

in the case of allyl cyanide and styrylacetic ester at the α - and β -carbon atoms, with migration of an α -hydrogen atom.

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NOTES

Some New *p*-Bromophenacyl Esters.—In using the method of Reid and Judefind [THIS JOURNAL, 42, 1043 (1920)] for the identification of organic acids, we have prepared the following *p*-bromophenacyl esters which are not listed by these authors: trimethylacetate, m. p. 76.5°; isocaproate, m. p. 77.3°; enanthate, m. p. 69.2°; isoheptylate, m. p. 75.5°; pelargonate, m. p. 63.5°.

CONTRIBUTION FROM THE
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Preparation of *N*-*o*-Chlorobenzoyl-*o*-chlorobenzenesulfonamide.—Several years ago an investigation was undertaken in this Laboratory having for its object the preparation of diphenic sulfinide ("Diphen-saccharin"). It was hoped that this compound might be sweet, or at least that its preparation would throw some light on the general problem of sweet taste *vs.* molecular structure. The method attempted was the internal condensation of chlorobenzoylchlorobenzenesulfonamide by loss of two atoms of chlorine from the molecule.

Preparation of *N*-*o*-Chlorobenzoyl-*o*-chlorobenzenesulfonamide, $\text{Cl-C}_6\text{H}_4\text{CONHSO}_2\text{C}_6\text{H}_4\text{Cl}$.—Ten grams of *o*-chlorobenzenesulfonamide was treated with 9.5 g. of *o*-chlorobenzoyl chloride and the mixture heated (180–190°) in an oil-bath for one hour. The dark brown mass was dissolved in acetone, the solution filtered, and the solid again precipitated by the use of petroleum ether. The solid was heated on a clay plate (70–80°) until it was perfectly dry and odorless. Repeated crystallizations from dilute ethanol or dilute acetic acid finally gave a product with a constant melting point of 154–155°; white platelets, having a faint bitter taste, yield about 11 g.

Anal. Calcd. for $\text{C}_{13}\text{H}_9\text{O}_2\text{Cl}_2\text{NS}$: C, 47.27; H, 2.72; N, 4.24; Cl, 21.52; S, 9.70. Found: C, 47.24; H, 2.60; N, 4.19; Cl, 21.40; S, 9.76.

In attempting to prepare diphenic sulfinide from the compound named above, it was heated alone and in different solvents, and treated with metals and other reagents under a variety of conditions. Seventy-two experiments were carried out, only two of which gave any indication of success. In these cases the material was heated in amyl alcohol solution with copper

powder and sodium iodide.¹ A compound was secured having a melting point of 255–258°. It was contaminated with amyl alcohol, which was removed in part by application of heat. The yield was small and complete purification was not possible. Analysis for sulfur gave 8.67%, while theory calls for 12.35%. The compound had a bitter taste. Repetitions of this experiment did not again yield this compound, and lack of starting materials forced the abandonment of the project. In view of the known instances in which seven- and eight-membered ring compounds have been made from diphenic acid, the failure of this synthesis is without explanation, and seems worthy of report.

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The *p*-Bromoanilides of Isobutyric and Isovaleric Acids.—For purposes of comparison in identification work in this Laboratory it was desired to have samples of the *p*-bromoanilides of a number of the paraffin acids. The most comprehensive list of such *p*-bromoanilides which appears in the literature is that reported by Robertson [Robertson, *J. Chem. Soc.*, 115, 1210 (1919)]. This list, however, does not contain the derivatives of isobutyric or isovaleric acids.

The procedure used for the preparation of the *p*-bromoanilides of the acids from acetic to stearic is a modification of Robertson's procedure and is as follows: One gram (1 mol) of the acid or its sodium salt was placed in a small flask or test-tube and treated with 1 mol of thionyl chloride and heated under a reflux condenser for thirty minutes. The reaction mixture was then cooled and treated with 2 mols of *p*-bromoaniline in 30 cc. of benzene. After warming on a steam-bath for a few minutes the benzene solution was cooled, transferred to a separatory funnel, washed twice with water, twice with 5% hydrochloric acid, once with 5% sodium hydroxide and finally with water. The benzene solution was then evaporated to dryness and the remaining bromoanilide recrystallized from ethyl alcohol. The melting points and analyses of these derivatives of isobutyric and isovaleric acids are

	M. p., °C.	Bromine, %	
		Calcd.	Found (Carius)
<i>p</i> -Bromoisobutyranilide	150–151	33.03	32.43
<i>p</i> -Bromoisovaleranilide	128–129	31.10	31.12

The *p*-bromoisobutyranilide has been reported by Norton [*Am. Chem. J.*, 7, 116 (1885)] as melting at 128°. Judging from the low melting point

¹ Finkelstein, *Ber.*, 43, 1530 (1910).

and satisfactory analysis reported for this *p*-bromoanilide it is quite probable that it was contaminated with some of the ortho isomer, as it was prepared by the bromination of isobutyranilide. *p*-Bromoisovaleranilide does not appear to have been described previously in the literature.

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COMMUNICATIONS TO THE EDITOR

THE α,β,γ -TRIMETHYLGLUTARIC ACIDS

Sir:

In a recent paper Michael and Ross¹ reported the failure to obtain α,β,γ -trimethyl- α -carboxyglutaric acid in a crystalline form. I had obtained this acid² and reported it as melting at 144–145°. Michael and Ross note that 145° is also the melting point of α,β -dimethyl- γ -carboxyglutaric acid, which suggests that the two are identical. The fact is that I obtained α,β,γ -trimethylglutaric acid melting at 134° from the decomposition of my acid, whereas α,β -dimethyl- γ -carboxyglutaric acid upon decomposition gives α,β -dimethylglutaric acid melting at 87°.³

Michael and Ross obtained α,β,γ -trimethyl- α -carboxyglutaric acid as a sirup which on distillation gave an acid melting at 115–125°. In my work on these compounds I found that it was necessary to obtain the tricarboxylic acid in a pure state before decomposing it in order to effect the purification of the α,β,γ -trimethylglutaric acid. Even so it required ten recrystallizations to reach the melting point of 134°. The compound which Michael and Ross describe as *cis*- α,β,γ -trimethylglutaric acid, which according to their statement "softened at 115° and melted at 125°," was probably an impure acid identical with mine, which melted at 134°. The liquid which they call *trans*- α,β,γ -trimethylglutaric acid was, apparently, the same as the liquid remaining in the mother liquors from the crystallization of the acid melting at 134°. Neither their work nor mine is sufficiently complete to characterize this liquid as a definite chemical individual. Inasmuch as modern theory predicts the occurrence of *three* stereoisomeric forms (one racemic and two meso acids) it would, in my opinion, be unfortunate if it should be so described in handbooks.

Michael and Ross attempted to separate their acids into a "*cis*" and a "*trans*" form by converting the "*cis*" form into the anhydride and the imide. Granting free rotation about a single bond *all three* of the possible

¹ Michael and Ross, *THIS JOURNAL*, **52**, 4607 (1930).

² Ray, *ibid.*, **50**, 558 (1928).

³ Thorpe, *J. Chem. Soc.*, **83**, 358 (1903).