

azidovalerate with hydrogen and 5% palladium on charcoal at 0–25° and atmospheric pressure was followed by hydrolysis to yield ornithine hydrochloride.

Experimental

Methyl 2,5-Dichlorovalerate.—A mixture of 2,5-dichloro-valeric acid (27.4 g., 0.16 mole), methanol (15.4 g., 0.48 mole), 2,2-dimethoxypropane (50 g., 0.48 mole), and a catalytic amount of dry, powdered Dowex 50-H⁺ was stirred at room temperature for 20 hr. and heated at 40–60° for 24 hr. After removal of the catalyst by filtration, distillation of the brown solution gave 18.1 g. (61% yield) of ester, b.p. 72–73° (1 mm.). Vapor phase chromatography showed one peak and a trace impurity.

Anal. Calcd. for C₈H₁₀O₂Cl₂: C, 38.94; H, 5.45; Cl, 38.32. Found: C, 39.34; H, 5.67; Cl, 38.69.

DL-Ornithine Hydrochloride.—Methyl 2,5-dichlorovalerate (9.40 g., 0.05 mole) was added to a mixture of 50 ml. of dimethyl sulfoxide and 13.0 g. (0.20 mole) of sodium azide and stirred for 5 hr. at 60–65°. Water was added and the orange solution extracted with ether. An aliquot of the total aqueous portion was found to contain 97.5% of the theoretical amount of inorganic chloride on titration with silver nitrate. The ether solution was washed, dried, and evaporated under reduced pressure to yield a bright yellow liquid, presumably methyl 2,5-diazidovalerate.⁵

This product was taken up in 50 ml. of 95% ethanol and placed in a reduction flask equipped with a stirrer, a sintered glass sparger, and a gas outlet tube. One gram of 5% palladium on charcoal suspended in 50 ml. of ethanol was added. With ice cooling, hydrogen was bubbled in for 2 hr. A small amount of fresh catalyst and 8 ml. of concentrated hydrochloric acid were added and reduction allowed to continue for 1 hr. with ice cooling and 4 hr. at room temperature. Filtration, evaporation, and refluxing with 40 ml. of 5 N hydrochloric acid for 4 hr. yielded a brown solution which was evaporated and redissolved in water. Passage through a column containing 70 g. of Dowex 50-H⁺ and washing with water until the eluate was chloride-free followed by elution with ammonia gave, on evaporation, a basic oil containing 65% of the theoretical amount of ornithine by hydrochloric acid titration. Addition of hydrochloric acid to pH 3.8 and evaporation gave a tan-colored oil which, on trituration with absolute methanol, yielded 5.8 g. (63% of theory) of DL-ornithine hydrochloride. An 85% recovery of white crystals containing 98.2% of the theoretical amount of chloride ion was obtained on recrystallization from water-ethanol. Comparison of our product with an authentic sample of DL-ornithine hydrochloride showed them to possess identical infrared and n.m.r. spectra and identical R_f values on paper chromatography of 0.03 in collidine-water (125:44) and 0.09 in *n*-butyl alcohol-acetic acid-water (40:10:50).

Hydrogen Bonding in Pyrrolymethenes¹

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Some time ago Vestling and Downing³ presented infrared spectral evidence for hydrogen bonding in 2,2'-(3,3',5,5'-tetramethyl-4,4'-diethoxycarbonyl)dipyrrolymethene (I) and in the 3,4,5-trimethyl-3',4'-diethoxycarbonyl-5'-bromo analog (II), both in carbon tetrachloride. The absence of dilution studies pre-

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(2) National Science Foundation Undergraduate Participant (NSF-G21628).

(3) C. S. Vestling and J. R. Downing, *J. Am. Chem. Soc.*, **61**, 3511 (1939).

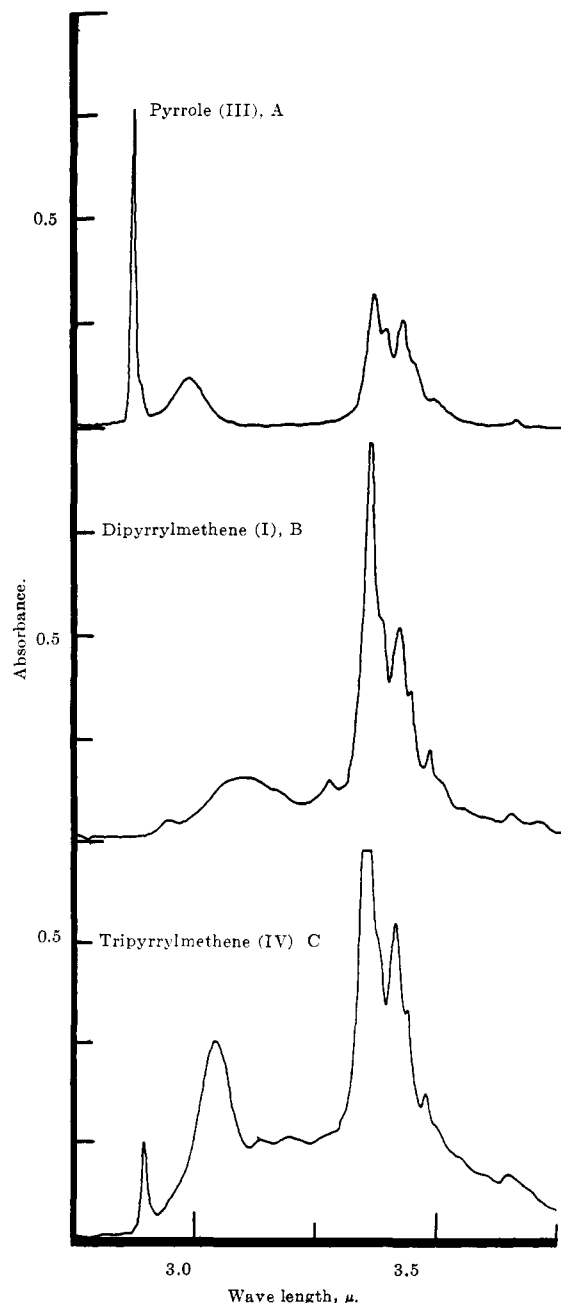
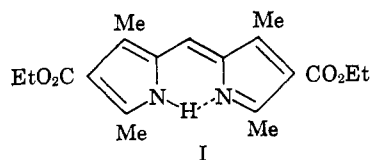


Fig. 1.—Infrared spectra in carbon tetrachloride. Letters (A, B, and C) refer to solutions marked in Table I.

vented a decision between intermolecular hydrogen bonding and an intramolecular bonding as presented for I. A proposal of the latter type has been made



independently by Brunings and Corwin⁴ from other considerations and such structures have been assumed⁵ *a priori*, although in fact this had not been established at

(4) K. J. Brunings and A. H. Corwin, *ibid.*, **66**, 337 (1944).

(5) Cf., A. Albert, "Heterocyclic Chemistry," The Athlone Press, University of London, London, 1959, p. 144.

TABLE I

Compound	Molarity $\times 10^2$	Alkyl		Type of NH stretch. vib.								
		Stretch. vib.		Free			Intermol. assoc.			Intramol. assoc.		
		λ, μ	<i>A</i>	λ, μ	<i>A</i>	<i>A/A_{Alk}</i>	λ, μ	<i>A</i>	<i>A/A_{Alk}</i>	λ, μ	<i>A</i>	<i>A/A_{Alk}</i>
Pyrrole (III)	2.954 ^a	3.413	0.260	2.875	0.765	2.9	2.987	0.123	0.47			
	2.265	3.413	.196	2.875	.610	3.1	2.982	.064	.33			
	1.482	3.415	.133	2.875	.440	3.3	2.980	.034	.26			
	1.133	3.412	.096	2.874	.343	3.6	2.978	.019	.20			
Dipyrromethene (I)	1.479 ^b	3.411 ^d	.518							3.098 ^d	0.158	0.31
	1.121	3.416	.399							3.099	.117	.29
	0.740	3.413 ^d	.259							3.101	.080	.31
	.560	3.415	.207							3.097	.062	.30
Tripyrromethene (IV)	1.252	3.415 ^d	.808	2.896 ^d	.271	0.34	3.045 ^d	.512	.63	3.138 ^d	.259	.32
										3.199 ^d	.267	.33
	1.242 ^c	3.413	.789	2.896	.250	.32	3.043	.504	.64	3.141	.262	.33
										3.201	.269	.34
	0.913	3.416	.575	2.896	.214	.37	3.046	.369	.64	3.142	.191	.33
										3.206	.198	.34
	.621	3.417	.393	2.895	.168	.43	3.047	.244	.62	3.142	.126	.32
										3.207	.130	.33
.457	3.415	.293	2.895	.140	.48	3.046	.170	.58	3.139	.090	.31	
									3.214	.093	.32	

^a Refers to A in Fig. 1. ^b B in Fig. 1. ^c C in Fig. 1. ^d Uncorrected, see Experimental.

the time the study reported upon here was undertaken.⁶

The spectra of carbon tetrachloride solutions of 2,4-dimethyl-3-ethoxycarbonylpyrrole (III) (Fig. 1 and Table I), which is related to I, shows free and associated NH absorption bands⁷ at 2.874–2.875 and 2.977–2.987 μ , respectively. The maximum of neither band follows Beer's law⁸ and that of the first shows a relative absorbance increase with dilution, whereas that of the second shows a relative absorbance decrease as seen in Table I. This is as would be expected for intermolecular association of the pyrrole. In striking contrast the spectra of solutions of methene I show no free NH and only a broad absorption with maxima at 3.097–3.101 μ at all concentrations. Accordingly, the hydrogen bonding in I, in carbon tetrachloride, is indeed intramolecular. This is presumably the case for 2,2'-(3,4',5-trimethyl-3',4'-diethoxycarbonyl-5'-bromo)dipyrromethene (II) and other 2,2'-dipyrromethenes.

The infrared absorption spectra of solutions of 2,2',-2''-(3,3',3'',5,5',5''-hexamethyl-4,4',4''-triethoxycarbonyl)tripyrromethene (IV) (see Fig. 1 and Table 1) show a free NH band at 2.895–2.896 μ , that which is apparently an intermolecular associated NH band at 3.043–3.047 μ , and absorption with maxima at 3.133–3.142 and 3.201–3.214 μ , which could be due to intramolecular association. This would be compatible with a structure wherein two of the rings are associated as shown for dipyrromethene (I) and the NH of the third ring is left free for involvement in intermolecular association.

(6) While this note was being written the abstract of the paper by L. P. Kuhn and G. C. Kleinspehn appeared, Abstracts of Papers, 142nd National Meeting, of the American Chemical Society, Atlantic City, N. J., September, 1962, p. 842. These workers report that in all 2,2'-dipyrromethenes studied by them an N-H . . . N band is present: [see *J. Org. Chem.*, **28**, 721 (1963)]. Since submitting the manuscript, G. M. Badger, R. L. N. Harris, R. A. Jones, and J. M. Sasse, *J. Chem. Soc.*, 4329 (1962), using a calcium fluoride prism, have defined the intramolecular hydrogen-bonded NH stretching vibration in such compounds as 3.021–3.100 μ in carbon tetrachloride. Our compound I is described as absorbing at the longer wave length and an intermolecular association band was stated as not observed for the methenes examined in dilute or concentrated solutions.

(7) N. Fuson, M. L. Josien, R. L. Powell, and E. Utterback, *J. Chem. Phys.*, **20**, 145 (1952).

(8) Obedience with this law is shown in a constant value for the relative absorbance, A/A_{Alk} .⁹ A plot of A_{Alk} as a function of concentration gives a straight line for each compound listed in Table I.

(9) Cf., L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 13, *et. seq.*

Upon dilution the relative absorbance of the free NH vibration band increases noticeably. However, a change of any magnitude in the relative absorbance of the intermolecular association band is found only upon comparing the two more dilute solutions. This is understandable upon consideration of the relative areas of the two bands; a small change in the intensity of the broad intermolecular association band is accompanied by a much larger change in the intensity of the narrow free NH band (see Fig. 1). The solubilities of the dipyrromethene (I) and the tripyrromethene (IV) in carbon tetrachloride are much less than that of the pyrrole (III). Consequently the upper limit of concentration that could be used for the methenes is less than that for the pyrrole. Although the most concentrated solutions listed in Table I for none of the three compounds corresponds to a saturated solution, those for the methenes are concentrations judged to be as high as could be readily handled without concern for separation of the solute from the solution. With all three compounds the accuracy of measurement of the low broad absorbances for the associated NH bands, especially at low concentrations, defines an additional restriction.

Experimental

Infrared absorption data were obtained with a Beckman IR-4 double beam spectrophotometer using a lithium fluoride prism and a compensating cell containing solvent in the reference beam. A fixed path length cell, 0.9787 mm., was used for the pyrrole solutions, and a variable path length cell, 3.1045 mm., was used for the solutions of the di- and tripyrromethene. Both types of cells were equipped with sodium chloride windows. Measurements were made using a scanning speed of 0.17 μ /min. and an instrument slit width of 0.23 mm. at 3.000 μ (spectral band width, 0.075 μ), which was automatically varied with the wave length according to the select control device of the instrument. The absorption bands of water at 2.856 μ and of polystyrene film at 3.3026 and 3.507 μ were used for calibration of the wave length. The precision of such measurements is $\pm 0.005 \mu$. Because of particular circumstances the calibration could not be applied to certain measurements in Table I and these are designated *d*.

Freshly distilled carbon tetrachloride was used as a solvent. Erroneous results were observed with methene I when this was not done.

Melting points were determined with a Fisher-Johns or a Kofler apparatus and are uncorrected.

2,4-Dimethyl-3-ethoxycarbonylpyrrole (III), m.p. 75.0–75.2° (lit.¹⁰ m.p. 75–76°), was prepared by the hydrolysis of 2,4-dimethyl-3,5-diethoxycarbonylpyrrole and decarboxylation of the resulting carboxylic acid as described by Knorr.¹⁰

2,2'-(3,3',5,5'-Tetramethyl-4,4'-diethoxycarbonyl)dipyrrylmethene (I) was synthesized through the condensation of 7.80 g. of 2-formyl-3,5-dimethyl-4-ethoxycarbonylpyrrole and 6.68 g. of 2,4-dimethyl-3-ethoxycarbonylpyrrole in the presence of 4.66 ml. of 48.3% hydrobromic acid in alcohol. A solution of the pyrrole in 50 ml. of absolute ethanol was added dropwise to a stirred, hot solution of the aldehyde and acid in 150 ml. of absolute alcohol during a period of 30 min. and the resulting mixture was refluxed for an additional 40 min. The mixture was cooled in an ice bath and 12.1 g. of the crude hydrobromide was collected. After two recrystallizations from a mixture of chloroform and cyclohexane 11.1 g. (65%) of the purified methene hydrobromide was obtained as red crystals, having a blue reflex, m.p. 212.0–213.5° dec. Portions of the purified methene hydrobromide in chloroform were shaken with an excess of ammonia in the same solvent. After filtering the resulting mixtures and evaporating the solvent, the residues were combined. The product was dissolved in a little chloroform and chromatographed on a column of Woelm alumina (nonalkaline, activity grade II). The middle fraction of the bright yellow ether eluate therefrom was collected, the solvent was evaporated, and the residue rechromatographed as before. Crystallization of the chromatographed product from acetone yielded beautiful, long, red needles of the methene (I), m.p. 186.8–188.1° dec. (lit.¹¹ m.p. 190°).

2,2',2''-(3,3',3'',5,5',5''-Hexamethyl-4,4',4''-triethoxycarbonyl)tripyrlylmethene (IV) was synthesized by the permanganate oxidation of the corresponding tripyrlylmethane¹² in different runs. In a typical case the methene, m.p. 215.0–216.5° dec. (lit.¹² m.p. 210.7–211.6°), was obtained in a yield of 63%.

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(10) L. Knorr, *Ann.*, **236**, 322 (1886).

(11) A. H. Corwin and K. J. Brunings, *J. Am. Chem. Soc.*, **64**, 2106 (1942).

(12) A. J. Castro, A. H. Corwin, J. F. Deck, and P. E. Wei, *J. Org. Chem.*, **24**, 1437 (1959).

A New Synthesis of Methyl Aryl Sulfones

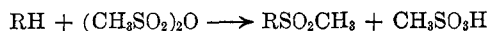
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Methyl aryl sulfones have been prepared by several methods^{1–4} all of which have limitations. We have

now found a new approach involving heating of an aromatic compound with methanesulfonic anhydride.



The data, summarized in Table I, indicate the scope of this procedure. It is evident that the CH_3SO_2 group enters primarily in the *para* position, although toluene also forms considerable *ortho* isomer. The structures indicated for new compounds were not proved, but for those derived from 1,4-xylene and from 1,2,4,5-tetramethylbenzene (compounds **3** and **6**), only one structure is possible if no rearrangement is assumed during reaction.

This procedure also has limitations under the conditions used. Use of pure reagents, especially with polymethylated benzenes, obviated tar formation, as did also use of fresh methanesulfonic anhydride, which deteriorates upon standing. Use of tetrachloroethylene as reaction solvent at reflux (b.p. 121°) generally gave a much cleaner reaction than employing an excess of the compound treated, as did also reduction of the standard reaction time of sixteen hours in a number of cases, as indicated in Table I. Less reactive and more volatile compounds, such as toluene and chlorobenzene, require longer periods of reaction. The following compounds did not react: 1,2-dichlorobenzene, phenyl benzoate, phenyl methanesulfonate, triphenyl phosphate, 2-nitroanisole, and 2-methoxybenzoic acid. Although anisole reacted normally, phenetole gave a good yield of phenyl methanesulfonate, as did also phenol and phenyl acetate. Intractable tars resulted from 1,2-xylene, 1,2,4-trimethylbenzene, pentamethylbenzene, phenoxyacetic acid, thioanisole, 2-methylanisole, and 3-methylanisole. Naphthalene, ethylbenzene, diphenyl oxide, and 2-phenylanisole appeared to react, but pure products could not be isolated. Infrared analysis of the product made from naphthalene showed it to comprise largely a mixture of the α - and β -methylsulfonyl derivatives. Where applicable, however, the present method appears simple and conveni-

(1) C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 660 ff.

(2) A. Schoeberl and A. Wagner, "Houben-Weyl Methoden der Organischen Chemie," 4th Ed., Vol. IX, Thieme, Stuttgart, 1955, p. 227 ff.

(3) L. Field and R. D. Clark, *J. Org. Chem.*, **22**, 1129 (1957).

(4) W. E. Truce and C. W. Vriesen, *J. Am. Chem. Soc.*, **75**, 5032 (1953).

TABLE I. METHYL ARYL SULFONES

No.	Compound reacted	Substituted methanesulfonylbenzene formed	Reflux time, hr.	Yield, % ^a	M.p., °C.		% Sulfur	
					Lit.	Found ^d	Theor.	Found
1	Toluene	2- and 4-Methyl	20	53 ^b	88 ^e	88	18.8	18.8
2	1,3-Xylene	2,4-Dimethyl	16	75	55 ^f	56	17.4	17.5
3	1,4-Xylene	2,5-Dimethyl	8	42	^g	45	17.4	17.5
4	1,2,3-Trimethylbenzene	3,4,5-Trimethyl	16	82 ^c	^g	121	16.2	16.6
4a	1,2,3-Trimethylbenzene	2,3,4-Trimethyl			^g	97	16.2	16.3
5	1,3,5-Trimethylbenzene	2,4,6-Trimethyl	8	75	130 ^f	131	16.2	16.4
6	1,2,4,5-Tetramethylbenzene	2,3,5,6-Tetramethyl	4	60	^g	133	15.1	15.1
7	Chlorobenzene	4-Chloro	24	10	98 ^f	97	16.6	16.7
8	Biphenyl	4-Phenyl	16	40	145 ^h	144	13.8	13.8
9	Anisole	4-Methoxy	16	70	120 ⁱ	120	17.2	17.3
10	4-Methylanisole	2-Methoxy-5-methyl	16	20	87 ⁱ	86	16.0	15.9
11	1,3-Dimethoxybenzene	2,4-Dimethoxy	8	50	^g	105	14.8	15.1

^a Average yields of fair quality crude. ^b Over half 2-isomer by infrared analysis. ^c Total for two isomers. ^d Uncorrected. ^e The 4-isomer of ref. 4. ^f J. Troeger and C. Budde, *J. prakt. Chem.*, (2) **66**, 149 (1902). ^g New compound. ^h A. Mangini, L. Ruzzier, and A. Tundo, *Bull. Sci. fac. chim. ind. Bologna*, **14**, 81 (1956); *Chem. Abstr.*, **52**, 19446 (1958). ⁱ Ref. 6. ^j D. T. Gibson and S. Smiles, *J. Chem. Soc.*, 2391 (1923).