dichlorophenol, b.p. 105–108° at 24 mm., and 368 g. of β-(2,4-dichlorophenoxy)-ethyl bromide, b.p. 157–159° at 10 mm., $n^{25}D$ 1.5785. The yield based upon the phenol is 69%.

Anal. Calcd. for $C_8H_7BrCl_2O$: C, 35.58; H, 2.59. Found: C, 36.03; H, 2.67.

3-Chlorobenzyl Alcohol.—This material had previously only been reported as being prepared by electrolytic reduction of 3-chlorobenzoic acid.[6] A more convenient laboratory procedure is as follows. In a 3-liter 3-neck flask equipped with stirrer, reflux condenser and dropping funnel there was prepared a solution of 52 g. (1.38 moles, 50% excess) of lithium aluminum hydride in 500 ml. of anhydrous ether. To this stirred solution there was added over a 2-hr. period, a slurry of 192 g. (1.23 moles) of 3-chlorobenzoic acid in 800 ml. of ether. The excess hydride was then carefully decomposed by dropwise addition of about 150 ml. (excess) ethyl acetate. The flask was cooled in an ice-bath and a stream of iced concentrated hydrochloric acid was slowly added. After vigorous stirring the solids partially dissolved into the aqueous layer. The ether was removed by decantation and 600 ml. of 10% sulfuric acid was added to the aqueous phase. This dissolved the remaining aluminum salts. The solution was washed with ether and both ether solutions combined. The ether was washed successively with water, potassium carbonate and dilute ferrous sulfate. The ether was removed by distillation and 3-chlorobenzyl alcohol was obtained as a white liquid, b.p. 131–132° at 19 mm. (lit.[6] value, 234° at atm. pressure), $n^{25}D$ 1.5521, yield 159 g. or 91%.

3-Chlorobenzyl Chloride and 3-Chlorobenzyl Ether.—The chloride had been prepared previously by the chlorination of toluene.[7] In our hands the following was a more convenient synthesis. To 100 g. (excess) of thionyl chloride in 100 ml. of benzene there was added 52 g. (0.36 mole) of 3-chlorobenzyl alcohol over a 10-min. period. The solvent and excess thionyl chloride were removed by distillation. There was obtained 34 g. (60%) of 3-chlorobenzyl chloride, b.p. 101–103° at 17 mm. (lit.[7] value, 104° at 17 mm.), $n^{25}D$ 1.5526.

Fractionation of the high-boiling pot residue yielded 8 g. (17%) of 3-chlorobenzyl ether, b.p. 195–199° at 4 mm., $n^{25}D$ 1.5787.

Anal. Calcd. for $C_{14}H_{12}Cl_2O$: C, 62.92; H, 4.50. Found: C, 62.95; H, 5.00.

Procedure for Herbicidal Assay.—The method is substantially that described by Thompson, *et al.*,[4] with the modifications noted by Schlesinger and Mowry.[8] Where compounds were tested with wheat, the procedure was the same except for substitution of wheat seeds for cucumber seeds in the petri dishes. The data obtained are listed in Table III.

Acknowledgment.—The authors wish to express their gratitude to Mrs. Emma Mori, Mr. Richard Martin and Dr. R. M. Hedrick for the herbicidal evaluation data and to Miss Mary Neal, Mrs. Betty Kosicki, Mrs. Winifred Harden, and Messrs. Paul Adams and Donald Stoltz for the microanalyses.

(6) C. Mettler, *Ber.*, **38**, 1745 (1905).

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(8) A. Schlesinger and D. Mowry, THIS JOURNAL, **73**, 2614 (1951).

DAYTON, OHIO

[CONTRIBUTION FROM STERLING-WINTHROP RESEARCH INSTITUTE]

Alkylaminoalkylamino Derivatives of Xanthones, Acridones and Anthraquinones

BY S. ARCHER, LOIS B. ROCHESTER AND MARY JACKMAN

RECEIVED SEPTEMBER 8, 1953

The three series mentioned in the title were prepared from appropriately halogenated nuclei and substituted alkylenediamines. The acridones and anthraquinones were ineffective schistosomicidal agents but moderately high activity against *S. mansoni* infections in mice was found among the xanthones.

At the time that we were preparing a series of basic thiaxanthones[1] for evaluation as schistosomicidal drugs we synthesized three groups of isosteric compounds in which the sulfur atom of the thiaxanthone nucleus was replaced by oxygen, imino and carbonyl groups to furnish the corresponding xanthones, acridones and anthraquinones. The description of the preparation of these substances and some of the preliminary chemotherapeutic results form the basis of this report.

Heller[2] prepared 1-chloro-4-methylanthraquinone and demonstrated the lability of the halogen by effecting a replacement reaction with aniline at high temperature.[3] We found that a 1-chloroanthraquinone and an alkylenediamine such as diethylaminopropylamine reacted smoothly in pyridine solution within a few hours to give the desired 1-aminoanthraquinone which was isolated and purified as the hydrochloride. The compounds listed in Table I were all prepared according to this general technique.

The 1-chloroacridones needed in this work were prepared by the customary Ullmann method. Since Nisbet[4] reported that a 1-piperidinoacridone could be prepared from piperidine and a 1-chloroacridone it seemed likely that the method used successfully for the synthesis of the basic anthraquinones could be used here. When a pyridine solution of 3-diethylamino-2-hydroxypropylamine and 1-chloro-4-methylacridone was refluxed for 16 hours only starting material was isolated from the reaction mixture. By omitting the pyridine it was possible to raise the reaction temperature sufficiently to permit the condensation to take place in a reasonable time. The method adopted for preparing the compounds listed in Table II is described in the Experimental part.

Mauss[5] prepared many 1-(2-dialkylaminoalkylamino)-xanthones, at least two of which showed high schistosomicidal activity. These were 1-(2-diethylaminoethylamino-4-methylxanthone (III, R = H) and the corresponding 7-chloro (III, R = Cl) derivative. The required nuclei (II) were prepared from 2-methyl-5-chlorophenol[6] and an appropriate 2-halobenzoic acid followed by ring closure of the intermediate phenoxybenzoic acid

(1) S. Archer and C. M. Suter, THIS JOURNAL, **74**, 4296 (1952).

(2) G. Heller and K. Schülke, *Ber.*, **41**, 3627 (1908).

(3) G. Heller, *ibid.*, **45**, 792 (1912).

(4) H. B. Nisbet, *J. Chem. Soc.*, 2772 (1932).

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(6) Th. Zincke and O. Preiss, *Ann.*, **417**, 207 (1918).

TABLE I

1-(DIALKYLAMINOALKYLAMINO)-ANTHRAQUINONE HYDROCHLORIDES

Anthraquinone	M.p., °C. (cor.)	Solvent	Formula	Nitrogen, % Calcd.	Nitrogen, % Found	Chlorine, % Calcd.	Chlorine, % Found
1-$(C_2H_5)_2NCH_2CH_2CH_2NH$,4-$CH_3$[a]	216.2–217.4	EtOH–ether	$C_{22}H_{26}N_2O_2 \cdot HCl$	7.24	7.20	9.16	9.15
1-$(C_2H_5)_2NCH_2CHOHCH_2NH$,4-$CH_3$	234–236	EtOH–ether	$C_{22}H_{26}N_2O_3 \cdot HCl$	6.97	6.84	8.82	9.13
1-$(C_2H_5)_2NCH_2CH_2CH_2CH_2NH$,4-$CH_3$	210–212	EtOH–ether	$C_{23}H_{28}N_2O_2 \cdot HCl$	6.99	6.96	8.85	9.05
1-$(C_2H_5)_2NCH_2CHOHCH_2NH$	211.5–212.5	EtOH–ether	$C_{21}H_{24}N_2O_3 \cdot HCl$	7.19	7.07	9.12	8.95
1-$(C_2H_5)_2NCH_2CH_2CH_2NH$	226.5–228.5	EtOH	$C_{21}H_{24}N_2O_2 \cdot HCl$	7.51	7.39	9.51	9.45
1-$(C_2H_5)_2NCH_2CH_2NH$	224–226	EtOH–ether	$C_{20}H_{22}N_2O_2 \cdot HCl$	7.81	7.60	9.88	9.60
1-$(C_2H_5)_2NCH_2CH_2CH_2NH$,3-Cl[b]	243.8–245	EtOH	$C_{21}H_{23}ClN_2O_2 \cdot HCl$	6.88	6.73	17.41	17.30
1-$(C_2H_5)_2NCH_2CHOHCH_2NH$,3-Cl[b]	240.5–242.6	EtOH	$C_{21}H_{23}ClN_2O_3 \cdot HCl$	6.62	6.49	16.75	16.49
1-$(C_4H_9)_2NCH_2CH_2NH$,4-CH_3	159–160	EtOH–acetone	$C_{25}H_{32}N_2O_2 \cdot HCl$	6.53	6.33	8.27	8.22

[a] The 1-chloro-4-methylanthraquinone was prepared by the method of Heller (ref. 2). [b] The 1,3-dichloroanthraquinone was prepared according to Goldberg, *J. Chem. Soc.*, 2829 (1931).

TABLE II

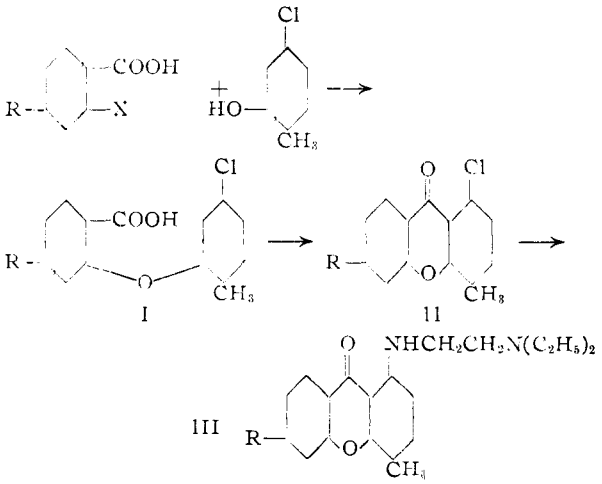
1-(DIALKYLAMINOALKYLAMINO)-ACRIDONES AND THEIR HYDROCHLORIDES

Acridone	M.p., °C. (cor.)	Solvent	Formula	Nitrogen, % Calcd.	Nitrogen, % Found	Chlorine, % Calcd.	Chlorine, % Found
1-$(C_2H_5)_2NCH_2CH_2CH_2NH$,4-Cl[a]	238.5–239	EtOH	$C_{20}H_{24}ClN_3O \cdot HCl$	10.66	10.38	17.98	17.80
1-$(C_2H_5)_2NCH_2CH_2CH_2(CH_3)CHNH$,4-Cl[a]	245–246.6	EtOH	$C_{22}H_{28}ClN_3O \cdot HCl$	9.77	9.67	16.82	16.62
1-$(C_2H_5)_2NCH_2CHOHCH_2NH$,4,6-di-Cl	160–162	Benzene–ligroin	$C_{20}H_{23}Cl_2N_3O$	10.29	10.11	17.37	17.11
1-$(C_2H_5)_2NCH_2CH_2CH_2NH$,3-Cl	269.8–270.8	EtOH–H_2O	$C_{20}H_{24}ClN_3O \cdot HCl$	10.66	10.57	17.98	17.88
1-$(C_2H_5)_2NCH_2CH_2CH_2NH$,4,6-di-Cl	256–258	EtOH	$C_{20}H_{22}Cl_2N_3O \cdot HCl$	9.85	9.75	24.93	24.69
1-$(C_4H_9)_2NCH_2CH_2NH$,4-CH_3	197.8–200	EtOH	$C_{24}H_{33}N_3O \cdot HCl$	10.10	9.77	8.52	8.24
1-$(C_4H_9)_2NCH_2CH_2NH$,4-CH_3,6-Cl	146.8–148.1	EtOH	$C_{24}H_{32}ClN_3O$	10.15	9.97	8.56	8.79

[a] 1,4-Dichloroacridone, Nisbet (ref. 4).

(I). The xanthones were then caused to react with diethylaminoethylamine in a closed system at elevated temperature to produce the compounds of formula III.

We prepared the desired 1-chloroxanthones (II) according to the usual methods. In the preparation of 1-chloro-4-methyl-6-methoxyxanthone (II, R = OCH_3) Mauss effected ring closure of the corresponding phenoxybenzoic acid (I, R = OCH_3) through the acid chloride. It was found that a one-step cyclization of the acid (I, R = OCH_3) could be carried out in sulfuric acid in fair yield with little loss due to sulfonation. The condensation between the diamines and the chloroxanthones was performed in open vessels by the methods described previously for the preparation of the thiaxanthones.[1] The diamines were available from the previous work.[1] The biologically more interesting xanthones are described in Table III.



Chemotherapeutic Results.—The method used for the evaluation of schistosomicidal agents was worked out by Berberian, Dennis and Freele of this Laboratory.[7] Two of the drug standards that were used were Miracil D[5] 1-(2-diethylaminoethylamino)-4-methylthiaxanthone and 1-(2-dibutylaminoethylamino)-4-methylthiaxanthone. The ED_{50} values for these drugs were 55 and 100 mg./kg., respectively. The dibutylamino homolog was interesting because of its low systemic toxicity which resulted in a rather favorable therapeutic index.

Most of the acridones and anthraquinones that are shown in Tables I and II were prepared before side chains having the structural requirements for high activity were discovered. Even the compounds which corresponded most closely to the active thiaxanthones, namely, 1-(2-dibutylaminoethylamino)-4-methylacridone and 1-(2-dibutylaminoethylamino)-4-methylanthraquinone, were ineffective at all dose levels tested.

Some of the xanthones listed in Table III showed considerable schistosomicidal activity. Of particular interest was number 10 which was active at doses of 25–50 mg./kg. Numbers 1, 8 and 12 were about half as effective. However, the thiaxanthones corresponding to these xanthones were all active at doses lower than 25 mg./kg.

(7) D. Berberian, E. W. Dennis and H. Freele, to be published. We wish to thank our colleagues for making available the biological results. Drug activity is expressed in terms of mg./kg. necessary to kill 50% of the adult worms of *S. mansoni* present in the infected mice. This value is the ED_{50} and has been used for comparative purposes in the preliminary screening. In the more intensive studies on the highly active drugs the minimum effective dose needed to kill all the worms was also determined.

TABLE III

1-(ALKYLAMINOALKYLAMINO)-XANTHONE HYDROCHLORIDES

No.	Xanthone	M.p., °C. (cor.)	Solvent	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
1	1-HOCH$_2$CH$_2$(C$_2$H$_5$)NCH$_2$CH$_2$NH, 4-CH$_3$, 6-Cl	202.7–203.7	EtOH	$C_{20}H_{25}ClN_2O_3$·HCl	58.40	58.46	5.88	6.04	6.81	6.80
2	1-HOCH$_2$CH$_2$(C$_2$H$_5$)NCH$_2$CH$_2$NH, 4-CH$_3$	178.1–181.5	EtOH	$C_{20}H_{24}N_2O_3$·HCl[a]					7.43	7.29
3	1-CH$_3$CHOHCH$_2$NHCH$_2$CH$_2$NH, 4-CH$_3$	203.6–205	EtOH	$C_{19}H_{22}N_2O_3$·HCl	62.89	63.14	6.39	6.67	7.72	7.98
4	1-CH$_3$CH$_2$CHOHCH$_2$NHCH$_2$CH$_2$NH, 4-CH$_3$	191–191.6	EtOH	$C_{20}H_{24}N_2O_3$·HCl	63.73	64.02	6.69	6.57	7.43	7.53
5	1-(CH$_3$)$_2$COHCH$_2$NHCH$_2$CH$_2$NH, 4-CH$_3$	220–221	EtOH	$C_{20}H_{24}N_2O_3$·HCl	63.73	63.57	6.69	6.57	7.43	7.23
6	1-(CH$_3$)$_2$COHCH$_2$NHCH$_2$CH$_2$NH, 4-CH$_3$, 6-Cl	254.2–254.8	EtOH	$C_{20}H_{23}ClN_2O_3$·HCl	58.40	58.70	5.88	5.77	6.81	6.84
7	1-CH$_3$CHOHCH$_2$(CH$_3$)NCH$_2$CH$_2$NH, 4-CH$_3$, 6-Cl	216–218	EtOH	$C_{20}H_{23}ClN_2O_3$·HCl	58.40	58.63	5.88	5.90	6.81	6.84
8	1-HOCH$_2$CH$_2$(C$_2$H$_5$)NCH$_2$CH$_2$NH, 4,6-di-CH$_3$	197.9–199.3	EtOH	$C_{21}H_{26}N_2O_3$·HCl	64.52	64.44	6.96	6.74	7.17	6.96
9	1-CH$_3$CH$_2$CHOHCH$_2$NHCH$_2$CH$_2$NH, 4-CH$_3$, 6-Cl	239–244	EtOH–ether	$C_{20}H_{23}ClN_2O_3$·HCl[b]					6.81	6.75
10	1-(CH$_3$)$_2$COHCH$_2$(C$_2$H$_5$)NCH$_2$CH$_2$NH, 4-CH$_3$, 6-Cl	210.4–212.4	EtOH–ether	$C_{22}H_{27}ClN_2O_3$·HCl[c]					6.38	6.26
11	1-HOCH$_2$CH$_2$(C$_2$H$_5$)NCH$_2$CH$_2$NH, 4-CH$_3$, 6-OCH$_3$	185.5–188	EtOH	$C_{21}H_{26}N_2O_4$·HCl[d]					6.89	6.86
12	1-CH$_3$CHOHCH$_2$(C$_2$H$_5$)NCH$_2$CH$_2$NH, 4-CH$_3$, 6-Cl	169.7–172.7	EtOH	$C_{21}H_{25}ClN_2O_3$·HCl[e]					6.59	6.71
13	1-CH$_3$CHOHCH$_2$(C$_4$H$_9$)NCH$_2$CH$_2$NH, 4-CH$_3$, 6-Cl	138–143	EtOH–ether	$C_{23}H_{29}ClN_2O_3$·HCl[f]					6.18	5.90

[a] Calcd.: Cl, 9.41. Found: Cl, 9.29. [b] Calcd.: Cl, 17.04. Found: Cl, 17.04. [c] Calcd.: Cl, 16.14. Found: Cl, 15.99. [d] Calcd.: Cl, 8.71. Found: Cl, 8.90. [e] Calcd.: Cl, 16.68. Found: Cl, 16.89. [f] Calcd.: Cl, 15.64. Found: Cl, 15.68.

Experimental[8]

3-Chloro-1-(3-diethylaminopropylamino)-anthraquinone Hydrochloride.—A mixture of 12 g. of 1,3-dichloroanthraquinone, 12 g. of 3-diethylaminopropylamine and 50 ml. of pyridine was refluxed for three hours and then steam distilled. The residue was taken up in ether and the red organic layer was washed with dilute hydrochloric acid. The aqueous layer was made alkaline and the product that separated was dissolved in chloroform. The dried chloroform solution was concentrated to leave a dark red residue which was dissolved in dry ether and then treated with alcoholic hydrogen chloride. The red powder that separated was filtered and dried; wt. 12.0 g. Upon recrystallization from alcohol the salt was obtained as bright red plates, m.p. 243.8–245° (cor.); wt. 9.0 g.

The other compounds described in Table I were prepared by essentially the same procedure.

1-Chloro-4-methylacridone.—A mixture of 21.4 g. of potassium *o*-bromobenzoate, 12.5 g. of 1-amino-4-chlorotoluene, 0.5 g. of copper powder and 50 ml. of amyl alcohol was stirred and refluxed for four hours, cooled and steam distilled. The residue was filtered and the solid was taken up in hot acetic acid and treated with Darco G-60. The filtrate was copiously diluted with water to precipitate 11.0 g. of the partially purified diphenylaminecarboxylic acid. The crystalline solid was dissolved in 83 ml. of sulfuric acid and the red solution was then heated on the steam-bath for 20 minutes. The reaction mixture was cooled and poured into a large volume of water. The acridone was collected on a filter and suspended in hot sodium carbonate solution. The crude acridone was recrystallized from dilute acetic acid to afford 7.8 g. of the pure substance, m.p. 298–300° (uncorr.) (Nisbet[7] reports m.p. 297–298°).

Anal. Calcd. for $C_{14}H_{10}ClNO$: Cl, 14.56. Found: Cl, 14.18.

1,4,6-Trichloroacridone.—Six grams of crude 2-(2′,5′-dichlorophenylamino)-4-chlorobenzoic acid (obtained from potassium 2,4-dichlorobenzoate and 2,5-dichloroaniline in the manner described directly above) was cyclized in sulfuric acid to furnish the corresponding trichloroacridone. After recrystallization from acetic acid 4.3 g. of the product was obtained, m.p. 242–243° (uncor.).

Anal. Calcd. for $C_{12}H_6Cl_3NO$: Cl, 35.63; N, 4.68. Found: Cl, 35.53; N, 4.56.

1,3-Dichloroacridone.—A mixture of 45 g. of potassium *o*-bromobenzoate and 30 g. of 3,5-dichloroaniline and 1.0 g. of copper powder suspended in 100 ml. of refluxing amyl alcohol furnished 28 g. of the crude diphenylaminecarboxylic acid. Cyclization of 26 g. of this acid in 170 ml. of sulfuric acid yielded 22 g. of the acridone. The analytical sample was obtained by recrystallization of the crude substance from pyridine, m.p. 310°.

Anal. Calcd. for $C_{13}H_7Cl_2NO$: Cl, 26.81; N, 5.3. Found: Cl, 26.48; N, 5.0.

4,6-Dichloro-1-(3-diethylamino-2-hydroxypropylamino)-acridone.—A mixture of 20 g. of 1,4,6-trichloroacridone and 50 g. of 3-diethylamino-2-hydroxypropylamine was heated under reflux for two hours and then cooled. The mixture was treated with a small amount of aqueous sodium hydroxide and then steam distilled. The residue, which had solidified on cooling, was filtered and dissolved in dilute hydrochloric acid. The solution was clarified by filtration and the filtrate was made alkaline. The crystalline product which separated was filtered and recrystallized from dilute ethanol to yield 20 g. of the base, m.p. 147–153°. After repeated crystallization from ethanol and then benzene–ligroin the pure product, m.p. 160–162° (cor.), was obtained.

The compounds listed in Table II were prepared by this method. The method was modified when hydrochlorides were prepared. After steam distillation the product was separated from any unreacted acridone with dilute hydrochloric acid. The acid solution was made alkaline and the liberated base was dissolved in chloroform. The oil layer was taken to dryness and the residue was dissolved in ether. The hydrochloride was precipitated with the aid of alcoholic hydrogen chloride.

When a condensation was attempted with 3-diethylamino-2-hydroxypropylamine and 1-chloro-4-methylacridone in the presence of pyridine, complete dissolution of the acridone was not observed after two hours of refluxing. Heating was continued for about another 16 hours but after the usual work-up only starting material was recovered.

1-Chloro-6-methoxy-4-methylxanthone.—A solution of 16.4 g. of 2-(5′-chloro-2′-methylphenoxy)-4-methoxybenzoic acid in 89 ml. of sulfuric acid was stirred and heated on the steam-bath for 50 minutes. The whole was poured into ice-water and then filtered. The solid was heated with dilute ammonium hydroxide and the suspension was filtered hot. The crude xanthone was recrystallized from acetic acid, wt. 10.3 g. (67%), m.p. 175–177° (uncor.) (Mauss[5] reports m.p. 176–177°).

1-(2-N-[2-Hydroxyethyl]-N-ethylamino)-ethylamino-4-methylxanthone Hydrochloride.—Six grams of 1-chloro-4-methylxanthone, 6 g. of N-(2-hydroxyethyl)-N-ethylethylenediamine and 6 g. of pyridine were refluxed overnight. To the cooled orange solution there was added 3 ml. of 50% potassium hydroxide solution. The mixture was steam distilled and the red oil that remained crystallized when cooled

(8) Analyses were carried out under the supervision of Messrs. M. E. Auerbach and K. D. Fleischer.

and then was covered with aqueous acetone. The solid was collected and dissolved in hot acetic acid. An equal volume of water was added to the solution to precipitate any unreacted xanthone. The neutral material was removed by filtration and the filtrate was then made alkaline. The product which separated was dissolved in chloroform. The solution was evaporated *in vacuo* to leave an oil which was dissolved in absolute alcohol. The alcohol solution was treated with dry hydrogen chloride whereupon the desired xanthone hydrochloride separated. After crystallization from absolute ethanol there was obtained 4.4 g. of the desired salt in a state of satisfactory purity, m.p. 178.5–181° (cor.).

The xanthones reported in Table III were prepared by the above method or some minor modification thereof.

RENSSELAER, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF DELAWARE]

The Effect of Alkali on Linear Polyurethans[1]

BY ELIZABETH DYER AND GEORGE W. BARTELS, JR.[2]

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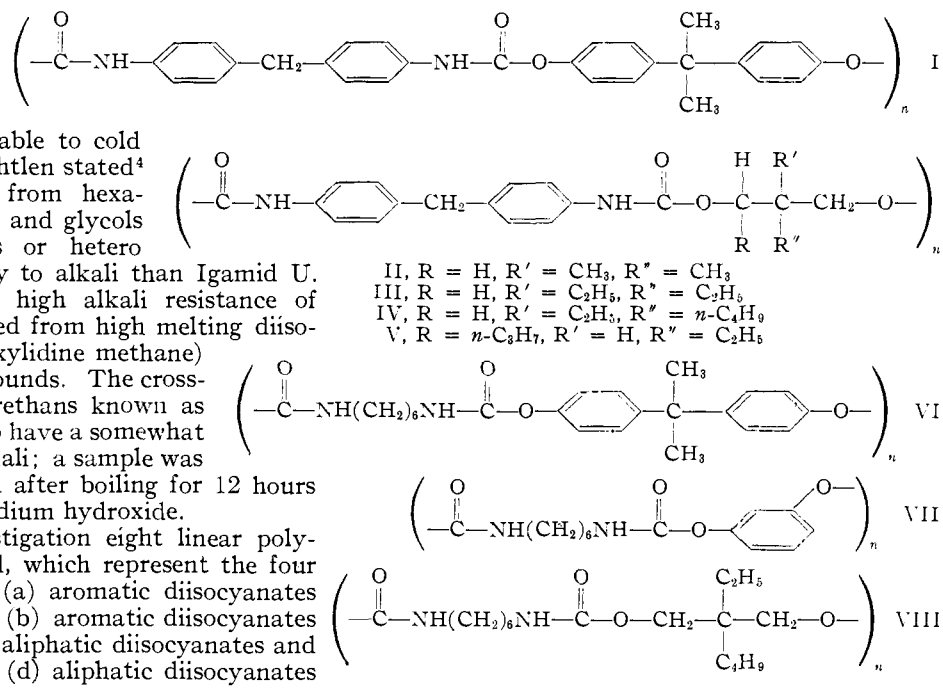
New polyurethans have been prepared by the reaction of methylene-bis-(4-phenyl isocyanate) and hexamethylene diisocyanate with various branched 1,3-diols and with two dihydric phenols. The polyurethans made from aliphatic diols were unaffected by 1% sodium hydroxide at 50°, whereas the polyurethans from phenols were attacked. Quantitative determinations were made of the hydrolysis products, which included carbon dioxide, the diamine, the phenol and a polyurea. The polyurea was shown to result from the action of the diamine on unchanged polyurethan.

The behavior of polyurethans toward alkali has been mentioned, but not described in detail. The fibrous polyurethan obtained by the action of hexamethylene diisocyanate on 1,4-butanediol (Igamid U) was reported[3] to be stable to cold and hot alkalies. Höchtlen stated[4] that polymers made from hexamethylene diisocyanate and glycols containing side chains or hetero atoms had less stability to alkali than Igamid U. Bayer mentioned[5] the high alkali resistance of molded plastics prepared from high melting diisocyanates (such as di-*p*-xylidine methane) and polyhydroxy compounds. The cross-linked polyester–polyurethans known as Vulcollans were said[6] to have a somewhat limited resistance to alkali; a sample was completely decomposed after boiling for 12 hours in contact with 15% sodium hydroxide.

In the present investigation eight linear polyurethans were prepared, which represent the four types obtainable from (a) aromatic diisocyanates and dihydroxy phenols, (b) aromatic diisocyanates and aliphatic diols, (c) aliphatic diisocyanates and dihydroxy phenols and (d) aliphatic diisocyanates and aliphatic diols.

These polyurethans were obtained from the interaction of the diisocyanate and the dihydroxy compound either in solution[5,7] using triethylamine as catalyst or in a melt[5,8] with no solvent and no catalyst. Polymers I, II and III were prepared by the solution method in yields of 73–95%, while the others were obtained by bulk polymerization in nearly quantitative yields. The chief advantage of the bulk method was the avoidance of products which differed from the desired polyurethans in having higher nitrogen contents, and decreased solubility and film-forming characteristics. It is probable that these products contained a homopolymer of the diisocyanate, since methylene-bis-(4-phenyl isocyanate) was shown to form an insoluble self-addition product in solvents containing triethylamine. The absence of such homopolymers in the polyurethans II–IX was shown by the fact that these substances were completely soluble in acetone, a non-solvent for the isocyanate homopolymer.



The properties of the polyurethans are given in Table I. The polymers were rather brittle in nature, formed films and frequently fibers, but had no

(1) From the Ph.D. dissertation of George W. Bartels, Jr., University of Delaware, Sept., 1953.

(2) Armstrong Cork Company Research Fellow, 1951–1953.

(3) J. DeBell, W. Goggin and W. Gloor, "German Plastics Practice," DeBell and Richardson, Cambridge, Mass., 1946, p. 305.

(4) A. Höchtlen, *Kunststoffe*, **42**, 303 (1952).

(5) O. Bayer, *Angew. Chem.*, **59**, 257 (1947).

(6) O. Bayer, E. Müller, S. Petersen, H. F. Piepenbrink and E. Windemuth, *ibid.*, **62**, 65 (1950).

(7) C. S. Marvel and J. H. Johnson THIS JOURNAL, **72**, 1674 (1950).

(8) J. H. Brewster, *ibid.*, **73**, 368 (1951).