benzenes, 1.2 moles of β-naphthol, and a trace of hydrochloric acid together for five and one-half hours. The yield after extracting the mixture with dilute alkali, distilling and crystallizing from methanol was about 40%, m. p. 76–78° and 80–81° after recrystallizing, b. p. 213° (3 mm.). A side product of the reaction was phenyl-β-naphthylamine.

Anal. Calcd. for $C_{20}H_{21}N$: C, 87.27; H, 7.71; N, 5.09. Found: C, 87.30; H, 7.74; N, 5.24.

The Preparation of Methyl-N-phenylanthranilate.—Baeyer and Villiger[17] prepared this compound as an oil in 60% yield by the saturation of a solution of N-phenylanthranilic acid in methanol with dry hydrogen chloride. The following directions give a better yield and also a product which is crystalline.

Dry hydrogen chloride was passed into 963 cc. of methanol until the weight had increased 289 g. One hundred and forty-seven grams (0.69 mole) of N-phenylanthranilic acid was then added and the mixture allowed to stand overnight and then refluxed for three hours. The mixture was cooled, 500 cc. of benzene added, then shaken with water (two volumes) and the layers separated. The water layer was then washed with benzene. The benzene layers were united, washed with dilute caustic until free of acid and finally with water. After drying over potassium carbonate the benzene solution was distilled. The product solidified in the receiver; yield 115 g. (91% after allowing for 27 g. of N-phenylanthranilic acid recovered from the alkaline wash water). After crystallizing from hexane 111 g. of pure product was obtained, m. p. 58–59°.

Anal. Calcd. for $C_{14}H_{13}NO_2$: C, 74.10; H, 5.77; N, 6.17. *Found*: C, 74.11; H, 5.78; N, 6.55.

The compound was also prepared in 93% yield (60% conversion) from the reaction of 21.3 g. (0.1 mole) of phenylanthranilic acid, 6 g. of potassium hydroxide, and 12.6 g. (0.1 mole) of methyl sulfate dissolved in 125 cc. of methanol. The mixture warmed up and after about an hour a considerable amount of solid had separated. It was allowed to stand overnight and worked up as in the case of the hydrochloric acid method.

Summary

1. The nitration of *t*-butylbenzene has been found to yield a mixture of *o*- and *p*-nitro-*t*-butylbenzenes, as reported by Senkowski.

2. *o*-Amino-*t*-butylbenzene was converted into *o*-*t*-butyldiphenylamine, which was also prepared by the reaction of methylmagnesium iodide with methyl-N-phenylanthranilate.

3. The following new diarylamines were prepared: *p*-*t*-butyldiphenylamine, *p*,*p*′-di-*t*-butyldiphenylamine, *p*,*p*′-di-*t*-butyl-N,N′-diphenyl-*p*-phenylenediamine, *p*-*t*-butylphenyl-β-naphthylamine and *p*-*t*-butylphenyl-α-naphthylamine.

4. The method for the preparation of methyl-N-phenylanthranilate was improved.

AKRON, OHIO RECEIVED NOVEMBER 2, 1934

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[17] Baeyer and Villiger, *Ber.*, **37**, 3201 (1904).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF ST. JOHN'S COLLEGE]

The Preparation of Some Normal Aliphatic Thiocyanates

BY PAUL ALLEN, JR.

In connection with other work straight-chain thiocyanates have been prepared to complete the series through the thirteen carbon member. The method of synthesis was to treat an alkyl bromide with potassium thiocyanate in alcohol.

Bromides.—Cyclohexyl, *n*-amyl and *n*-octyl bromides were Eastman Kodak Co. chemicals and were used without further purification. The others were made from the corresponding alcohols using hydrobromic acid.

Alcohols.—The nonyl alcohol was an Eastman product; decyl and dodecyl (lauryl) alcohols were prepared by reduction of the methyl esters[1] of the corresponding acids by sodium and absolute alcohol; undecyl and tridecyl alcohols were made by the reaction between formaldehyde and decyl and dodecyl magnesium bromides, respectively.

Thiocyanates.—The proportions of materials were one mole of bromide to one and a half moles of potassium thiocyanate to about 340 cc. of ethanol. About a third of the potassium salt dissolves in this amount of boiling alcohol. To the mixture, boiling under reflux, was added the alkyl bromide drop by drop; refluxing was continued for two hours. When small quantities of material were involved water was added at this point, without distilling off any of the alcohol, and the mass extracted with ether. The extract was dried over calcium chloride, the ether evaporated off and the residue distilled under vacuum. Usually one fractional distillation sufficed, but in a few cases two were needed to obtain a product boiling over a narrow range.

THIOCYANATES

	Yield, %	B. p., °C.	Pressure, mm.	d_4^{25}	n_D^{25}	Sulfur, % Calcd.	Sulfur, % Found
Amyl	84.5	90–91	16	0.9412	1.4620	24.8	24.8
Octyl	83.5	141–142	19	.9149	1.4642	18.7	18.5
Nonyl	67.3	156–157	19	.9091	1.4649	17.3	17.4
Decyl	95.3	154–155	15	.9047	1.4652	16.1	16.0
Undecyl	86.5	160–161	10	.9007	1.4653	15.0	14.7
Dodecyl	92.9	170–172	10	.8958	1.4657	14.1	14.1
Tridecyl	88.0	173–176	7	.8935	1.4661	13.3	13.1
Cyclohexyl	31.2	111–112	16	1.0402	1.5055	22.7	22.8

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(1) Noller, Millner and Gordon, THIS JOURNAL, **55**, 1227 (1933).

In the preparation of cyclohexyl thiocyanate ammonium thiocyanate was used instead of the potassium salt. This proved to be unsatisfactory due to some of it being carried into the ether extract; it may have been responsible for the low yield.

The thiocyanates are water-white liquids with an ethereal odor, quite strong in the amyl and cyclohexyl but faint in the tridecyl compound.

They are insoluble in water, but readily soluble in ether, carbon tetrachloride, benzene, absolute methyl and ethyl alcohols, glacial acetic acid and ethyl acetate. The mutual solubility with 96% ethanol appears to decrease with increasing molecular weight of the thiocyanate.

Summary

The series of normal aliphatic thiocyanates has been completed through the thirteen carbon member; cyclohexyl thiocyanate has been prepared.

ANNAPOLIS, MARYLAND RECEIVED NOVEMBER 3, 1934

[CONTRIBUTION FROM THE ORGANIC CHEMICAL LABORATORY OF THE UNIVERSITY OF FLORIDA]

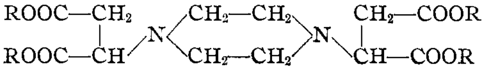
Derivatives of Piperazine. III. Reactions with Unsaturated Esters, Part 1

BY C. B. POLLARD, J. P. BAIN AND DAVID E. ADELSON

Reference to previous work on the addition of amines to esters of fumaric and maleic acids reveals that only two cases have been reported wherein the amine adds to the ethenoid linkage. These are ammonia and methylamine, which yield under drastic conditions aspartic ester and methylaspartic ester, respectively.[1]

More recently Clemo and Graham[2] have reported that methyl maleate is isomerized into the corresponding fumarate in the presence of a variety of primary and secondary amines, including piperazine. They state that no additive complexes involving the ethenoid linkage and the catalyst could be isolated, although they admit that there is no adequate reason why some of the additive complexes should not reach a stable maturity. These authors postulate a mechanism involving a coördinate link between the hydrogen atom of the base and the carbonyl oxygens of the ester. This would lead to an uncertain electronic system and thus to a very unstable complex. In this fashion Clemo and Graham attempt to account for the non-isolation of an intermediate additive compound.

In this paper stable compounds involving the addition of piperazine to the ethenoid linkage of a series of esters of fumaric and maleic acids are described (Table I). The mechanism of the reaction between piperazine and the maleic ester seems to involve two consecutive stages, first, a conversion of the ester from the maleinoid to the fumaroid form, and, second, the addition of the piperazine to the ethenoid linkage of the fumarate. When one mole of anhydrous piperazine is added to two moles of methyl maleate, the latter isomerizes instantly to the fumarate. A mixed melting point determination indicates that a mixture of piperazine and methyl fumarate is now present. Likewise, piperazine can be identified in the mixture by conversion into the 1,4-dinitroso compound.[3] Upon heating this mixture to 100° and subsequently extracting with dioxane, pure piperazino-1,4-bis-(methyl succinate) crystallizes out. When the ester is initially in the fumaroid form, the addition takes place directly. In either case identical compounds are formed resulting from the addition of one molecule of piperazine to two molecules of the ester



Piperazino-1,4-bis-(alkyl succinate)

The reactions are definitely exothermic.

The authors have duplicated the experimental work of Clemo and Graham[2] with special attention to the conversion taking place in the presence of piperazine. That this isomerization does not concern the formation of an additive compound involving the ethenoid linkage is shown by the fact that the type of compound described below does not cause the transformation of pure methyl maleate into the fumarate.

These syntheses are effected by refluxing for a short time 0.05 mole of piperazine and 0.1 mole of the ester in 100 cc. of the appropriate solvent. Upon cooling, the pure additive compound crystallizes out. These compounds can also be made in the proper solvent at room temperature. Either the hexahydrate or the anhydrous form of piperazine may be used, although the latter is preferable in most cases. Anhydrous piperazine may easily be prepared by placing the hexahydrate *in vacuo* over solid potassium hydroxide for one week. The average yield of

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[1] Körner and Menozzi, *Ber.*, **21R**, 86 (1888); **22R**, 735 (1889).

[2] Clemo and Graham, *J. Chem. Soc.*, 213 (1930).

[3] Ladenburg, *Ber.*, **24**, 2401 (1891).