Condensation of Diethyl Tartrate with Cyclic Ketones and the Molecular Rotation of the Resulting Compounds.*

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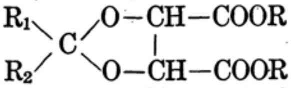
It was reported in the previous papers⑴ that alkyl tartrates can be condensed with some simple carbonyl compounds giving bridged derivatives of tartaric acid of the type  , and was shown that these compounds would afford suitable materials for the study of the optical activity of tartaric acid. Thus it was pointed out that the molecular rotation of these compounds shows a certain regularity, i.e. the power of the strong lævo-rotation of these compounds falls off as the bulk of the radicals R_1 and R_2 increases, and on the other hand it increases with the increasing bulk of the radical R. And further the rotatory dispersion of these bridged derivatives of tartaric acid was in-

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* Synthesis of bridged derivatives of tartaric acid and their optical activity. IV.

(1) Y. Tsuzuki, this Bulletin, **10** (1935), 255; **11** (1936), 362.

vestigated, with a view to interpret the complex nature of the optical activity of tartaric acid and of its derivatives, the results of which brought out a suggesting relation between the radicals R_1 and R_2 and the optically active absorption bands of the compounds.(2) The number of these compounds are, however, very small, so that materials must be substantiated, in order to consolidate the above statement. The present paper aimes to supply some materials for this purpose and to give some simple suggestion of the tendency of the molecular rotation of the newly synthesized bridged compounds. The author has, in the first place, prepared condensation products with one cyclic radical instead of the separate two radicals R_1 and R_2 which were contained in the already synthesized compounds.

Condensation. Diethyl tartrate has been condensed with the following cyclic ketones: cyclopentanone, cyclohexanone, *o*-methylcyclohexanone, *m*-methylcyclohexanone, and *p*-methylcyclohexanone. Cyclopentanone was prepared by distilling adipic acid with barium hydroxide at 315–320°. The three methylcyclohexanones were prepared by oxidising the corresponding alcohols with Beckmann's mixture. *o*-Methyl- and *m*-methylcyclohexanols were Takeda samples and *p*-compound(3) was prepared from *p*-cresol by catalytic hydrogenation. Cyclopentanone, b.p. 128.5–129.5° (760 mm.), $n_D^{20} = 1.4358$. Cyclohexanone, b.p. 153–154° (760 mm.), $n_D^{20} = 1.4506$. *o*-Methylcyclohexanone, b.p. 164° (760 mm.), $n_D^{20} = 1.4482$. *m*-Methylcyclohexanone, b.p. 165° (755 mm.), $n_D^{20} = 1.4482$. *p*-Methylcyclohexanone, b.p. 163–164° (751 mm.), $n_D^{20} = 1.4448$.

The condensation reaction proceeds very smoothly in every case. The yield is fairly good, from 50 to 70% of the theoretical amount. The purification of the condensation product is easy. As the condensation reagent phosphorus pentoxide was employed exclusively, which proved to be very useful, but in the reactions(1) previously performed, various condensation reagents had to be applied according to the nature of the carbonyl compound.(2)

The condensation and the purification of the product has been carried out in the following way: to the mixture of diethyl tartrate (1/20 mol) and cyclic ketone (1/20 mol) is added in portions 10 g. phosphorus pentoxide at 80–90°, in the course of 30–60 minutes. The solid phase of the phosphorus pentoxide is coloured quite strongly, but the liquid mixture remains almost colourless, only in some cases faintly yellowish coloured. In the case of higher members of the ketone homologue the

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(2) Y. Tsuzuki, this Bulletin, **11** (1936), 586.

(3) The author is grateful to Dr. K. Ishimura who kindly afforded this material.

temperature must be raised comparatively higher and the duration of reaction must be prolonged. After the whole of phosphorus pentoxide has been added, the heating of the reaction mixture is further continued at that temperature for 30–60 minutes, with occasional stirring. Then the liquid mixture is decanted from the phosphorus pentoxide portion and evaporated at 130° under the pressure 20–30 mm., by which process the unchanged ketone distils over. The product is dissolved in 70 c.c. ether. The ethereal solution is shaken 4 times with each 30 c.c. saturated aqueous solution of borax, whereby the unchanged ethyl tartrate can be almost completely removed into the borax layer, and further shaken with water and dried with anhydrous sodium sulphate. After the ether was evaporated off, the remaining liquid is distilled under reduced pressure.

Reaction products. The condensation products thus obtained and purified are all transparent colourless liquid, but they show some pale yellowish colouration when freshly distilled, which fades away on standing for a few days. This is probably due to some similar cause of the phenomenon, which was observed by Patterson long ago in the case of diethyl tartrate—green colouration produced by its vacuum distillation and disappearance of the colour on its standing—and quite recently given a plausible explanation by the same author.(4)

The physical constants of the new condensation products thus obtained will not be individually described, but are put into Table 1, together with the analytical data.

Molecular rotation. As seen in Table 2 the molecular rotation of the condensation product decreases in magnitude with the increasing bulk of the ketone-residue in the compound, thus the molecular rotation of diethyl cyclopentylidene-tartrate is smaller than that of diethyl isopropylidene-tartrate, but larger than that of diethyl cyclohexylidene-tartrate.

These facts will be understood by the molecular theory of de Malleman(5) as well as of Boys(6), who regards the volumes of the radicals as a dominating factor of the optical activity. In fact the molecular rotation goes almost inversely proportional with the parachor, a quantity equivalent to the molecular volume of the radical.

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(4) T. S. Patterson, *J. Chem. Soc.*, **121** (1922), 1042; T. S. Patterson and A. H. Lamberton, *J. Chem. Soc.*, **1937**, 963.

(5) *Trans. Faraday Soc.*, **26** (1930), 281.

(6) *Proc. Roy. Soc.* (London), A, **144** (1934), 655.

Table 1. The Physical Constants and the Analytical Data of the Bridged Derivatives of Tartaric Acid Obtained by Condensing Diethyl Tartrate with Cyclic Ketones.

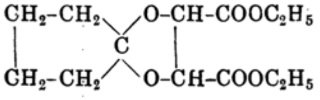
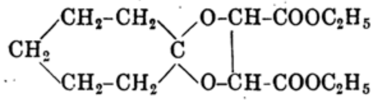
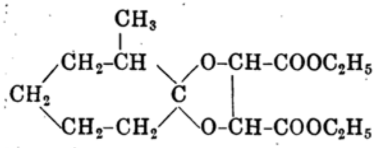
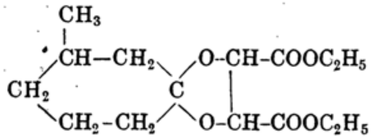
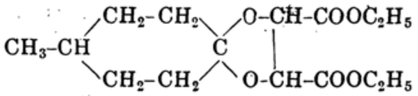
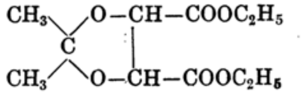
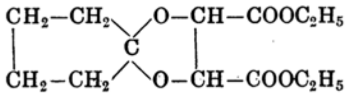
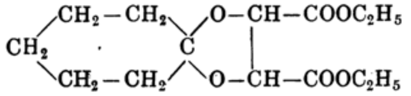
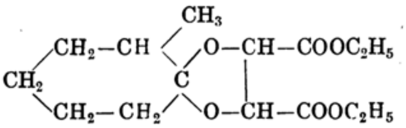
Substance	Structural Formula	Boiling Point (corr.)	d_4^{20}	n_D^{20}	Molecular Refraction	$[\alpha]_D^{20}$	$[M]_D^{20}$	Elementary Analysis		Yield (%)
								Found	Calc.	
Diethyl cyclopentylidene-tartrate		170–171° (12 mm.)	1.1468	1.4560	obs. 64.50 calc. 64.44	-40.55°	-110.4°	C 57.07 H 7.35	C 57.31 H 7.41	49
Diethyl cyclohexylidene-tartrate		178° (12 mm.)	1.1329	1.4605	obs. 69.25 calc. 69.05	-35.57°	-101.8°	C 58.63 H 7.77	C 58.70 H 7.75	51
Diethyl o-methylcyclo-hexylidene-tartrate		184° (14 mm.)	1.1140	1.4590	obs. 73.66 calc. 73.66	-21.81°	-65.48°	C 59.63 H 8.11	C 59.96 H 8.06	52
Diethyl m-methylcyclo-hexylidene-tartrate		186° (14 mm.)	1.1085	1.4572	obs. 73.78 calc. 73.66	-35.42°	-106.3°	C 59.73 H 7.96	C 59.96 H 8.06	61
Diethyl p-methylcyclo-hexylidene-tartrate		188° (14 mm.)	1.1109	1.4580	obs. 73.73 calc. 73.66	-30.49°	-91.53°	C 59.66 H 8.06	C 59.96 H 8.06	69

Table 2. Molecular Rotation and Parachor of the Condensation Products.

	Molecular Rotation at 20°	Parachor of Ketone-residue
	−120.9°	117.0
	−110.4°	160.8
	−101.8°	199.8
	−65.48°	238.8

The introduction of one methyl group in the cyclohexylidene residue tends to decrease the molecular rotation of the resulting compound. But it is seen that the position of a substituent exerts a great influence on the molecular rotation. The ortho-position has the most diminishing effect, while the meta-position has the least effect, rather an increasing effect. Although these methylcyclohexylidene residues may have the same magnitude of parachor, but their volumes effective to the asymmetric carbon atoms of the compounds must be different. The nearest ortho-position exerts a most intense influence and the meta-position at the least. In the flexible cyclohexane-ring structure of Sachse and Mohr the group attached to the meta-position is situated a little farther than that of the para-position. The differences of these influences by position are, however, quite remarkable, so that the electronic effect due to the position of a group must also be considered in these cases, in order to comprehend more satisfactorily the molecular rotation. Similar phenomena of the effects of position have been already known in the absorption of light in aromatic compounds, where the ortho effect is largest and the meta effect is least or none.(7) These facts would be understood by the electronic theory of aromatic substitution.

Summary.

(1) It has been shown that the condensation of diethyl tartrate with cyclic ketones can be effected with great ease by the use of phosphorus pentoxide as condensation reagent.

(2) New products obtained by condensing diethyl tartrate with cyclic ketones, namely cyclopentanone, cyclohexanone, and three isomeric methylcyclohexanones, have been described, and their physical constants have been compared in a table.

(3) The molecular rotation of these homologous compounds decreases as the parachor of the ketone-residue in the condensation product increases, but the influence by the position of the substituent is noticed: the substitution of a methyl group at ortho-position is the most effective, and that of meta-position is nearly ineffective.

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(7) Y. Shibata, *Acta Phytochim.* (Japan), **1** (1923), 91; S. Hattori, *ibid.*, **6** (1932), 131.