502. *Some Nuclear-methylated Styrenes and Related Compounds. Part I.*

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The effects, on the properties of styrene and ethylbenzene, of the introduction of nuclear methyl groups have been investigated by measuring physical properties of suitable hydrocarbons of this type, and of binary systems containing them. The presence of two *o*-methyl groups has a profound effect on the nature of styrene; that of one *o*-methyl group has a much smaller effect. Values of physical constants are recorded for certain pure hydrocarbons homologous with styrene and ethylbenzene.

In the last decade, styrene has found application in many fields as the precursor of polystyrene, used for electrical and other purposes, and of Buna-S and similar synthetic rubbers. The present work was initiated in an attempt to find homologues of styrene which would yield polymers of enhanced value. Experiments in this direction in the U.S.A. led to the development of the chlorostyrenes (Michalek and Clark, *Chem. Eng. News*, 1944, **22**, 1559) and provided information on a large variety of other nuclear-substituted analogues (*e.g.*, Marvel *et al.*, *J. Amer. Chem. Soc.*, 1946, **68**, 736, 1085, 1088).

The availability of *m*- and *p*-ethyltoluene, mesitylene, and *ψ*-cumene from natural crude oils (*e.g.*, Morton and Richards, *J. Inst. Petroleum*, 1943, **29**, 67) directed attention to *m*- and *p*-methylstyrene and to 2 : 4 : 6- and 2 : 4 : 5-trimethylstyrene. These styrene derivatives have been described previously, but the available physical data, on both the monomers and the polymers, are inadequate.

The large-scale production of styrene is normally effected by the catalytic dehydrogenation of ethylbenzene, which, on account of the position of the thermodynamic equilibrium, does not proceed to completion at the temperatures used. An important step in this process is therefore the separation, normally by fractional distillation at reduced pressure, of the styrene from unchanged ethylbenzene, the latter being re-cycled to the dehydrogenation stage. Before such a process could be applied to the homologues of styrene and ethylbenzene, determination of their vapour pressure–temperature relations and volatility ratios was necessary.

It is to be expected, especially by analogy with the *n*-paraffin–alk-1-ene equilibria (Kilpatrick *et al.*, *J. Res. Nat. Bur. Stand.*, 1946, **36**, 559), that the equilibrium constant at a given temperature for the reaction nuclear-methylated ethylbenzene $\rightleftharpoons$ nuclear-methylated styrene + H_2 will be largely independent of the number and position of substituent methyl groups. Evidence in support of this has been obtained by calculation, by use of the method of increments and values of the necessary thermodynamic functions recently available from the work largely of the U.S. National Bureau of Standards and of Pitzer and his collaborators at California (Beckett and Pitzer, *J. Amer. Chem. Soc.*, 1946, **68**, 2213; Pitzer and Scott, *ibid.*, 1943, **65**, 803; Prosen, Johnson, and Rossini, *J. Res. Nat. Bur. Stand.*, 1946, **36**, 455; Taylor *et al.*, *ibid.*, 1946, **37**, 95; Wagman *et al.*, *ibid.*, 1945, **34**, 143). Such calculations for all the compounds under consideration give values of the equilibrium constant which are not significantly different. As has been shown by Guttman, Westrum, and Pitzer (*J. Amer. Chem. Soc.*, 1943, **65**, 1246), such experimental data as are available on the ethylbenzene $\rightleftharpoons$ styrene + H_2 equilibrium are in moderate agreement with calculation, so that it may be expected in turn that nuclear-methylated ethylbenzenes will be dehydrogenated under conditions similar to those necessary for ethylbenzene.

Stanley reported (*Chem. and Ind.*, 1938, **57**, 93) that styrene may be separated from ethylbenzene by freezing. Since the freezing points of the 2 : 4 : 5-trimethyl analogues (2 : 4 : 5-trimethylstyrene and 1 : 4 : 5-trimethyl-2-ethylbenzene) are much higher, separation of this pair by such a method would be far more practicable, provided that the system did not form solid solutions. It was with this in mind that the freezing diagram of the system was examined.

The measurements recorded show that the presence of even one methyl group, but especially two, *ortho* to the vinyl group in vinylbenzenes considerably affects many physical properties of the molecule. The classic example of a benzene derivative having a polar substituent between two *o*-methyl groups is nitrodurene, whose dipole moment is reduced from the normal value (as in nitrobenzene) nearly to its value in aliphatic nitro-compounds (Birtles and Hampson, *J.*, 1937, 10); such effects are normally due to steric interaction of the *o*-methyl groups on the adjacent polar substituent hindering the assumption by the molecule of a coplanar configuration, and hence in turn reducing the resonance with the benzene nucleus. Recently, ultra-violet absorption has been shown to be a valuable means of indicating the presence and extent of this *ortho* effect (see references in Part III of this series), which has received much attention in molecules containing groups such as Ac, NO_2, and NMe_2 but produces phenomena no less definite in the relatively more simple hydrocarbons of the styrene series. A preliminary note on some of this work has already been published (*Nature*, 1948, **162**, 103).

EXPERIMENTAL.

All fractional distillations were effected through a 2 ft. × 1 in. column packed with $\frac{1}{16}$-in. phosphor-bronze gauze ferrules. The styrenes were stored at −20° and freshly distilled *in vacuo* before use.

Preparation of Materials.—Ethylbenzene and styrene were obtained from commercial samples by fractional distillation. A mixture of *m*- and *p*-ethyltoluene was extracted from suitable fractions of re-formed naphtha by sulphonation followed by hydrolysis; by ultra-violet absorption it was shown to contain 74% of *m*-ethyltoluene, 21% of *p*-ethyltoluene and 5% of *n*-propylbenzene. 985 Ml. of this material were sulphonated by the addition, with stirring, of 1200 ml. of 98% sulphuric acid, and the final mixture was hydrolysed by boiling after addition of sufficient water to give a liquid temperature of about 120° at the initial boiling point. During this process water was dropped in at a rate rather lower than that at which it was removed as distillate, so as to cause the hydrolysis temperature to rise slowly. Under these conditions the sulphonic acid of *m*-ethyltoluene is readily hydrolysed at 130—140°, whereas the *p*-isomer and *n*-propylbenzene are only slowly produced until the temperature has risen above 140°. In this way 660 ml. of a *m*-ethyltoluene concentrate were obtained, which, after a further similar treatment, yielded 520 ml. of *m*-ethyltoluene, which was finally redistilled under reduced pressure. The *p*-isomer could not be detected in the final material by ultra-violet analysis.

p-Ethyltoluene was obtained by Clemmensen reduction of *p*-methylacetophenone prepared from toluene (a pure grade used as a reference fuel) by the method of Noller and Adams (*J. Amer. Chem. Soc.*, 1924, **46**, 1889). 1 : 4 : 5- and 1 : 3 : 5-Trimethyl-2-ethylbenzene were obtained similarly from *ψ*-cumene and mesitylene, respectively, which had been purified from crude materials extracted from petroleum, by sulphonation, crystallisation of the sulphonic acids from hydrochloric acid, and hydrolysis. These three compounds were finally purified by fractional distillation, centre fractions of constant refractive index being bulked.

p-Methylstyrene and 2 : 4 : 5- and 2 : 4 : 6-trimethylstyrene were obtained by reduction of the ketones obtained as above to the corresponding carbinols, followed by dehydration by the method of Brooks (*J. Amer. Chem. Soc.*, 1944, **66**, 1295). The reduction of the ketones was effected with hydrogen at 100—120°/100 atm. in presence of copper chromite, in a Baskerville–Lindsay hydrogenator. Reductions were also carried out by the Ponndorf method, using aluminium *iso*propoxide, but this method was later abandoned on account of its inconvenience on anything but a small scale, and also since 50% of the reaction product in the case of *p*-methylacetophenone was the *iso*propyl ether of the carbinol.

m-Methylstyrene was obtained from *m*-xylene (separated and purified from mixed isomers by the methods described above for *m*-ethyltoluene, etc.) by oxidation with manganese dioxide and sulphuric acid to *m*-tolualdehyde, which was converted into the carbinol by methylmagnesium chloride. The carbinol was finally dehydrated in the manner mentioned above.

Freezing Points and Determination of Purities.—Freezing curves were obtained by a simplification of the technique used by the U.S. National Bureau of Standards (*e.g.*, Glasgow, Streiff, and Rossini, *J. Res. Nat. Bur. Stand.*, 1945, **35**, 355); 20-ml. samples and single-junction iron–constantan thermocouples calibrated at the freezing point of mercury and the sublimation point of carbon dioxide were used, e.m.f.s being measured to ±0·01 mv. (equivalent to ±0·2°) with a portable potentiometer. *m*-Methylstyrene was still liquid at −70°; a higher degree of refrigeration than that given by solid carbon dioxide was not available. Similarly, determinations were not made on *m*- and *p*-ethyltoluene since these hydrocarbons freeze at −95° and −64°, respectively. From the methods of purification used it is likely, however, that these materials, as well as the ethylbenzene and styrene, had a purity of better than 95%.

Freezing point diagram for the system 1 : 4 : 5-*trimethyl*-2-*ethylbenzene*–2 : 4 : 5-*trimethylstyrene.* Time–temperature freezing curves were obtained for a series of mixtures of known composition, by use of a simple air-jacketed freezing tube holding 5-ml. samples, mechanical stirrer, and a calibrated alcohol thermometer reading to ±0·1°. The positions of the solidus lines were approximately determined by observing the temperatures at which melting commenced on small samples of mixtures of several compositions contained in capillary tubes (the thaw–melt method). Further evidence for the position of these solidus lines was obtained from the form of the freezing curves; in the composition range of about 10—36 moles-% of 1 : 4 : 5-trimethyl-2-ethylbenzene freezing took place over a range of several degrees, whereas in the range 50—100 moles-% the freezing range was never greater than 1°; in the latter range, therefore, any mixture behaved much as though it were a nearly pure compound, illustrating the care necessary in determining purity from freezing curves when the impurity can form a solid solution with the major component.

Refractive indices and densities. Refractive indices (n_D) and dispersions (n_F–n_C) were determined on an Abbé refractometer (carefully calibrated for both these quantities on a series of pure hydrocarbons), whose prisms were kept at constant temperature by the circulation of water at 20° ± 0·1°. Densities were obtained to 0·001 or better, using a Westphal balance.

Boiling points. These were determined for each compound at a series of pressures in a modified Othmer equilibrium still (see next section). Temperatures were measured to ±0·1° on a mercury thermometer, graduated in 0·5° divisions, which had been previously calibrated by use of liquids of accurately known boiling points; stem corrections were applied in the usual way, the temperature of the emergent stem being measured on a second thermometer. Pressures, held constant by means of a simple manostat, were measured to ±0·5 mm. on a full-length mercury manometer of the closed-limb type. Measurements on the styrenes were made as rapidly as possible to minimise errors due to polymerisation, which was inhibited by the presence of a trace of free sulphur.

Relative volatilities. Attempts were made to determine the relative volatility (α) experimentally for each of the systems ethylbenzene–styrene, *m*-ethyltoluene–*m*-vinyltoluene, *p*-ethyltoluene–*p*-vinyltoluene and 1 : 4 : 5-trimethyl-2-ethylbenzene–2 : 4 : 5-trimethylstyrene, with use of a modification (having a boiler capacity of 50 ml.) of Othmer's apparatus (*Ind. Eng. Chem.*, 1943, **35**, 614). Analyses were effected by refractive index. Polymerisation of styrenes in the boiler was inhibited by the presence of a trace of free sulphur. After a series of measurements, the " liquid " sample was tested for the presence of polymer by addition (after filtration from sulphur) to an excess of methanol. Precipitation of polymer was seldom observed; if it was, the series of measurements was discarded. Measurements on the above four systems were carried out at 100, 40, 40, and 20 mm., respectively, these pressures being chosen to give an operating temperature close to 100° in each case.

RESULTS AND DISCUSSION.

Freezing Points and Purities.—These are collected in Table I, along with data from the literature where available.

2 : 4 : 6-Trimethylstyrene is anomalous in this series in having a freezing point lower than that of its ethyl analogue.

The freezing point diagram for the 1 : 4 : 5-trimethyl-2-ethylbenzene–2 : 4 : 5-trimethylstyrene system is shown in Figure 1. It belongs to the rather unusual class showing a continuous series of solid solutions interrupted by a transition or peritectic point (see, *e.g.*, Glasstone, " Textbook of Physical Chemistry," Macmillan, 1938, p. 758). Clearly the separation of the two components by freezing is not possible.

TABLE I.

Hydrocarbon.	Estimated minimum purity (moles-%).	Observed f. p.	F. p. (literature).
Ethylbenzene	—	—	−94·98° [a]
Styrene	—	—	−30·63 [a]
m-Methylethylbenzene	—	—	−95·55 [a]
m-Methylstyrene	—	−70°	—
p-Methylethylbenzene	—	—	−62·35 [a]
p-Methylstyrene	98·5	−37·8	—
1 : 4 : 5-Trimethyl-2-ethylbenzene	99·0	−13·0	−13·58 [b]
2 : 4 : 5-Trimethylstyrene	97·5	+ 2·5	—
1 : 3 : 5-Trimethyl-2-ethylbenzene	97·5	−12·2	−15·56 [b]
2 : 4 : 6-Trimethylstyrene	98·0	−37·0	—

[a] " Selected Values of Properties of Hydrocarbons," American Petroleum Institute Research Project 44, June 1948.

[b] Smith and Keiss, *J. Amer. Chem. Soc.*, 1939, **61**, 284.

TABLE II.

	B. p. at 760 mm.		n_D^{20}.		Density.		Specific dispersion, $(n_F-n_C)/d$ $\times 10^4$ at 20°.	
Hydrocarbon.	This work.	Literature.*	This work.	Literature.*	This work.	Literature.*	This work.	Literature.*
Ethylbenzene	136·2°	136·187° [a]	1·4959	1·49594 [a]	—	d_4^{20} 0·86702 [a]	175	173·9 [a]
Styrene	145·1	145·2 [a]	1·5465	1·54682 [a]	—	d_4^{20} 0·90600 [a]	263	265 [a]
m-Methylethylbenzene	161·0	161·301 [a]	1·4966	1·49661 [a]	d_4^{14} 0·871	d_4^{20} 0·86452 [a]	176	172·1 [a]
m-Methylstyrene	169·8	168 [a]	1·5406	1·542 [a]	d_4^{18} 0·902	d_4^{20} 0·900 [a]	250	265 [a, e]
p-Methylethylbenzene	161·5	161·985 [a]	1·4952	1·49497 [a]	d_4^{14} 0·869	d_4^{20} 0·86118 [a]	174	173·5 [a]
p-Methylstyrene	170·5	169 [a]	1·5421	1·541 [a]	d_4^{24} 0·893	d_4^{20} 0·897 [a]	258	265 [a, e]
1 : 4 : 5-Trimethyl-2-ethylbenzene	212·0	210 [b] (725 mm.)	1·5098	1·5075 [b]	$d_4^{17\cdot5}$ 0·888	d_4^{14} 0·8890 [c]	168	170 [d]
2 : 4 : 5-Trimethylstyrene	216·8	—	1·5462	1·5379 [c] (17°)	$d_4^{16\cdot5}$ 0·916	d_4^{17} 0·9137 [c]	236	—
1 : 3 : 5-Trimethyl-2-ethylbenzene	210·2	210 [b] (725 mm.)	1·5101	1·5075 [b]	d_4^{18} 0·888	$d_4^{18\cdot5}$ 0·8907 [c]	170	174 [d]
2 : 4 : 6-Trimethylstyrene	209·0	206 [c] (755 mm.)	1·5323	1·5296 [c] (17·5°)	d_4^{21} 0·906	$d_4^{17\cdot5}$ 0·9073 [c]	206	—

* The most recent work is cited when a value is quoted in more than one source.

[a] " Selected Values of Properties of Hydrocarbons," American Petroleum Institute, 1947 or later.

[b] Smith and Keiss, *J. Amer. Chem. Soc.*, 1939, **61**, 284.

[c] Klages and Keil, *Ber.*, 1903, **36**, 1635.

[d] Von Auwers, *Annalen*, 1919, **419**, 92.

See discussion in text.

TABLE III.

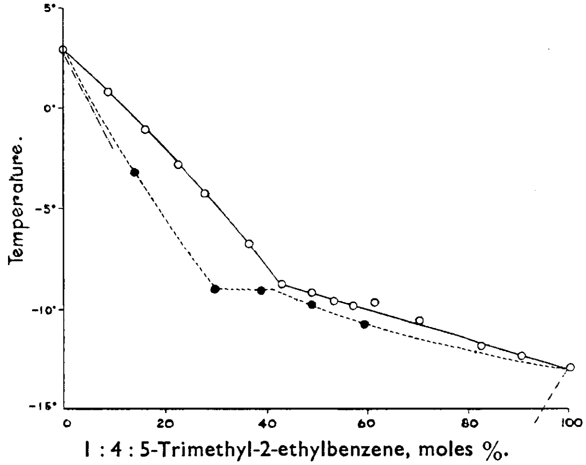
Temp.	Pressure (mm.).	Temp.	Pressure (mm.).	Temp.	Pressure (mm.).	Temp.	Pressure (mm.).
Ethylbenzene.		Styrene.		*m*-Ethyltoluene.		*m*-Vinyltoluene.	
63·3°	63	66·7°	51	62·1°	23·0	67·6°	20·2
67·7	76	75·4	74	74·0	40·4	72·3	25·8
75·2	105	82·4	100	77·9	47·2	80·7	37·0
82·6	140	88·0	125	85·4	65·2	87·0	49·0
91·6	195	91·7	142	91·3	81·6	93·8	62·8
99·0	254	95·1	163	95·1	95·8	96·5	73·0
108·1	342	98·2	185	102·1	125·8	106·9	108·0
112·7	395	119·1	361	115·3	198	121·0	180
117·6	457	132·6	536	122·5	257	128·3	228
120·5	496	145·0	755	129·8	318	138·5	312
124·6	566			140·7	437	147·6	411
129·3	638			148·5	544	159·2	568
135·9	756			160·3	747	169·1	748
p-Ethyltoluene.		*p*-Vinyltoluene.		1 : 3 : 5-Trimethyl-2-ethylbenzene.		2 : 4 : 6-Trimethylstyrene.	
66·8°	28·8	68·6°	20·8	88·5°	11·8	89·9°	14
77·4	45·8	70·6	22·4	91·3	13·8	97·1	19
79·4	49·4	75·1	28·0	96·3	17·8	102·2	25
83·5	60·0	78·8	33·0	102·0	22·8	109·9	32
87·9	71·0	80·6	35·4	107·0	28·0	114·5	40
90·2	78·0	82·7	39·0	110·1	32·0	117·7	46
94·0	90·0	84·2	41·8	115·4	39·0	123·7	58
105·8	139·8	87·9	49·2	119·0	46·6	134·5	88
122·7	249	94·1	64·2	122·2	53·0	139·2	101
131·7	331	104·4	96·2	125·1	58·0	141·7	111
136·9	385	115·1	142·2	130·0	70·0	147·5	134
144·2	477	131·9	249	133·9	80·5	151·8	155
152·5	598	144·0	360	140·5	103	155·8	178
161·1	756	154·7	493	151·9	151	165·2	238
		163·7	624	161·2	204	172·8	297
		170·0	748	174·0	300	176·4	328
				185·0	401	179·1	354
				195·9	528	182·4	388
				210·2	760	186·4	432
						192·9	500
						197·1	570
						199·8	611
						205·0	694
						207·9	750
1 : 4 : 5-Trimethyl-2-ethylbenzene.		1 : 4 : 5-Trimethyl-2-ethylbenzene.		2 : 4 : 5-Trimethylstyrene.		2 : 4 : 5-Trimethylstyrene.	
87·3	11	141·2	98	79·5	5	165·8	188
98·3	16	150·7	135	97·9	13	177·0	261
100·2	19	161·2	197	106·8	21	198·4	470
101·7	20	169·1	245	113·6	28	216·3	754
103·6	21	174·3	285	142·0	83		
109·4	27	182·8	360				
109·1	28	187·9	412				
117·4	39	197·9	537				
122·2	50	205·0	640				
126·3	58	207·2	680				
132·1	71						

Boiling Points, Refractive Indices, Densities, and Specific Dispersions.—These constants are collected in Table II for all the hydrocarbons used, the normal boiling points being obtained from the vapour-pressure data (next section). The elevation of refractive index and specific dispersion, characteristic of styrenes (in comparison with alkylbenzenes, and of alkenylbenzenes in which at least two single bonds intervene between the ethylenic bond and the nucleus), is markedly reduced in 2 : 4 : 6-trimethylstyrene. This hydrocarbon shows also an appreciably lower optical exaltation (1·0) than the other styrenes examined (1·3—1·8); 2 : 4-, 2 : 5-, and 3 : 4-dimethylstyrenes also have exaltations in the range 1·5—1·9 (B.P. 598,069).

A significant comparison may be made of the physical properties of 2 : 4 : 6-trimethylstyrene and of α-methylstyrene, which also has an abnormally low boiling point, refractive index, and optical exaltation (see ref. *a*, Table II). Resonance between the external double bond and the benzene nucleus is diminished to a similar extent in both compounds, by steric restriction of rotation, about the bond between the nucleus and the ethylenic system, caused by interaction between the α-hydrogen atom and *o*-methyl groups in the first, and between the α-methyl group and *o*-hydrogen atoms in the second, compound respectively.

The specific dispersions of all five monomethylstyrenes quoted by the A.P.I. (*loc. cit.*) as 265 are almost certainly incorrect, particularly for α-methylstyrene, for which von Auwers and Eisenlohr (*J. pr. Chem.*, 1910, **82**, 65) found a value of 230, which is more in line with the other properties of this hydrocarbon.

FIG. 1.



○ *Liquidus points from freezing curves.* ● *Solidus points from thaw-melt method.*
—·—·— *Calculated ideal behaviour.*

Vapour Pressures.—The experimental data on the variation of boiling point with pressure are collected in Table III.

For each compound the data were plotted in the form log p against $1/T$. By measurement of the slopes of these curves at a series of values of log p, the results were fitted for the temperature range 80—120° to equations of the form, $\log_{10} p = a/T + b \log_{10} T + c$, where p is the vapour pressure (mm.) at an absolute temperature T, and a, b, and c are constants. The latent heats of vaporisation were also calculated from the slopes of the log p–$1/T$ plots at a series of temperatures. The results obtained for the four tetra-substituted compounds are less consistent than for the others; this is particularly so in the low-temperature region where the pressures are so low as to make possible a large percentage error in their measurement. Hence the detailed variation of the heat of vaporisation with temperature could not be measured for these compounds. The results of these calculations are given in Tables IV and V.

A comparison with data in the literature, when this is available, shows satisfactory agreement (vapour pressures of ethylbenzene, Willingham *et al.*, *J. Res. Nat. Bur. Stand.*, 1945, **35**, 219, of styrene, Patnode and Scheiber, *J. Amer. Chem. Soc.*, 1939, **61**, 3449, and Burchfield, *ibid.*, 1942, **64**, 2501; latent heats of vaporisation of ethylbenzene, styrene, and *m*- and *p*-ethyltoluene, Haggenmacher, *J. Amer. Chem. Soc.*, 1947, **69**, 707, Pitzer, Guttman, and Westrum, *ibid.*, 1946, **68**, 2209, U.S. National Bureau of Standards, unpublished observations cited by Wood and

TABLE IV.

Values of a, b, *and* c *in the equation* $\log_{10} p = a/T + b \log_{10} T + c$, *representing the variation of vapour pressure with temperature in the range* 80—120°.

Hydrocarbon.	*a.*	*b.*	*c.*
Ethylbenzene	−3225	−7·553	30·49
Styrene	−3151	−6·294	26·92
m-Methylethylbenzene	−3155	−5·663	25·08
m-Methylstyrene	−3563	−7·553	30·90
p-Methylethylbenzene	−2939	−4·406	21·27
p-Methylstyrene	−3476	−6·923	29·03

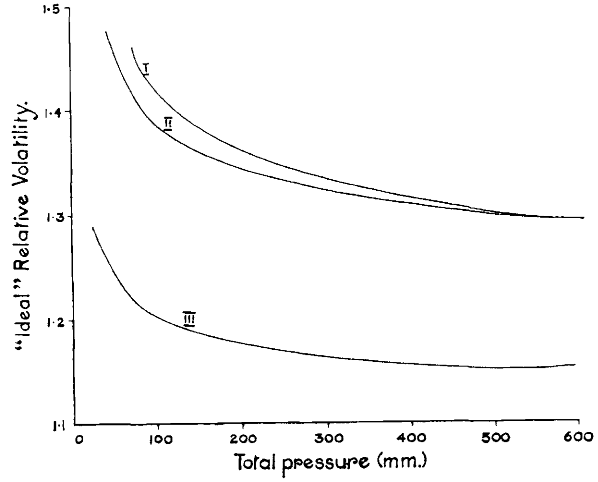
TABLE V.

Hydrocarbon.	Temp.	Latent Heat of Vaporisation, kcals./mole. This work.	Latent Heat of Vaporisation, kcals./mole. Lit.*
Ethylbenzene	25°	10·25	10·07
	50	9·85	9·68
	100	9·15	9·04
	140	8·55	8·44
Styrene	25	10·55	10·50
	145·2	9·25	9·04
m-Methylethylbenzene	25	11·1	11·22
p- ,, ,,	25	10·85	11·15
1 : 4 : 5-Trimethyl-2-ethylbenzene	80—120	12·4	—
,, ,, ,,	120—200	11·3	—
2 : 4 : 5-Trimethylstyrene	80—120	13·6	—
,, ,,	120—200	12·0	—
1 : 3 : 5-Trimethyl-2-ethylbenzene	80—120	11·8	—
,, ,, ,,	120—200	11·3	—
2 : 4 : 6-Trimethylstyrene	80—120	11·8	—
,, ,,	120—200	11·3	—

* See text for references.

Higgins, *Petroleum Refiner*, 1943, **22**, 87, and Prosen, Johnson, and Rossini, *J. Res. Nat. Bur. Stand.*, 1946, **36**, 455). The only published vapour-pressure data for 1 : 4 : 5- and 1 : 3 : 5-trimethyl-2-ethylbenzene (Smith and Keiss, *J. Amer. Chem. Soc.*, 1939, **61**, 284) have little self-consistency and, judged from freezing points (cf. Table I), were carried out on materials of lower purity than those obtained here.

FIG. 2.



I. *Ethylbenzene–styrene.*
II. *Methylethylbenzene–methylstyrene* (m- *or* p-*isomer*).
III. 1 : 4 : 5-*Trimethyl-2-ethylbenzene*–2 : 4 : 5-*trimethylstyrene.*

The fact that 1 : 4 : 5-trimethyl-2-ethylbenzene boils at a rather higher temperature than does the 1 : 3 : 5-compound is not anomalous. The reverse might be expected by comparison with durene and *iso*durene (b. p. 193° and 196°, respectively), but an *o*-methyl group raises the boiling point more than does an *o*-ethyl group, as shown by the boiling points of the xylenes and the ethyltoluenes (Egloff, " Physical Constants of Hydrocarbons," Vol. III, Reinhold, 1946).

The anomalous behaviour of 2 : 4 : 6-trimethylstyrene is reflected in a low heat of vaporisation as well as a high vapour pressure.

Relative Volatilities.—On account of the comparatively low values (about 1·3) of the relative volatilities (α) of the systems examined, the experimental errors inherent in the method of analysis were too large to permit accurate representation of the variation of α with composition or a significant test of thermodynamic consistency. Nevertheless, the accuracy was sufficient to show that all the systems approximated to ideality (in terms of Raoult's law), with a tendency towards lower values of α as the concentration of the ethyl component increased, except for the 1 : 2 : 4 : 5-substituted system where the reverse was true.

The approximation to ideal behaviour of these systems is sufficiently close to justify an analysis of the variation in α with changing pressure, using values of α calculated from the vapour pressure data of the previous section. The result of this is shown in Figure 2. At any given value of the total pressure, the value of α for the system 1 : 4 : 5-trimethyl-2-ethylbenzene–2 : 4 : 5-trimethylstyrene is about 0·15 below the corresponding value for the other systems. This effect appears to be connected with the presence of an *o*-methyl group rather than with increasing similarity of the components as more methyl groups are added, for the following reason. The introduction of one *m*- or *p*-methyl group has virtually no effect on α, but, from the limited vapour pressure data available for *o*-ethyltoluene and *o*-vinyltoluene (Egloff, *loc. cit.*) it is clear that the value of α for this system is only about 1·11 at atmospheric pressure; it appears that two additional methyl groups lower α further only if one of them is in the second *ortho* position. Thus, at atmospheric pressure, for the system 1 : 3 : 5-trimethyl-2-ethylbenzene–2 : 4 : 6-trimethylstyrene, α is about 0·96, but for the 1 : 2 : 4 : 5- system is about 1·15. The decrease (1·2° at 760 mm.) in boiling point which accompanies the dehydrogenation of 1 : 3 : 5-trimethyl-2-ethylbenzene may be compared with the similar decrease (1·7°) accompanying the change from *n*-propyl- to allyl-benzene (Egloff, *loc. cit.*); in the latter compound no resonance is possible between the side-chain double bond and the benzene ring, indicating (even if other evidence were not available) that the resonance of the vinyl double bond with the nucleus in 2 : 4 : 6-trimethylstyrene is less complete than in styrene, whose normal boiling point is 9° above that of ethylbenzene.

The effects of *o*-methyl groups on the dipole moment (Everard and Sutton, *Nature*, 1948, **162**, 104) and on the ultra-violet and infra-red absorption spectra (Part III of this series) of styrene have also been measured.

Two main results of the present work have been to show that *ortho* effects are often pronounced in benzene derivatives containing small and relatively non-polar groups such as vinyl, and that they may be revealed in the value of almost every physical property of such molecules. Some form of electronic field effect may also contribute to these abnormalities, but the steric explanation is simplest, and probably the most useful in predicting the likelihood of such effects.

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