9. $C_{24}H_{16}O,C_{13}H_5N_3O_7$ requires C, 69·9; H, 3·3; N, 6·6%), $\lambda_{max.}$ (in EtOH) 253 (ε 30,770), 270 (ε 21,760), 294 (ε 14,250), and 317 mμ (ε 11,000).

1,2-*Diphenyldibenzofuran* (VI). The mixture of ketones M (19·6 g., 0·074 mole) was refluxed with phenylmagnesium bromide (from 0·22 mole of bromobenzene and 0·23 g.-atom of

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[1] Part II, preceding paper.

[2] Gilman, " Organic Chemistry," John Wiley, New York, 1953, Vol. IV, p. 734.

[3] Chatterjea and Ray, *Chem. Ber.*, 1959, **92**, 998; Stetter and Lauterbach, *Annalen*, 1962, **652**, 40.

[4] McCall, Neale, and Rawlings, *J.*, 1962, 4900.

[5] Bergmann and Szmuszkovicz, *J. Amer. Chem. Soc.*, 1953, **75**, 3226.

magnesium) in tetrahydrofuran for 4 hr. and gave a pale yellow oil (18·3 g.), b. p. 238—250°/2·3 mm. The oil was heated with 5% palladium–charcoal (5 g.) for 5 hr. at 310°, and extraction with benzene then gave an oil (11·7 g.), b. p. 220—238°/0·8 mm., which after repeated crystallisation from benzene gave colourless needles of 1,2-*diphenyldibenzofuran*, m. p. 188—189° (Found: C, 90·0; H, 5·0%; *M*, 332), $\lambda_{max.}$ (in EtOH) 245 (ε 37,100) and 289 mμ (ε 16,250). The material recovered from the benzene had m. p. 103—130° and, crystallised from ethanol, m. p. 110—113°. It was identical (infrared spectrum) with 1,4-diphenyldibenzofuran obtained from the ketone (IV).

We are grateful to Mr. K. Salisbury and Mr. L. Hughes for experimental assistance.

MONSANTO CHEMICALS LIMITED,
RUABON, WREXHAM, DENBIGHSHIRE.

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1012. *The Dipole Moments of* 4-*Nitrobenzo*[c]*cinnoline and its* N-*Oxide.*

By K. E. BAUGE and J. W. SMITH.

THE dipole moments of materials prepared by Corbett, Holt, and Vickery,[1] and believed from spectrochemical data to be the above-named compounds, have been determined from the dielectric constants of benzene solutions at 25°. The dielectric constants (ε), relative to benzene = 2·28410, and the orientation polarisations (${}_{\mu}P$) and dipole moments (μ) derived from them were as follows:

4-Nitrobenzo[*c*]cinnoline

$10^6 w$	229	508	892	1126	${}_{\mu}P$ = 1058 c.c., μ = 7·19 D.
ε	2·27983	2·28690	2·29638	2·30169	

4-Nitrobenzo[*c*]cinnoline *N*-oxide

$10^6 w$	299	351	443	605	${}_{\mu}P$ = 1179 c.c., μ = 7·58 D.
ε	2·28247	2·28344	2·28542	2·28980	

The low solubilities restricted the measurements to very dilute solutions, of which the refractive indices were almost indistinguishable from that of the pure solvent. Hence the dipole moments were deduced by application of the approximate relationship[2] ${}_{\mu}P_2 = 3M_2\alpha v_1/(\varepsilon_1 + 2)^2$, where v_1 and ε_1 are the specific volume and the dielectric constant, respectively, of the pure solvent and α is the mean value of $d\varepsilon/dw$ over the concentration range studied, w being the weight fraction of solute.

From the moments of benzo[*c*]cinnoline[3] and nitrobenzene (3·93 and 4·01 D, respectively), and with the assumption that the rings are coplanar, the calculated moments of 3- and 4-nitrobenzo[*c*]cinnoline are 5·61 and 7·66 D, respectively. The observed value confirms the assignment of structure made by Corbett, Holt, and Vickery. The fact that it is lower than the calculated moment suggests that either the $C-NO_2$ bond is appreciably deflected in the plane of the rings or the nitro-group cannot assume coplanarity with the rings. Thus the result could be accounted for by a reduction of the effective moment of the nitro-group to about 3·53 D, almost the value for an aliphatic nitro-group. An analogous result was obtained with 1-nitrobenzo[*c*]cinnoline, for which an isolated measurement indicated that the moment is about 1·60 D, as compared with a calculated value of 2·05 D.

The observed moment of the *N*-oxide also supports the structural assignment made,[3]

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[1] Corbett, Holt, and Vickery, *J.*, 1962, 4384.
[2] Smith, *Trans. Faraday Soc.*, 1950, **46**, 394.
[3] Corbett, Holt, and Vickery, unpublished work.

the fact that the difference between the moments of 4-nitrobenzo[*c*]cinnoline and of its *N*-oxide is less than that (1·3 D) observed by Calderbank and Le Fèvre [4] for benzo[*c*]-cinnoline and its *N*-oxide being attributable to the different inclinations of the additional N–O moment to the axis of the molecular dipole.

BEDFORD COLLEGE, LONDON, N.W.1.

[*Received, March* 13*th*, 1962.]

[4] Calderbank and Le Fèvre, *J.*, 1948, 1949.

1013. *The Activation of Reduced Nickel Catalysts by Metallic Oxides for the Hydrogenation of Ethyl Oleate.*

By E. R. MAXTED and S. M. ISMAIL.

THE present work relates to the activation of reduced nickel catalysts by the use of various metallic oxides as supports in the hydrogenation, $\sim$160°/1 atm., of ethyl oleate, the oxides including thoria, zirconia, chromium sesquioxide, ceria, titania, magnesia, lanthanum sesquioxide, and silica in the form of kieselguhr. With an increase in the amount of the support, the activation curves, in general, rise to a maximum value and then fall. With a particular type of thoria employed, the maximum activity of the supported nickel was 13—14 times that of the unsupported nickel.

Experimental.—Hydrogenation was carried out at atmospheric pressure with a stirring device described earlier.[1] The reduced supported nickel was made by suspending the oxide in a reaction pipette, to which was added a known amount of nickel formate in aqueous ammonia. The ammonia was then boiled off at a low temperature, thorough and uniform impregnation of the supports being obtained in this way. The contents of the pipette were then dried overnight; precautions were taken against exposure to temperatures higher than $\sim$60°, otherwise a green and less readily reducible nickel oxide was formed. The dry catalyst was ground in an agate mortar. A current of pure hydrogen, regulated by a flow meter, was passed through the pipette, which was placed in an electric furnace, the temperature of which was gradually raised to 280°C and kept thereat for an hour; black reduced supported nickel was thus obtained. The pipette was then removed from the furnace and allowed to cool to room temperature, after which 10 c.c. of ethyl oleate were introduced, with precautions against oxidation of the catalyst by air.

The hydrogenation was carried out in a mechanical shaker operating at a constant speed, the activity of the catalyst being taken as equivalent to the number of c.c. of hydrogen absorbed during the first 0·5 hr. The reaction was approximately of zero order and the rate remained constant for the stated period. Results are shown in the Figures.

Discussion.—0·17 g. of reduced nickel, weighed as the corresponding amount of the formate, was used throughout, and the hydrogenation rate of the reduced nickel in the absence of a support was taken as a standard. This was found to be 18 c.c. in 30 minutes. The order of the activities of the supports was found to be: ThO_2 (120—150 mesh) $>$ Th_2O (120—200 mesh) $>$ ThO_2 (passing 200 mesh) $>$ ThO_2 (150—200 mesh) $>$ Cr_2O_3 $>$ kieselguhr $>$ TiO_2 $>$ MgO $>$ LaO_2 $>$ ZrO_2 $>$ CeO_2; ceria was more active than certain varieties of ZrO_2. ZrO_2 (120—150 mesh) was the least active support, having a hardly appreciable effect on the hydrogenation rate. A study of the effect of thoria in the presence of kieselguhr was also made, but, contrary to expectations, the activity was lower than that of either thoria or kieselguhr alone. The distribution of the catalyst, of the order of several Å thickness, over the surface of the support is more desirable to give an active

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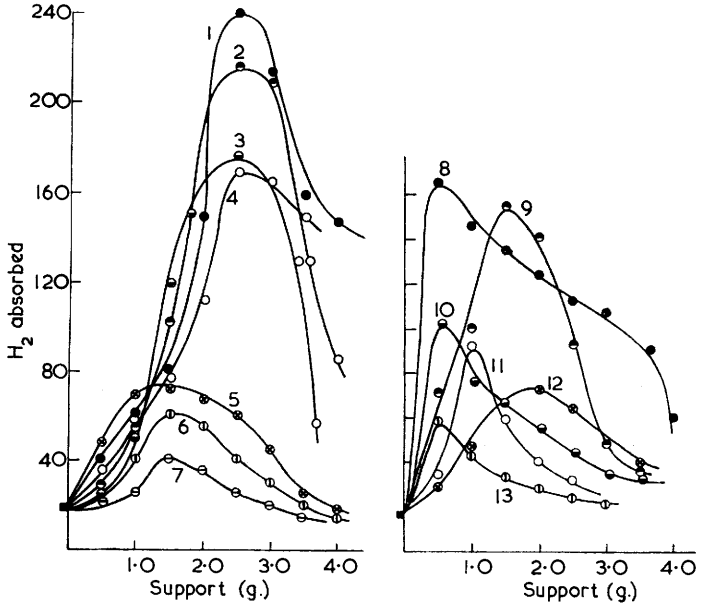
[1] Maxted and Ismail, *J.*, 1962, 2330.

catalytic surface, since it has been shown by Selwood [2] that the crystallites of nickel are dispersed to a very high degree, giving a lower activity.

Support	Total micro-pore (vol. ml./g.)	Amount of support corresponding to peak activity (g.)	Surface area of support (m.^{2}/g.)	Calc. surface area of support corresponding to peak activity (m.^{2}/g.)
ZrO_2I	0·285	1·5	11·9	7·9
ThO_2I	0·279	2·5	20·9	8·4
TiO_2...............	0·639	0·5	95·5	19·1
Cr_2O_3	0·364	0·5	45·6	9·1
MgO..............	0·608	1·0	24·2	24·2
Kieselguhr	—	1·5	26·9	17·9

The activation effects in two- and in three-component systems, consisting respectively of thoria, chromia, and titania, and of thoria, chromia, and kieselguhr, was also studied. In the first, a maximum activity of 136 c.c. in 30 minutes was obtained when the proportion of $ThO_2 : Cr_2O_3 : TiO_2$ was 60 : 20 : 20. This is an appreciable rise of activity over that obtained when only one or two components are present. In the ThO_2–Cr_2O_3–kieselguhr system, maxima were observed, lying between those obtained when the proportions of $ThO_2 : Cr_2O_3$: kieselguhr are 40 : 20 : 40 and 60 : 20 : 20.



Effect of support on the rate of hydrogenation (c.c. in 30 min.): 1, ThO_2 I (120—150 mesh); 2, ThO_2 IV (used as such); 3, ThO_2 III (passing 200 mesh); 4, ThO_2 II (150—200 mesh); 5, ZrO_2 III (passing 200 mesh); 6, ZrO_2 II (150—200 mesh); 7, ZrO_2 I (120—150 mesh); 8, Cr_2O_3; 9, kieselguhr; 10, TiO_2; 11, MgO; 12, LaO_2; 13, CeO_2. Unsupported nickel is represented by the black squares on the left of each diagram, at 18 c.c.

It has been shown by Polanyi [3] that the dissociation of hydrogen into atoms on the catalyst surface is an essential factor in the activation of the hydrogen molecules involved; and Schmidt [4] has also found that this activation by metals of the nickel group occurs in the micropores of the catalyst which, for a high activity, must be porous. For this reason, a

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[2] Hill and Selwood, *J. Amer. Chem. Soc.*, 1949, **71**, 2522.

[3] Polanyi, *Z. Elektrochem.*, 1929, **35**, 561.

[4] Schmidt, *Z. phys. Chem.*, 1925, **118**, 193; 1933, *A.*, **165**, 209; 1936, *A*, **176**, 237.

study was made of the micropores and of the surface areas of the various supports. This is summarised in the Table.

The temperature coefficient of hydrogenation processes is also of considerable importance. By virtue of the dependence of the reaction velocity on the absorbed concentration, a decrease in the hydrogenation velocity, as the temperature is increased, may occur at high temperatures. A change in the kinetic form with increasing temperature has been observed in liquid-phase hydrogenation by Maxted and Moon.[5] For this reason, the hydrogenation temperature was kept as low as possible, an optimum value being found to be at 160°C.

One of us (S. M. I.) acknowledges with thanks the grant of a study leave by C.S.I.R. (Pakistan), which enabled this work to be done.

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[*Received, March* 19*th*, 1962.]

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[5] Maxted and Moon, *J.*, 1935, 1190.

1014. *Tropylium Salts. Part III.*[1] *The Introduction of Tropyl (Cycloheptatrienyl) and Benzyl Groups into Anisole by Tropylium Halides.*

By D. BRYCE-SMITH and N. A. PERKINS.

To ascertain whether a Friedel–Crafts type of substitution into the benzene ring can occur without an added acceptor catalyst when the reagent contains a pre-existing carbonium ion, we have examined the reactions of tropylium chloride and bromide with benzene and anisole. Several examples are known of *C*-tropylation by tropylium halides at active methylene groups,[2] but no corresponding case of aromatic substitution by the tropylium ion has yet been reported.

The reactions in benzene at 80° were slow and apparently complex. No phenylcycloheptatriene was found. On the other hand, anisole, a stronger nucleophile than benzene, reacted with tropylium chloride at 85—90° during 5 hours, to give *p*-methoxyphenylcycloheptatriene. The use of tropylium bromide in place of the chloride led to a 2 : 3 mixture of this product with *p*-benzylanisole.

These reaction mixtures were heterogeneous, tropylium salts being generally highly insoluble in ethers. The reactions were repeated in the presence of sufficient nitromethane to render the systems homogeneous. Tropylium chloride gave no clearly defined products under these conditions, but tropylium bromide surprisingly gave *p*-benzylanisole (3—10%, depending on the reaction temperature) free from *p*-methoxyphenylcycloheptatriene.

In control experiments, tropylium chloride and bromide gave no recognisable amounts of benzyl halide when heated in nitromethane, although some decomposition occurred with evolution of hydrogen halide. Benzyl bromide was largely unchanged after being heated for five hours under reflux (108°) with nitromethane, although the solution became orange and a little hydrogen bromide was evolved. These facts appear to render unlikely any possibility that the observed benzylation involves initial isomerisation to benzyl halide: in principle, this could be expected to occur more readily in solution than in the crystalline state of the tropylium salt. Benzyl bromide did indeed react very slowly with anisole at 158° without added catalyst, to give 1·5% of a mixture of benzylanisoles, apparently largely the *ortho*- and the *para*-isomer (cf. Nenitzescu *et al.*[3]). It has also been shown that *p*-methoxyphenylcycloheptatriene does not rearrange to *p*-benzylanisole or suffer any other perceptible change at 85—90° in nitromethane.

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[1] Part II, Bryce-Smith and Perkins, *J.*, 1962, 1339.

[2] Jordan and Elliott, *J. Org. Chem.*, 1962, **27**, 1445, and references therein.

[3] Nenitzescu, Isăcescu, and Ionescu, *Annalen*, 1931, **491**, 210.

In view of the traditional catalytic activity of aluminium chloride in alkylation, it is interesting that tropylium tetrachloroaluminate[4] gave no trace of methoxyphenylcycloheptatriene or benzylanisole when heated with anisole at 85°.

Consideration of the mechanism of these substitutions is rendered difficult by the very low yields (*ca.* 1—10%) of the products. Our conclusion at present is that the exclusively *para*-substitution products with anisole and the failure to observe corresponding reactions with benzene are consistent with attack by an electrophile, possibly a weak one having limited stability under the conditions of the experiments. The rearrangement is evidently promoted by nitromethane, and appears not to involve directly either the starting materials or the products.

Added in Proof.—After the present manuscript had been submitted, Nozoe and Kitahara described the nuclear introduction of a tropyl group into phenol by di(cycloheptatrienyl) ether.[4a] Direct nuclear attack was thought possible, rather than the Claisen-type rearrangement of an intermediate *o*-derivative which had previously been suggested for reactions of this type.[4b] These authors did not report a concurrent benzylation reaction. We observed no reaction between di(cycloheptatrienyl) ether and anisole under conditions similar to those described in the present work.

Experimental.—Tropylium chloride was prepared from di(cycloheptatrienyl) ether and hydrogen chloride,[1] tropylium bromide by Doering and Knox's method,[5] and tropylium tetrachloroaluminate by reaction of cycloheptatriene, aluminium chloride, and t-butyl chloride.[4] Anisole was fractionated over sodium; a middle fraction was used.

Reaction of anisole with tropylium chloride. A suspension of tropylium chloride (2·38 g.) in anisole (55 ml.) was stirred at 85—90° for 5 hr. in the dark with passage of a stream of nitrogen. Hydrogen chloride was evolved. Dry ether (100 ml.) was added to the cooled solution, and insoluble matter removed by filtration. Fractional distillation of the filtrate in nitrogen gave p-*methoxyphenylcycloheptatriene* (0·03 g., 0·8%) as a colourless oil, b. p. *ca.* 115°/1·5 mm., having ultraviolet and infrared spectra identical with those of material prepared as described below from *p*-methoxyphenylmagnesium bromide and tropylium bromide (Found: C, 84·8; H, 7·2. $C_{14}H_{14}O$ requires C, 84·8; H, 7·1%). In one only of several experiments conducted on twice the foregoing scale, was the infrared spectrum of the product identical with that of a synthetic mixture of the cycloheptatriene (80%) and *p*-benzylanisole (20%).

Reaction of anisole with tropylium chloride in nitromethane. A solution of tropylium chloride (4·3 g.) in anisole (100 ml.) and nitromethane (30 ml.) was stirred at 85° in the dark for 5 hr. in a stream of nitrogen. The yield of products other than tar was so small that pure material was not obtained; but the presence of *p*-methoxyphenylcycloheptatriene and *p*-benzylanisole in traces of a brown oily fraction was inferred from the infrared spectrum.

Reaction of anisole with tropylium bromide. A suspension of tropylium bromide (3·3 g.) in anisole (40 ml.) was stirred at 85—90° for 5 hr. in the dark with passage of a stream of nitrogen. Hydrogen bromide was evolved. Working up as above gave an oil (0·08 g.), b. p. *ca.* 116°/1·3 mm., having an infrared spectrum identical with that of a synthetic mixture of *p*-methoxyphenylcycloheptatriene (40%) and *p*-benzylanisole (60%) (Found: C, 84·7; H, 7·1%). Chromatography on alumina gave enriched fractions, but no clean separation.

Reaction of anisole with tropylium bromide in nitromethane. The previous experiment was repeated with the addition of nitromethane (12 ml.) to render the reaction mixture homogeneous. The product was a colourless oil (0·12 g., 3·1%), b. p. 115°/0·8 mm. This soon solidified, and was identified as *p*-benzylanisole by elemental analysis, m. p. and mixed m. p. (24°), and by infrared and ultraviolet spectra ($\lambda_{max.}$ 208, 228, 280, 287; $\lambda_{min.}$ 221, 249—250, 284; shoulders at 264, 271 mμ).

Repetition of the foregoing experiment at 120° with tropylium bromide (3·45 g.), anisole (100 ml.), and nitromethane (30 ml.) gave *p*-benzylanisole (0·41 g., 10·3%), b. p. 105—110°/0·15 mm., which after removal of a trace of brown impurity by chromatography in ether

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[4] Bryce-Smith and Perkins, *J.*, 1961, 2320.

[4a] Nozoe and Kitahara, *Chem. and Ind.*, 1962, 1192; cf. Nozoe, Itô, and Tezuka, *ibid.*, 1960, 1088.

[4b] Nozoe, *Progr. Org. Chem.*, 1961, **5**, 132.

[5] Doering and Knox, *J. Amer. Chem. Soc.*, 1957, **79**, 352.

over basic alumina had m. p. 22°, mixed m. p. 23°, and the correct analysis and infrared and ultraviolet spectra.

Reaction of anisole with tropylium tetrachloroaluminate. A mixture of tropylium tetrachloroaluminate (4·13 g.) and anisole (40 ml.) was stirred at 85—90° for 5 hr. in the dark with passage of a stream of nitrogen. Hydrogen chloride was evolved. The product was tarry, and no *p*-methoxyphenylcycloheptatriene or *p*-benzylanisole was detected.

Reaction of benzyl bromide with anisole. A mixture of benzyl bromide (17·1 g.) and anisole (43·2 g.) was heated under reflux (158°) for 5 hr. in nitrogen. A little hydrogen bromide was evolved. Fractional distillation gave benzylanisoles as a colourless oil (0·3 g., 1·5%), b. p. 118—121°/1·1 mm. (Found: C, 84·5; H, 7·2%). The infrared spectrum showed all the maxima corresponding to the *para*-isomer, and extra maxima at 9·5 and 13·2 μ are attributed to the *ortho*-isomer.

Preparation of p-*methoxyphenylcycloheptatriene.* The Grignard reagent from *p*-bromoanisole (18·7 g.) and magnesium (2·4 g.) in ether (40 ml.) was treated with a suspension of tropylium bromide (7·0 g.) in dry ether (130 ml.). The mixture was heated under reflux for 40 min. Conventional procedures gave colourless *p*-methoxyphenylcycloheptatriene (4·58 g., 56·5%), b. p. 103—106°/0·08 mm., m. p. 14° (Found: C, 84·45; H, 6·85%), $\lambda_{max.}$ (in cyclohexane) 207, 280, 287, $\lambda_{min.}$ 257, 284 mμ. The strongest infrared maxima over the range 3—15 μ were at 3·34, 6·20, 6·63, 6·88, 7·82, 7·90, 8·08, 8·50, 9·64, 12·06, 13·42, and 14·20 μ.

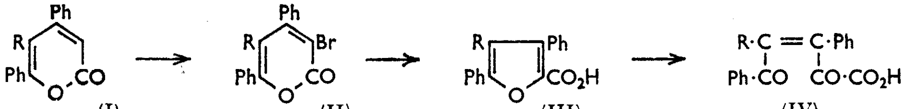
One of us (N. A. P.) thanks Albright and Wilson Ltd. for a maintenance grant.

CHEMISTRY DEPARTMENT, THE UNIVERSITY, READING. [*Received, May* 28*th*, 1962.]

1015. *Polysubstituted Furans from 2-Pyrones.*

By IBRAHIM EL-SAYED EL-KHOLY and FATHI KAMEL RAFLA.

WE have shown that 4,5,6-triphenyl-2-pyrone [1] (I; R = Ph) and 5-phenoxy-4,6-diphenyl-2-pyrone [2] (I; R = OPh) undergo bromination (cf. ref. 3) to the 3-bromo-2-pyrones (II; R = Ph or OPh) which are characterised by strong carbonyl absorption at 1721 and 1724 cm.$^{-1}$, respectively. These 3-bromopyrones are converted by alcoholic alkali into the furancarboxylic acids (III) that are very easily decarboxylated. Their esters show strong absorption at 1712 and 1715 cm.$^{-1}$ characteristic of αβ-unsaturated carboxylic esters.[4]



(I) (II) (III) (IV)

Nitric acid in acetic acid oxidise the acid (III; R = Ph) to 2,5-dioxo-3,4,5-triphenylpent-3-enoic acid (IV; R = Ph).[5]

Experimental.—3-*Bromo*-4,5,6-*triphenyl*-2-*pyrone* was prepared by addition of bromine (4·9 g.) in chloroform (20 ml.) to a boiling solution of 4,5,6-triphenyl-2-pyrone (10 g.) in chloroform (200 ml.). It was isolated, by distillation of the solvent, washing with cold methanol, and crystallisation from acetic acid, in pale yellow needles, m. p. 193° (Found: C, 68·6; H, 3·8; Br, 19·7. $C_{23}H_{15}BrO_2$ requires C, 68·5; H, 3·75; Br, 19·8%).

3,4,5-*Triphenyl*-2-*furoic acid.* This was prepared when 3-bromo-4,5,6-triphenyl-2-pyrone

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[1] Soliman and El-Kholy, *J.*, 1955, 2911.

[2] El-Kholy, Rafla, and Soliman, *J.*, 1961, 4490.

[3] Elderfield, "Heterocyclic Compounds," John Wiley and Sons, Inc., New York, 1950, Vol. I, p. 134.

[4] Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1959, p. 179.

[5] Chi-kang Dien and Lutz, *J. Org. Chem.*, 1957, **22**, 1355.

(2 g.) was refluxed with 5% methanolic potassium hydroxide (20 ml.) for 20 min. The mixture was then diluted with water and extracted with ether, and the alkaline solution acidified and extracted with ether. The latter ethereal solution yielded an oil (2 g.) from which the free acid (0·4 g.) was obtained. It crystallised from benzene in needles, m. p. 166° (decomp.), which gradually decomposed in the process of purification. Its *methyl ester* was prepared by diazomethane and crystallised from methanol in prisms, m. p. 130° (Found: C, 81·6; H, 5·1; OMe, 8·8. $C_{24}H_{18}O_3$ requires C, 81·3; H, 5·1; OMe, 8·75%).

2,5-*Dioxo*-3,4,5-*triphenylpent*-3-*enoic acid.* A solution of the foregoing furoic acid (0·7 g.) in acetic acid (35 ml.) was treated dropwise with concentrated nitric acid (1·5 ml.) at room temperature and then kept in the ice-chest for 24 hr. The *pentenoic acid* (0·6 g.) was recovered by dilution with water and crystallised from benzene–light petroleum (b. p. 50—70°) and recrystallised from methanol in elongated prisms, m. p. 211° (decomp.) (Found: C, 77·4; H, 4·6. $C_{23}H_{16}O_4$ requires C, 77·5; H, 4·5%). The same acid was also obtained from the oily residue left after crystallisation of 3,4,5-triphenyl-2-furoic acid. Its *methyl ester*, prepared by diazomethane, crystallised from dilute methanol in needles, m. p. 156—157° (Found: C, 77·95; H, 5·0; OMe, 8·25. $C_{24}H_{18}O_4$ requires C, 77·8; H, 4·9; OMe, 8·4%), $\nu_{max.}$ 1664 (C=O) and 1706 cm.$^{-1}$ (ester C=O).

3-*Bromo*-5-*phenoxy*-4,6-*diphenyl*-2-*pyrone.* Bromine (0·85 g.) was added to 5-phenoxy 4,6-diphenyl-2-pyrone (1·7 g.) in boiling chloroform (20 ml.). The *bromo-pyrone* (1·8 g.) crystallised from benzene in yellow prismatic needles, m. p. 192° (Found: C, 66·0; H, 3·7; Br, 19·1. $C_{23}H_{15}BrO_3$ requires C, 65·9; H, 3·6; Br, 19·1%).

4-*Phenoxy*-3,5-*diphenyl*-2-*furoic acid.* The foregoing pyrone (1 g.) was refluxed with 5% methanolic potassium hydroxide (20 ml.) for 10 min. The *acid* (0·4 g.) was isolated as described above and crystallised from benene–light petroleum (b. p. 50—70°) in plates, m. p. 219—221° (decomp.) (Found: C, 77·4; H, 4·5. $C_{23}H_{16}O_4$ requires C, 77·5; H, 4·5%). Its *methyl ester* crystallised from methanol in plates, m. p. 134—135° (Found: C, 77·6; H, 4·9; OMe, 8·4. $C_{24}H_{18}O_4$ requires C, 77·8; H, 4·9; OMe, 8·4%).

The authors thank Professor Gabra Soliman, Chemistry Department, Faculty of Science, Alexandria University, for his interest in this work.

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1016. *Biphenylenes. Part IX.*[1] *Biphenylene-2-aldehyde.*

By J. F. W. McOMIE and S. D. THATTE.

AROMATIC aldehydes can be obtained by thermal decarboxylation of the corresponding glyoxylic acid which in turn can be made by the oxidation of the appropriate aryl methyl ketone.[2] In this way biphenylene-2-aldehyde has been prepared. It readily condenses with malonic acid and with acetophenone, to give β-2-biphenylenyl-acrylic acid and -acrylophenone, respectively. For comparison with the latter the isomeric ketone, 2-cinnamoylbiphenylene, was made.

Biphenylene did not react when it was heated with dimethylformamide and phosphoryl chloride (Vilsmeier–Haack aldehyde synthesis).[3] This is in agreement with the suggestion of Buu-Hoï *et al.*[4] that non-*peri*-condensed aromatic polycyclic hydrocarbons will undergo formylation by this method only if the index of free valency at any position is not less than 0·510. With biphenylene the indices of free valency for positions 1 and 2 are 0·43 and 0·41, respectively.[5]

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[1] Part VIII, Blatchly, McOmie, and Thatte, *J.*, 1962, 5090.
[2] Cymerman-Craig, Loader, and Moore, *Austral. J. Chem.*, 1956, **9**, 222.
[3] Minkin and Dorofeenko, *Russ. Chem. Rev.*, 1960, 599.
[4] Buu-Hoï, Lavit, and Chalvet, *Tetrahedron*, 1960, **8**, 7.
[5] Roberts, Streitwieser, and Regan, *J. Amer. Chem. Soc.*, 1952, **74**, 4579.

Experimental.—*2-Biphenylenylglyoxylic acid.* Potassium permanganate (5·0 g.) in water (250 ml.) was added slowly to a stirred mixture of 2-acetylbiphenylene [6] (1·5 g.), potassium hydroxide (2·0 g.), pyridine (200 ml.), and water (100 ml.) at 10—15°, and stirring was continued for 2 more hours. The excess of potassium permanganate was destroyed by addition of sodium hydrogen sulphite. After being filtered, the solution was acidified with 10N-hydrochloric acid, and the precipitated biphenylene-2-carboxylic acid (15%) was removed. The filtrate was extracted with ether and yielded the glyoxylic acid (0·84 g., 49%) as an orange solid which could not be obtained analytically pure. It formed a *semicarbazone*, m. p. 222—224° (decomp.) (Found: C, 64·5; H, 4·2; N, 15·35. $C_{15}H_{11}N_3O_3$ requires C, 64·05; H, 3·9; N, 14·9%).

Biphenylene-2-aldehyde. The above glyoxylic acid (0·5 g.) and dimethylaniline (1·5 ml.) were heated together at 110—120° for 4 hr. After being cooled, the mixture was diluted with n-hexane and washed several times with dilute hydrochloric acid and then with water. Removal of the organic solvent under reduced pressure left a yellow residue which was sublimed at 70—75°/112 mm., giving *biphenylene-2-aldehyde* (0·08 g., 21%) as yellow needles, m. p. 78—79° (Found: C, 86·4; H, 4·4. $C_{13}H_8O$ requires C, 86·65; H, 4·5%), $\lambda_{max.}$ (in EtOH) 240, 249, 270, 345 mμ ($\log_{10} \varepsilon$ 4·47, 4·65, 4·41, 3·56). It yielded a deep red *2,4-dinitrophenylhydrazone*, m. p. 312—314° (decomp.) (Found: C, 63·5; H, 3·3; N, 16·0. $C_{19}H_{12}N_4O_4$ requires C, 63·3; H, 3·4; N, 15·6%).

β-*2-Biphenylenylacrylic acid.* A mixture of biphenylene-2-aldehyde (60 mg.), malonic acid (100 mg.), pyridine (0·3 ml.), and one drop of piperidine was heated on a water-bath for 8 hr. Next day the mixture was acidified with 10N-hydrochloric acid and the resulting precipitate was crystallised from ethanol. The *acrylic acid* formed deep yellow needles, m. p. 228—229° (Found: C, 81·2; H, 4·4. $C_{15}H_{10}O_2$ requires C, 81·1; H, 4·5%). The acid in ethanol had $\lambda_{max.}$ 239, 248, 283, 383 mμ ($\log_{10} \varepsilon$ 4·43, 4·48, 4·59, 4·02).

β-*2-Biphenylenylacrylophenone.* A mixture of biphenylene-2-aldehyde (100 mg.), acetophenone (80 mg.), and sodium hydroxide (1·2 g.) in ethanol (30 ml.) was stirred for 2 hr., then kept overnight in an ice-box. The *product* was recrystallised from aqueous ethanol and formed deep yellow needles, m. p. 128—129° (Found: C, 88·8; H, 4·8. $C_{21}H_{14}O$ requires C, 89·3; H, 5·0%).

2-Cinnamoylbiphenylene. Benzaldehyde (270 mg.) in ethanol (10 ml.) was added gradually to a stirred solution of 2-acetylbiphenylene (500 mg.) and sodium hydroxide (1·2 g.) in the same solvent (25 ml.). After the mixture had been stirred for 2 hours more, the precipitate was collected and recrystallised from ethanol, giving the *2-cinnamoylbiphenylene* (620 mg.) as yellow plates, m. p. 142—144° (Found: C, 89·0; H, 4·6. $C_{21}H_{14}O$ requires C, 89·3; H, 5·0%), $\lambda_{max.}$ (in EtOH) 237, 243, 265, 281, 313, 369, 394 mμ ($\log_{10} \varepsilon$ 4·48, 4·50, 4·34, 4·34, 4·43, 3·95, 3·94.)

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[6] Baker, Boarland, and McOmie, *J.*, 1954, 1476.

1017. *Methyl-substituted αβ-Unsaturated Acids. Part III.*[1]

By J. M. WHITELEY and N. POLGAR.

IN continuation of earlier studies [1] *trans*-10-hydroxy-2-methyldec-2-enoic acid has been prepared for comparison of its biological properties with those of *trans*-10-hydroxydec-2-enoic acid ("royal jelly acid").[2] The starting point was the known [3] 8-bromo-octyl acetate, obtained from 1,8-dibromo-octane by the action of silver acetate. The product, containing some unchanged dibromide and the diacetate, was condensed with the sodio-derivative of ethyl methylmalonate; the procedure described in the Experimental section then gave methyl 10-hydroxy-2-methyldecanoate. We then turned to the preparation of the corresponding αβ-unsaturated ester.

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[1] Part II, Bailey, Polgar, Tate, and Wilkinson, *J.*, 1955, 1547.

[2] Townsend and Lucas, *Biochem. J.*, 1940, **34**, 1155; Fray, Jaeger, Morgan, Robinson, and Sloan, *Tetrahedron*, 1961, **15**, 18.

[3] Pattison, Howell, McNamara, Schneider, and Walker, *J. Org. Chem.*, 1956, **21**, 739.

Hydrolysis of the above hydroxy-ester, followed by acetylation of the resulting acid, gave the 10-acetoxy-acid. Bromination of this acid in the presence of red phosphorus under the usual [1] conditions of the Hell–Volhard–Zelinsky method, followed by treatment with methanol, resulted in the formation of a dibromo-ester; we, therefore, performed the bromination in the presence of carbon tetrachloride according to the directions given by Howe and Pietrusza.[4] On treatment of the brominated material with methanol the resulting bromo-ester showed hydroxyl absorption in its infrared spectrum, presumably owing to removal of the acetoxy-group as a result of transesterification. Re-acetylation, followed by dehydrobromination with pyridine, gave the αβ-unsaturated acetoxy-ester showing $\lambda_{max.}$ 2120 Å (ε 9850), the somewhat low ε value indicating incomplete bromination in the earlier stage. Vapour-phase chromatography of this product afforded the acetoxy-ester with ε 10,900 at 2130 Å; hydrolysis of the ester gave 10-hydroxy-2-methyldec-2-enoic acid ($\lambda_{max.}$ 2180 Å; 10,000) which from its method of preparation is regarded as the *trans*-isomer.

Experimental.—Alumina used for chromatography (Spence, type H) was deactivated by being shaken with 7% of its weight of aqueous 10% acetic acid; its activity was tested according to Brockmann and Schodder's method.[5] Petrol refers to light petroleum, b. p. 40—60°.

Methyl 10-*hydroxy*-2-*methyldecanoate*. 1,8-Dibromo-octane [3] was converted by the action of silver acetate [3] into 8-bromo-octyl acetate. The crude product (60 g.), b. p. 140—156°/10 mm., was refluxed for 12 hr. with ethyl sodiomethylmalonate (from 60 g. of ethyl methylmalonate, 8 g. of sodium, and 205 ml. of ethanol). After dilution with water the product was isolated by means of ether, then refluxed with potassium hydroxide (56 g.) in 1 : 2 aqueous methanol (240 ml.) for 4 hr. Most of the methanol was then distilled off, and the residue poured into dilute hydrochloric acid. The product, isolated by extraction with ether, was decarboxylated by heating it at 180° for 2 hr.; it was then refluxed with potassium hydroxide (16 g.) in 1 : 1 aqueous methanol (240 ml.) for 4 hr. in order to hydrolyse any ester or lactone present. After removal of most of the methanol by distillation, the residue was acidified with hydrochloric acid and extracted with ether from which the acidic fraction was removed with 5% aqueous potassium hydroxide. The acid liberated by hydrochloric acid was esterified with refluxing 5% methanolic sulphuric acid (400 ml.; 3 hr.), and the product chromatographed in petrol on alumina (1500 g.; activity IV). The fractions eluted by petrol–benzene (1 : 1) were rejected; further elution with ether gave *methyl* 10-*hydroxy*-2-*methyldecanoate* as an oil (22 g.) (Found: C, 67·1; H, 11·3. $C_{12}H_{24}O_3$ requires C, 66·6; H, 11·2%).

10-*Hydroxy*-2-*methyldec*-2-*enoic acid*. The above methyl ester (25 g.) was hydrolysed by refluxing aqueous-methanolic 10% potassium hydroxide (3 hr.), and the liberated acid, isolated by ether-extraction, was treated with acetic anhydride (100 ml.) and fused sodium acetate (1·5 g.) at the b. p. for 4 hr. The product (isolated by removal of the excess of acetic anhydride by distillation, followed by addition of water and extraction with ether) showed in its infrared spectrum the presence of anhydride; it was refluxed with glacial acetic acid (100 ml.) for 2 hr. Removal of the acetic acid by distillation gave the acetoxy-acid (26 g.). To a mixture of the acetoxy-acid (5 g.), red phosphorus (0·8 g.), carbon tetrachloride (50 ml.), and water (0·5 ml.), bromine (12 g.) was added dropwise during 1 hr. with stirring. Stirring was continued for a further hr., the temperature being kept below 50°, after which the carbon tetrachloride was distilled off. Further bromine (3 g.) was then added (below 50°), and the mixture was heated at 100° for 45 min.; this procedure was repeated with a further quantity (1·5 g.) of bromine. The product was then cooled, methanol (30 ml.) added, and the mixture refluxed for 3 hr. Dilution with water and extraction with ether afforded the crude bromo-ester which showed in its infrared spectrum a band at 3448 cm.$^{-1}$ (OH). It was, therefore, re-acetylated with acetic anhydride (as above), and the resulting acetoxy-ester and pyridine (15 g.) were refluxed for 18 hr. The mixture was then cooled and poured into dilute hydrochloric acid, and the product isolated, with ether, as a liquid, b. p. 145—155° (bath)/0·1 mm. (1·22 g.). It showed in its infrared spectrum bands at 1739 (ester), 1709 (conjugated ester), and 1650 cm.$^{-1}$ (conjugated C=C), and had $\lambda_{max.}$ 2120 Å (ε 9850). Vapour-phase chromatography of this material

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[4] Howe and Pietrusza, *J. Amer. Chem. Soc.*, 1949, **71**, 2581.

[5] Brockmann and Schodder, *Ber.*, 1941, **74**, 73.

on a column containing 30% of Apiezon " L " on " Embacel " at 197° gave *methyl* 10-*acetoxy*-2-*methyldec*-2-*enoate* as the major fraction, $\lambda_{max.}$ 2130 Å (ε 10,900) (Found: C, 65·5; H, 9·4. $C_{14}H_{24}O_4$ requires C, 65·6; H, 9·4%). Hydrolysis of this ester afforded the hydroxy-acid, n_D^{19} 1·4820, $\lambda_{max.}$ 2180 Å (ε 10,000); the α-*naphthylurethane* had m. p. 90—91° after crystallisation from light petroleum (b. p. 100—120°) (Found: C, 71·4; H, 7·5; N, 4·1. $C_{22}H_{27}NO_4$ requires C, 71·5; H, 7·4; N, 3·8%).

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1018. *Synthesis and Purification of* m-*Ethylphenol.*

By J. E. CONNETT and J. B. DITCHAM.

IN continuation of work[1] on the determination of the thermodynamic properties of oxygen-containing compounds, substantial amounts of very pure *m*-ethylphenol were required. Kenner and Statham[2] prepared this compound from acetophenone by way of the *m*-nitro-, *m*-amino-, and *m*-hydroxy-compounds. Variants of their process, or parts of it, have been described by others.[3,4]

We used Kenner and Statham's method with modifications described below, the following points being notable. *m*-Nitroacetophenone is best precipitated from the reaction mixture in water containing solid carbon dioxide,[3] and it should be twice crystallised before use in the next stage. It can be conveniently reduced to *m*-ethylaniline in one stage by hydrazine and potassium hydroxide in boiling diethylene glycol.[5] *m*-Ethylphenol obtained by the diazo-reaction from the amine always had a brownish-yellow colour which infrared evidence and the further discoloration in contact with aqueous alkali suggested was due to a quinonoid impurity; this was not removed by distillation *in vacuo* or in steam, or by passage of the phenol through its adduct with *o*-toluidine.[6] It was, however, removed when the phenol was treated with zinc and hydrochloric acid (which would reduce any quinone present) before being purified as this adduct. Final distillation and fractional freezing gave *m*-ethylphenol with a purity of 99·94 ± 0·02%, as estimated by cryoscopy.

Experimental.—m-*Nitroacetophenone.* Redistilled acetophenone (150 g.) was nitrated by Cobb's method.[3] The brownish-yellow precipitate gave a pale yellow solid from alcohol (charcoal), and almost white crystals of *m*-nitroacetophenone in 70—72% yield when recrystallised from aqueous acetic acid. Different preparations having m. p. between 77° and 82° were sufficiently pure for use in the next stage.

m-*Ethylaniline.* Hydrazine hydrate (99—100%; 160 ml.) was added to a stirred suspension of *m*-nitroacetophenone (100 g.) in diethylene glycol (750 ml.), and the mixture was refluxed for 30 min., then cooled to 77° (12 min.), and a solution of potassium hydroxide (134 g.) in water (80 ml.) was added during 4 min. Heating was resumed and the mixture was refluxed 30 min. Water was then distilled off until the liquid temperature reached 198°, whereupon refluxing was resumed for 60 min. The amine was isolated by steam-distillation and separated from non-basic impurities by shaking an ether extract of the distillate with 4N-hydrochloric

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[1] Andon, Biddiscombe, Cox, Handley, Harrop, Herington, and Martin, *J.*, 1960, 5246; Green, *J.*, 1961, 2236, 2241; Cox, *Trans. Faraday Soc.*, 1961, **57**, 1674; Green, *ibid.*, p. 2132.

[2] Kenner and Statham, *J.*, 1935, 299.

[3] Cobb, *Proc. S. Dakota Acad. Sci.*, 1945, **25**, 64.

[4] Rupe and Majewski, *Ber.*, 1900, **33**, 3407; Morgan and Watson, *J. Soc. Chem. Ind.*, 1936, **55**, 29T; Simpson, Atkinson, Schofield, and Stephenson, *J.*, 1945, 646; Lock, *Monatsh.*, 1954, **85**, 802; Oki and Sato, *Bull. Chem. Soc. Japan*, 1957, **30**, 508; Landa and Maćak, *Chem. Listy*, 1957, **51**, 1851; Helferich and Rullman, *J. prakt. Chem.*, 1960, **11**, 233.

[5] Huang-Minlon, *J. Amer. Chem. Soc.*, 1948, **70**, 2802; Campbell, Ginsig, and Schmid, *Helv. Chim. Acta*, 1953, **36**, 1489.

[6] Reilly Tar and Chemical Corporation, U.S.P. 2,490,671.

acid. The acid extract was rendered alkaline with sodium hydrogen carbonate and re-extracted with ether. The ethereal solution was dried ($MgSO_4$) and after removal of the solvent the *m*-ethylaniline was distilled, yielding a base (57 g., 77%), b. p. 56°/0·25 mm.

m-*Ethylphenol.* A stirred solution of *m*-ethylaniline (150 g.) in concentrated sulphuric acid (*d* 1·84; 135 ml.) and water (1 l.) was cooled in an ice–salt bath, and ice (1 kg.) was added. When the mixture had cooled to between $-3°$ and $-5°$, a solution of sodium nitrite (95 g.) in water (200 ml.) was added, the temperature being kept below 0° during the addition and for 1 hr. afterwards. The mixture was then heated to 70°, and when the effervescence ceased the crude *m*-ethylphenol was steam-distilled. The distillate was extracted with ether, the solvent removed, and the residue stirred vigorously with zinc dust (10 g.) in N-hydrochloric acid (375 ml.) at 80° for 10 min. The suspension was filtered and the filtrate steam-distilled. The material obtained by ether-extraction of the distillate was distilled, yielding nearly colourless *m*-ethylphenol (89 g., 59%), b. p. 48—53°/0·3 mm.

Purification of m-*ethylphenol.* A stirred solution of *m*-ethylphenol (100 ml.) and *o*-toluidine (176 ml.) in light petroleum (b. p. 40—60°; 1 l.) was cooled to $-5°$ and a few crystals of the adduct (previously obtained by cooling a mixture of *o*-toluidine and *m*-ethylphenol in solid carbon dioxide–alcohol) were added. Rapid crystallisation was accompanied by a rise in temperature to $+5°$, and cooling was continued until the temperature was again $-5°$. The crystals were filtered off and washed rapidly with light petroleum (b. p. 40—60°; 1 l.) which had been precooled to *ca.* $-20°$. As much solvent as possible was removed on the filter, and the crystals were decomposed by addition to 4% sodium hydroxide solution (1 l.). The organic phase (*o*-toluidine) was removed by steam-distillation, and the remaining sodium *m*-ethylphenoxide solution was cooled and acidified with hydrochloric acid (*d* 1·18; 96 ml.). The mixture was steam-distilled and the organic phase was dried ($MgSO_4$) and distilled *in vacuo*, yielding *m*-ethylphenol (62 g.), b. p. 37°/0·05 mm. To this was added, after further treatment with *o*-toluidine, the material obtained by ether-extraction of the aqueous phase. The purification was repeated, if necessary, until the gas chromatogram showed only one peak. The overall yield calculated on acetophenone was 20%.

Final purification was effected by slow fractional freezing under nitrogen. The *m*-ethylphenol then had a cryoscopically determined purity of 99·94 moles %.

The purity determinations were carried out by Mr. D. Harrop, and the gas chromatography by Messrs. T. R. D. Chandler and D. Harrop.

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1019. *Heterocyclic Compounds of Nitrogen. Part V.*[1] *The Preparation of* 1,3-*Diacetyl- and* 3-*Acetyl*-1-*methyl*-3-*phenyloxindole.*

By J. MALCOLM BRUCE.

TREATMENT of 3-phenyloxindole with acetic anhydride yields the 1-acetyl derivative, whilst in the presence of an acidic catalyst 2-acetoxy-1-acetyl-3-phenylindole is formed.[2] With sodium acetate as catalyst a different diacetyl derivative, having the ultraviolet absorption spectrum of a 1-acetyl-3-phenyloxindole,[2] results, and the same product is obtained when 1-acetyl-3-phenyloxindole is similarly acetylated. The infrared spectrum shows three carbonyl bands, but the compound fails to form ketonic derivatives, and yields 3-phenyloxindole when treated[2] with ethanolic hydrazine hydrate. These properties, together with the fact that 3-methyl-3-phenyloxindole yields only the 1-acetyl derivative when acetylated under similar conditions, suggest that the compound is 1,3-diacetyl-3-phenyloxindole. This is confirmed by the absence of absorption in the 5—6

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[1] Part IV, Bruce, *J.*, 1962, 1514.
[2] Bruce and Sutcliffe, *J.*, 1957, 4789.

τ region of its proton magnetic resonance spectrum; the 3-proton in 1-acetyl-3-phenyloxindole absorbs at 5·47.

1-Methyl-3-phenyloxindole similarly yields a 3-acetyl derivative. Both compounds are readily hydrolysed by aqueous-ethanolic sodium hydroxide, in agreement with the properties reported [3] for other 3-acyloxindoles.

Experimental.—Sublimation and bulb-to-bulb distillation temperatures are those of the heating-bath. Infrared spectra, for Nujol mulls, were measured in a Perkin-Elmer model 21 double-beam spectrometer, and ultraviolet spectra, for dioxan solutions, in a Unicam S.P. 500 spectrophotometer. Nuclear magnetic resonance spectra, in carbon tetrachloride, were determined at 60 Mc./sec. with an Associated Electrical Industries model RS2 spectrometer, tetramethylsilane being used as internal standard. M. p.s are corrected.

1,3-*Diacetyl*-3-*phenyloxindole.* A mixture of 3-phenyloxindole [2] (0·42 g.), powdered anhydrous sodium acetate (1·2 g.), and acetic anhydride (10 c.c.) was refluxed for 3 hr., the solvent was removed, and the residue was shaken with water (10 c.c.) and extracted with ether. The extract was washed with water and dried (Na_2SO_4), and the solvent was removed. Distillation (bulb-to-bulb, 120°/0·01 mm.) of the residue, and crystallisation of the distillate from ethanol, gave the *oxindole* (0·48 g., 81%) as plates, m. p. 102·5—104° raised to 105° by recrystallisation (Found: C, 73·8; H, 5·0; N, 5·0; Ac, 30·6. $C_{18}H_{15}NO_3$ requires C, 73·7; H, 5·1; N, 4·8; Ac, 29·4%), $\lambda_{max.}$ nil, $\nu_{max.}$ 1767, 1734, 1711 cm.$^{-1}$, τ 7·47, 7·88 in the ratio 1 : 1 (cf. 1-acetyl-3-phenyloxindole, τ 5·47, 7·55 in the ratio 1 : 3). Identical (m. p., mixed m. p., and infrared spectrum) material was obtained in 77% yield when 1-acetyl-3-phenyloxindole [2] was similarly acetylated; 3-methyl-3-phenyloxindole gave a 90% yield of its 1-acetyl derivative,[2] m. p. and mixed m. p. 113°.

Cleavage of 1,3-*diacetyl*-3-*phenyloxindole.* A mixture of the diacetyl compound (0·88 g.), 99% hydrazine hydrate (1·8 c.c.), and ethanol (15 c.c.) was refluxed for 8 hr., the solvent was removed, and the residue was dissolved in ethanol (5 c.c.). Addition of water (20 c.c.), and sublimation of the precipitate at 180°/0·01 mm. gave 3-phenyloxindole (0·58 g., 93%), m. p. and mixed m. p. 191—192°. Removal of the solvent from the aqueous phase and treatment of the residue with acetone afforded acetone acetylhydrazone (0·42 g., 62%), m. p. 135—136° raised by crystallisation from acetone to 139—139·5° (lit.,[4] 138°, 139·5—140°) (Found: N, 24·5. Calc. for $C_5H_{10}N_2O$: N, 24·6%).

3-*Acetyl*-1-*methyl*-3-*phenyloxindole.* Acetylation of 1-methyl-3-phenyloxindole [2] (0·45 g.) as described for 3-phenyloxindole, distillation (bulb-to-bulb, 150°/0·01 mm.) of the ether-soluble material, and crystallisation of the distillate from light petroleum (b. p. 60—80°) gave the *oxindole* (0·29 g., 53%) as prisms, m. p. 85° (Found: C, 76·8; H, 5·6; N, 5·5; Ac, 16·4. $C_{17}H_{15}NO_2$ requires C, 77·0; H, 5·7; N, 5·3; Ac, 16·2%), $\lambda_{max.}$ 261 mμ (log ε 3·89), $\nu_{max.}$ 1737, 1706 cm.$^{-1}$, τ 6·93, 7·92 in the ratio 1 : 1 (cf. 1-methyl-3-phenyloxindole, τ 5·63, 6·94 in the ratio 1 : 3).

The author thanks Mrs. R. C. Hignett for the measurement of nuclear magnetic resonance spectra.

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MANCHESTER. [*Received, July* 16*th*, 1962.]

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[3] Julian, Magnani, Pikl, and Karpel, *J. Amer. Chem. Soc.*, 1948, **70**, 174; Julian, Pikl, and Wantz, *ibid.*, 1935, **57**, 2026.

[4] Elks and Phillipps, *J.*, 1956, 4326; Turner, *J. Amer. Chem. Soc.*, 1947, **69**, 875.