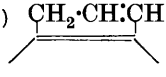
LXIII.—*The Mobility of Symmetrical Triad (Prototropic) Systems. Part IV. Mobility in the Simple Three-carbon System terminated by Aryl Groups.*

By CHRISTOPHER KELK INGOLD and CHARLES WILLIAM SHOPPEE.

THE importance, from the point of view of the modern theory of reactivity-distribution in molecules, of the study of equilibria in simple * three-carbon prototropic systems has recently been emphasised (Ingold and Rothstein, this vol., p. 8), but no systematic examination of the subject has yet been taken up. The main available examples of three-carbon prototropy may be grouped as follows: (I) Indene, its derivatives and analogues (Ingold and Piggott, J., 1923, **123**, 1469; Goss and Ingold, J., 1928, 1268); (II) propenylbenzene and its substitution products (Tiffeneau, *Compt. rend.*, 1904, **139**, 482; Shoppee, J., 1928, 2567; *inter alia*); (III) propenylammonium derivatives (Ingold and Rothstein, *loc. cit.*).

(I.)  Aryl·CH_2·CH:CH_2 (II)

$R_3\overset{+}{N}$·CH_2·CH:CH_2 (III.)

(IV.) Aryl·CH_2·CH:CH·Aryl′ $R_3\overset{+}{N}$·CH_2·CH:CH·$\overset{+}{N}R_3$′ (V.)

The great mobility of systems (I) renders them unsuitable for investigations on the position of equilibrium. Systems (II) and (III), on the other hand, undergo isomeric change only in the presence of an added proton-attractor (usually ethoxide ions †), and the equilibrium, once attained, can readily be fixed by destruction of the catalyst. The difficulty with regard to these systems, however, is that the equilibrium is too one-sided to permit of accurate determination. It therefore seemed that by the introduc-

* The adjective is introduced to indicate the exclusion of pentad "three-carbon systems" (*e.g.*, pentad keto-enol, CH·C:C·C:O, etc.).

† The order of proton-affinity of the more commonly employed alkaline catalysts is OH′<OMe′<OEt′, and illustrations of these inequalities are given in this paper.

tion of a balancing group, as in (IV) or (V), series might be obtained in which both the mobility and the position of equilibrium would be of a convenient order. This paper records a preliminary investigation in which systems of type (IV) have been quantitatively studied with tolerably satisfactory results.

The methoxyhydrocarbons (VI) and (VII) were originally described by Ingold and Piggott (J., 1922, **121**, 2381) : they underwent no interconversion at 220—230°, and each yielded its own dibromide. We have confirmed these results and found, further, that no interconversion occurs in the presence of hot dilute alkali solution, and that on ozonolysis each isomeride yields exclusively products corresponding to its constitution. These observations establish the stability of the isomerides under the condition which we have employed to isolate and examine the products of their partial or complete equilibration. Moreover, we found that each methoxyhydrocarbon could be quantitatively regenerated, without any interconversion, from its pure dibromide by the action of zinc dust, and this gave the means of obtaining the isomerides in the high degree of purity required for the study of their isomerisation by a physical method.

$$\underset{\text{(VI, 29·5\%.)}}{p\text{-MeO}\cdot C_6H_4\cdot CH_2\cdot CH{:}CHPh} \rightleftharpoons \underset{\text{(VII, 70·5\%.)}}{p\text{-MeO}\cdot C_6H_4\cdot CH{:}CH\cdot CH_2Ph}$$

Interconversion was effected in 1·45*N*-ethyl-alcoholic sodium ethoxide at 85°, and, after 4 hours or longer at this temperature, mixtures were obtained which gave, on ozonolysis, products derived from both isomerides, and yielded mixtures of dibromides from which, even when (VI) was the starting point, up to 58% of the dibromide of (VII) could be isolated in a state of purity. The attainment of equilibrium was thereafter studied refractometrically. The coefficient (k_1+k_2) for the velocity of interconversion was 0·79 hour^{-1}, and the equilibrium ratio (k_1/k_2) was 0·42, the corresponding percentages being as indicated beneath the formulæ above.

During the preparation of the methoxyhydrocarbons considerable quantities of the β-carboxy-derivatives (VIII and IX) were accumulated, and it appeared of interest to examine the equilibration of these under the conditions used for the methoxyhydrocarbon, since the position of the carboxyl group is such that neither substance is a pentad keto-enol tautomeride. This was done (by thermal analysis), but the composition–time curves exhibited a curious semi-rectilinear character, which was traced to the separation of the sodium salts of the acids under the conditions used : the equilibration was non-homogeneous. Therefore, although the same equilibrium mixture (indicated below the formulæ) was obtained

from each isomeride, the numerical data given in the experimental portion cannot be expressed as velocity coefficients :

$$p\text{-MeO}\cdot C_6H_4\cdot CH_2\cdot C(CO_2H):CHPh \underset{\text{anions}}{\overset{\text{as}}{\rightleftharpoons}} p\text{-MeO}\cdot C_6H_4\cdot CH:C(CO_2H)\cdot CH_2Ph$$

(VIII, 44·0%.) (IX, 56·0%.)

The acids were therefore converted into their methyl and ethyl esters, and the purity of these was proved by finding conditions in which they could be hydrolysed quantitatively to the corresponding pure acids. The same method of hydrolysis, combined with thermal analysis of the acids, gave a convenient method for the analysis of mixtures of isomeric esters. Observations on the interconversion of the isomeric methyl esters in the presence of methyl-alcoholic sodium methoxide at the b. p. and at 100° showed that this catalyst, although it effected some isomerisation at the higher temperature, was inconveniently slow in its action. The ethyl esters were therefore selected for quantitative study. They readily came into equilibrium at 85° in the presence of alcoholic sodium ethoxide of the concentration used for the methoxyhydrocarbons, and the composition–time curves exhibited the normal unimolecular character. The velocity coefficient (k_1+k_2) was 0·0585 hour^{-1}, and the equilibrium ratio (k_1/k_2) was 0·770, the corresponding percentages being as shown beneath the following formulæ :

$$p\text{-MeO}\cdot C_6H_4\cdot CH_2\cdot C(CO_2Et):CHPh \rightleftharpoons p\text{-MeO}\cdot C_6H_4\cdot CH:C(CO_2Et)\cdot CH_2Ph$$

(X, 43·5%.) (XI, 56·5%.)

The theoretical significance of these results, in so far as it is not apparent from previous publications, will be discussed on a future occasion.

EXPERIMENTAL.

(1) *Interconversion of the Methoxyhydrocarbons.*

α - p- *Methoxyphenyl* - γ - *phenyl* - Δ^{β} - *propene* (VI).—*p*-Methoxycinnamic acid was prepared in good yield by condensing *p*-anisaldehyde with malonic acid in pyridine solution on the steam-bath with the addition of a little piperidine, and reduced (220 g.) at about 45° with 3% sodium amalgam (15 kg.) to the dihydro-acid, which was crystallised from 30% acetic acid below 60° (yield, 200 g.), and converted into its sodium salt. Ingold and Piggott's method of condensing this salt with benzaldehyde was modified to the following. The melt obtained by heating the salt (165 g.), benzaldehyde (105 g.), and acetic anhydride (105 g.) successively for 5 hours at 150°, 4 hours at 160°, and 1 hour at 170° was poured into a solution of excess of crystallised sodium carbonate and extracted with ether. The extract was washed with 2*N*-sodium hydroxide

and water, dried, and evaporated, and the residue carefully distilled in a vacuum by means of a metal-bath and a short column. The methoxyhydrocarbon was obtained (10·5 g.) as a pale yellow liquid, b. p. 211—213°/15 mm., $n_{5461}^{26°}$ 1·60194; an independent preparation had b. p. 208—211°/14 mm. and $n_{5461}^{26°}$ 1·60194. It was converted into its dibromide, the m. p. of which was raised to the constant value of 94° by repeated crystallisation from ligroin (Found: C, 50·0; H, 4·2. Calc.: C, 50·0; H, 4·2%). The purified bromide was treated with excess of zinc dust, followed by a small amount of "molecular" silver in boiling absolute alcohol, and the methoxy-compound extracted with ether from the diluted and acidified filtrate. It had b. p. 179—180°/3 mm. and $n_{5461}^{26°}$ 1·60246. The regenerated methoxyhydrocarbon yielded the same crystalline dibromide, and repeated distillation, and boiling for several hours with dilute sodium hydroxide solution, did not alter this property or the refractive index. Successive treatment with ozone and water yielded benzaldehyde (semicarbazone instantly precipitated), *p*-methoxyphenylacetaldehyde, and benzoic acid, but no *p*-methoxyphenylacetic acid.

*α-Phenyl-γ-*p*-methoxyphenyl-Δ$^{\beta}$-propene* (VII).—Sodium β-phenylpropionate (225 g.), *p*-anisaldehyde (160 g.), and acetic anhydride (160 g.), condensed as in the last example, yielded 46 g. of the methoxyhydrocarbon, b. p. 211—215°/14—15 mm., $n_{5461}^{26°}$ 1·60659. This may be a mixture of geometrical isomerides, since the purified dibromide, m. p. 119°, on treatment with zinc and silver as described above, gave specimens having b. p. 185—186°/3 mm. and $n_{5461}^{26°}$ 1·60598. Its stability to heat and aqueous alkali was proved as for the isomeride. Ozonolysis yielded anisaldehyde (semicarbazone instantly precipitated), phenylacetaldehyde, and anisic acid, but no phenylacetic acid.

Interconversion.—Either methoxyhydrocarbon (1 part) was heated at 85° for various times up to 18 hours with a solution of sodium (1 part) in ethyl alcohol (30 parts). The product was poured into water and extracted with ether and the extract was washed with calcium chloride solution, dried, and evaporated. The residual oil was then completely distilled under a pressure of about 1 mm.

Qualitative Examination.—Some of the products thus obtained were converted into their dibromides, from which considerable quantities (up to 58%) of the dibromide of α-phenyl-γ-*p*-methoxyphenylpropene were isolated when the period of heating of either methoxyhydrocarbon had been 4 hours or longer. Other products were also submitted to ozonolysis; benzoic and anisic acids were then obtained and partly separated, and likewise the rapidly precipitated semicarbazones of benzaldehyde and anisaldehyde.

Quantitative Examination.—The linearity of the mixture law for the refractive indices of the isomeric methoxyhydrocarbons (VI and VII) was confirmed experimentally, and the interconversion was then followed refractometrically. The drum of the Pulfrich instrument was used as in the measurement of dispersion, so that differences of refractive index could be observed with greater accuracy than their absolute values; by using a narrow auxiliary slit, and carefully focusing the green line from a powerful mercury arc on the cross-wires, very accurate settings could be obtained. All the measurements were taken over a short interval of time; the temperature recorded, which is that of the water-jacket of the refractometer, was constant throughout the measurements.

Refractive Indices of the Methoxyhydrocarbons and their Mixtures.

VI (%)	0·0	25·5	73·0	100·0
$n_{5461}^{26·0°}$	1·60598	1·60511	1·60342	1·60246
VI (% calc.) *	—	25·0	73·0	—

* From linear law.

Interconversion of Isomerides.

Isomeride used.	Time at 85° with NaOEt (hrs.).	$n_{5461}^{26·0°}$.	Isomeride VI (%).	$k_1 + k_2$ (hour^{-1}).
VII	0·0	1·60598	0·0	—
	1·0	540	16·5	0·82
	2·0	519	23·0	0·76
	4·0	498	28·5	0·84
	18·0	494	29·5	—
VI	18·0	494	29·5	—
	0·0	246	100·0	—

Equilibrium: VI (29·5%) $\rightleftharpoons$ (70·5%) VII; velocity coefficient $(k_1 + k_2) = 0·79$ hour^{-1}; $k_1/k_2 = 0·42$; $k_1 = 0·23$; $k_2 = 0·56$.

(2) *Interconversion of the Methoxy-acids.*

α-p-*Methoxybenzylcinnamic Acid* (VIII).—An almost pure specimen (23·5 g.) of this acid was obtained by acidifying the sodium hydroxide washings obtained in the preparation of α-*p*-methoxyphenyl-γ-phenylpropene, and a further quantity was isolated from the sodium carbonate solution as described by Ingold and Piggott (m. p. 165·5°).

p-*Methoxy*-α-*benzylcinnamic Acid* (IX).—This acid was isolated and purified exactly as described by Ingold and Piggott, attempts to employ fractional crystallisation or extraction being unsuccessful (m. p. 171·5°).

Interconversion.—Interconversion was effected by heating either acid with sodium ethoxide, under the conditions described for the methoxyhydrocarbons, for various times up to 48 hours. Ice-water and hydrochloric acid were added, and the organic acids extracted

completely with pure ether. The extract was dried and evaporated, and the last trace of ether removed at 100°.

Qualitative Examination.—Products obtained by heating α-*p*-methoxybenzylcinnamic acid with sodium ethoxide for 24 hours or longer under the above conditions had m. p. about 130—140° (Found : C, 75·5; H, 5·9. Calc. : C, 76·1; H, 6·1%). Three crystallisations from dilute alcohol gave crystals, m. p. 171°, consisting of pure *p*-methoxy-α-benzylcinnamic acid. Other portions of these and similar products obtained from the same initial acid were treated with ozonised oxygen in glacial acetic acid solution for 24 hours, and the ozonide was decomposed with water. The products were separated into neutral and acid portions with ether and sodium carbonate. The main constituent of the acid fraction was *p*-anisic acid, which was readily purified by crystallisation from alcohol. The neutral portion yielded an immediate precipitate of semicarbazones, the major constituent of which was anisaldehyde-semicarbazone, m. p. 203°; the soluble semicarbazones were not examined. These experiments afford qualitative proof of the reaction in the direction (VIII) ⟶ (IX).

Products obtained by heating *p*-methoxy-α-benzylcinnamic acid with sodium ethoxide for 24 hours or longer as indicated above were oxidised at 0° with the theoretical quantity of dilute permanganate solution, and the oxidation acids isolated in the usual way. Extraction with warm ligroin yielded phenylacetic acid, which separated from the solvent on cooling, and from the sparingly soluble residue benzoic acid was sublimed and identified. The residue, principally *p*-anisic acid, was purified by crystallisation from dilute alcohol. The isolation of benzoic acid indicates the presence of α-*p*-methoxybenzylcinnamic acid in the material oxidised. A control oxidation experiment with pure *p*-methoxy-α-benzylcinnamic acid gave the same results except that no benzoic acid could be removed by sublimation. This proves that the interconversion also proceeds in the direction (IX) ⟶ (VIII).

Quantitative Examination.—In order to avoid sampling, the *whole* of the products obtained in interconversion experiments were transferred to the freezing-point apparatus.

The following f. p.'s are uncorrected, but were determined under identical conditions with the same apparatus. The f. p.'s of artificial mixtures of the isomerides lie on a two-branch curve, the eutectic point of which corresponds to a mixture containing 56·8% of (VIII), having f. p. 113·8°. After determining the f. p.'s of the products of interconversion experiments, a pure isomeride was added and a further f. p. taken in order definitely to locate the corresponding point on the f. p. diagram. It was shown that these

products of the interconversion experiments were strictly binary in character, and that the process of isolation did not introduce impurities affecting the f. p.

F. p.'s of Mixtures of Acids (VIII) *and* (IX).

VIII (%) ...	0·0	16·9	35·0	49·8	60·1	71·5	83·65	100·0
F. p.	169·5°	156·5°	139·0°	122·5°	118·5°	133·5°	148·5°	163·3°

Interconversion of Isomerides.

Acid IX used.	Time (hrs.)	0·0	4·0	8·0	16·0	24·0	48·0		
	F. p.	169·5°	164·0°	156·0°	141·0°	129·0°	129·0°		
	VIII (%)...	0·0	7·5	17·5	33·0	44·0	44·0		
Acid VIII used.	Time (hrs.)	0·0	1·0	2·0	3·5	12·0	16·0	18·0	24·0
	F. p.	163·3°	158·5°	155·5°	149·0°	122·5°	128·5°	129·0°	129·0°
	VIII (%)...	100·0	94·0	90·5	84·0	49·8	44·5	44·0	44·0

Equilibrium : VIII (44·0%) $\rightleftharpoons$ (56·0%) IX.

(3) *Interconversion of Methyl and Ethyl Methoxy-esters.*

Preparation of Esters.—The following esters were obtained both by way of the acid chlorides, which were prepared by means of thionyl chloride, and also by the action of methyl iodide on the appropriate silver salts. *Methyl* α-p-*methoxybenzylcinnamate* is a colourless oil, b. p. 237—238°/14—15 mm., n_{6563}^{19} 1·58904, $n_{5893}^{19°}$ 1·59684, $n_{5461}^{19°}$ 1·60221 (Found : C, 76·7; H, 6·5. $C_{18}H_{18}O_3$ requires C, 76·6; H, 6·4%). Its isomeride, *methyl* p-*methoxy-α-benzylcinnamate*, b. p. 245°/11—12 mm., solidified and separated from ligroin in rhombic prisms, m. p. 55° (Found : C, 76·7; H, 6·5%). *Ethyl* α-p-*methoxybenzylcinnamate*, a colourless oil, has b. p. 235°/13—14 mm., $n_{5893}^{22°}$ 1·58334, $n_{5461}^{22°}$ 1·58972 (Found : C, 77·0; H, 6·7. $C_{19}H_{20}O_3$ requires C, 77·3; H, 6·8%), and the isomeric *ethyl* p-*methoxy-α-benzylcinnamate*, b. p. 240—241°/10—11 mm., separates from ligroin or dilute alcohol as prismatic needles, m. p. 45° (Found : C, 77·0; H, 6·7%).

Alkaline Hydrolysis of Esters.—After some exploratory work the following method was evolved for use as described subsequently. The ester (1 part) was boiled for 0·5 hour with an aqueous-alcoholic solution of sodium hydroxide prepared from sodium (1 part), methyl *or* ethyl alcohol (30 parts), and water (22 parts). The acids were isolated as indicated in section (2). The yields and m. p.'s were as follows :

True m. p. of acid.	Ester used.	Yield of acid (unpurified).	M. p. (unpurified).
165·5°	Methyl	98·8%	165·0°
	Ethyl	98·3	165·5
171·5	Methyl	98·4	171·5
	Ethyl	98·4	171·5

These results establish (*a*) that no interconversion of isomerides takes place in the presence of hydroxide ions at 100° under the

conditions stated (contrast interconversion by OMe′ and OEt′), (*b*) that, since the yields of acids are constant and almost quantitative, and since no impurities affecting the m. p.'s of the acids are introduced, hydrolysis under the conditions described and subsequent thermal analysis of the acids can be used to follow the interconversion of the esters.

Stability of the Esters to Heat.—Redistillation of the esters and subsequent hydrolysis gave the same results, wherefore it follows that the esters, like the methoxyhydrocarbons, undergo no interconversion on being heated alone to temperatures somewhat above 220°.

Stability of the Methyl Esters to Sodium Methoxide.—The methyl esters (1 part) were boiled, for times up to 24·5 hours, with a solution of sodium methoxide prepared from sodium (1 part) and methyl alcohol (30 parts). Hydrolysis under the conditions described above, followed by f. p. determinations, showed that the esters were entirely unaltered.

Methyl α-*p*-methoxybenzylcinnamate was heated with a similar solution of sodium methoxide at 100° for 72 hours. The f. p. of the acid was 122·0°, and was lowered by addition of *p*-methoxy-α-benzylcinnamic acid. Hence 37% of the ester has been converted into its isomeride. Since, at equilibrium, about 56% is expected to be converted, it is obvious that the catalytic activity of methoxide ions is small.

Interconversion of Ethyl Esters by Sodium Ethoxide.—This was effected at 85° under the conditions used for the methoxy-acids and methoxyhydrocarbons. The approach towards equilibrium from either side was followed by hydrolysis, after addition of the amount of water necessary to produce aqueous-alcoholic sodium hydroxide of the strength stated above, and thermal analysis of the mixtures of acids formed. The f. p.'s were taken under the same conditions as those relating to the f. p. data in section (2).

Isomeride used.	Time at 85° with NaOEt (hrs.).	F. p. of acids.	Isomeride X (%).	$k_1 + k_2$ (hour^{-1}).
XI	0·0	169·5°	0·0	—
	8·0	156·5	17·0	0·066
	16·0	150·5	24·5	0·052
	23·0	149·0	26·0	0·051
	72·0	130·5	43·0	—
X	72·0	129·5	44·0	—
	28·0	115·0	56·0	0·054
	16·0	121·0	62·5	0·067
	4·0	152·5	88·0	0·060
	2·0	158·0	93·5	0·059
	0·0	163·3	100·0	—

Equilibrium: X(43·5%) $\rightleftharpoons$ (56·5%)XI; velocity coefficient, $k_1 + k_2$ (mean) = 0·0585 hr.$^{-1}$; $k_1/k_2 = 0·770$; $k_1 = 0·0255$; $k_2 = 0·0330$.

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