at 25.0 ± 0.1°, by thermostating solutions in advance and by use of a thermostated cell compartment.

TABLE II

RATE DATA FOR REACTION OF DIPHENYLDIAZOMETHANE WITH CARBOXYLIC ACIDS, RCOOH, IN ETHANOL AT 25°

Subst., R	Concn. of acid, mole/l.	Concn. of DDM, mole/l.	k_2, l. mole min.$^{-1}$
$CNCH_2$	0.0637	0.00333	18.0
	.0429	.00308	19.0
	.0318	.00330	18.5
$ClCH_2$	.0570	.00310	13.1
	.0380	.00305	12.7
$C_6H_5(OH)CH$	.0328	.00279	6.86
	.0539	.00302	6.68
	.0773	.00319	6.77
$HOCH_2$	.0410	.00332	3.01
	.0730	.00319	3.02
$(C_6H_5)_2CH$	.0459	.00319	2.22
	.0306	.00310	2.34
	.0459	.00266	2.29
	.0525	.00224	2.41
H	.0965	.00354	2.32
	.0483	.00345	2.18
	.0483	.00327	2.18
$ClCH_2CH_2$	.0870	.00306	2.30
	.0438	.00316	2.22
	.0525	.00310	2.20
$C_6H_5CH_2$	.0559	.00554	1.43
	.0559	.00495	1.49
	.0559	.00532	1.55
	.0461	.00236	1.49
	.0461	.00230	1.40
$C_6H_5CH_2CH_2$	.0451	.00307	1.01
	.0315	.00317	1.17
C_6H_5	.0452	.00326	0.965
	.0928	.00290	.946
	.0618	.00385	.966
CH_3	.0758	.00347	.468
	.0505	.00332	.461
	.1516	.00330	.460
n-C_5H_{11}	.0578	.00339	.449
	.0771	.00226	.433
	.0385	.00447	.445
t-C_4H_9	.0460	.00297	.297
	.0307	.00258	.307
	.0460	.00179	.284

Materials.—DDM was prepared from benzophenone hydrazone by the method in "Organic Syntheses."[7] The method was modified in that a flask and stirrer were used in place of a pressure bottle and mechanical shaker. After the reaction mixture was filtered, an equal volume of ethanol was added to the solution of DDM in pentane, and the bulk of the material was stored under refrigeration. The pentane was boiled off of small portions of the bulk material, under reduced pressure, prior to use in the rate determinations. Ethanol was then added until the desired concentration was obtained. The preparation of DDM was done by Mr. Monis J. Manning.

The anhydrous ethanol used in the present work was obtained from commercial grade ethanol by refluxing it over magnesium turnings for several hours.

The acids used were C.P. grade Fisher Scientific or Eastman organic chemicals. Benzoic acid was recrystallized from water. Diphenyl- and phenylacetic acids were recrystallized from 50% aq. ethanol. A center cut from a fractionation of n-caproic acid was supplied by Mr. William A. Pavelich. Other acids were used without further purification.

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(7) *Org. Syntheses*, **24**, 53 (1944).

Reactions of Toluic Acids with Sulfur. II. 4,4'-Bibenzyldicarboxylic Acid

BY WM. G. TOLAND, JR., AND JOHN B. WILKES

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The reaction of p-toluic acid and sulfur to form 4,4'-stilbenedicarboxylic acid and tetra-(p-carboxyphenyl)-thiophene has been reported in a previous paper.[1] The present investigations show that the reaction of p-toluic acid and sulfur under a pressure of hydrogen sulfide produces, in addition, 4,4'-bibenzyldicarboxylic acid. The amounts of tetra-(p-carboxyphenyl)-thiophene formed are greatly reduced in the presence of hydrogen sulfide, and the yields of dimer acids (4,4'-stilbenedicarboxylic acid and 4,4'-bibenzyldicarboxylic acid) are correspondingly increased. The reduction of 4,4'-stilbenedicarboxylic acid to 4,4'-bibenzyldicarboxylic acid by hydrogen sulfide in a p-toluic acid solution was carried out, and additional dimer acids were formed by reaction of the p-toluic acid with the sulfur liberated in the reaction.

Aronstein and Van Nierop[2] found that the action of sulfur upon m- and p-xylenes in sealed tubes gave dimethyl stilbenes which were partially reduced to dimethylbibenzyls by the hydrogen sulfide formed. The presence of even relatively unreactive substituents had a great effect on this reaction as the reaction of toluene under the same conditions gave stilbene and tetraphenylthiophene, but no bibenzyl. The substitution of a highly reactive functional group, such as the carboxyl group, would be expected to have an even greater effect than the substitution of a methyl group into the benzene ring. The effect was found to be appreciable. In contrast to the reactions of sulfur and toluene and m- and p-xylenes, which occur to a slight extent at reflux temperatures[2] and which are relatively rapid at 200°, the reactions of sulfur and toluic acids are not detectable below about 245°.[1] Furthermore, whereas m- and p-xylenes react equally well with sulfur at 200°, m-toluic acid reacts with sulfur much more slowly than does p-toluic acid, and the yield of stilbenedicarboxylic acid is much lower from m-toluic acid than from p-toluic acid.

Experimental

Materials.—The materials used have been previously described.[1]

Reaction Conditions.—The reactions were conducted in a stainless steel bomb of 200-cc. capacity, equipped with a thermowell, valve and bursting disk, and fitted with a glass liner, open at the top. The bomb was heated without shaking by immersion in a bath of Dow-Corning 550 fluid. The time of reaction was taken from the time the thermo-

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(1) W. G. Toland, Jr., J. B. Wilkes and F. J. Brutschy, THIS JOURNAL, **75**, 2263 (1953).

(2) L. Aronstein and A. S. Van Nierop, *Rec. trav. chim.*, **21**, 448 (1902).

well registered the bath temperature. In some runs, hydrogen sulfide was added to the bomb before heating the reaction mixture, while other runs were conducted in which the hydrogen sulfide pressure was allowed to develop autogeneously. Excess hydrogen sulfide could be bled off through the valve to permit study of the reaction over a limited pressure range.

Product Separations.—The crude reaction mixture was extracted with boiling xylene to remove *p*-toluic acid, sulfur and some of the by-products, and the residue was then extracted with boiling dioxane to remove most of the remaining by-products[1] and any remaining sulfur. The insoluble material consisted of a mixture of 4,4′-stilbenedicarboxylic acid and 4,4′-bibenzyldicarboxylic acid, which were separated as follows through the potassium salts: 45 g. of crude dimer acids was boiled with 700 ml. of water and 22 g. of potassium hydroxide, the hot solution was filtered, and the filter cake washed with about 100 ml. of hot water. A clear, light yellow solution was obtained from most reactions. The hot solution was stirred with 25 g. of potassium chloride for a few minutes, and the mixture was cooled to precipitate the potassium salt of 4,4′-stilbenedicarboxylic acid, which was collected and washed with a small amount of saturated potassium chloride solution. The filtrate was heated to about 90°, and the 4,4′-bibenzyldicarboxylic acid was precipitated with an excess of hydrochloric acid. After a period of digestion the acid was collected, washed and dried. The product usually contained about 10% 4,4′-stilbenedicarboxylic acid. Further purification was effected by recrystallizations of the potassium salts, when desired.

The potassium salts of the acids were dissolved in hot water with added base, and the free acids precipitated in the same manner as the 4,4′-bibenzyldicarboxylic acid. This fraction usually contained 85 to 90% of 4,4′-stilbenedicarboxylic acid, the remainder being 4,4′-bibenzyldicarboxylic acid.

4,4′-Stilbenedicarboxylic Acid.—4,4′-Stilbenedicarboxylic acid was identified by its characteristic ultraviolet adsorption spectrum, fluorescence, solubility of its potassium salt, and its reaction with dilute solutions of permanganate in neutral or alkaline solutions.[1]

4,4′-Bibenzyldicarboxylic Acid.—The dimethyl ester, m.p. 119°,[3] was formed through the acid chloride. As 4,4′-bibenzyldicarboxylic acid reacts slowly with dilute alkaline permanganate solution, the amount of 4,4′-stilbenedicarboxylic acid in a mixture of the two acids can be determined approximately by permanganate titration in dilute caustic solution. The acid has a neutral equivalent of 135. The best samples, containing about 1.5% of 4,4′-stilbenedicarboxylic acid, melted at 378–385° in a sealed tube. Spectroscopic examination of the acid and ester showed that absorption spectra closely resemble the spectrum of *p*-toluic acid, both in the position of the absorption maxima, and in the intensity of the absorption.

Tetra-(*p*-carboxyphenyl)-thiophene.—The dioxane-soluble, xylene-insoluble brown product formed in the reaction had the same properties as the tetra-(*p*-carboxyphenyl)-thiophene previously described.[1]

Discussion

Temperature.—The reaction was studied at 288 and 315°. While the reaction was faster at the higher temperature, the yield of dimer acids decreases sharply with increasing reaction time at 315°. There is no evidence of such an effect at 288°. The products of reaction at 315° are more highly colored than the products from reaction at 288°, when the same purification technique is used.

Hydrogen Sulfide Pressure.—Increasing hydrogen sulfide pressure decreases the rate of dimerization of *p*-toluic acid considerably. While sulfur will completely react with *p*-toluic acid at a 1:2 mole ratio in two hours at atmospheric pressure and 275°, reaction was not complete at 288° in 6.5 hours with a hydrogen sulfide pressure at 27–38 atm. 4,4′-Bibenzyldicarboxylic acid is produced by treating a mixture of 4,4′-stilbenedicarboxylic acid and *p*-toluic acid with hydrogen sulfide. The *p*-toluic acid acted as a solvent for the 4,4′-stilbenedicarboxylic acid, and also reacted with the sulfur liberated in the reaction. When 4,4′-stilbenedicarboxylic acid was added to a reaction mixture with *p*-toluic acid and sulfur the ratios of stilbene- and bibenzyldicarboxylic acids obtained in the final products were similar to the ratios obtained when the stilbenedicarboxylic acid was omitted and more bibenzyldicarboxylic acid was produced from the same amount of sulfur and toluic acid. Higher conversions are obtained due to the sulfur liberated by reaction of hydrogen sulfide with stilbenedicarboxylic acid.

The presence of hydrogen sulfide pressure greatly decreased the amount of tetra-(*p*-carboxyphenyl)-thiophene formed. The reaction of *p*-toluic acid with sulfur under hydrogen sulfide pressure gave yields of dimer acids (4,4′-stilbenedicarboxylic acid plus 4,4′-bibenzyldicarboxylic acid) varying from 67.5 to 80.8% at 288°, when conversions were held below about 50% of the toluic acid. This compares[1] to yields of 50 to 60% (based on toluic acid converted) at 270–275° and similar conversions at atmospheric pressure. The fraction of 4,4′-bibenzyldicarboxylic acid in the dimer acid varies from 39% with reaction at 288° and 17 atm. for three hours to 100% with reaction at 315° and 38 atm. for six hours.

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[3] C. Liebermann and P. Mitter, *Ber.*, **45**, 1210 (1912).

Amine Glutamates

BY BRUNO VASSEL AND W. G. SKELLY

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During the course of an investigation on the properties of certain L-glutamic acid derivatives a number of previously unreported amine salts were prepared.

Table I presents the melting points of the octyl-, decyl-, dodecyl- and cyclohexylamine glutamates, analytical data on these salts, as well as the boiling points of the rectified amines used.

TABLE I

Amine glutamate	B.p. of amine cut used, °C.	M.p. (cor.) of amine glutamate,[1] °C.	α-Carboxyl-C (Van Slyke),[2] % Theory	Found	Nitrogen, % (Micro Kjeldahl) Theory	Found
n-Octylamine	176–178	150.5	4.35	4.67	10.15	9.99
n-Decylamine	216–218	160.9	3.95	4.29	9.21	9.25
n-Dodecylamine	119–122[3]	165.0	3.56	3.85	8.45	8.37
Cyclohexylamine	134	157.7	4.87	4.61	11.39	10.88

TABLE II

Amine glutamate	Solubility at 25°, in G./100 ml. soln. Water	1-Butanol	Distribution coefficient
n-Octylamine	30.79	0.106	0.0035
n-Decylamine	23.08	.071	.0031
n-Dodecylamine	36.27	.064	.0018
Cyclohexylamine	6.58	.080	.012

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(1) Fisher–Johns melting point block.

(2) An excess of ninhydrin must be used because of the presence of the amine.

(3) At 5 mm.