material was prepared in 78% yield from a 70-mole reaction involving the condensation of phenylmagnesium bromide with methyl ethyl ketone (n^{20}D 1.3788). The ether was removed by distillation after the mixture was hydrolyzed with a saturated solution of ammonium chloride. Careful fractionation *in vacuo* gave the carbinol with little or no dehydration. The properties of a selected sample were: b. p. 97° at 15 mm. and 107.5° at 20 mm., n^{20}D 1.5195 and d^{20} 0.97696 g./ml.

Anal. Calcd. for $C_{16}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.93; H, 9.39.

2,2-Diphenylbutane. Rearrangement and Bimolecular Condensation Products from Friedel-Crafts Reaction.—In a typical synthesis 1202 g. (8 moles) of 2-phenyl-2-butanol, 1875 g. (24 moles) of benzene and 536 g. (4 moles) of aluminum chloride reacted in a 5-l. flask equipped with a stirrer, dropping funnel and condenser. One-third of the benzene was used as solvent for the carbinol and the remainder was added to the reaction flask containing the aluminum chloride. The addition of the carbinol-benzene mixture required three hours during which time the temperature of the reactants was kept below 20° by means of an ice-bath. Stirring was maintained for an additional 24 hours with the ice-bath removed and the reaction mixture was hydrolyzed by pouring the flask contents into dilute sulfuric acid and ice. The hydrocarbon layer was washed and dried and the benzene and low boiling impurities were removed by distillation. The remainder, after combination with similar material from a total of four identical runs (32 moles), was fractionally distilled *in vacuo* to give 750 g. (11%) of 2,2-diphenylbutane which was refractionated on a Podbielniak column.

The initial distillation also gave 40 g. of biphenyl and 240 g. (4%) of the solid and liquid isomers of 2,3-diphenylbutane. The identity of the isomeric rearrangement products was established by comparison of their physical properties and infrared spectra with those of *meso*- and *dl*-2,3-diphenylbutanes prepared from α-bromoethylbenzene.

The principal product from the Friedel-Crafts reaction was a viscous liquid which partially crystallized on standing. The solid, following recrystallization from ethanol, melted at 50.5–52° and is presumably 1-methyl-1,3-diethyl-3-phenylhydrindene formed by the bimolecular condensation of the reaction intermediate.

Anal. Calcd. for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 90.85; H, 9.13.

The preparation of 1,1,3-trimethyl-3-phenylhydrindene (m. p. 51–52°) by an analogous procedure has been discussed in a previous paper of the series.[1] The mixing of the two solids for a mixed melting point determination gave a liquid at room temperature.

Preparation of Dicyclohexylbutanes. 1,4-Dicyclohexylbutane.—As previously stated, the saturated hydrocarbons were generally prepared by the total hydrogenation of the purified aromatic hydrocarbon. In a typical procedure, 1013 g. (4.8 moles) of 1,4-diphenylbutane dissolved in an equal volume of methylcyclohexane was hydrogenated in a rocker-type autoclave of 4½ l. capacity using 150 g. of U.O.P. nickel catalyst. Reaction occurred at 170–180° at 1700 p.s.i. and the temperature was maintained at a maximum of 200° until the theoretical amount of hydrogen was consumed. Following filtration of the catalyst, the solvent was removed by distillation. The remaining material was fractionally distilled *in vacuo* to give 967 g. (91%) of 1,4-dicyclohexylbutane. Selected fractions were refractionated on a Podbielniak column and the product was passed through silica gel prior to the determination of the physical properties.

CLEVELAND, OHIO RECEIVED JUNE 7, 1951

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

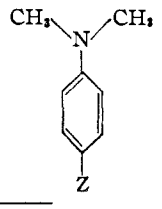
Steric Effect of Methylene Groups. VI

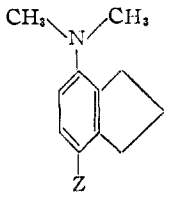
BY RICHARD T. ARNOLD, VINCENT J. WEBERS[1,2] AND R. M. DODSON

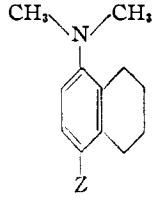
A number of *p*-substituted dimethylamino derivatives of the benzene, indan, tetralin and *o*-xylene series have been prepared. Comparison of their absorption spectra in the ultraviolet and near visible region has further demonstrated that the steric effect of an ortho methylene group in a six-membered ring is greater than that in a corresponding five-membered ring. New chemical data also supports this view.

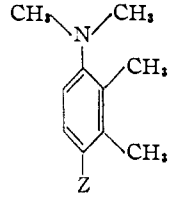
In several previous papers[3] considerable physical and chemical evidence has been presented which strongly indicates that the steric effect of a methylene group is not constant, and, in particular, that the ortho methylene groups in indan derivatives offer less steric hindrance to ring substituents than those in corresponding tetralin analogs.

During this study we prepared the sixteen compounds indicated below and examined their spectra in the ultraviolet and near visible region.









[Z = —CH=NOH, —C≡N, —N=N—C_6H_5, —N=N—C_6H_4—NO_2-*p*]

Table I gives the position and intensity of the major absorption band in the region studied. Two facts are immediately evident. In the first place, with some particular group "Z," the absorption intensity diminishes regularly through the benzene, indan and tetralin series. Secondly, both the position and the intensity of the absorption bands for the tetralin and *o*-xylene derivatives are remarkably similar.

With substituted aromatic amines, it has been reasonably well established[3,4] that the intensity of

(1) Taken from the Ph.D. thesis of Vincent J. Webers, 1949.

(2) Allied Chemical and Dye Corporation fellow 1947–1948; du Pont fellow 1948–1949.

(3) Paper V of this series, R. T. Arnold and P. N. Craig, THIS JOURNAL, **72**, 2728 (1950).

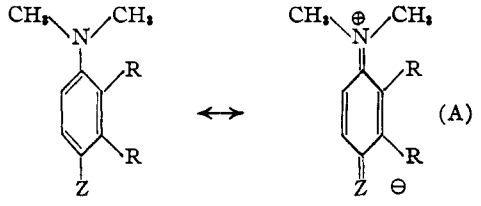
(4) W. R. Remington, *ibid.*, **67**, 1838 (1945).

TABLE I[a]

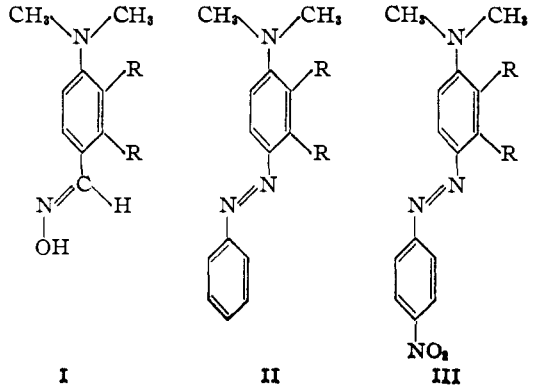
Group Z	Dimethylaniline deriv.	λ_{max}, in mμ	ϵ_{max}
Phenylazo-	Dimethylaniline	407	27,500
	4-Dimethylaminoindan	393	19,400
	5-Dimethylaminotetralin	380	17,300
	Dimethyl-2,3-xylidine	377	17,400
p-Nitro-	Dimethylaniline	478	32,100
phenylazo-	4-Dimethylaminoindan	466	21,800
	5-Dimethylaminotetralin	430	18,200
	Dimethyl-2,3-xylidine	425	17,900
Aldoxime-	Dimethylaniline	302	23,700
	4-Dimethylaminoindan	296	14,900
	5-Dimethylaminotetralin	294	11,700
	Dimethyl-2,3-xylidine	289	11,400
Cyano-	Dimethylaniline	294	27,200
	4-Dimethylaminindan	301	19,000
	5-Dimethylaminotetralin	296	12,600
	Dimethyl-2,3-xylidine	293	12,300

[a] The absorption spectra were taken in 95% ethanol using a Beckman spectrophotometer.

the absorption band in question and the contribution made by the limiting resonance structure (A) are at a maximum when the molecule conforms to a planar configuration.

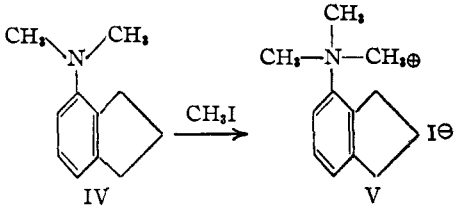


As the "effective" size of "R" increases, coplanarity between $(CH_3)_2N$– and the benzenoid ring becomes increasingly difficult. Steric inhibition of resonance and therefore the steric hindrance afforded by "R" may be measured in a relative sense by the extent to which intensity of absorption is lowered from that of the parent (R = H) substance. In the cases reported here, the major repulsion which resists coplanar configurations probably involves the dimethylamino group and the methylene substituent adjacent to it. Obviously, the linear —C≡N is not appreciably affected by the neighboring methylene grouping. As shown in I, II and III, the three substituents —CH=N—OH, —N=N—C_6H_5, and —N=N—C_6H_4—NO_2-*p* are able to assume preferred positions (with respect to "R") which lead to minima in potential energy.



I II III

It has been well established[5,6] that N,N-dimethylaniline derivatives having a substituent ortho to the amino group react slowly with methyl iodide to form quaternary salts. In view of this well known generalization it is noteworthy that 4-N,N-dimethylaminoindan (IV) reacts readily with methyl iodide to form (V). Indeed this reaction



IV V

proceeds so rapidly that (V) is always produced as one of the major products in the preparation of (IV) by direct methylation of 4-aminoindan with methyl iodide. In agreement with the stereochemical view expressed in this and previous papers from this Laboratory, the corresponding N,N-dimethylamino derivatives in the tetralin and *o*-xylene series are quite unreactive toward methyl iodide under comparable experimental conditions.

Experimental[7]

Tertiary Amines.—The aromatic primary amines were methylated by standard procedures with 2.5 moles of methyl iodide per mole of amine in the presence of excess sodium carbonate in water. Partially methylated material was removed by treatment of the crude product with acetic anhydride followed by acid extraction.

N,N-Dimethyl-4-indanamine.—From 100 g. of 4-indanamine was obtained 52 g. of quaternary iodide (23%, m.p. 210–211°), and 73.6 g. (61%) of the desired tertiary amine; b.p. 125–126° (18 mm.). This amine[8] gave a picrate; m.p. 145.5–147°.

N,N-Dimethyl-5,6,7,8-tetrahydro-1-naphthylamine.—From 101.6 g. of 5-aminotetralin by methylation with methyl iodide there was obtained 99.7 g. of tertiary amine; b.p. 138° (20 mm.)[8] a picrate of this product melted at 170–170.5°.

No quaternary salt was isolated during the above methylation. In a separate experiment 0.026 mole of the above tertiary amine was treated with 0.078 mole of methyl iodide in 100 ml. of dry ether at room temperature. After 55 days, 97% of the starting tertiary amine and 0.21 g. (2.7%) of the quaternary salt were isolated.

N,N-Dimethyl-2,3-xylidine.—From 60.5 g. of 2,3-xylidine there was obtained 64.9 g. (87%) of tertiary amine; b.p. 112° (38 mm.). This substance gave a picrate which after recrystallization from ethanol melted at 139.3–140°. The melting point previously reported[8] is 127–128°.

Anal. Calcd. for $C_{10}H_{15}N \cdot C_6H_3N_3O_7$: C, 50.79; H, 4.79. Found: C, 50.93; H, 4.84.

N,N-Dimethyl-*p*-phenylazoaniline.—This substance was prepared in the usual way by coupling 3.63 g. of dimethylaniline with the diazonium chloride from 2.80 g. of aniline. The crude product was crystallized from methanol, chromatographed from benzene on activated alumina and again crystallized from methanol; yield 3.4 g. (50%); m.p. 116.5–117.5°; reported m.p. 117°.[9]

Azo Compounds.—Except for the unsubstituted compound reported above, the remaining azo compounds were prepared by coupling in aqueous pyridine. A solution of the diazonium salt was prepared by diazotization of 0.02 mole of aniline (or *p*-nitroaniline) using a minimum of

(5) J. v. Braun and O. Kruber, *Ber.*, **46**, 3470 (1913).

(6) W. G. Brown and S. Fried, THIS JOURNAL, **65**, 1841 (1943).

(7) Microanalyses by Jay S. Buckley, Jr., William Cummings and Roger Amidon.

(8) J. v. Braun, Z. Arkuszewski and Z. Kohler, *Ber.*, **51**, 282 (1918).

(9) A. Shattenstein and E. Israilewitsch, *Acta Physicochim. U. R. S. S.*, **13**, 88 (1940).

water and ice, 3.3 g. of sodium acetate and 30 ml. of cold pyridine. To this was added a solution of the tertiary amine (regenerated from 0.02 mole of its picrate) containing 40 ml. of cold pyridine. The reaction mixture was allowed to stand in the refrigerator from 1–3 days. Dilution with water followed by filtration gave the crude product.

N,N-Dimethyl-7-phenylazo-4-indanamine.—The crude product, obtained as indicated above, was chromatographed using petroleum ether (b.p. 60–70°) and activated alumina. The main fraction from this separation was converted to its hydrochloride and regenerated with aqueous ammonia. Recrystallization from ethanol–water and then from ethyl ether (at −80°) gave 1.7 g. (32%) of orange crystals; m.p. 65.5–66°.

Anal. Calcd. for $C_{17}H_{19}N_3$: C, 76.95; H, 7.21. Found: C, 77.11; H, 7.18.

N,N-Dimethyl-4-phenylazo-5,6,7,8-tetrahydro-1-naphthylamine.—The crude product from the coupling reaction was crystallized twice from methanol, chromatographed using benzene and activated alumina, and recrystallized from methanol to give an orange-red compound melting at 91.5–92.5°.

Anal. Calcd. for $C_{18}H_{21}N_3$: C, 77.38; H, 7.58. Found: C, 77.76; H, 7.75.

N,N-Dimethyl-4-phenylazo-2,3-xylidine.—Pyridine was removed by steam distillation after completion of the coupling reaction. Chromatography using petroleum ether (b.p. 60–70°) gave an oil. This substance was converted to its hydrochloride and regenerated with ammonia. Repetition of this procedure gave a crystalline solid which after recrystallization from ether (at −80°) and from ethanol–water gave a pure product weighing 0.85 g. (16.8%); m.p. 44.5–45°.

Anal. Calcd. for $C_{16}H_{19}N_3$: C, 75.86; H, 7.56. Found: C, 75.63; H, 7.59.

N,N-Dimethyl-*p*-(*p*-nitrophenylazo)-aniline.—The crude product was crystallized from toluene then from butanol and finally chromatographed using benzene and activated alumina. No separation on alumina was apparent so two fractions melting at 230 and 226° were obtained from two arbitrarily taken eluate samples. The first was crystallized from butanol giving 1.0 g. (18.5%) of a dark purple powder; m.p. 232–233°; reported[10] 234.5–235°.

Anal. Calcd. for $C_{14}H_{14}N_4O_2$: C, 62.21; H, 5.22. Found: C, 62.21; H, 5.35.

N,N-Dimethyl-7-(*p*-nitrophenylazo)-4-indanamine.—The crude product from the coupling reaction was chromatographed using benzene and activated alumina, and recrystallized three times from butanol to give 3.5 g. (56.5%) of a dark purple powder; m.p. 146–146.5°.

Anal. Calcd. for $C_{17}H_{18}N_4O_2$: C, 65.79; H, 5.85. Found: C, 66.04; H, 5.72.

N,N-Dimethyl-4-(*p*-nitrophenylazo)-5,6,7,8-tetrahydro-1-naphthylamine.—The crude product was chromatographed from benzene on activated alumina, crystallized from ethyl acetate, and then from butanol, to give 3.5 g. (54%) of dark rose needles, m.p. 149–149.5°.

Anal. Calcd. for $C_{18}H_{20}N_4O_2$: C, 66.65; H, 6.22. Found: C, 66.35; H, 6.40.

N,N-Dimethyl-4-(*p*-nitrophenylazo)-2,3-xylidine.—The crude product was chromatographed from benzene on activated alumina, crystallized from ethyl acetate and from butanol to give 2.5 g. (42%) of deep red needles, m.p. 151–152°.

Anal. Calcd. for $C_{16}H_{18}N_4O_2$: C, 64.41; H, 6.08. Found: C, 64.61; H, 6.10.

Aldoximes.—The aldehydes were all prepared by the Vilsmeier[11] reaction with some variation in conditions. As the reaction is described in the literature, one-half of the initial amine is used to neutralize hydrochloric acid generated in the reaction. It was found that substitution of pyridine for one-half of the dimethylaniline gave higher yields, but an increase in the amount of pyridine over this amount gave a decrease in yield. The aldehydes were converted directly to the oximes.

***p*-Dimethylaminobenzaldoxime.**—A solution of 10 g. of phosphorus oxychloride (0.066 mole) and 8.9 g. of N-methylformanilide (0.066 mole) was allowed to stand for one hour. The solution was cooled to 5°, then 8.0 g. of dimethylaniline (0.066 mole) was added, one-half cc. at a time, during which time the temperature was held between 0 and 10°. The reaction mixture was kept in a refrigerator overnight. It was cautiously hydrolyzed, neutralized and steam distilled until the solid product began to appear in the distillate. The organic material in the distilling flask solidified on cooling. The *p*-dimethylaminobenzaldehyde was dried in a vacuum desiccator and distilled, b.p. 166–170° (13.5 mm.); reported[12] b.p. 176–177° (17 mm.). The yield of crude aldehyde was 3.9 g. (40%). In a second experiment, all quantities were doubled except dimethylaniline, which was dissolved in 6.4 cc. of pyridine (0.066 mole plus one cc.); 5.9 g. of product (60%) was obtained. When tributylamine was used instead of pyridine, none of the desired product was obtained.

The crude aldehyde prepared above was converted to the oxime in the usual way in 92% yield. The crude product was crystallized from benzene, sublimed at 0.5 mm., and reprecipitated from basic solution to give a product melting at 142.5–143.5°. After successive crystallizations, from benzene, benzene–petroleum ether (60–68°), and twice from ethanol–water, the melting point was 145–148°, 144.5–147.5°, 144.5–147° and 145–146.5°, respectively. The final yield was 3 g. (28%). The reported[13] m.p. is 144°.

7-Dimethylamino-4-indancarboxaldoxime.—A solution of 0.05 mole of N,N-dimethyl-4-indanamine (from 19.5 g. of picrate) in 20 cc. of dry pyridine was added during 1.5 hours to a solution of 10.1 cc. (0.110 mole) of phosphorous oxychloride and 13.7 cc. (0.110 mole) of N-methylformanilide. The mixture was held at about 40° during the addition. After standing overnight at room temperature, the mixture was cautiously hydrolyzed, neutralized and steam distilled until no more oil appeared in the distillate. The organic residue was taken up in benzene; the benzene solution was washed with water and extracted with dilute hydrochloric acid; the acid solution was neutralized with ammonia; the product was taken up in ether; the ether solution was dried over sodium sulfate; the ether was evaporated, and the product was distilled, b.p. 145–150° (4 mm.). This material, 2.6 g. (27.5%), was converted directly to the oxime in 100% yield. A second run on a 0.075 mole scale using only 7.5 cc. of pyridine (0.085 mole) gave 5.2 g. (43.8%) of material, which was converted to the oxime in a yield of 73%.

The 7-dimethylamino-4-indancarboxaldoxime (7.7 g.) was purified by solution in dilute aqueous sodium hydroxide, precipitation with carbon dioxide and crystallization of the solid so obtained from ethyl acetate and then from benzene; m.p. 118.5–119°.

Anal. Calcd. for $C_{12}H_{16}N_2O$: C, 70.55; H, 7.90. Found: C, 70.60; H, 8.02.

4-Dimethylamino-5,6,7,8-tetrahydro-1-naphthaldoxime.—This substance was prepared from 0.05 mole of dimethylaminotetralin picrate in substantially the same manner as the first method (*i.e.*, excess of pyridine) described above for the indan derivative. The yield of crude product, b.p. 145–150° (3.5 mm.) was 1.9 g. (18%) of material, from which the oxime was prepared in a crude yield of 88%. A second run, corresponding to the second run under the indan derivative, differed from that above in that only 5 cc. of pyridine (0.055 mole) was used, and that the reaction mixture was held at 40° for five hours after addition was complete. This gave 3.7 g. (36%) from which the oxime was prepared in 78% crude yield. The 4-dimethylamino-5,6,7,8-tetrahydro-1-naphthaldoxime so obtained (3.7 g.) was sublimed at 0.5 mm., crystallized from ethanol–water and chromatographed from chloroform on activated alumina. The chloroform solution obtained on elution of the chromatogram was extracted with dilute hydrochloric acid; the acid solution was neutralized with ammonia; the product was crystallized from benzene, benzene–petroleum ether (60–68°), and finally from ethanol–water. The yield was 1.4 g., m.p. 143–144°.

Anal. Calcd. for $C_{13}H_{18}N_2O$: C, 71.52; H, 8.31. Found: C, 71.19; H, 8.40.

4-Dimethylamino-2,3-xylaldoxime.—This substance was prepared according to the second procedure (only a slight

(10) A. Pongratz, G. Markgraf and E. Mayer-Pitsch, *Ber.*, **71**, 1257 (1938).

(11) A. Vilsmeier and A. Haack, *ibid.*, **60**, 119 (1927).

(12) H. Well, *ibid.*, **27**, 3317 (1894).

(13) O. L. Brady and F. P. Dunn, *J. Chem. Soc.*, **105**, 2573 (1914).

excess of pyridine) described above, except that the reaction mixture was held at 43° for 25 hours and then at room temperature for another 20 hours after addition was complete. The yield was 4.8 g. (27%) of material, b.p. 135–150° (3–3.5 mm.), which gave the crude oxime in 56% yield.

This oxime (2.9 g.) was chromatographed from chloroform on activated alumina. The product was extracted from the chloroform eluate with dilute hydrochloric acid and reprecipitated with dilute sodium hydroxide solution. After crystallization from benzene and benzene–petroleum ether, there remained 1.2 g. of pure material, m.p. 148.5–149.5°.

Anal. Calcd. for $C_{11}H_{16}N_2O$: C, 68.72; H, 8.39. Found: C, 68.91; H, 8.41.

Nitriles.—For each gram of oxime, about 10 cc. of acetic anhydride was added, and the solution was heated on the steam-bath for one hour in the preparation of dimethylaminobenzonitrile, and for five hours with the other examples. Water was then added, and the acetic acid solution was neutralized with ammonia, whereupon the crude nitrile precipitated.

***p*-Dimethylaminobenzonitrile.**—The crude product was chromatographed from benzene on activated alumina, and crystallized three times from methanol–water. From 1.67 g. of oxime was obtained 0.42 g. (32%) of the nitrile, m.p. 75–76°; reported[13,14] m.p. 75–76°.

(14) K. Matsumura, THIS JOURNAL, **57**, 955 (1935).

7-Dimethylamino-4-indancarbonitrile.—The crude product was extracted from benzene solution with dilute hydrochloric acid, and then reprecipitated with ammonia. It was then chromatographed from benzene on activated alumina, and crystallized from methanol–water. From 1.5 g. of the oxime was obtained 0.39 g. (29%) of nitrile, m.p. 55–56°.

Anal. Calcd. for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58. Found: C, 77.06; H, 7.67.

4-Dimethylamino-5,6,7,8-tetrahydro-1-naphthonitrile.—The crude product was chromatographed from benzene on activated alumina. From 0.69 g. of the oxime was obtained 0.36 g. (56%) of nitrile, m.p. 46.5–47.5°. After two crystallizations from methanol–water, there remained 0.26 g. (41%) of the desired nitrile; m.p. 46–47°.

Anal. Calcd. for $C_{13}H_{16}N_2$: C, 77.96; H, 8.05. Found: C, 77.84; H, 8.37.

4-Dimethylamino-2,3-xylonitrile.—The crude product was chromatographed from benzene on activated alumina, and crystallized from methanol at −80°. The yield from 0.63 g. of oxime was 0.34 g. (60%) of nitrile, m.p. 25–26°.

Anal. Calcd. for $C_{11}H_{14}N_2$: C, 75.82; H, 8.10. Found: C, 75.52; H, 8.30.

MINNEAPOLIS 14, MINNESOTA RECEIVED JULY 6, 1951

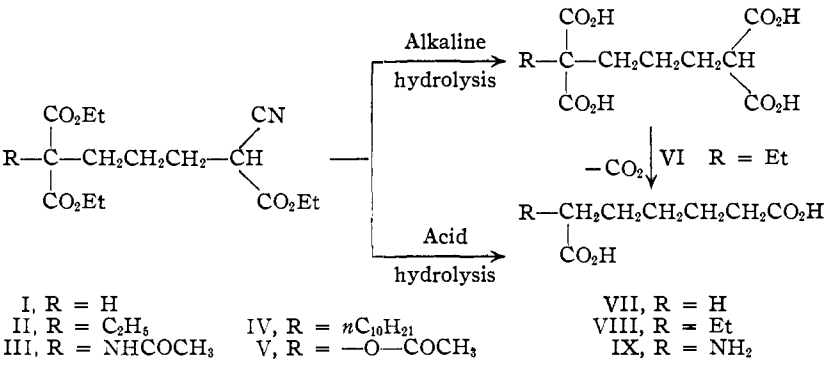
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, GENERAL MILLS, INC.]

Synthesis of Pimelic Acid and α-Substituted Pimelic Acid and Intermediates[1]

BY DONALD T. WARNER AND OWEN A. MOE

Several aldehydo compounds, obtained by 1,4-addition reactions of malonate systems with acrolein, have been utilized in simultaneous condensation–reduction reactions with ethyl cyanoacetate. The resulting products are intermediates in the synthesis of pimelic acid and mono-α-substituted pimelic acids. The hydrolyses of three of the intermediates and the identification of pimelic acid, α-aminopimelic acid and α-ethylpimelic acid are described.

The 1,4-additions of malonate systems to α,β-unsaturated aldehydes have resulted in the convenient preparation of a number of aldehydo compounds.[2] These compounds have been utilized for the preparation of amino acids and other products.[3] In the present work, these aldehydes have been condensed with ethyl cyanoacetate[4] to produce intermediates which may be hydrolyzed to pimelic acid and mono-α-substituted pimelic acids. The results obtained indicate that the aldehydo compounds, although formed by a reversible 1,4-addition reaction, can be conveniently used with the mild alkaline catalysts required in this method.

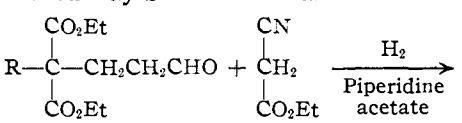


I, R = H
II, R = C_2H_5
III, R = NHCOCH$_3$

IV, R = $nC_{10}H_{21}$
V, R = —O—COCH$_3$

VII, R = H
VIII, R = Et
IX, R = NH_2

The compounds studied and the reactions involved may be illustrated as



All of the aldehydo compounds tested readily undergo a simultaneous condensation–reduction with ethyl cyanoacetate to form the pimelic acid intermediates I–V. We have used alcohol as the solvent for these reductions with satisfactory results. The cyanotricarboxylate products may be purified by distillation without decomposition even at the elevated distillation temperatures which are required in some instances.

Since the yields of the condensation–reduction products are known to be dependent upon the purity of the aldehydo compounds,[4] we have attempted to determine the optimum results when freshly distilled γ,γ-dicarbethoxy-caproaldehyde was employed in the preparation of II. The condensation–reduction product was obtained in a yield of 75% based on the weight of redistilled II.

The cyanotricarboxylate compounds I, II and III

(1) Paper No. 122, Journal Series, Research Laboratories, General Mills, Inc.

(2) For previous references to this work see O. A. Moe, D. T. Warner and M. I. Buckley, THIS JOURNAL, **73**, 1062 (1951).

(3) (a) O. A. Moe and D. T. Warner, *ibid.*, **71**, 1251 (1949); (b) D. T. Warner and O. A. Moe, *ibid.*, **70**, 2765 (1948); (c) D. T. Warner and O. A. Moe, *ibid.*, **70**, 3918 (1948).

(4) E. R. Alexander and A. C. Cope, *ibid.*, **66**, 886 (1944).