aminopyridine with acrylonitrile, a non-cyclic analog of 2-vinylpyridine, also have failed.[8]

It should be noted that while cyclohexylamine was pyridylethylated in 60% yield under acidic conditions, the same reaction failed when it was attempted earlier[5] under non-catalytic conditions.

The mechanism for the acid-catalyzed pyridylethylation of primary amines is probably the same as that suggested earlier[4] for the analogous reactions with secondary amines.

Experimental

Reaction of Equivalents of Aniline, 2-Vinylpyridine[9] and Acetic Acid in Methanol Solution.—A solution of aniline (85.0 g., 0.914 mole), 2-vinylpyridine (96.0 g., 0.914 mole), glacial acetic acid (54.8 g., 0.914 mole) and 250 ml. of absolute methanol was refluxed for eight hours, allowed to cool to room temperature and then allowed to stand at room temperature for nine hours. The methanol was removed at atmospheric pressure and the reaction mixture was then poured onto ice and made strongly basic with 10% sodium hydroxide solution. The basic solution was extracted with ether, the extracts dried over anhydrous sodium sulfate, the solvent removed at atmospheric pressure and the residue distilled in vacuum to give 142 g. (78%) of 2-(2-anilinoethyl)-pyridine, b.p. 167–168° at 2.5 mm., m.p. 40.6–41.5° (from 60–70° petroleum ether). *Anal.* Calcd. for $C_{13}H_{14}N_2$: C, 78.79; H, 7.07; N, 14.14. Found: C, 78.62; H, 6.78; N, 13.88. The amine gave a monopicrate, m.p. 169.5–170.5° (from 95% ethanol). *Anal.* Calcd. for $C_{19}H_{17}O_7N_5$: N, 16.39. Found: N, 16.45. From this reaction there were also obtained 11.0 g. of 2-vinylpyridine, b.p. 80–82° at 50 mm., 14.7 g. of aniline, b.p. 74–80° at 23 mm., and 12.0 g. of a non-distillable tarry nitrogenous residue. The procedure described above was used in all the pyridylethylations.

Reaction of Aniline with 2-Vinylpyridine Using Clifford's Procedure.—A mixture of aniline (93.0 g., 1.0 mole), 2-vinylpyridine (105 g., 1.0 mole), glacial acetic acid (4.5 g., 0.075 mole) and copper(II) acetate (0.7 g., 0.04 mole) was refluxed for ten hours and then distilled directly to give 126.0 g. (64%) of 2-(2-anilinoethyl)-pyridine, b.p. 166–168° at 2.5 mm., m.p. 40.5–41.4° (from 60–70° petroleum ether); 38.7 g. of aniline, b.p. 58° at 2 mm.; 1.0 g. of 2-vinylpyridine, b.p. 65–70° at 32 mm., and 31.0 g. of a non-distillable tarry nitrogenous residue. Mixed melting points between the pyridylethylated aniline obtained in this experiment with the material of the same melting point obtained in the preceding experiment as well as mixed melting points of their respective monopicrates showed no depression.

Preparation of 2-Pyridylacetanilide.—A solution of ethyl 2-pyridylacetate[7] (10.0 g., 0.06 mole) and aniline (7.5 g., 0.08 mole) was heated at 170° for three hours and then allowed to cool to room temperature. The solid which precipitated was filtered and recrystallized from benzene to give 8.2 g. (65%) of 2-pyridylacetanilide, m.p. 134–135°.[10]

Alkylation of 2-(2-Anilinoethyl)-pyridine with Methyl Iodide.—To an ether solution of phenyllithium, prepared from 5.6 g. (0.8 mole) of lithium ribbon, 62.8 g. (0.4 mole) of bromobenzene and 400 ml. of anhydrous ether, was added 79.2 g. (0.4 mole) of 2-(2-anilinoethyl)-pyridine, dissolved in 100 ml. of anhydrous ether followed by 56.8 g. (0.4 mole) of methyl iodide, dissolved in 100 ml. of anhydrous ether and added at such a rate that the ether refluxed gently. After the addition of the methyl iodide was completed, the reaction mixture was refluxed for one hour, poured onto ice and made strongly basic by 10% sodium hydroxide solution. The mixture was extracted with several portions of ether, the combined extracts were dried over sodium sulfate and the solvent was removed at atmospheric pressure. The residue was distilled in vacuum to give 57.7 g. (65%) of 2-(2-N-methylanilinoethyl)-pyridine, b.p. 148–151° at 3.5 mm., and 19.4 g. of a non-distillable tarry residue. The 2-(2-N-methylanilinoethyl)-pyridine formed a monopicrate, m.p. 167–167.7° alone and when mixed with a sample prepared from the material made by the pyridylethylation of N-methylaniline.[4]

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(8) F. C. Whitmore, H. S. Mosher, R. R. Adams, R. B. Taylor, E. C. Chapin, C. Weisel and W. Yanko, THIS JOURNAL, **66**, 725 (1944).

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The Structure of Tribromophenol Bromide

BY JOHN A. PRICE

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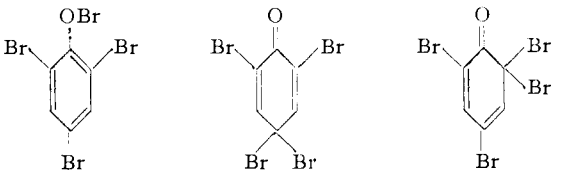
It has not been possible to choose with confidence between the structures I[1] and II[2] for the product obtained from the further bromination of 2,4,6-tribromophenol. However, II appears to be favored by the most recent physical evidence[2c] and the results of Forman and Sears on the halogenation of 3-methyl-4,6-di-*t*-butylphenol[3] and of Coppinger and Campbell on the bromination of 2,6-di-*t*-butyl-4-methylphenol.[4]



I II III

A clear choice in favor of II can be made on the basis of its infrared spectrum, which shows a characteristic strong maximum at 5.99 μ, clearly indicative of a conjugated carbonyl. Infrared absorption at closely similar wave lengths was observed with the related cyclohexadienones studied by Forman and Sears[3] and by Coppinger and Campbell.[4] Furthermore, its ultraviolet spectrum which shows a maximum at 280 mμ, ϵ 9270,[5] allows a choice between the cross-conjugated *p*-quinonoid structure II and the *o*-quinonoid form III in favor of the former. The values show excellent correspondence with those of IV, λ_{max} 274 mμ, ϵ 10,600, and may be contrasted with those of V, λ_{max} 296, ϵ 19,400.[6]

IV V

III would be expected to absorb at even longer wave lengths than V.[7]

Experimental

Tribromophenol bromide was prepared according to Benedikt[1a] and recrystallized from chloroform, m.p. 124°

(1) (a) R. Benedikt, *Ann.*, **199**, 127 (1879); (b) W. M. Lauer, THIS JOURNAL, **48**, 442 (1926); (c) I. Ssuknewitsch and S. Budnitzkii, *J. prakt. Chem.*, **138**, 22 (1933).

(2) (a) J. Thiele and H. Eichwede, *Ber.*, **33**, 673 (1900); (b) J. H. Kastle and R. Speyer, THIS JOURNAL, **27**, 40 (1902); (c) C. H. R. Elston, A. T. Peters and F. M. Rowe, *J. Chem. Soc.*, 367 (1948).

(3) L. E. Forman and W. C. Sears, THIS JOURNAL, **76**, 4977 (1954).

(4) G. M. Coppinger and T. W. Campbell, *ibid.*, **75**, 735 (1953).

(5) Compare the spectrum of the related tribromophenol chloride examined by Elston, Peters and Rowe, ref. 2c, which has λ_{max} 275–280, ϵ 10,000.

(6) L. Dorfman, *Chem. Revs.*, **53**, 47 (1953).

(7) R. B. Woodward, THIS JOURNAL, **64**, 72 (1942).

with evolution of bromine vapor. Additional peaks occur at 6.33, 7.66, 11.08 μ.

Infrared spectra were determined in Nujol mulls in a cell of 0.025-mm. thickness with a Perkin–Elmer spectrophotometer, model 12AB; the slit width in the region of 6 μ was 0.043 mm. Ultraviolet spectra were taken in chloroform on a Cary ultraviolet spectrophotometer, model 11.[8]

(8) These spectra have been deposited as Document number 4614 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance $1.25 for photoprints, or $1.25 for 35 mm. microfilm payable to Chief, Photoduplication Service, Library of Congress.

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Fractionation and Stabilization of Fatty Acid Cyclohexyl Esters by Means of Thiourea[1]

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Previous work showed that fatty acids can be separated from mixtures by fractional inclusion in urea. Furthermore, it was found that inclusion protects autoxidizable fatty acids or esters against attack by oxygen.[2] Experiments showing segregation and protection by thiourea inclusion are reported here. The results show the strong resemblance of thiourea to urea. Mixtures of molecules of equal chain length can be fractionated by means of thiourea according to their degree of unsaturation. As with urea, the more saturated components react preferentially.

These effects were indicated strongly when commercial terpinolene or other terpene mixtures were used to form inclusion compounds with thiourea. Due to the low stability of such adducts it is difficult to obtain results as clear-cut as those obtained with urea and fatty acids. Although McLaughlin and McClenahan reported that thiourea can react with straight chain hydrocarbons,[3] the instability of such compounds doubtless would not permit practical studies of the fractionation and preservation of natural fatty acids or their common esters. Introducing the cyclohexane ring as an ester group, however, enhances greatly the stability of the thiourea–fatty ester compound. It is even possible to bind the cyclohexyl esters of the more unsaturated, autoxidizable fatty acids. These adducts are resistant to attack by oxygen. On the other hand, the same esters, because of their long alkyl chains, still react with urea, and the two including molecules, urea and thiourea, can be compared in their reactions with the same substrate. The components of the mixtures of esters exhibit the same order in their reactivity for both cases. Unsaturation shifts the equilibria toward dissociation for both urea and thiourea inclusion complexes. This is in agreement with previous observations.[4]

Experimental

Cyclohexyl esters of fatty acids were prepared from commercial corn oil and from cottonseed oil by means of alkaline interesterification. The esters boiled at 1 mm. pressure between 168 and 183°, the yields being 70–80%. In a representative experiment, 30 g. of corn oil fatty esters was added to a warm solution of 90 g. of thiourea in 900 ml. of methanol. After cooling slowly and crystallizing at 4°, the precipitate was filtered and dried. The crystals had the typical appearance of thiourea adducts, they weighed 56.2 g. and contained 27% esters (15.1 g.). An additional 60 g. of thiourea was added to the mother liquor and a second fraction was obtained at 4°, which weighed 57.7 g. This fraction contained only 20% esters (11.4 g.) and obviously consisted of adduct and free thiourea. The recovery of the esters from the adducts or from the mother liquor was carried out as with urea compounds.[5] Data for this and other experiments are given in Table I.

TABLE I

FRACTIONATION OF FATTY ACID CYCLOHEXYL ESTERS

Type of esters	Precipitant	Methanol, ml.	Percentage of total esters bound in Fraction 1	Fraction 2	M.L.
30 g. corn oil, I.V. 104	90 + 60 g. thiourea	900	50.4, I.V. 85	38.0, I.V. 121	7.7, I.V. 119
30 g. cottonseed, I.V. 86	90 + 60 g. thiourea	900	48.8, I.V. 58	31.8, I.V. 96	11.3, I.V. 100
30 g. cottonseed, I.V. 86	90 g. thiourea	450	78.2, I.V. 72		18.8, I.V. 115
30 g. cottonseed, I.V. 86	90 g. urea	300	63.2, I.V. 63		30.7, I.V. 123
30 g. cottonseed, I.V. 86	90 g. urea	900	17.1, I.V. 16	8.0,[a] I.V. 45	..., I.V. 108

[a] This fraction was obtained by cooling to −10°. The precipitate contained only 3.8% ester.

The tests for autoxidation were carried out in a Warburg apparatus, as previously described for adducts of urea,[5] or other host molecules.[6] An aliquot of the second adduct fraction described above, equivalent to 60 mg. of cyclohexyl esters, released 372 μl. of gas in 50 hours[7] and showed no further gas release or absorption for an additional 90 hours. In contrast, 100 mg. of the esters recovered from this adduct absorbed 2880 μl. in 77 hours. The rate of autoxidation then was still increasing.

From Table I it is seen that virtually all components of the mixture can be bound by thiourea, whereas urea will not bind the more unsaturated esters. The first fractions of the thiourea adducts contained between 26 and 28% esters. The subsequent fractions always contained considerable amounts of free thiourea.

Terpinolene and thiourea reacted on mixing the components in a mortar in presence of enough methanol to form a thick paste. We failed to establish a reproducible ratio of host to guest molecules. The oxygen uptake of typical samples after two hours in the Warburg apparatus were: commercial terpinolene, 1200 μl.; fraction recovered from adduct, 260 μl.; fraction recovered from mother liquor, 2500 μl; thiourea adduct (17% hydrocarbon), −85 μl. after 30 hours, no change after 10 additional hours.

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(5) H. Schlenk and R. T. Holman, THIS JOURNAL, **72**, 5001 (1950).

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(7) The negative values often encountered in such experiments are discussed in ref. 6.