Experimental

Ethyl β-Phenyl-γ-nitrobutyrate.—To a stirred solution of 48.8 g. (0.8 mole) of nitromethane and 15 g. of benzyltrimethylammonium butoxide solution in butanol (Rohm and Haas Company) was added 35.2 g. (0.2 mole) of ethyl cinnamate. While the reaction mixture was stirred for 68 hours at 65–70°, additional 5-g. portions of catalyst were added at 24-hour intervals. The mixture was acidified with 1 *N* hydrochloric acid, an equal volume of ethylene dichloride was added, and the ethylene dichloride layer was washed with water. The solvent was removed and the residual oil was fractionally distilled in vacuum. Unchanged ethyl cinnamate (18.0 g.) was recovered at 100–110° (1 mm.), and the ethyl β-phenyl-γ-nitrobutyrate was collected as a light yellow oil; b.p. 156–158° (1 mm.); $n^{20}{}_{\mathrm{D}}$ 1.5085; $d^{20}{}_{4}$ 1.162; yield 17.6 g. (76% based on unrecovered ethyl cinnamate).

Anal. Calcd. for $C_{12}H_{15}NO_4$: N, 5.90; *MR*D, 61.40. Found: N, 5.90; *MR*D, 60.91.

1-Ethyl-3-phenylpyrrolidine by Reductive Cyclization.—A solution of 3.2 g. (0.014 mole) of ethyl β-phenyl-γ-nitrobutyrate in 34 ml. of dioxane was hydrogenated in the presence of 3 g. of copper chromite catalyst at 265° and 250 atm. during 3 hours. After removal of the catalyst and solvent in the usual manner,[1] the residue was fractionally distilled, and the product boiling at 64.5° (0.12 mm.) was collected; $n^{19}{}_{\mathrm{D}}$ 1.5238; yield 0.8 g. (40%).

Anal. Calcd. for $C_{12}H_{17}N$: N, 7.99. Found: N, 8.13.

1-Ethyl-3-phenylpyrrolidine Picrate (Picrate 1).—Prepared in ether and recrystallized from methanol, the picrate formed yellow elongated prisms, m.p. 153–155°.

Anal. Calcd. for $C_{18}H_{20}N_4O_7$: C, 53.46; H, 4.99; N, 13.86. Found: C, 53.41; H, 5.23; N, 14.00.

1-Ethyl-3-phenylpyrrolidine Picrolonate (Picrolonate 1).—Prepared in ethanol and recrystallized from methanol, the picrolonate formed yellow microcrystals, m.p. 149.5–151.5°.

Anal. Calcd. for $C_{22}H_{25}N_5O_5$: C, 60.13; H, 5.73; N, 15.94. Found: C, 59.90; H, 5.82; N, 16.20.

1-Ethyl-3-phenylsuccinimide.—A mixture of 35.0 g. (0.20 mole) of phenylsuccinic anhydride[2] and 25.6 g. (0.40 mole) of 70% aqueous ethylamine was heated gradually under a reflux air condenser to 280°. When the temperature had reached 280°, the reaction mixture was maintained there for 1 hour, then cooled and distilled twice *in vacuo* using a short-path apparatus; b.p. 140–146° (1.5–2.5 mm.); $n^{20}{}_{\mathrm{D}}$ 1.5501; $d^{20}{}_{4}$ 1.1574; yield 25.9 g. (65%).

Anal. Calcd. for $C_{12}H_{13}NO_2$: C, 70.91; H, 6.45; N, 6.89. Found: C, 70.95; H, 7.17; N, 6.95.

The infrared spectrum indicated the absence of any absorption due to N–H, and the presence of carbonyl absorption similar to that exhibited by succinimide.[3]

1-Ethyl-3-phenylpyrrolidine by Lithium Aluminum Hydride Reduction.—The procedure which was followed was identical with that described by Nystrom and Brown[4] for the reduction of amides by their lithium aluminum hydride reagent. The product was a colorless liquid, b.p. 77–78° (1.4–1.5 mm.); $n^{20}{}_{\mathrm{D}}$ 1.5240; $d^{20}{}_{4}$ 0.9608; yield 71%.

Anal. Calcd. for $C_{12}H_{17}N$: C, 82.23; H, 9.78; N, 7.99; *MR*D, 55.97. Found: C, 82.11; H, 9.82; N, 8.13; *MR*D, 55.82.

The picrate (Picrate 2), m.p. 153–155°, was undepressed on mixing with the picrate of 1-ethyl-3-phenylpyrrolidine obtained by reductive cyclization (Picrate 1).

Anal. Calcd. for $C_{18}H_{20}N_4O_7$: C, 53.46; H, 4.99; N, 13.86. Found: C, 53.50; H, 5.28; N, 13.91.

The picrolonate (Picrolonate 2), m.p. 149.5–151°, was undepressed on mixing with Picrolonate 1.

Anal. Calcd. for $C_{22}H_{25}N_5O_5$: C, 60.13; H, 5.73; N, 15.94. Found: C, 60.19; H, 5.92; N, 16.10.

THE NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS
RECEIVED OCTOBER 14, 1950

---

[2] P. E. Verkade and H. Hartman, *Rec. trav. chim.*, **52**, 945 (1933).

[3] *Infrared analysis by Miss Elizabeth M. Petersen.*

[4] R. F. Nystrom and W. G. Brown, THIS JOURNAL, **70**, 3738 (1948).

The Molar Absorbancy Indices of Some 2,4-Dinitrophenylhydrazones

BY E. E. LOCKHART, M. C. MERRITT AND C. D. MEAD[1]

The molar absorbancy indices of several 2,4-dinitrophenylhydrazones of saturated aliphatic aldehydes have already been published.[2,3] However, for a continuing investigation of the carbonyl fraction of food products, it became necessary to prepare and study the spectral characteristics of hydrazones of other members of the aliphatic series. The results of this study are reported here (Table I), to provide a more complete picture of this group of compounds.

TABLE I

MOLAR ABSORBENCY INDICES OF SOME 2,4-DINITROPHENYLHYDRAZONES

	Maximum		
Aldehyde	Primary $a_M \times 10^{-2}$	Secondary $a_M \times 10^{-2}$	Minimum $a_M \times 10^{-2}$
Isobutyr-	230	156	22
n-Valer-	231	157	22
Isovaler-	232	160	21
n-Capro-	238	161	21
n-Capryl-	218	149	21
n-Nonyl-	217	146	21
n-Decyl-	216	146	19
n-Dodecyl-	216	148	20

Our results agree essentially with those previously reported, with respect to wave lengths of maximum and minimum absorption. We were unable, however, to obtain any indication that a third or fourth absorption band might be present in the spectra studied, as suggested by Braude and Jones.[2] The resolution possible with their equipment may account for this discrepancy. With the exception of the formaldehyde hydrazone, all maxima occur at 224–226 mμ (secondary) and 357–358 mμ (primary). The minima are located at 282–283 mμ.

A portion of this study included a repetition of the earlier work. The results obtained, together with those reported here, seemed to indicate that the length of the alkyl chain has some small effect on the intensity of resonance. There is a relatively regular increase in the molar absorbancy indices with increase in chain length, until a maximum is reached at $C_5 \cdot CH{=}$. Chain lengths greater than this seem to have a damping effect on resonancy. The significance of this effect is being tested by a study of other carbonyl series.

Experimental.—The 2,4-dinitrophenylhydrazones were prepared according to the method of Allen.[4] They were recrystallized from 95% ethyl alcohol until a constant melting point was obtained. A Beckman model DU ultraviolet spectrophotometer and 1.000-cm. silica cells were used throughout this work. The absorption data were obtained from solutions containing uniformly 0.0125 mg. of hydrazone per ml. The solvent was 95% U.S.P. ethyl alcohol (U.S.I. synthetic). Preliminary work indicated that heating solid–liquid mixtures to facilitate dissolution of the hydrazones caused decomposition. It was necessary, therefore, to dissolve the compounds at room temperature. The time required varied from several hours to several days.

---

[1] C. D. Mead, S.B. Thesis, Dept. Food Tech., Mass. Inst. Tech., 1949.

[2] E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 498 (1945).

[3] J. D. Roberts and C. Green, THIS JOURNAL, **68**, 214 (1946).

[4] C. F. H. Allen, *ibid.*, **52**, 2955 (1930); C. F. H. Allen and J. H. Richmond, *J. Org. Chem.*, **2**, 222 (1937–1938).

Solutions were apparently stable at room temperature for at least one week. Reproducible data were obtained only if this procedure was followed.

Acknowledgment.—This investigation was conducted with the assistance of grants-in-aid from the following organizations: American Can Company, Maywood, Illinois; Dow Chemical Company, Midland, Michigan; Nestlé Company, New York, New York; Pillsbury Mills, Inc., Minneapolis, Minnesota; Standard Brands, Inc., New York, New York; Wilson & Company, Chicago, Illinois.

DEPARTMENT OF FOOD TECHNOLOGY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASS. RECEIVED SEPTEMBER 25, 1950

Some Alkanesulfinic Acids and their Derivatives[1]

BY C. S. MARVEL AND N. A. MEINHARDT

In connection with a study of alkanesulfinic acids as activators in an oxidation–reduction type polymerization recipe[2] we have had occasion to prepare the C_8 to C_{18} even-numbered carbon straight-chain members of the alkanesulfinic acid series and have characterized them with derivatives. The methods of preparation for the acids and derivatives are those recently described for 1-dodecanesulfinic acid.[3]

1-Octanesulfinic acid and 1-decanesulfinic acid are low melting and rapidly become colored in air. They obviously oxidize and/or rearrange very quickly and they have only been prepared in a crude state. Their derivatives, however, have been obtained as pure crystalline compounds.

Experimental.—The magnesium salts of the alkanesulfinic acids were prepared by the method of Houlton and Tartar[4] and converted into the various derivatives by standard methods.[3] The results of the work are presented in the tables.

This series of compounds is unstable and decomposes on standing for a few days. This makes their analysis unsatisfactory.

TABLE I

ALKANESULFINIC ACIDS RSO_2H

Decane	Yield of acid from Mg salt, %	M. p., °C.	Analyses, %					
			Carbon		Hydrogen		Sulfur	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
1-Tetra-	65.5	48–48.4	64.12	64.46	11.43	11.51	12.2	12.06
1-Hexa-	58	54–55	66.21	65.90	11.71	11.58	11.05	11.15
1-Octa.	69.2	60–60.5	67.92	67.68	11.94	12.14	10.05	10.20

TABLE II

N,N-DI-(1-ALKANESULFONYL)-HYDROXYLAMINES $(RSO_2)_2NOH$

	Yield based on sodium salt, %	M. p., °C.	Analyses, %					
			Carbon		Hydrogen		Nitrogen	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
1-Octane	77.1	64–65	49.9	50.02	9.09	9.20	3.64	3.43
1-Decane	91.8	68–69	54.44	54.76	9.73	9.45	3.18	3.06
1-Tetradecane	90	74–75	60.75	60.77	10.68	10.77	2.53	2.45
1-Hexadecane	77	75–75.5	63.1	62.87	11.00	10.83	2.30	2.16
1-Octadecane	78.8	83–84	65.00	65.25	11.28	11.10	2.10	2.06

TABLE III

O-ACETYL-N,N-DI-(1-ALKANESULFONYL)-HYDROXYLAMINES $(RSO_2)_2NOCOCH_3$

	Yield based on hydroxylamine, %	M. p., °C.	Analyses, %					
			Carbon		Hydrogen		Nitrogen	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
1-Octane	65.6	24–25	50.58	50.19	8.66	8.6	3.29	3.00
1-Decane	72.3	43–45	54.66	54.45	9.31	9.66	2.90	2.69
1-Tetradecane	62	54–57.5	60.49	61.25	10.25	10.75	2.35	2.42
1-Hexadecane	65.9	74–75	62.66	63.05	10.59	11.32	2.14	2.19
1-Octadecane	70.4	78–79	64.5	65.10	10.89	11.39	1.98	2.27

TABLE IV

TRI-(1-ALKANESULFONYL)-AMINE OXIDES $(RSO_2)_3NO$

	M. p., °C.	Analyses, %					
		Carbon		Hydrogen		Nitrogen	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
1-Octane	39–40	51.3	51.14	9.26	8.90	2.49	2.76
1-Decane	47–48	55.8	55.86	9.77	9.57	2.17	2.35
1-Tetradecane	69–70	62.0	62.3	10.70	10.45	1.72	1.76
1-Hexadecane	74.5–76	64.25	64.3	11.02	11.25	1.56	1.74
1-Octadecane	76–77	66.06	66.10	11.31	11.49	1.43	1.64

TABLE V

1-ALKANESULFONYLACETIC ACIDS $RSO_2CH_2CO_2H$

	Yield based on sodium salt, %	M. p., °C.	Analyses, %			
			Carbon		Hydrogen	
			Calcd.	Found	Calcd.	Found
1-Octane	82	95–96	50.9	51.2	8.47	8.57
1-Decane	52.6	102–103.5	54.6	54.73	9.09	9.09
1-Tetradecane	47.7	110–111	60.0	60.10	10.00	9.91
1-Hexadecane	47.5	113–114	62.1	62.18	10.34	10.43
1-Octadecane	45	116–117	63.8	64.49	10.62	10.69

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS RECEIVED SEPTEMBER 11, 1950

---

[1] This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the U. S. Government Synthetic Rubber Program.

[2] Office of the Publication Board, U. S. Department of Commerce, Item P. B. No. 1636—Activation of Buna-S Polymerization in Mersolat Emulsion with Reducing Agents, Sherlock Swann, Jr., and N. M. Elias.

[3] C. S. Marvel and R. S. Johnson, *J. Org. Chem.*, **13**, 822 (1948).

[4] H. G. Houlton and H. V. Tartar, THIS JOURNAL, **60**, 544 (1938).