## 234. Organic Molecular Compounds. Part III. Compounds of Phenols with Some Synthetic Cyclic Oxides.

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The tendency of the cyclic oxide cineole (inset) to form stable molecular compounds with phenols (Bellucci and Grassi, Gazzetta, 1913, 43, 712; Morgan and Pellett, J. Soc. Chem.
 Ind., 1935, 54, 22) has hitherto remained a unique phenomenon. It may be regarded as indicating both an oxygen atom in a specially active state, and a general structure which favours stable solid complexes. High donating power in the oxygen atom of cineole is to be expected in view of its attachment on either side to tertiary carbon atoms, and in view also of the fact that the oxygen atom is a member of a ring, since ring formation appears to increase the basic activity of oxygen (cf., e.g., Bennett and Philip, J., 1928, 1937). Furthermore, the formation of a stable crystal assemblage is doubtless favoured by the rigidity of the strutted ring system and the compactness of the tertiary carbon groups.

In order to put these considerations to the test, we have synthesised four cyclic oxides which might be expected to resemble cineole from this point of view. The method by which we proposed to study the formation of compounds with phenols required, for convenient working with small quantities of material, that the m. p.'s of the oxides should be well above laboratory temperature, and of the four new cyclic oxides three were suitable for study, and each, as we had anticipated, yields complexes with a number of phenols.

The method of synthesis adopted was the conversion of a dicarboxylic ester, $\mathrm{A}\left(\mathrm{CO}_{2} \mathrm{R}\right)_{2}$, by the action of a large excess of methylmagnesium iodide into the glycol, $\mathrm{A}\left(\mathrm{CMe}_{2} \cdot \mathrm{OH}\right)_{2}$, and dehydration of this by the action of $60-70 \%$ sulphuric acid to yield the oxide $\mathrm{A}<_{\mathrm{CMe}_{2}}^{\mathrm{CMe}_{2}}>\mathrm{O}$ (cf. preparation of $\alpha \alpha \alpha^{\prime} \alpha^{\prime}$-tetramethyltetramethylene oxide; Pogorzesky, $J$. Russ. Phys. Chem. Soc., 1903, 35, 882). The esters used were methyl phthalate, $\beta$-phenylglutarate, phenylsuccinate, and diphenate, also ethyl camphorate.

The action of organomagnesium compounds on phthalic esters has been investigated several times (Shibata, J., 1909, 95, 1449 ; Hewitt and Steinberg, P., 1912, 28, 140; Ott and Schurmann, Ber., 1928, 61, B, 2122), and the last-named authors isolated $o$-xylylene glycol, m. p. $166^{\circ}$. We find that this substance is readily converted by $60 \%$ sulphuric acid into the cyclic oxide tetramethylphthalan, m. p. $72^{\circ}$.

Methylmagnesium iodide in ethereal solution converted methyl $\beta$-phenylglutarate into 4-phenyl-2 : 6-dimethylheptane-2:6-diol, m. p. $71^{\circ}$, which yielded on dehydration the cyclic oxide 4-phenyl-2:2:6:6-tetramethyltetrahydropyran, m. p. 57.5 .

Methyl phenylsuccinate by similar reactions furnished the glycol, 3-phenyl-2:5-di-methylhexane-2:5-diol, m. p. 62 ${ }^{\circ}$, and the oxide 3 -phenyl-2:2:5:5-tetramethyltetrahydrofuran, m. p. $40^{\circ}$. From methyl diphenate the glycol, oo'-di-( $\alpha$-hydroxyisopropyl)diphenyl, $\mathrm{m} . \mathrm{p} .139^{\circ}$, was obtained and converted into its cyclic oxide, m. p. $92^{\circ}$.

No pure individual substance could be isolated from the products of heating ethyl camphorate with an excess of methylmagnesium iodide in boiling toluene for 24 hours, a result which we attribute to steric hindrance.

These oxides do not yield crystalline compounds with hydrogen chloride, boron trifluoride, or perchloric acid, but a study of the thermal diagrams for systems of these substances with certain phenols and acids gave interesting results (see e.g., Figs. l-6). A wide range of substances was taken with the simplest oxide tetramethylphthalan : a few only were used with each of the others.

Tetramethylphthalan yields compounds with $\alpha$-naphthol (1:1), m. p. $92.6^{\circ}$; with $\beta$-naphthol ( 2 oxide : 1 naphthol) of congruent m. p. $79 \cdot 3^{\circ}$; with $p$-bromophenol ( $1: 1$ ), m. p. $54 \cdot 3^{\circ}$; with $p$-iodophenol (1:1), m. p. $51 \cdot 8^{\circ}$; with catechol (1:1), m. p. $85 \cdot 5^{\circ}$; with resorcinol ( 2 oxide : 1 phenol), congruent m. p. $88.5^{\circ}$; with $p$-xylenol ( $1: 1$ ), m. p. $40.5^{\circ}$; but it gives no evidence of combination with $s$-trichloro- or $s$-tribromo-phenol or with phenylacetic or $o$-toluic acid.

Phenyltetramethyltetrahydropyran forms compounds with $\alpha$-naphthol (1:1), m. p. $69^{\circ}$; with catechol (1:1), m. p. $78^{\circ}$; with resorcinol ( 2 oxide : 1 resorcinol), congruent m . p. $67.5^{\circ}$; but it does not form any stable compound with $\beta$-naphthol.

The cyclic oxide from methyl diphenate yields an unstable compound with $\alpha$-naphthol ( 2 oxide: 1 naphthol) having an incongruent m . p. of $76^{\circ}$, but none with catechol.

There can be little doubt that the association of the oxide oxygen with the hydroxyl group of the phenol is the principal factor determining the existence of these molecular compounds. The union by co-ordination through hydrogen is now regarded as a resonance phenomenon (Sidgwick, Ann. Reports, 1933, 30, 112). The compounds are in general equimolecular in composition, as this conception requires. The results for two different oxides with resorcinol and catechol and the failure to combine with the trihalogenophenols are consistent with this view, for it is easy to understand that for steric reasons or because of chelate co-ordination, only one of the two hydroxyl groups of catechol may be able to function as a point of attachment, whereas in resorcinol each hydroxyl group may attach an oxide molecule separately to itself; and the hydroxyl group of the trihalogenophenols may be rendered inactive owing to chelation or to steric hindrance.

At the same time, the formation of a compound of two molecules of tetramethylphthalan with one of $\beta$-naphthol, and that of two of the cyclic oxide from methyl diphenate with one of $\alpha$-naphthol suggests that the composition of the solid complex is partly determined in these cases by forces of a lower order concerned in the packing of molecules into the crystal assemblage.

In this connection it is noteworthy that the thermal diagrams do, in fact, provide evidence of the existence of compounds in the liquid phase. The form taken by the curves near the m. p. of a molecular compound which dissociates incompletely in the liquid phase was discussed in detail by van Laar (Proc. K. Akad. Wetensch. Amsterdam, 1906, 8, 699), and a method was indicated for an approximate determination of the degree of such dissociation. We have applied this method in two cases, and find that the extent of dissociation at the m . p . of the complexes of tetramethylphthalan with $\alpha$-naphthol and $p$-bromophenol is of the order $58 \%$ and $40 \%$ respectively.

Since the law of mass action is assumed to hold when molecular concentrations of the components are used, departure from ideal behaviour of the solutions is ignored, and there is, moreover, some uncertainty in the determination of the heat $Q_{0}$ of fusion of the compound with partial dissociation, so these values can have little quantitative significance. They suffice, however, to emphasise the fact that the complexes persist to a considerable extent in solution.

As regards the absence of solid complexes of an oxide with two carboxylic acids examined, it may be pointed out that such complexes would be far lower in compactness of structure and in rigidity than those derived from the phenols, and that consequently it need not be regarded as surprising if they have m. p.'s too low for observation.

## Experimental.

Tetramethylphthalan.-Methylmagnesium iodide ( $\mathbf{1} \mathrm{mol}$.) was prepared in the usual manner in ether ( 350 c.c.), the ether evaporated, and dry benzene ( 250 c.c.) added. Methyl phthalate ( $\frac{1}{8}$ mol.) was gradually added, the mixture left over-night, and boiled under an upright condenser ( 8 hours). The mixture was added to ice and dilute sulphuric acid, and the whole extracted five times with ether. The extract, dried over potassium carbonate, on evaporation left oxylylene glycol as a pinkish solid, which was freed from oil (yield of crude glycol, 40\%) and twice recrystallised from benzene, forming colourless needles with a straight extinction, m. p. 166 ${ }^{\circ}$ (Found: C, $\mathbf{7 4 \cdot 1}$; H, 9.2. Calc.: C, $\mathbf{7 4 \cdot 2}$; H, $9.3 \%$ ).

When the foregoing operation was conducted in ethereal solution, the only definite product isolated was a white substance, m. p. 108-111 ${ }^{\circ}$. This has the composition of a keto-alcohol $\mathrm{C}_{6} \mathrm{H}_{4}(\mathrm{COMe}) \cdot \mathrm{CMe}_{2} \cdot \mathrm{OH}$ (Found: C, $74 \cdot 0 ; \mathrm{H}, \mathbf{7 . 8} . \mathrm{C}_{11} \mathrm{H}_{14} \mathrm{O}_{2}$ requires $\mathrm{C}, 74 \cdot 2 ; \mathrm{H}, 7.9 \%$ ), but it was not further examined.

The glycol ( 10 g .) was shaken for 1 hour with $60 \%$ sulphuric acid ( 75 c.c.) at $50-60^{\circ}$; the mixture was then diluted, extracted five times with ether, and the extract dried over potassium carbonate and evaporated. $\alpha \alpha \alpha^{\prime} \alpha^{\prime}$-Tetramethylphthalan ( I , in figs. and tables) was left as a white solid, and after successive crystallisations from benzene and aqueous alcohol formed colourless plates of characteristic, slightly camphoraceous odour, m. p. 71-72 (Found : $\mathrm{C}, 8 \mathrm{l} \cdot 7 ; \mathrm{H}, 9 \cdot 0 . \quad \mathrm{C}_{12} \mathrm{H}_{18} \mathrm{O}$ requires $\mathrm{C}, 81 \cdot 7 ; \mathrm{H}, \mathbf{9 . 1 5} \%$ ).

Phenyltetramethyltetrahydropyran.-Methyl $\beta$-phenylglutarate (m. p. $86^{\circ}$ ) was boiled with methylmagnesium iodide ( 8 mols .) in ether for 12 hours, and the product isolated as before. The glycol, 4-phenyl-2:6-dimethylheptane-2: 6-diol, was obtained (yield, $80 \%$ ) in colourless monoclinic plates, m. p. $70-71^{\circ}$, from light petroleum (Found : C, 76.2; H, 10.2. $\mathrm{C}_{15} \mathrm{H}_{14} \mathrm{O}_{2}$ requires $\mathrm{C}, \mathbf{7 6 . 2} ; \mathrm{H}, \mathbf{1 0 . 2 \%}$ ). Dehydration of this glycol ( 1 part) was effected by shaking it at $65^{\circ}$ for ${ }^{\frac{1}{2}}$ hours with $70 \%$ sulphuric acid ( 8 parts), diluting the liquid, and extracting it five times with ether. The product, recovered from the extract after drying over potassium carbonate, was crystallised successively from light petroleum and aqueous alcohol. 4-Phenyl-2:2:6:6-tetramethyltetrahydropyran (III, in figs. and tables) was thus obtained in colourless prisms with an oblique extinction, m. p. $57.5^{\circ}$ (Found: $\mathrm{C}, \mathbf{8 2 . 3} ; \mathrm{H}, \mathbf{1 0 . 2} . \mathrm{C}_{15} \mathrm{H}_{22} \mathrm{O}$ requires C, $82 \cdot 5 ; \mathrm{H}, \mathbf{1 0} \cdot 2 \%$ ).

Phenyltetramethyltetrahydrofuran.-Methyl phenylsuccinate was converted precisely as in the preceding case into 3 -phenyl-2: 5-dimethylhexane-2:5-diol which crystallises from light petroleum in hair-like needles with a straight extinction, m. p. $61-62^{\circ}$ (yield, 62\%) (Found: C, 75.8; $\mathrm{H}, 9.9 . \mathrm{C}_{14} \mathrm{H}_{22} \mathrm{O}_{2}$ requires $\mathrm{C}, \mathbf{7 5 \cdot 6} ; \mathrm{H}, \mathbf{1 0 . 0} \%$ ). The glycol ( 1 part) was shaken at $30-40^{\circ}$ for 2 hours with $70 \%$ sulphuric acid ( 8 parts), the mixture diluted, and the product isolated as before. The oil solidified, and was recrystallised in succession from paraffin and from aqueous alcohol (yield, 68\%). 3-Phenyl-2:2:5:5-tetramethyltetrahydrofuran was thus obtained as colourless monoclinic plates with an optic axis emerging perpendicular to the plane of the plate. It has a faintly camphoraceous odour and m. p. 39-40 (Found: C, 82.0; H, 9.7. $\mathrm{C}_{14} \mathrm{H}_{20} \mathrm{O}$ requires $\mathrm{C}, 82 \cdot 3 ; \mathrm{H}, \mathbf{9 . 9} \%$ ).

Cyclic Oxide from Methyl Diphenate.-The ester (m. p. $74^{\circ}$ ) was boiled with a benzene solution of the reagent ( 8 mols.) for 18 hours, and the product isolated as before. The viscous brown oil so obtained was left exposed to the air and slowly deposited crystals, which were separated with the aid of light petroleum. The solid (yield, $25 \%$ of the weight of ester taken) was recrystallised successively from absolute ethyl and methyl alcohol, $2: 2^{\prime}-d i-(\alpha-h y d r o x y$ isopropyl)diphenyl being obtained in small colourless crystals, m. p. $139^{\circ}$ (Found: C, 79.9; H, 8.1. $\mathrm{C}_{18} \mathrm{H}_{22} \mathrm{O}_{2}$ requires $\mathrm{C}, 80 \cdot 0 ; \mathrm{H}, 8 \cdot 2 \%$ ).

Dehydration was effected by shaking for 2 hours at $25-30^{\circ}$ with $70 \%$ sulphuric acid ( $\mathbf{1 5}$ parts) and a little ether to facilitate mixing. The mixture was diluted, and the product isolated in the usual manner. The cyclic oxide (II, in figs. and tables) thus obtained (yield, 72\%) was repeatedly crystallised from methyl alcohol and formed well-defined monoclinic prisms, m. p. $90-91.8^{\circ}$, with $\beta=118^{\circ}$ (Found: C, $85.9,85.3 ; \mathrm{H}, 7.9,7.9 . \mathrm{C}_{18} \mathrm{H}_{20} \mathrm{O}$ requires C, 85.7; H, $8.0 \%$ ).

Figs. 1-6.


Thermal diagrams for some systems of cyclic oxides with phenols.

## Examination of Phase Diagrams in Some Binary Systems of Three Cyclic Oxides.

Method of Experiment.-Observations were made of eutectic temperatures, $T_{1}$ (thawpoints), and melting temperatures, $T_{2}$, small quantities being used in m. p. capillaries according to the "thaw-point method" of Rheinboldt and Kircheisen (J. pr. Chem., 1926, 113, 348). The readings were taken on a thermometer graduated to $0 \cdot 1^{\circ}$ and are of considerable precision, although they may presumably be subject to a slight positive error. Any such error should, however, be fairly constant. No correction has been applied for the exposed stem of the thermometer, as this would be in the opposite direction to the error referred to and of the same order of magnitude.

A selection of the results is shown graphically in Figs. 1-6, and the complete data are tabulated below.

Systems with Tetramethylphthalan (Oxide I).
a-Naphthol (Curve 1).

| Oxide, mols. \% | 0 | $12 \cdot 1$ | $25 \cdot 8$ | $34 \cdot 0$ | $39 \cdot 8$ | $44 \cdot 9$ | $49 \cdot 8$ | $55 \cdot 0$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $T_{1} \ldots \ldots . . . . . . . . . . . .$. | $95 \cdot{ }^{\circ}$ | $76.3{ }^{\circ}$ | $76.4{ }^{\circ}$ | $76 .{ }^{\circ}$ | $76 .{ }^{\circ}$ | $76.4{ }^{\circ}$ | $89 \cdot{ }^{\circ}$ | $75.8{ }^{\circ}$ |
| $T_{2} \quad \ldots \ldots \ldots \ldots . . .$. | 96.2 | $90 \cdot 3$ | $81 \cdot 0$ | $79 \cdot 4$ | $88 \cdot 1$ | $91 \cdot 6$ | $92 \cdot 5$ | 92-1 |
| Oxide, mols. \%...... | $60 \cdot 2$ | $67 \cdot 1$ | 76.3 | $84 \cdot 2$ | $90 \cdot 0$ | $93 \cdot 1$ | 100 |  |
| $T_{1} \ldots \ldots \ldots \ldots \ldots . . . . .$. | $64.6{ }^{\circ}$ | $64 \cdot 2^{\circ}$ | $64 \cdot 3{ }^{\circ}$ | $64 \cdot 3^{\circ}$ | $64.2{ }^{\circ}$ | $63.9{ }^{\circ}$ | $71 \cdot 1^{\circ}$ |  |
|  | 90.5 | $86 \cdot 1$ | $78 \cdot 3$ | $69 \cdot 8$ | $66 \cdot 6$ | $68 \cdot 9$ | $72 \cdot 1$ |  |

The curve shows a well-defined compound ( $1: 1$ ) with congruent m. p. $92 \cdot \mathbf{6}^{\circ}$; eutectic

$\beta$-Naphthol.

| Oxide, mols. \%... | 0 | $21 \cdot 4$ | $32 \cdot 5$ | $41 \cdot 4$ | $44 \cdot 7$ | $50 \cdot 5$ | $60 \cdot 4$ | $69 \cdot 4$ | 81.5 | $88 \cdot 1$ | $95 \cdot 3$ | 100 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $T_{1} \ldots \ldots \ldots \ldots \ldots$. | $121 \cdot{ }^{\circ}$ | $69.7{ }^{\circ}$ | $69.9{ }^{\circ}$ | $70 \cdot{ }^{\circ}$ | $70 \cdot{ }^{\circ}$ | $70 \cdot 0^{\circ}$ | $70.9{ }^{\circ}$ | $65 \cdot{ }^{\circ}$ | $65.3{ }^{\circ}$ | $65 \cdot{ }^{\circ}$ | $65.0{ }^{\circ}$ | $71 \cdot 1^{\circ}$ |
| $T_{2}$ | $122 \cdot 0$ | 107.5 | 95-8 | $81 \cdot 7$ | $76 \cdot 1$ | $74 \cdot 4$ | $78 \cdot 2$ | $78 \cdot 9$ | $75 \cdot 5$ | 69.4 | $69 \cdot 1$ | $72 \cdot 1$ |

A well-defined compound ( 2 oxide : 1 naphthol) is revealed with congruent m. p. 79.3 ${ }^{\circ}$; eutectic points at $\mathbf{7 0} \cdot 1^{\circ}, \mathbf{4 7} \cdot 5 \mathrm{mols}$. $\%$ oxide; and $\mathbf{6 5 \cdot} \cdot \mathbf{1}^{\circ}, 91 \mathrm{mols} . \%$ oxide.
p-Bromophenol.

| Oxide, mols. \% | 0 | $17 \cdot 1$ | $28 \cdot 9$ | $35 \cdot 0$ | $37 \cdot 8$ | $44 \cdot 8$ | $51 \cdot 3$ | $55 \cdot 3$ | $61 \cdot 6$ | $65 \cdot 7$ | $69 \cdot 7$ | 83 | 100 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $T_{1} \ldots \ldots . . . . . . . .$. | $63.0^{\circ}$ | $29 \cdot{ }^{\circ}$ | $29.9{ }^{\circ}$ | $30 \cdot 1{ }^{\circ}$ | $29.5{ }^{\circ}$ | $30 \cdot{ }^{\circ}$ | $52 \cdot{ }^{\circ}$ | $41 \cdot 2^{\circ}$ | $40 \cdot 6{ }^{\circ}$ | $40 \cdot{ }^{\circ}$ | $39.5{ }^{\circ}$ | $39.9{ }^{\circ}$ | $71 \cdot 1^{\circ}$ |
| $T_{2}$ | $4 \cdot 0$ | $49 \cdot 2$ | 37-4 | $39 \cdot 1$ | $46 \cdot 1$ | $52 \cdot 2$ | $54 \cdot 2$ | 53-2 | $49 \cdot 8$ | $46 \cdot 8$ | $45 \cdot 5$ | $59 \cdot 4$ | 72•1 |

A well-defined compound is formed (1:1) with congruent m. p. 54.3 ${ }^{\circ}$; eutectic points at $29 \cdot 9^{\circ}, 33 \cdot 5 \mathrm{mols}$. \% oxide; and $40 \cdot 1^{\circ}, 68 \mathrm{mols} . \%$ oxide.

| p-Iodophenol. |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Oxide, mols. \%..... | 0 | $13 \cdot 9$ | $24 \cdot 1$ | $31 \cdot 9$ | 36.8 | $40 \cdot 2$ | $43 \cdot 8$ | 46.2 |
| $T_{1} \ldots \ldots . . . . . . . . . . . .$. | $91.6{ }^{\circ}$ | $42.9{ }^{\circ}$ | $42.0{ }^{\circ}$ | $43 \cdot{ }^{\circ}$ | $42.5{ }^{\circ}$ | $42.8{ }^{\circ}$ | $42 \cdot 1^{\circ}$ | $42 \cdot{ }^{\circ}$ |
| $T_{2} \quad \ldots \ldots \ldots \ldots \ldots \ldots .$. | 92.5 | $83 \cdot 1$ | $72 \cdot 6$ | $58 \cdot 8$ | $47 \cdot 6$ | $48 \cdot 1$ | $49 \cdot 7$ | $51 \cdot 2$ |
| Oxide, mols. \%...... | $49 \cdot 2$ | $54 \cdot 4$ | $59 \cdot 0$ | $62 \cdot 9$ | $71 \cdot 6$ | $80 \cdot 7$ | $89 \cdot 6$ | 100 |
| $T_{1}$ | $43 \cdot{ }^{\circ}$ | $39 \cdot 2^{\circ}$ | $38.8{ }^{\circ}$ | $38 \cdot 5^{\circ}$ | $39.6{ }^{\circ}$ | $39 \cdot 1^{\circ}$ | $39 \cdot{ }^{\circ}$ | $71 \cdot 1^{\circ}$ |
| $T_{2}$ | 51.7 | $51 \cdot 1$ | $48 \cdot 4$ | $44 \cdot 9$ | $47 \cdot 7$ | 57-8 | $65 \cdot 3$ | $72 \cdot 1$ |

The curve shows the formation of a compound ( $1: 1$ ) with congruent m. p. $51 \cdot 8^{\circ}$; eutectic points at $42 \cdot 2^{\circ}, 38$ mols. $\%$ oxide; and $38 \cdot 9^{\circ}, 67$ mols. $\%$ oxide.

|  |  |  |  | $\mathrm{s}-\mathrm{Tr}$ | or | nol. |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Oxide, mols. \% | 0 | $10 \cdot 0$ | $22 \cdot 1$ | $28 \cdot 4$ | 39.9 | $47 \cdot 4$ | $51 \cdot 9$ | $60 \cdot 0$ | $67 \cdot 1$ | $75 \cdot 8$ | $86 \cdot 4$ | 100 |
| $T_{2}$ | $66.7{ }^{\circ}$ | $62.7{ }^{\circ}$ | $55.1^{\circ}$ | 48.3 ${ }^{\circ}$ | $36.2{ }^{\circ}$ | $20.3{ }^{\circ}$ | $9 \cdot 1^{\circ}$ | $10 \cdot 6{ }^{\circ}$ | $41.8{ }^{\circ}$ | $56.1^{\circ}$ | $66.5{ }^{\circ}$ | $72 \cdot 1$ |

The eutectic temperature was not observed : mixtures between 52 and $60 \mathrm{mols} . \%$ of oxide did not solidify. The curve is of the simple eutectic type without compound formation, and the eutectic point is about - $10^{\circ}, 56 \mathrm{mols} . \%$ oxide.
s-Tribromophenol (Curve 2).

| Oxide, mols. \%...... | 0 | $13 \cdot 1$ | $27 \cdot 8$ | $39 \cdot 2$ | $47 \cdot 4$ | $49 \cdot 9$ | $54 \cdot 0$ | $58 \cdot 6$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $T_{1}$.................... | $91.6{ }^{\circ}$ | $38 \cdot{ }^{\circ}$ | $38 \cdot{ }^{\circ}$ | $38.5{ }^{\circ}$ | $38 \cdot{ }^{\circ}$ | $39 \cdot{ }^{\circ}$ | $38.2{ }^{\circ}$ | $38 \cdot{ }^{\circ}$ |
| $T_{2}$ | $92 \cdot 9$ | $86 \cdot 9$ | $78 \cdot 0$ | $68 \cdot 5$ | $60 \cdot 1$ | $57 \cdot 1$ | $52 \cdot 6$ | $45 \cdot 2$ |
| Oxide, mols. \%...... | $63 \cdot 7$ | $68 \cdot 1$ | $76 \cdot 4$ | 84-3 | $93 \cdot 9$ | 100 |  |  |
| $T_{1} \ldots \ldots \ldots \ldots \ldots \ldots$. | $37 \cdot{ }^{\circ}$ | $38 \cdot{ }^{\circ}$ | $38.5{ }^{\circ}$ | $38.7{ }^{\circ}$ | $38 \cdot 8{ }^{\circ}$ | $71 \cdot 1^{\circ}$ |  |  |
| $T_{2}$ | $42 \cdot 3$ | $49 \cdot 1$ | $57 \cdot 8$ | $63 \cdot 2$ | $69 \cdot 0$ | $72 \cdot 1$ |  |  |

The curve shows a simple eutectic with no combination. The eutectic point is $38 \cdot 1^{\circ}, 62$ mols. \% oxide.

Catechol.

| Oxide, | 0 | 9.7 | $20 \cdot 3$ | $31 \cdot 6$ | $40 \cdot 2$ | $48 \cdot 6$ | 59.7 | 66.0 | $74 \cdot 8$ | $80 \cdot 3$ | $87 \cdot 1$ | 93.9 | 100 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| T | $03.9^{\circ}$ | $79.8{ }^{\circ}$ | $80 \cdot 2{ }^{\circ}$ | $79 \cdot 6{ }^{\circ}$ | $79 \cdot{ }^{\circ}$ | $80 \cdot 1^{\circ}$ | $57.9^{\circ}$ | $58.7{ }^{\circ}$ | $58.5{ }^{\circ}$ | $59.2{ }^{\circ}$ | $58 \cdot 9^{\circ}$ | $59 \cdot{ }^{\circ}$ | $71 \cdot 1^{\circ}$ |
| $T_{2}$ | 1047 | $100 \cdot 4$ | 93.5 | $84 \cdot 6$ | 83.7 | $85 \cdot 2$ | 83.7 | $80 \cdot 4$ | $73 \cdot 3$ | $66 \cdot 1$ | 62.2 | $68 \cdot 2$ | 72.1 |

The curve shows a compound (1:1) with congruent m. p. $85 \cdot 5^{\circ}$ and eutectic points at $79 \cdot 6^{\circ}$, $36 \mathrm{mols} . \%$, and $58.9^{\circ}$, $84 \mathrm{mols} . \%$ oxide.

Resorcinol (Curve 3).

| Oxide, mols. \% | 0 | $9 \cdot 4$ | 26.1 | $39 \cdot 8$ | $49 \cdot 5$ | $52 \cdot 6$ | $57 \cdot 1$ | $61 \cdot 7$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $T_{1} \ldots \ldots . . . . . . . .$. | $109.0^{\circ}$ | $71.6{ }^{\circ}$ | $72 \cdot{ }^{\circ}$ | $72 \cdot 8^{\circ}$ | $72 \cdot{ }^{\circ}$ | $73 \cdot{ }^{\circ}$ | $73 \cdot 0^{\circ}$ | $72 \cdot{ }^{\circ}$ |
| $T_{2} \ldots \ldots \ldots \ldots \ldots \ldots \ldots$ | $110 \cdot 1$ | $106 \cdot 3$ | $97 \cdot 5$ | $87 \cdot 9$ | $77 \cdot 8$ | $77 \cdot 9$ | $82 \cdot 4$ | $86 \cdot 1$ |
| Oxide, mols. \%...... | $67 \cdot 2$ | $75 \cdot 9$ | $83 \cdot 2$ | $89 \cdot 1$ | $\mathbf{9 4 \cdot 4}$ | 100 |  |  |
| $T_{1}$................... | $81.6{ }^{\circ}$ | $65.8{ }^{\circ}$ | $66.8{ }^{\circ}$ | $67 \cdot{ }^{\circ}$ | $65 \cdot 4{ }^{\circ}$ | $71.1^{\circ}$ |  |  |
| $\mathrm{T}_{2}$ | 88.5 | $85 \cdot 9$ | $80 \cdot 1$ | 72.5 | $68 \cdot 1$ | 72-1 |  |  |

A well-defined compound is revealed ( 2 oxide $: 1$ resorcinol) with congruent m. p. $88 \cdot 5^{\circ}$. The eutectic points are at $72 \cdot 5^{\circ}, 52 \mathrm{mols} . \%$ oxide; and $65 \cdot 5^{\circ}, 93 \mathrm{mols} . \%$ oxide.

| p-Xylenol. |  |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Oxide, mols. \%...... | 0 | $25 \cdot 6$ | $40 \cdot 0$ | $45 \cdot 1$ | $51 \cdot 2$ | $55 \cdot 0$ | $60 \cdot 0$ | $61 \cdot 1$ | $65 \cdot 2$ | $75 \cdot 2$ | 88.5 | 100 |
| $T_{1} \ldots \ldots \ldots \ldots \ldots . . . .$. | $76.0{ }^{\circ}$ | $37.9{ }^{\circ}$ | $36.8{ }^{\circ}$ | $36.8{ }^{\circ}$ | $34.5{ }^{\circ}$ | $34.8{ }^{\circ}$ | $34.4{ }^{\circ}$ | $33.8{ }^{\circ}$ | $34 \cdot{ }^{\circ}$ | $33.5{ }^{\circ}$ | $34 \cdot 3{ }^{\circ}$ | $71.1^{\circ}$ |
| $T_{2}$ | $77 \cdot 5$ | $60 \cdot 4$ | $45 \cdot 3$ | $39 \cdot 8$ | 39.7 | $40 \cdot 2$ | 38.7 | 36.5 | 41-8 | 53-1 | $64 \cdot 6$ | 72•1 |

A relatively unstable compound ( $1: 1$ ) with congruent m. p. $40 \cdot 5^{\circ}$ is present, and the eutectic points are at $36 \cdot 8^{\circ}, 44 \mathrm{mols} . \%$; and $34 \cdot 1^{\circ}, 62 \mathrm{mols} . \%$ oxide.

Phenylacetic acid.

| Ox | 0 | 9 | 19 | $29 \cdot 8$ | $38 \cdot 9$ | $48 \cdot 9$ | $54 \cdot 1$ | $59 \cdot 5$ | $70 \cdot 6$ | $78 \cdot 8$ | $90 \cdot 3$ | , |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $T_{1} \ldots \ldots . . . .$. | $76.8{ }^{\circ}$ | $37.4{ }^{\circ}$ | $37 \cdot{ }^{\circ}$ | $36.9{ }^{\circ}$ | $37.0^{\circ}$ | $37 \cdot{ }^{\circ}$ | $36.8{ }^{\circ}$ | $36.9{ }^{\circ}$ | $37 \cdot{ }^{\circ}$ | $37 \cdot{ }^{\circ}$ | $37 \cdot{ }^{\circ}$ | $71.1^{\circ}$ |
| T | 77.7 | $73 \cdot 1$ | 66.4 | $59 \cdot 1$ | 51.8 | $41 \cdot 8$ | $40 \cdot 1$ | $46 \cdot 5$ | $55 \cdot 0$ | $60 \cdot 6$ | 67.4 | 72-1 |

There is no compound formation, the eutectic point being at $37 \cdot 0^{\circ}, 68 \mathrm{mols} . \%$ oxide.

| o-Toluic acid. |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Oxide, mols. \%. | 0 | $19 \cdot 8$ | $30 \cdot 2$ | $40 \cdot 1$ | $50 \cdot 1$ | 56.3 | $64 \cdot 1$ | $74 \cdot 8$ | 88.2 | 100 |
| $T_{1}$ | $103.9^{\circ}$ | $49.2{ }^{\circ}$ | $49 \cdot{ }^{\text {o }}$ | $49 \cdot{ }^{\circ}$ | $49 \cdot 3^{\circ}$ | $49.5{ }^{\circ}$ | $49 \cdot 2^{\circ}$ | $49 \cdot{ }^{\circ}$ | $49 \cdot 6{ }^{\circ}$ | $71 \cdot 1^{\circ}$ |
| $T_{2}$ | 104.7 | $92 \cdot 6$ | 85•1 | 76.5 | $68 \cdot 4$ | 62.6 | $54 \cdot 1$ | 55.5 | $65 \cdot 5$ | 72•1 |

The system forms a simple eutectic at $49 \cdot 3^{\circ}, 52 \mathrm{mols} . \%$ oxide.

| Systems with Oxide II, a-Naphthol (Curve 4). |  |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |  |  |  |  |  |  |
| Oxide, mols. \%..... | 0 | $15 \cdot 7$ | 29.0 | 36-8 | 47.7 | $57 \cdot 1$ | 63.7 | $67 \cdot 0$ | 71.2 | $75 \cdot 9$ | 82.0 | 100 |
| $T_{1} \ldots \ldots . . . . . .$. | $95 \cdot{ }^{\circ}$ | $65.2{ }^{\circ}$ | $65 \cdot{ }^{\circ}$ | $65 \cdot{ }^{\circ}$ | $64.8{ }^{\circ}$ | $64.6{ }^{\circ}$ | $70 \cdot 2^{\circ}$ | $73 \cdot{ }^{\circ}$ | $72.5{ }^{\circ}$ | $72.8{ }^{\circ}$ | $72.7^{\circ}$ | $90.0^{\circ}$ |
| $T_{2}$ | 96.2 | $88 \cdot 1$ | $79 \cdot 0$ | 71.4 | $70 \cdot 5$ | 74-1 | $75 \cdot 7$ | 76.2 | 76.4 | $79 \cdot 4$ | $82 \cdot 6$ | 91-8 |

There is an unstable compound ( 2 oxide $: 1$ naphthol) with an incongruent $m$. p. at $76^{\circ}$. The eutectic point at $65 \cdot 2^{\circ}, 42$ mols. \% oxide, is well defined. The second eutectic arrest is at $72 \cdot 7^{\circ}$.

## Catechol.

| Oxide, mols. \% | 0 | $25 \cdot 1$ | $41 \cdot 8$ | $51 \cdot 6$ | $58 \cdot 1$ | $73 \cdot 7$ | $85 \cdot 5$ | 100 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $T_{1}$. | $103.9^{\circ}$ | $73.9{ }^{\circ}$ | $74.0{ }^{\circ}$ | $73.8{ }^{\circ}$ | $73 \cdot{ }^{\circ}$ | $74 \cdot 2^{\circ}$ | $73.9{ }^{\circ}$ | $90.0{ }^{\circ}$ |
| $T_{1}$ | $104 \cdot 7$ | $\mathbf{9 4 \cdot 4}$ | 86.8 | $80 \cdot 8$ | $77 \cdot 1$ | $79 \cdot 8$ | $85 \cdot 5$ | $91 \cdot 8$ |

The curve is simple, with a eutectic point at $73 \cdot 8^{\circ}, 63$ mols. \% oxide.
Systems with Phenyltetramethyltetrahydropyran (Oxide III). $\alpha$-Naphthol (Curve 5).

| Ox | 0 | 12 | $25 \cdot 3$ | 35 | 40 | $45 \cdot 8$ | 52.9 | $60 \cdot 6$ | $72 \cdot 2$ | $80 \cdot 1$ | 90 | 100 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $T_{1}$ | $95 \cdot{ }^{\circ}$ | $62 \cdot{ }^{\circ}$ | $61.6{ }^{\circ}$ | $61.8^{\circ}$ | $61.3{ }^{\circ}$ | $61.4{ }^{\circ}$ | $48 \cdot 6{ }^{\circ}$ | $48 \cdot 0^{\circ}$ | $48 \cdot 3^{\circ}$ | $48 \cdot{ }^{\circ}$ | $48 \cdot{ }^{\circ}$ | $56.2^{\circ}$ |
| $T_{2}$ | 96.2 | $90 \cdot 2$ | $78 \cdot 8$ | $67 \cdot 0$ | $65 \cdot 9$ | $68 \cdot 0$ | $68 \cdot 4$ | $65 \cdot 8$ | $58 \cdot 8$ | $50 \cdot 9$ | $53 \cdot 8$ | 57.5 |

The curve shows a single compound (1:1) with congruent m. p. 68.9 ${ }^{\circ}$ and eutectic points at $61 \cdot 5^{\circ}, 38$ mols. $\%$ oxide ; and $48 \cdot 2^{\circ}, 82$ mols. $\%$ oxide.

| $\beta$-Naphthol. |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Oxide, mols. \%..... | 0 | $19 \cdot 0$ | 41.2 | $49 \cdot 2$ | 64-1 | $79 \cdot 5$ | $91 \cdot 8$ | 100 |
| $T_{1} \ldots \ldots . . . . . . . . . . . .$. | $119.5^{\circ}$ | $36.9{ }^{\circ}$ | $37.1{ }^{\circ}$ | $37 \cdot{ }^{\circ}$ | $35.2^{\circ}$ | $37.4{ }^{\circ}$ | $37.6{ }^{\circ}$ | $56.2{ }^{\text {² }}$ |
| $T_{2}$. $\ldots$................. | $120 \cdot 8$ | $108 \cdot 4$ | $85 \cdot 3$ | $74 \cdot 5$ | 42.7 | $48 \cdot 4$ | $54 \cdot 2$ | $57 \cdot 6$ |

The curve is simple, with a eutectic point at $37 \cdot 3^{\circ}, 66 \mathrm{mols} . \%$ oxide.
Catechol (Curve 6).

| xide, mols. \% | 0 | $21 \cdot 3$ | $38 \cdot 6$ | $43 \cdot 3$ | $47 \cdot 6$ | $51 \cdot 4$ | $58 \cdot 2$ | 66.5 | $80 \cdot 4$ | 88.5 | $93 \cdot 7$ | 100 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $T_{1}$ | $103.9^{\circ}$ | $74.7{ }^{\circ}$ | $75 \cdot{ }^{\circ}$ | $75 \cdot{ }^{\circ}$ | $74.4{ }^{\circ}$ | $65.8{ }^{\circ}$ | $51.5{ }^{\circ}$ | $50.9{ }^{\circ}$ | $51.1^{\circ}$ | $50.9{ }^{\circ}$ | $50.7{ }^{\circ}$ | $56.2{ }^{\circ}$ |
| $T_{2}$ | 104.7 | $94 \cdot 6$ | $82 \cdot 6$ | 78.2 | $77 \cdot 6$ | 77.9 | 76.7 | $73 \cdot 2$ | $63 \cdot 1$ | 53.9 | $54 \cdot 8$ | 57.5 |

The curve shows the formation of an unstable compound ( $1: 1$ ) of m. p. $77 \cdot 9^{\circ}$; there is a eutectic point at $51 \cdot 0^{\circ}, 90$ mols. \% oxide, and the eutectic arrest for mixtures rich in catechol is at $\mathbf{7 4} \cdot \mathbf{8}^{\circ}$.

Resorcinol.

| O | 0 | 23.5 | 38.0 | 48.5 | $54 \cdot 7$ | $60 \cdot 3$ | $67 \cdot 9$ | $72 \cdot 1$ | $78 \cdot 7$ | $84 \cdot 7$ | 88.5 | 93.0 | 100 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $T_{1}$ | $109.0^{\circ}$ | $60 \cdot{ }^{\circ}$ | $58.9{ }^{\circ}$ | $59.5{ }^{\circ}$ | $59 \cdot 3^{\circ}$ | $60 \cdot{ }^{\circ}$ | $63 \cdot{ }^{\circ}$ | $52.7{ }^{\circ}$ | $52 \cdot{ }^{\circ}$ | $52.7^{\circ}$ | $51.9^{\circ}$ | $51.6{ }^{\circ}$ | $56.2{ }^{\circ}$ |
| $T_{2}$ | $110 \cdot 1$ | 96.5 | 83.9 | 69.2 | 63.2 | 65.8 | $67 \cdot 1$ | 66.3 | 64.6 | $60 \cdot 2$ | $54 \cdot 3$ | $55 \cdot 1$ | 57.5 |

The curve shows the existence of a well-defined compound ( 2 oxide : 1 resorcinol) with congruent m. p. at $67 \cdot 5^{\circ}$. The eutectic points are at $59 \cdot 5^{\circ}, 53 \mathrm{mols} . \%$ oxide ; and $52 \cdot 1^{\circ}, 90 \mathrm{mols}$. \% oxide.

Examination of the Extent of Dissociation on Melting in Two Instances.-It was shown by van Laar (loc. cit.) that, provided the law of mass action holds when molecular concentrations are used, and that a binary compound dissociates at its $\mathrm{m} . \mathrm{p} ., T_{0}$, in the liquid phase to a degree $\alpha_{0}$ which is not too small (at least $0 \cdot 2$ ), then

$$
\begin{equation*}
T_{0}-T=\frac{R T_{0}^{2}}{Q_{0}} \cdot \frac{x^{2}(1+x)}{4 x_{0}} \tag{l}
\end{equation*}
$$

in which $T$ is the temperature to which $T_{0}$ is depressed by the presence of a mol.-fraction $x$ of one of its constituents, $R$ is the gas constant, and $Q_{0}$ is the heat of fusion of the compound with partial dissociation. $Q_{0}$ may be determined from

$$
\begin{equation*}
(d T / d x)_{0}=-R T^{2} / Q_{0} \tag{2}
\end{equation*}
$$

where $x$ is now the molecular proportion of an added foreign solute (cf. Kremann and Grasser, Monatsh., 1916, 37, 761).

The compounds of oxide I with $(a) \alpha$-naphthol and $(b) p$-bromophenol were examined, naphthalene being used as foreign solute.
(a) Compound with $\alpha$-naphthol; $M=320$. Naphthalene, $M=128$.


The degree of dissociation is of the order 0.58 .
(b) Compound with $p$-bromophenol; $M=349$. Naphthalene, $M=128$.
$\begin{array}{ccccc}\text { Compound, g. } & \text { Added } \mathrm{C}_{10} \mathrm{H}_{8}, \mathrm{~g} . & \text { Mol.-fraction, } x . & \Delta T . & Q_{0} \text { [by equation (2)], cals. } \\ 0 \cdot 2269 & 0 \cdot 1040 & 0 \cdot 144 & 5 \cdot 3^{\circ} & 5700 \\ & 0 \cdot 0234 & 0 \cdot 220 & 8 \cdot 8 & 5300 \\ & & & & \text { Mean } 5500\end{array}$
From the original m. p. curve :
Oxide, mols. \% M.p. Added oxide, mols. \%. $\quad$. $\quad$. $\quad$ [by equation (1)].

| $50 \cdot 0$ | $54 \cdot 3^{\circ}$ |  |
| :--- | :--- | :--- |
| $55 \cdot 3$ | $53 \cdot 2$ | $0 \cdot 192$ |
| $61 \cdot 6$ | $\mathbf{4 9 \cdot 8}$ | $0 \cdot 376$ |


| $1 \cdot 1^{\circ}$ | 0.39 |
| :--- | :--- |
| $4 \cdot 5$ | 0.41 |

The degree of dissociation is of the order $0 \cdot 40$.
The University, Sheffield.
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