NOTES.

Composition, Pressure, and Temperature Relationships in Binary Azeotropic Systems. By O. REDLICH.

THE recent paper by Coulson and Herington (*J.*, 1947, 597; see also *Nature*, 1946, **158**, 198) follows the discussion of the azeotropic equilibrium presented by the author and the late Professor P. W. Schutz (*J. Amer. Chem. Soc.*, 1944, **66**, 1007) in various steps, namely, in the enumeration of the relationships between composition, pressure, and temperature, in the procedure of deriving these relationships, and in the application to available data regarding the azeotropic temperature range and Wrewski's rule. There are, however, differences in three points :

(1) The quantities $(\partial a/\partial T)_{N_2}$ and $(\partial a/\partial N_2)_T$ in Coulson and Herington's eqn. (4) are undefined as long as no instruction is given as to how the pressure is to be varied in the calculation of these derivatives. In view of the interdependence of the variables the pressure cannot be kept constant, but it is to be considered as a function either of N_2 or, more conveniently, of T. A simple calculation shows that the expression $[\partial(\ln p_1/p_2)/\partial T]_{N_2}$ in eqn. (8) is not to be derived at constant pressure, as we should expect without further instruction, but with the pressure varying according to the shift of the azeotropic equilibrium. Consequently this term must not be replaced by $(\bar{H}_1 - \bar{H}_2)/RT^2$ as suggested by Coulson and Herington but by $(\bar{H}_1 - \bar{H}_2 + v\Delta H)/RT^2$ in precise agreement with eqn. (10) of our paper. This equation follows in a straightforward way from our eqn. (4) which expresses a total differentiation in precise terms. The belief that three independent variables appear in our eqn. (4) rests on a misunderstanding.

The term $v\Delta H$ is quite frequently *not* negligible compared with $\bar{H}_1 - \bar{H}_2$. It may be even of the same order of magnitude, for instance, if both components approximately satisfy Trouton's rule or deviate from this rule by approximately equal amounts.

(2) Coulson and Herington suggest a linear relationship between T and N_2 for determining the azeotropic temperature range, and represent data for aqueous solution of hydrogen chloride by a straight line in their Fig. 1. They overlook our strict conclusion that systems with a dissociating component have an infinite azeotropic temperature range. A linear relationship is inconsistent with this conclusion.

(3) The fact that the N_2-T curves can be approximated by straight lines even for not " strictly regular " solutions results in the case of hydrogen chloride solutions simply from the smallness of the composition range $(0.107 < N_2 < 0.131)$. For ethyl acetate–ethanol a systematic deviation is noticeable; it would be more conspicuous if the point at 0° were added (see Fig. 1 of our paper). No conclusion can be drawn from the fact that data in a limited range can be imperfectly represented by a relationship with two coefficients *derived from the same data*. In our discussion, on the other hand, the results for hydrochloric acid were derived from *entirely different* data (activity coefficients, etc.).

No objection is raised against the simplification of general thermodynamic relationships by justified assumptions. The danger of oversimplification is sufficiently illustrated by the example of the hydrogen chloride solutions. In a case like this significant results cannot be obtained without somewhat laborious calculations. The legitimate range of application of the " strictly regular " solution is so narrow that the general relationships cannot be dispensed with. The special case was only briefly mentioned in our discussion because all essential aspects were fully discussed by Kireev and, in principle, even earlier by Herzfeld and Heitler (*Z. Elektrochem.*, 1925, **31**, 536).

A few decades ago quite a few physical chemists believed that general thermodynamic relationships are " formal " and not useful in practical applications because at that time convenient methods were developed only for the perfect solution. We should avoid a similar restriction to " strictly regular " solutions.—BERKELEY, CALIFORNIA. [*Received, September 19th,* 1947.]

Remarks on Redlich's Note on Composition, Pressure, and Temperature Relationships in Binary Azeotropic Systems. By E. A. COULSON and E. F. G. HERINGTON.

THROUGH the courtesy of Dr. Redlich we have been able to see a copy of the preceding Note. Our critical review of prior work led us to extend the discussion to include "strictly regular" solutions which allowed us to obtain explicit relationships between composition and pressure and temperature. This is beyond the scope of Redlich and Schutz's treatment (*loc. cit.*) even if the latter had been formally accurate.

The first point is the central issue between us. The pressure is precisely specified in our treatment as being throughout the total pressure of the vapour phase, so that the differentials to which Redlich draws attention are completely defined. Redlich and Schutz's equations (4) and (9) cannot be reconciled with our corresponding equations (4) and (8). The difference is fundamental. Redlich now disputes that three independent variables appear in his equation (4), thus tacitly admitting that there should not be more than two independent variables, but there can, we think, be no question that three independent

variables have in fact been employed by Redlich. Moreover, no explanation has been furnished, even now, why the phase rule is ignored in this way.

The second and the third point are of minor interest. They raise matters upon which opinions may legitimately differ and do not seem to warrant further discussion at this stage.—CHEMICAL RESEARCH LABORATORY, TEDDINGTON, MIDDLESEX. [*Received, October 7th, 1947.*]


The Action of Hydrochloric Acid on 5 : 5-Dichloro-6-hydroxy-6-methyl-5 : 6-dihydrouracil.
By J. W. CORNFORTH and H. T. HUANG.

JOHNSON (*J. Amer. Chem. Soc.*, 1943, **65**, 1220; 1944, **66**, 146) has reported that 5 : 5-dichloro-6-hydroxy-6-methyl-5 : 6-dihydrouracil (I) on treatment with hot hydrochloric acid or acetic anhydride gave a substance to which he ascribed the " bicyclouracil " structure (II).

(I.) (II.) (III.) (IV.) (V.)
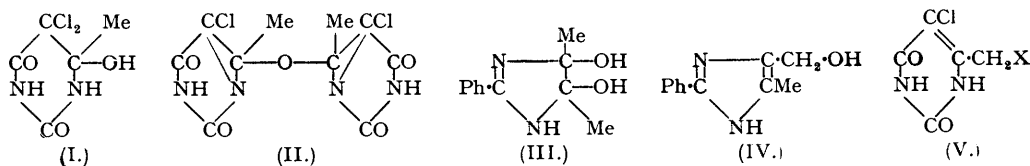
The action of hydrochloric acid on 4 : 5-dihydroxy-2-phenyl-4 : 5-dimethyl-4 : 5-dihydroglyoxaline (III) has been shown by us (this vol., p. 731) to give 2-phenyl-5-methyl-4-hydroxymethylglyoxaline (IV). The analogy between (I) and (III) prompted a repetition of Johnson's experiment : the
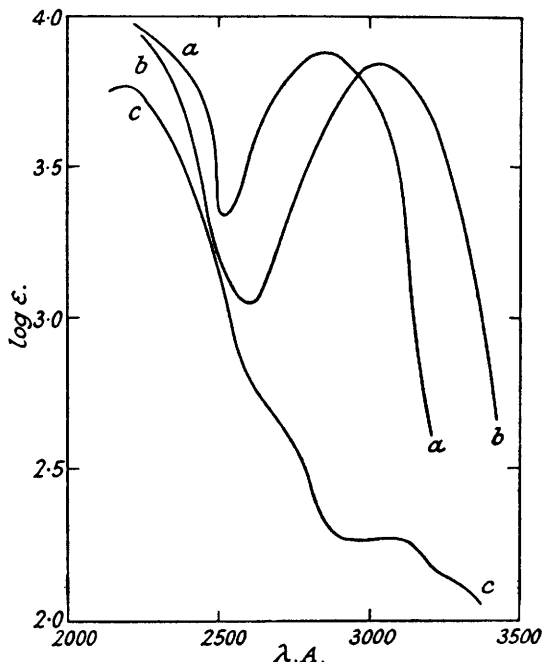
Ultra-violet absorption (*in* N/20 NaOH) *of* (a) 5-*chloro*-6-*methyluracil*, (b) 5-*chloro*-6-*chloromethyluracil*, (c) 5 : 5-*dichloro*-6-*hydroxy*-6-*methyl*-5 : 6-*dihydrouracil*.

dihydrouracil (2 g. : Behrend, *Annalen*, 1886, **236**, 59) was refluxed with concentrated hydrochloric acid (20, 30, 40, 50 c.c.) for periods of 2—12 hours. The product (1·2—1·5 g.) was the same in every case; it crystallised from hot water, dilute hydrochloric acid, or glacial acetic acid in shining prisms, m. p. 270—275° (somewhat variable) with decomposition after decrepitation at 220° and darkening from 250°. The m. p. is that given by Johnson but a different composition was found on analysis (Found, after drying at 100—110° : C, 31·1, 31·2, 30·7, 30·9; H, 2·4, 2·1, 2·3, 2·2; N, 14·7; Cl, 36·3, 36·3, 35·9, 36·6, 36·4. $C_5H_4O_2N_2Cl_2$ requires C, 30·8, H, 2·1; N, 14·4; Cl, 36·4%). The ultra-violet absorption spectrum showed λ max. 3025 A. (log ϵ, 3·83), λ min. 2600 A. (log ϵ, 3·05). The presence of a true uracil ring was established by comparison with the spectra of 5-chloro-6-methyluracil (V; X = H; Behrend, *loc. cit.*), which had λ max. 2840 A. (log ϵ, 3·87), λ min. 2510 A. (log ϵ, 3·34), and of the dihydrouracil (I), which showed only end absorption. The substance is therefore 5-*chloro*-6-*chloromethyluracil* (V; X = Cl), and is evidently produced from (I) by dehydration and anionotropic change as postulated (*loc. cit.*) for the conversion of (III) into (IV). The same substance (V; X = Cl) was formed in poor yield by the action of acetic

anhydride on (I). When the chloromethyluracil (V; X = Cl) was refluxed in acetic acid for 4 hours with an equal weight of zinc dust, 5-chloro-6-methyluracil (V; X = H) was formed, m. p. 330—332° (decomp.) after crystallisation from water (Found: C, 37·8; H, 3·2; N, 17·0; Cl, 21·4. Calc. for $C_5H_5O_2N_2Cl$: C, 37·4; H, 3·1; N, 17·4; Cl, 22·1%). The chloromethyluracil (V; X = Cl) dissolved in dilute aqueous sodium hydroxide without decomposition, though, on keeping, chloride ion was slowly liberated; it was recovered unchanged (Found: Cl, 36·7%) after being kept for a fortnight with nitric acid (d 1·42) at room temperature. No product having the composition of (II) could be obtained by treating (I) with hydrochloric acid and no explanation of Johnson's results can be offered.

The Action of Amines upon Esters. Part II. By HARRY IRVING and HOWARD I. FULLER.

IT has now been confirmed that the formation of amines (III; X = H, alkyl, aryl, NHAr, etc.) rather than the amides expected by the action of ammonia and its substitution products upon certain esters (I; R = Ac) results from the addition of these amines to the double bond of the nitro-olefin (II) postulated as a reaction intermediate (Irving, *J.*, 1936, 797).*

$$CCl_3 \cdot CH(OR) \cdot CH_2 \cdot NO_2 \xrightarrow[-ROH]{(NH_2X)} CCl_3 \cdot CH{:}CH \cdot NO_2 \xrightarrow{+ NH_2X} CCl_3 \cdot CH(NHX) \cdot CH_2 \cdot NO_2$$
$$\text{(I.)} \qquad\qquad\qquad \text{(II.)} \qquad\qquad\qquad \text{(III.)}$$

Though elimination of acetic acid from the ester (I; R = Ac) by refluxing in ethereal solution with potassium hydrogen carbonate (cf. Schmidt and Rutz, *Ber.*, 1928, **61**, 2142) did not prove a satisfactory method of preparation, (II) was readily obtained by distilling the nitro-alcohol (I; R = H; 1 mol.) with phosphoric oxide (3 mols.) under reduced pressure (45 mm., oil-bath at 150°). 3 : 3 : 3-*Trichloro*-1-*nitropropene* (II) is a highly lachrymatory, pale yellow, oily liquid, b. p. 80—81°/13 mm., insoluble in water, but miscible with organic solvents (Found: C, 19·5; H, 1·3; N, 6·7; Cl, 55·8. $C_3H_2O_2NCl_3$ requires C, 18·9; H, 1·05; N, 7·35; Cl, 55·9%). It did not react with water during 2 months, or decolourise bromine within 48 hours but, as expected, it reacted exothermically with an alcoholic solution of phenylhydrazine (1 equiv.) to give a practically quantitative yield of 1 : 1 : 1-trichloro-3-nitro-2-phenylhydrazinopropane (III; X = NHPh), m. p. 119—120° from alcohol, identical with an authentic specimen prepared from phenylhydrazine and the nitro-ester (I; R = Ac); *p*-toluidine and (II) reacted in chloroform to give 1 : 1 : 1-trichloro-3-nitro-2-(*p*-toluidino)propane, which crystallised as pale yellow rhombs, m. p. 62° from petrol (b. p. 40—60°) or alcohol (cf. Chattaway, *J.*, 1936, 356). The nitro-olefin did not react with phenylhydrazine hydrochloride.

In ethyl alcohol at 20° the reaction between phenylhydrazine (0·046, 0·048, and 0·047 g.-mol./l.) and 1 : 1 : 1-trichloro-3-nitro-2-acetoxypropane (I; R = Ac; 0·075, 0·15, and 0·30 g.-mol./l.) was 50% completed in 60, 23, and 13 minutes, respectively. Under comparable conditions the ester did not react with phenylhydrazine hydrochloride and only slowly with phenylhydrazine acetate. The reaction with phenylhydrazine itself was found to be strongly catalysed by various bases; it could be stopped immediately by adding 2N-hydrochloric acid, and the rate determined by estimating excess phenylhydrazine iodometrically (Meyer, *J. pr. Chem.*, 1887, **36**, 115; as modified by Ardagh, *J. Amer. Chem. Soc.*, 1932, **54**, 721).—THE INORGANIC CHEMISTRY LABORATORY, OXFORD UNIVERSITY. [*Received, December 31st,* 1947.]

Preparation of Mannose. By F. SMITH.

HITHERTO the best source of mannose has been the vegetable ivory nut (Reiss, *Ber.*, 1889, **22**, 609). The preparation of mannose from ivory nut mannan worked out by Hudson (*Org. Synth.*, Coll. Vol. 1, 371) involves a lengthy hydrolysis of the mannan using considerable amounts of sulphuric acid. The mannose is purified by the formation of α-methylmannoside which is then reconverted into mannose in the usual way (Hudson and Jackson, *J. Amer. Chem. Soc.*, 1934, **56**, 958). Instead of ivory nut mannan which is relatively stable to acids, it is believed that carob gum, from the carob bean *Ceratonia siliqua*, a galactomannan containing 80% mannose, is a better source of mannose. This polysaccharide undergoes hydrolysis with ease, and high yields of α-methylmannoside can be obtained from it.

Experimental.—Carob gum (sometimes called St. John's bread), from the carob bean, *Ceratonia siliqua* (100 g.), is heated for 9 hours on the boiling water-bath with 0·5N-sulphuric acid (500 c.c.). After removal of a flocculent precipitate on the centrifuge, the solution ([α]$_D$ + 22·5°) is neutralised with a solution of barium hydroxide, treated with a little charcoal, and filtered hot. Evaporation of the filtrate to dryness under reduced pressure gives a glassy residue which is then boiled for 6 hours with 3% methyl-alcoholic hydrogen chloride (250 c.c.). The solution is concentrated under reduced pressure to half volume and cooled, and the crystalline α-methylmannoside is filtered off, washed with cold methyl alcohol, and dried (yield, 44 g.). A further 5—6 g. can be obtained from the mother liquors. After crystallisation from water the α-methylmannopyranoside shows m. p. 195°, [α]$_D^{18°}$ + 80° in water (c, 1·0).

Hydrolysis of the α-methylmannoside with N-sulphuric acid (5 parts) on a boiling water-bath until

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* After this paper had been submitted, Heath and Rose (*J.*, 1947, 1487) showed that the addition of amines to nitro-olefins is a general reaction, but, although noting that the latter can advantageously be replaced by esters of the corresponding nitro-alcohols, they do not comment on the mechanisms of these " abnormal " reactions (cf. Irving, *loc. cit.*).

the rotation is constant gives rise to mannose, which can be isolated and crystallised in the usual manner (cf. Hudson and Jackson, *loc. cit.*), m. p. 127—128°, $[\alpha]_D^{18°}$ + 14° equilibrium value in water (*c*, 2).—THE UNIVERSITY, MINNEAPOLIS, MINNESOTA, U.S.A. THE UNIVERSITY, EDGBASTON, BIRMINGHAM 15, ENGLAND. [*Received, November 26th*, 1947.]

The Dimerisation of Acenaphthylene. By V. A. CRAWFORD and C. A. COULSON.

IN the presence of ultraviolet light the acenaphthylene hydrocarbon (I) forms a colourless dimer (II). The nature and quantum efficiency of this process have recently been discussed by Bowen and Marsh (*J.*, 1947, 109). It seems probable that the mechanism is not a simple " collisional " one, but depends on the existence of van der Waals complexes in the solution.

In the case of a relatively non-polar molecule such as acenaphthylene, the formation of these complexes is probably facilitated by the presence of a high " free valence " at the reacting carbon atoms (Coulson,
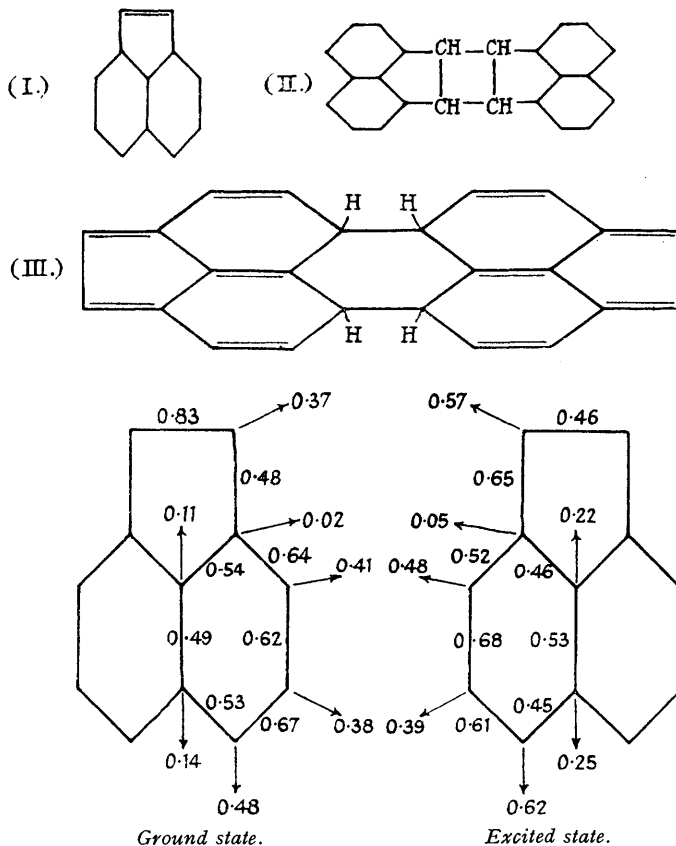
Bond orders and free valence in the ground and the excited state. For comparison, bond order in benzene is 0·67 and free valence is 0·35. In ethylene, they are 1·00 and 0·68, respectively.

Trans. Faraday Soc., to appear). For that reason, and in order to throw further light on the process, we have calculated the bond orders and free valences in this molecule, both in its ground state and in the lowest excited state. This latter is presumably the one into which the molecule is thrown by the absorption of the mercury 4360, 4050 and 3650 A. radiation used by Bowen and Marsh. We have adopted the standard molecular-orbital technique (see, *e.g.*, Coulson, *Quart. Reviews*, 1947, **1**, 144) for calculating bond orders and interpreting the lowest excited level. In these calculations we have neglected, as is usual, the overlap integral between adjacent carbon π orbitals.

The numerical results for the two electronic states are shown in the diagram. The figures along a bond denote the mobile bond order *p* (100*p* may be called percentage double-bond character), and the figures at the arrowheads denote the free valence at the appropriate carbon atom. As the molecule is symmetrical, bond orders and free valences on the one side are equal to those on the other side.

These figures show that the effect of excitation is to diminish the bond order of the ethylene-type linkage much more than that of any other part of the molecule. It is approximately, though not entirely, true to say that the excitation resides largely in this region. As a result, the free valence at each end of this bond is considerably enhanced, this increase much exceeding the increase at any other part of the

molecule. It is not in any way surprising, therefore, that the dimerisation takes place at this ethylene-type linkage, and that it is greatly facilitated by ultra-violet absorption. If our interpretation is correct, we have a good illustration of the fact that a high bond order is not, *per se*, an advantage in promoting reactivity of a homolytic kind. Rather is it true to say that the reactivity is increased when, as a result of electronic excitation, the high bond order has been sacrificed to create an enhanced free valence.

However, if we accept this large free valence at the outer link as an explanation of the dimerisation there, we have still to understand why no reaction takes place at the opposite vertices (4, 5 —) of the naphthalene nucleus, where the calculated free valence is also large. It seems fairly well established that dimerisation does not take place at these centres, even though, in the presence of a catalyst, naphthalene itself does react slightly in this manner to form dinaphthyl (Moureu, Chovin, and Rivoal, *Compt. rend.*, 1946, **223**, 951). The explanation is quite simple. For if we suppose the dimerisation to take place in such a way that (III) is formed, then, as the bond diagram shows, we are left with a molecule in which only quinonoid structures can be drawn, so that the aromatic character of both naphthalene nuclei has been destroyed. Indeed a system such as (III) must be much less favoured energetically than one such as (II) in which the resonance in both naphthalene nuclei is retained. This example shows that free valence, by itself, is not a sufficient guide to reactivity, even of homolytic type. It requires at least to be supplemented by a discussion of the stability of the final products.—DEPARTMENT OF THEORETICAL PHYSICS, KING'S COLLEGE, LONDON. [*Received, December 23rd, 1947.*]

Fluorides of the Natural Radioactive Elements. By H. J. EMELÉUS, A. G. MADDOCK, G. L. MILES, and A. G. SHARPE.

BROMINE trifluoride reacts rapidly and quantitatively at temperatures below its boiling point with most uranium compounds and forms the volatile hexafluoride. It has been established that under the same conditions, none of the other naturally occurring elements of atomic number greater than 80 (apart from radon) volatilises quantitatively with this reagent. This reaction is thus useful in the analysis of mixtures of radioactive materials and in the final stages of the preparation of large uranium-X_1 sources. Very thin uranium-X_1 sources have been prepared by solvent extraction of the bulk of the uranium in a sample of uranyl nitrate containing uranium decay products, followed by fluorination of the residue with bromine trifluoride. The evidence presented in no way excludes the formation of a volatile fluoride by an element such as polonium by other methods, *e.g.*, direct fluorination.

Experimental.—The elements other than uranium which might conceivably form volatile fluorides on treatment with bromine trifluoride are thallium, lead, bismuth, polonium, thorium, and protoactinium. As far as possible each of these was examined both by macro- and by tracer procedures. In the first case a weighed quantity of a compound of the element was treated with excess of liquid bromine trifluoride in a silica vessel attached by a train of traps to a vacuum apparatus. After allowing time for reaction, the excess of bromine trifluoride was pumped off and condensed. Finally, the reaction vessel was warmed to 120° at a pressure of less than 0·01 mm. The distillates were collected and analysed for the element under investigation.

No visible residue remained when 200-mg. samples of uranium metal, UO_2, UO_3, or U_3O_8 were treated. Gravimetric and colorimetric analysis of the distillate showed that the uranium had been volatilised quantitatively. No volatile products were obtained from thallium oxides, lead chloride, lead fluoride, or thorium oxide. The condensate obtained by treating bismuth trioxide gave a detectable reaction with hydrogen sulphide.

The tracer experiments were carried out by depositing the active material on glass or metal-foil discs, such as were used for counting. The activity of the deposit on the disc was measured before and after treatment with bromine trifluoride. The activity of the condensate was determined when that of the original deposit was decreased by the fluorination.

Three 100-mg. samples of U_3O_8 retained an average of 0·04% ± 0·01% of their α-activity after a short treatment with bromine trifluoride. The condensate, after correction for the uranium-X_1 grown since the time of distillation, possessed no activity. Thus uranium isotopes are volatile and those of thorium non-volatile under this treatment. With glass discs, mechanical losses prevented efficient recovery of the uranium-X_1, but with metal discs more than 90% of the β-activity remained on the discs. Rapid examination of the β-activity of the residues from the uranium oxide fluorination proved that the short-lived uranium-X_2 is also non-volatile under these conditions. This was confirmed by treatment of four foils supporting carrier-free ^{233}Pa. In each case the loss of activity by the foil was less than the counting error (± 1·5%). Similar results were obtained when using natural ^{231}Pa. Duplicate experiments with foils carrying thorium oxide containing mesothorium (an isotope of Ra) and mesothorium-2 (an isotope of Ac) showed no significant loss in activity.

A series of nine polonium foils gave a mean loss of 4·5% ± 1·0% on fluorination, but it was found that the same loss was experienced in blank experiments in which bromine trifluoride was omitted. It must therefore be attributed to the pseudo-volatility or recoil effect investigated by Lawson (*Nature*, 1919, **102**, 465). This is supported by the observation that less than 0·01% of the polonium reached the condensation trap. Four experiments with a mixture of Ra-D, Ra-E, and Ra-F on a lead oxide carrier showed that about 6% of the more penetrating β-active body (Ra-E) volatilised. Examination of the condensate showed the presence of 5% of the Ra-E originally present in the sample. This isotope of bismuth presumably volatilised as the pentafluoride, which has a sublimation pressure of 1 atm. at 550° (von Wartenburg, *Z. anorg. Chem.*, 1940, **244**, 337), as was indicated by the macro-experiments already described.—UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, January 15th, 1948.*]

The Condensation of Benzoin with Quinol or Resorcinol. By R. J. W. Le Fèvre, C. R. Taylor, and R. N. Whittem.

Japp and Meldrum (*J.*, 1899, **75**, 1035), by the condensation of benzoin with quinol or with resorcinol in 73% sulphuric acid obtained " para- or meta-benzotetraphenyldifurfuran," respectively, but made no decision between the obvious alternative formulæ, (I) or (II), (III) or (IV) (see Beilstein, " Handbuch," XIX, 62) :

(I.)   (II.)   (III.)   (IV.)
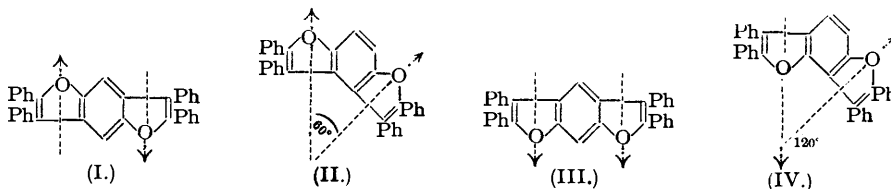
Such ambiguities should be resolvable by dipole-moment measurements since the molecular resultants to be expected are, for (I) *ca.* zero, for (II) *ca.* $\sqrt{3}\mu$, for (III) *ca.* 2μ, and for (IV) *ca.* μ, where μ is of the order of those observed for furan (0·63 D., Hunter and Partington, *J.*, 1931, 2062; 0·71 D., Smyth and Walls, *J. Amer. Chem. Soc.*, 1932, **54**, 3230), coumarone (0·79 D., Syrkin and Schott-Lvova, *J. Physical Chem. U.S.S.R.*, 1938, **12**, 479), and diphenylene oxide (0·88 D., Bretscher, *Helv. Physica. Acta*, 1929, **2**, 257), in benzene solutions.

We find, in fact, that in this solvent the quinol derivative has $\mu < 0.5$ D., while that from resorcinol has $\mu = 1.65$ D. It should be noted, however, (a) that the structure (I) has features liable to cause an anomalous solvation moment (Jenkins, *J.*, 1936, 910; Bauer, *J. Chem. Physics*, 1936, **4**, 458; Frank and Sutton, *Trans. Faraday Soc.*, 1937, **33**, 1307; cf., however, Coop and Sutton, *J.*, 1938, 1269) which might easily account for an " apparent " μ of 0·2 or 0·3 D., and (b) that in the calculation from the observed 5 c.c. excess of total polarisation over the molecular refraction for Na light, the atomic polarisation (which, while not additive, often increases with the number of atoms in a molecule, cf. Sugden, *Trans. Faraday Soc.*, 1934, **30**, 734; Coop and Sutton, *loc. cit.*) has not been fully subtracted. If, following the common convention, we were to take the distortion polarisation as $1.05 \times [R_L]_D$ the figure obtained, 159·6 c.c., would actually exceed our experimental result.

We conclude therefore that (I) and (III) are indicated as the correct formulæ.

Chemical Evidence.—These condensations have been studied also by Dischendorfer (*Sitzungsber. Akad. Wiss. Wien*, 1933, **142**, 69; *Monatsh.*, 1933, **62**, 263; 1935, **66**, 201) who, by chromic acid oxidation of the chief products in acetic acid, isolated the dibenzoates of 2 : 5-dihydroxy-1 : 4-dibenzoyl- and 2 : 4-dihydroxy-1 : 5-dibenzoyl-benzene, respectively (cf. Desai and Radha, *Proc. Indian Acad. Sci.*, 1940, **12**, A, 46). Such degradations are in accord with the conclusion reached from the present measurements.

Material and Apparatus.—The condensations were effected by the procedure described by Dischendorfer or Japp and Meldrum (*loc. cit.*), followed by recrystallisation from hot acetic acid (since the resorcinol derivative separated from benzene with solvent of crystallisation). The m. p.s observed were : resorcinol product, 223° (217—219°, J. and M.; 221—222°, D.); quinol product, 280—281° (278°, J. and M.; 281°, D.).

The apparatus used is described by Calderbank and Le Fèvre (this vol., p. 1950) except that for the present work a dielectric cell constructed of concentric brass cylinders sealed into an annular glass envelope (compare the description given in *Trans. Faraday Soc.*, 1947, **43**, 377) replaced the usual silvered Sayce–Briscoe condenser.

The necessary experimental data are set out below, followed by the calculation of results, under headings explained previously (*J.*, 1937, 1805) :

100 ω_1.	$\epsilon_{25°}$.	$d_4^{25°}$.	$\alpha\epsilon_2$.	β.	100 ω_1.	$\epsilon_{25°}$.	$d_4^{25°}$.	$\alpha\epsilon_2$.	β.
0	2·2725	0·87378	—	—	0	2·2725	0·87378	—	—

" p-Benzotetraphenyldifurfuran."					" m-Benzotetraphenyldifurfuran."				
0·2452	2·2740	0·87447	0·612	0·322	0·3280	2·2762	0·87464	1·128	0·300
0·2824	2·2742	0·87462	0·602	0·343	0·6232	2·2795	0·87540	1·123	0·298
0·2922	2·2742	0·87464	0·582	0·337	1·174	2·2858	0·87689	1·133	0·303

Substance.	Mean $\alpha\epsilon_2$.	Mean β.	$_\infty P_1$.	$[R_L]_D.$*	μ, D.
" p-Benzotetraphenyldifurfuran "	0·599	0·334	156·9	151·6	0·51
" m-Benzotetraphenyldifurfuran "	1·128	0·300	208·3	151·6	1·65

* Calc. from : $2 \times R_{stilbene}$ (Chilesotti, *Gazzetta*, 1900, **30**, 153) $+ 1 \times R_{benzene} + 2 \times E_{ether\ oxygen} - 8 \times R_H = 130.9 + 26.2 + 3.3 - 8.8 = 151.6$ c.c.

Some Tri- and Tetra-nitro-4-methyldiphenylamines. By A. F. CHILDS and S. G. P. PLANT.

THE only reference in the literature to a tetranitro-derivative of 4-methyldiphenylamine relates to a compound, m. p. 219°, obtained by Reverdin and Crépieux (*Ber.*, 1903, **36**, 29; *Bull. Soc. chim.*, 1903, **29**, 235) by the nitration of 2′ : 4′-dinitro-4-methyldiphenylamine. Its constitution was not established, and its composition was determined only by a nitrogen determination. It has now been found that the product of the reaction carried out under conditions similar to those used by these authors is 2 : 2′ : 4′-trinitro-4-methyldiphenylamine, m. p. 221°, identified by synthesis from 1-chloro-2 : 4-dinitrobenzene and 3-nitro-*p*-toluidine. 3 : 2′ : 4′-Trinitro-4-methyldiphenylamine, m. p. 207°, has been prepared, for comparison, from 1-chloro-2 : 4-dinitrobenzene and 2-nitro-*p*-toluidine. Further nitration of the 2 : 2′ : 4′-trinitro-compound under more vigorous conditions gave 2 : 6 : 2′ : 4′-tetranitro-4-methyldiphenylamine, m. p. 169°, the constitution of which followed from the fact that it was also obtained by the nitration of 2 : 6-dinitro-4-methyldiphenylamine. 2 : 2′ : 4′ : 6′-Tetranitro-4-methyldiphenylamine has been made, for comparison, from picryl chloride and 3-nitro-*p*-toluidine.

2 : 2′ : 4′-Trinitro-4-methyldiphenylamine.—(*a*) When 2′ : 4′-dinitro-4-methyldiphenylamine (7·5 g., prepared from 1-chloro-2 : 4-dinitrobenzene and *p*-toluidine as described by Reitzenstein *J. pr. Chem.*, 1903, **68**, 251) was heated for an hour on a steam-bath with nitric acid (60 c.c., *d* 1·23), the scarlet needles were converted into an orange-yellow solid. After addition of water, the product (6·8 g.), m. p. 210° (after previous softening), was collected and dried. On crystallisation from ethyl acetate, 2 : 2′ : 4′-trinitro-4-methyldiphenylamine was obtained in orange-yellow needles, m. p. 221° (Found : C, 48·8; H, 3·1; N, 17·4. $C_{13}H_{10}O_6N_4$ requires C, 49·1; H, 3·2; N, 17·6%). (*b*) After a mixture of 1-chloro-2 : 4-dinitrobenzene (2 g.), 3-nitro-*p*-toluidine (1·6 g.), and potassium carbonate (1·4 g.) had been heated at 150—180° for 1½ hours, the solid mass was ground with warm dilute hydrochloric acid, dried, and boiled with ethyl acetate containing a little charcoal. When the solution was filtered and cooled, 2 : 2′ : 4′-trinitro-4-methyldiphenylamine, identical (mixed m. p.) with the product described above, separated.

3 : 2′ : 4′-Trinitro-4-methyldiphenylamine.—A mixture of 1-chloro-2 : 4-dinitrobenzene (6 g.), 2-nitro-*p*-toluidine (4·8 g.), and potassium carbonate (4·2 g.) was heated at 150—160° for an hour, and the product, after being washed with warm dilute hydrochloric acid, was crystallised from glacial acetic acid (charcoal). 3 : 2′ : 4′-*Trinitro-4-methyldiphenylamine* was obtained in golden brown plates, m. p. 207° (Found : C, 49·5; H, 3·1; N, 17·5%). This compound is mentioned in a German patent (D.R.-P., 148,113; Friedlaender, " Fortschritte der Teerfarbenfabrikation," **7**, 341), but no properties are given and no details of its preparation except that the starting materials were the same as those now used.

2 : 6 : 2′ : 4′-Tetranitro-4-methyldiphenylamine.—(*a*) When 2 : 2′ : 4′-trinitro-4-methyldiphenylamine (1 g.) was heated on a steam-bath with concentrated nitric acid (25 c.c., *d* 1·42), it gradually dissolved during about 5 minutes. The solution was poured into ice–water, and 2 : 6 : 2′ : 4′-*tetranitro-4-methyl-diphenylamine* was precipitated. By crystallisation from alcohol, it was obtained in bright yellow needles, m. p. 169° (Found : C, 42·7; H, 2·4; N, 18·9. $C_{13}H_9O_8N_5$ requires C, 43·0; H, 2·5; N, 19·3%). (*b*) 2 : 6-Dinitro-4-methyldiphenylamine (0·5 g., prepared from 3 : 5-dinitro-*p*-cresol as described by Ullmann and Nádai, *Ber.*, 1908, **41**, 1870) was added to nitric acid (15 c.c., *d* 1·42) at 90°, and the solution, after ½ minute, was poured on ice. When the precipitate was crystallised from alcohol, 2 : 6 : 2′ : 4′-tetranitro-4-methyldiphenylamine, identical (mixed m. p.) with the material described above, was obtained in lemon-yellow needles, m. p. 169°. Jackson and Ittner (*Amer. Chem. J.*, 1897, **19**, 1) state that 2 : 6-dinitro-4-methyldiphenylamine is converted by nitric acid (*d* 1·36) into a " yellow substance, probably a nitro compound ", but the product was not examined further.

2 : 2′ : 4′ : 6′-Tetranitro-4-methyldiphenylamine.—When a mixture of picryl chloride (2·5 g.) and 3-nitro-*p*-toluidine (1·5 g.) was heated to 160°, a reaction set in accompanied by considerable frothing. After 20 minutes at this temperature, the product was cooled and crystallised from glacial acetic acid. 2 : 2′ : 4′ : 6′-*Tetranitro-4-methyldiphenylamine* separated in golden brown plates, m. p. 217—219° (Found : C, 43·5; H, 2·4; N, 19·5%).

We are indebted to Sir Robert Robinson for his interest in these investigations, and to the Chief Scientific Officer, Ministry of Supply, for permission to publish the work.—DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, January 30th, 1948.*]

Tetrahydrofurans related to Amidone. By WALTER WILSON.

SCHULTZ, ROBB, and SPRAGUE (*J. Amer. Chem. Soc.*, 1947, **69**, 2454) obtained 2-imino-3 : 3-diphenyl-5-methyltetrahydrofuran from propylene oxide, diphenylmethyl cyanide, and potassium *tert.*-butoxide, and refer to unpublished work by Easton, Gardner, and Stevens * in which the same compound was made with sodamide as the condensing agent. The same structure had been assigned independently in these laboratories to the product obtained using sodamide, on the basis of the acid hydrolysis to *αα*-diphenyl-*γ*-valerolactone (described by Schultz, Robb, and Sprague, *loc. cit.*) and the experiments appended.

The basic imino-compound gave an *N*-acetyl derivative with acetic anhydride in pyridine. The orientation of the methyl group in *αα*-diphenyl-*γ*-valerolactone was established by a synthesis of the lactone by acid hydrolysis of 1-cyano-1 : 1-diphenylbut-2-ene (new preparation using sodamide). The inert amide corresponding to this cyanide was the only product of alkaline hydrolysis. Cautious acidification of a solution of the lactone in alkali afforded a labile solid acid, which reverted to the lactone even on careful drying for analysis.

Ethylmagnesium bromide and the lactone yielded 2-hydroxy-3 : 3-diphenyl-5-methyl-2-ethyltetra-hydrofuran, which was converted into the acetate, and dehydrated by methyl- or ethyl-alcoholic hydrogen

* *Added in Proof.*—Details are now available (*J. Amer. Chem. Soc.*, 1947, **69**, 2941). These workers also describe the conversion of cyanobutene into *αα*-diphenyl-*γ*-valerolactone.

chloride to 3 : 3-diphenyl-5-methyl-2-ethylidenetetrahydrofuran, without formation of the 2-alkoxytetra-hydrofurans (" furanosides ").

The above 2-hydroxytetrahydrofuran is the stable cyclic semi-acetal of a hypothetical hydroxy-ketone closely related to the new analgesic drug " Amidone ", $Ph_2C(CO \cdot C_2H_5) \cdot CH_2 \cdot CH(NMe_2) \cdot CH_3$. The stability of the cyclic form is indicated by the failure to obtain ketonic derivatives, and recalls the rapid formation of αα-diphenyl-γ-valerolactone from the corresponding hydroxy-acid and the isolation of 2-imino-3 : 3-diphenyl-5-methyltetrahydrofuran instead of the expected open-chain hydroxy-cyanide in the condensation of propylene oxide with diphenylmethyl cyanide.

2-Imino-3 : 3-diphenyl-5-methyltetrahydrofuran.—Diphenylmethyl cyanide (77 g.) in dry benzene (300 c.c.) was stirred (3 hours at 40—50°) with sodamide (24 g.). Propylene oxide (23 g.) in benzene (50 c.c.) was added dropwise, and the mixture heated until the colour had changed from deep green to pale yellow. The benzene solution was washed with water. Distillation of the benzene and trituration of the residue with ether–petroleum (b. p. 40—60°) afforded the imino-compound (86 g., 86% yield ; m. p. 116—118°, b. p. 155—160°/0·3 mm.). The pure material formed white prisms, m. p. 116·5—118° (Schultz, Robb, and Sprague, *loc. cit.*, give m. p. 114—115°). Warm dilute hydrochloric or lactic acid yielded quantitatively αα-diphenyl-γ-valerolactone, m. p. 115° (Schultz, Robb, and Sprague give m. p. 111—112°).

2-Acetimido-3 : 3-diphenyl-5-methyltetrahydrofuran.—The imino-compound (2·5 g.) and acetic anhydride (1·5 c.c.) were heated at 100° for 1½ hours. The solid (2·8 g. ; m. p. 110—112°) obtained on pouring into water was crystallised from benzene–petroleum (b. p. 40—60°), giving white prisms of the *acetimido*-compound, m. p. 114·5—116·5° (Found : N, 4·95. $C_{19}H_{19}O_2N$ requires N, 4·8%).

1-Cyano-1 : 1-diphenylbut-2-ene.—Diphenylmethyl cyanide (28 g.), sodamide (7·0 g.), and benzene (125 c.c.) were stirred at 40° for 1½ hours, then allyl bromide (17·6 g.) in benzene (25 c.c.) was added dropwise. The reaction was completed by heating to 90°, and the product (30 g.) isolated by washing with water and distillation; b. p. 162°/1·5 mm., m. p. 25° (Found : N, 5·7. Calc. for $C_{17}H_{15}N$: N, 6·0%). (Schultz, Robb, and Sprague, *loc. cit.*, obtained this compound by the potassium *tert.*-butoxide method, and give b. p. 129—131°/1·5 mm.)

2 : 2-Diphenylpent-4-en-1-carboxyamide.—The above cyanide (2 g.), potassium hydroxide (4 g.), water (2 c.c.), and ethylene glycol (20 c.c.) were boiled for 20 hours. Traces of ammonia were evolved, and a neutral product (0·75 g., m. p. 130—135°) was obtained on cooling. Recrystallisation from benzene–petroleum (b. p. 60—80°) afforded glistening white flakes of the *amide*, m. p. 163—164° (Found : N, 5·8. $C_{17}H_{17}ON$ requires N, 5·6%).

αα-Diphenyl-γ-valerolactone from 1-Cyano-1 : 1-diphenylbut-2-ene.—The cyanide (2·3 g.) and 80% (by weight) sulphuric acid (10 g.) were heated at 185° for 1½ hours. Water (10 c.c.) and alcohol (5 c.c.) were added, and the mixture refluxed for 30 minutes. On cooling, αα-diphenyl-γ-valerolactone (1·2 g., m. p. 105—109°) separated; recrystallisation from petroleum (b. p. 80—100°) gave the pure lactone, m. p. 112·5—115°, not depressed on mixing with a specimen prepared by hydrolysis of the imino-compound.

Hydrolysis of αα-Diphenyl-γ-valerolactone.—The lactone (1·0 g.), potassium hydroxide (4·0 g.), water (10 c.c.), and alcohol (5 c.c.) were boiled for 3 hours. The solution was diluted, cooled, and carefully acidified with acetic acid (4 c.c.). The solid acid (1·07 g. ; m. p. 94—96°) formed small needles, m. p. 95—95·5°, from ethyl acetate–petroleum (b. p. 40—60°). Prolonged heating during the m. p. determination, or even drying for analysis in a desiccator, regenerated the original lactone, m. p. and mixed m. p. 114·5—116°.

2-Hydroxy-3 : 3-diphenyl-5-methyl-2-ethyltetrahydrofuran.—αα-Diphenyl-γ-valerolactone (5·0 g.) in dry benzene (50 c.c.) was refluxed for 18 hours (dry nitrogen atmosphere) with an excess of Grignard reagent prepared from ethyl bromide (8·8 g.), magnesium (2·0 g.), and ether (75 c.c.). The ether solution was treated with dilute hydrochloric acid, washed with water, and dried (Na₂SO₄). Distillation of the ether and trituration with petroleum (b. p. 40—60°) afforded a solid (4·9 g. ; m. p. 121—122°). The hydroxy-compound formed fluffy white needles, m. p. 124·5—125° after three crystallisations from benzene–petroleum (b. p. 60—80°) (Found : C, 80·15; H, 8·3. $C_{19}H_{22}O_2$ requires C, 80·9; H, 7·8%). The compound was stable to boiling aqueous-alcoholic sodium hydroxide, and no ketonic derivatives were obtained with alcoholic solutions of semicarbazide or 2 : 4-dinitrophenylhydrazine sulphate.

2-Acetoxy-3 : 3-diphenyl-5-methyl-2-ethyltetrahydrofuran.—The hydroxy-compound (1·0 g.), pyridine (6 c.c.), and acetic anhydride (0·7 c.c.) were heated at 100° for 6 hours. Decomposition with water and extraction with ether–benzene afforded the *acetate* (0·4 g. ; m. p. 110—111°, b. p. 170—175°/5 mm.), crystallising from petroleum in white needles, m. p. 111—112·5° (Found : C, 77·5; H, 7·9. $C_{19}H_{20}O_3$ requires C, 77·8; H, 7·4%). Boiling with aqueous-alcoholic sodium hydroxide regenerated the original hydroxy-compound, m. p. and mixed m. p. 124—125°.

3 : 3-Diphenyl-5-methyl-2-ethylidenetetrahydrofuran.—The hydroxy-compound (1·0 g.) was boiled for 2 hours with methanol (50 c.c.) containing dry hydrogen chloride (1·0 g.). Removal of the solvent and trituration with water gave a solid, which was recrystallised from aqueous methanol. The *ethylidene* compound was obtained in large white prisms, m. p. 90—91° (Found : C, 86·0; H, 8·0; OMe, 0·4. $C_{19}H_{20}O$ requires C, 86·4; H, 7·6; OMe, 0·0%). The same substance was obtained with ethyl-alcoholic hydrogen chloride.

The Preparation of N-(2 : 4-*Dinitrophenyl*)- *and of* N-(2 : 6-*Dinitrophenyl*)-*phthalimide.* By HERBERT
H. HODGSON and DOUGLAS P. DODGSON.

DURING attempts to obtain a better isolation of the 20—25% yield of the 1-chloro-2 : 6-dinitrobenzene
which is formed during the mononitration of *o*-chloronitrobenzene, the crude nitration product (Hodgson
and Dodgson, this vol., p. 1006) was fused for 30 minutes at 120° with potassium phthalimide. A
readily crystallisable compound of m. p. 195—196° was obtained from the reaction complex, which,
however, did not correspond with any of the simple possible reaction products anticipated, *viz.*, the
N-(2 : 4- and 2 : 6-dinitrophenyl)phthalimides and the *N*-(2 : 4 : 6-trinitrophenyl)phthalimide prev-
iously made by Schmidt (*Ber.*, 1889, **22**, 3249), and has so far not been identified. The above *N*-dinitro-
phenylphthalimides, however, have not been previously reported and are now described. Attempts
to prepare *N*-(2 : 4-dinitrophenyl)phthalanilic acid by the method of Sherrill, Schaeffer, and Shoyer
(*J. Amer. Chem. Soc.*, 1928, **50**, 474), whereby 2 : 4-dinitroaniline is refluxed with phthalic anhydride
in chloroform solution, showed that no reaction had occurred even after 9 hours.

N-(2 : 4-*Dinitrophenyl*)*phthalimide* was obtained when 2 : 4-dinitroaniline (1·8 g.) was heated with
phthalic anhydride (1·5 g.) for 5 hours at 260°. After cooling, the powdered mass was triturated with
cold N-sodium hydroxide, and the solid *N*-(2 : 4-dinitrophenyl)phthalimide filtered off; it crystallised
from glacial acetic acid (charcoal) in cream-yellow plates, m. p. 192° (Found : N, 13·6. $C_{14}H_7O_6N_3$
requires N, 13·4%).

N-(2 : 6-*Dinitrophenyl*)*phthalimide*, prepared in like manner from 2 : 6-dinitroaniline (1·8 g.) and
phthalic anhydride (1·5 g.), crystallised from glacial acetic acid (charcoal) in lemon-yellow prisms,
m. p. 202° (Found : N, 13·6. $C_{14}H_7O_6N_3$ requires N, 13·4%).