NOTES

Di-*n*-propylgermanium Esters, Halides, Oxide and Sulfate

By Herbert H. Anderson[1]

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To previously prepared alkylgermanium oxides, esters, halides and sulfates[2] there is now added di-*n*-propylgermanium oxide trimer and some derivatives. Bis-(tri-*n*-propylgermanium) oxide is converted into tri-*n*-propylgermanium fluoride, which upon bromination and subsequent hydrolysis yields a mixture of di-*n*-propylgermanium oxide and bis-(tri-*n*-propylgermanium) oxide; this procedure follows the Flood method.[3] These oxides must be converted into fluorides (or conceivably even chlorides) for easy separation by distillation; the hydrolysis of pure di-*n*-propylgermanium difluoride yields pure di-*n*-propylgermanium oxide, which oxide is trimeric according to molecular weight determinations. This trimeric oxide melts at 5.8°, but upon standing changes into a form melting at 153°—which when melted reverts to the form melting at 5.8°. Thus the new oxide resembles diethylgermanium oxide.

Table I

Properties of New Di-*n*-propylgermanium Derivatives

Compound[a]	B.p., °C.	M.p., °C.	d^{20}_4	n^{20}	Mol. wt. (camphor) Calcd.	Found	Halogen or ester, % Calcd.	Found	Distilled at °C.	Mm.
$(n\text{-}Pr_2GeO)_3$	320	5.8	1.240	1.4730	524	500	(41.5	40.8% Ge)	148–149	1
$n\text{-}Pr_2GeF_2$	182.8	0.5	1.248	1.4128	196.8	204	19.3	19.3, 19.2	181.8–182.1	764[b]
$n\text{-}Pr_2GeCl_2$	209.5	−45.0	1.275	1.4725	229.7	222	30.9	31.1, 31.0	209.4–210.2	777
$n\text{-}Pr_2GeBr_2$	240.5	−52.0	1.689	1.5173	318.5	324	50.2	50.2, 50.2	111.8–112.3	12
$n\text{-}Pr_2GeI_2$	276.5	−53.5	2.024	....	412.6	400	61.5	61.3, 61.5	128.2–128.6	9
$n\text{-}Pr_2Ge(CH_3COO)_2$	244.6	35.6	...	....	276.8	260	42.6	42.2	89	1
$n\text{-}Pr_2Ge(CH_2ClCOO)_2$	296 dec.	....	1.374	1.4793	345.8	260	54.1	54.4	143–145	2
$(n\text{-}Pr_2GeSO_4)_2$	.....	129	...	....	509.7	470	37.7	37.4		

[a] All compounds are colorless. Molar refractions in white light, oxide to bromide, 39.6, 39.3, 50.5, 57.1 ml., respectively (n^2 formula); monochloroacetate, 71.1. [b] B.p. of fluoride at 764 mm. is uncorrected.

This method of preparing di-*n*-propylgermanium oxide is tedious, but avoids any possible rearrangement of propyl into isopropyl groups.

Di-*n*-propylgermanium oxide nearly quantitatively furnishes di-*n*-propylgermanium dichloride, dibromide and diiodide with concentrated halogen acid, or furnishes the diacetate with acetic anhydride. Transesterification of the diacetate with monochloroacetic acid gives di-*n*-propylgermanium bis-(monochloroacetate), while transesterification of the monochloroacetate with a slight deficiency of 100% sulfuric acid gives dimeric di-*n*-propylgermanium sulfate.

In transesterifications the less volatile acid displaces the more volatile acid apparently without regard for dissociation constants[2,4] which are so important in esterifications; in preparing an organogermanium sulfate by transesterification rather than by esterification water is not a product and cannot hydrolyze the sulfate.

Experimental

Table I presents the numerical data.

Di-*n*-propylgermanium Difluoride.—Tri-*n*-propylgermanium fluoride, b.p. 203°, was prepared from 40 g. of bis-(tri-*n*-propylgermanium) oxide and excess 48% hydrofluoric acid in a transparent plastic container; after extraction of the fluoride with (30–60°) petroleum ether and evaporation of the solvent, the fluoride was treated with 0.5 g. of iron powder and 33 g. of bromine, added stepwise, with reflux for six hours on a steam-bath. Following hydrolysis with alkali, then extraction with petroleum ether, 29 g. of oxides inseparable by distillation resulted. However, when converted into fluorides and then distilled under 760 mm. pressure, 10.2 g. of di-*n*-propylgermanium difluoride boiled at 182° and 8.8 g. of tri-*n*-propylgermanium fluoride boiled at 201°.

Thirty grams of tri-*n*-propylgermanium fluoride and 10 g. of iodine did not react at the boiling point of the mixture, even in the presence of aluminum iodide. This mixture, plus 0.3 g. of iron powder and 24 g. of bromine, was heated 16 hours on the steam-bath; after alkaline hydrolysis, the resultant oxides were converted into fluorides, yielding 13 g. of di-*n*-propylgermanium difluoride and 4 g. of tri-*n*-propylgermanium fluoride.

Distillation of 19 g. of 80% pure di-*n*-propylgermanium difluoride in a total-reflux, variable-takeoff column, 50 cm. long and 8 mm. i.d., filled with stainless steel helices yielded 1.9 g. boiling at 181–182°, 7.5 g. of pure difluoride at 181.8–182.1°, 3.9 g. at 182.1–182.8°, 1.6 g. at 183–191° and 3.8 g. higher boiling; all temperatures are uncorrected, at 764 mm. pressure.

Trimeric Di-*n*-propylgermanium Oxide.—Hydrolysis of 8.5 g. of the pure difluoride with 30 g. of 20% aqueous sodium hydroxide and then extraction of the solution with carbon tetrachloride, followed by evaporation of the solvent, gave 7.4 g. of a colorless liquid oxide distilling at 148–149° under 1 mm. pressure. Trimeric, the oxide melts at 5.8°, but slowly changes into another form melting at about 153°; in melting the 153° form reverts to the form melting at 5.8°.

Di-*n*-propylgermanium Dichloride and Dibromide.—In each case a mixture of 5.6 g. of di-*n*-propylgermanium oxide and 23 g. of concentrated halogen acid was heated to boiling, then cooled for two hours and extracted with petroleum ether. After distilling the solvent, approximately 0.2 g. of the oxide was added to react with free hydrogen halide, and the product distilled, with a quantitative yield.

Di-*n*-propylgermanium Diiodide.—A mixture of 5.6 g. of the oxide and 33 g. of freshly-prepared 48% hydriodic acid was shaken thoroughly at 70°, let stand overnight and extracted with petroleum ether. Dried over sodium sulfate, the solution finally gave a 96% yield of the diiodide after removal of solvent.

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[1] 1932 Commonwealth Ave., Auburndale 66, Mass.

[2] H. H. Anderson, This Journal, **71**, 1799 (1949); **72**, 194, 2089 (1950); **73**, 5439, 5440 (1951).

[3] E. A. Flood, *ibid.*, **54**, 1665 (1932).

[4] H. H. Anderson, *ibid.*, **73**, 5798 (1951).

Di-*n*-propylgermanium Diacetate.—Upon reflux for three hours and then distillation of excess anhydride, 3.5 g. of the oxide and 4.5 g. of acetic anhydride gave a 90% yield of the diacetate.

Di-*n*-propylgermanium Bis-(monochloroacetate).—Upon refluxing 3.60 g. of the diacetate and 2.50 g. of monochloroacetic acid at 43 mm. pressure, 1.55 ml. of crude acetic acid distilled. When distilled at very low pressure the center fraction of the resultant monochloroacetate contained no hydrolyzable chlorine; boiling at 760 mm. darkens the product and gives a positive test for hydrolyzable chlorine.[4]

Dimeric Di-*n*-propylgermanium Sulfate.—Heating 0.74 g. of 100% sulfuric acid and 3.05 g. (10% excess) of di-*n*-propylgermanium bis-(monochloroacetate) at a pressure of 17 mm. yielded as distillate 1.28 g. of monochloroacetic acid, a displacement of 90%. Recrystallization of the white solid residue from benzene, and then washing with petroleum ether followed; a second recrystallization furnished long, slender, colorless or white needles of the dimeric sulfate. The solubility of the easily hydrolyzed compound in benzene is 18 g./liter at 27° and over 90 g./liter at 70°.

Table I lists the properties of the compounds, all of which were center fractions obtained in equipment bearing ground joints. Analysis was based on titration primarily.

CHEMICAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE 38, MASSACHUSETTS

Monoethylgermanium and Alkylsilicon Esters, Dimethylgermanium Diacetate

BY HERBERT H. ANDERSON[1]

RECEIVED NOVEMBER 28, 1951

Organogermanium oxides of the type $(R_3Ge)_2O$ or $(R_2GeO)_{3 \text{ or } 4}$ react with acetic anhydride to yield the corresponding monoacetate or diacetate, respectively, but the oxide $[(RGeO)_2O]_n$ does not react with acetic anhydride.[2] Although anhydrous sodium acetate and alkylchlorosilanes furnish alkylacetoxysilanes with yields of approximately 50%, this[3] method is less desirable for precious germanium compounds than the use of silver, lead or thallous salts, which are more covalent than the corresponding sodium salts. Tri-*n*-propylbromosilane and silver acetate yielded tri-*n*-propylacetoxysilane,[4] while thallous acetate[5] and germanium tetrachloride reacted in acetic anhydride furnishing germanium tetraacetate, m.p. 156°; probably the chief advantages of the anhydride were repression of hydrolysis and easy solution of germanium tetraacetate. Solvolysis[5] may not be so important as the authors feel.

Lead formate is a suitable reagent for preparing some formates, but not for others; organogermanium formates are not all completely stable, since ethylgermanium triformate loses water and carbon monoxide, and has no definite b.p. at 760 mm. Lead formate and $MeSiI_3$ yielded no stable product, although they reacted. Therefore formate stabilities apparently increase from silicon to lead, and from triformate to monoformate. Di-*n*-propylgermanium diiodide and lead formate did not react; previously[2] diethylgermanium oxide and formic acid gave a 30% yield, while bis-(triethylgermanium) oxide and formic acid gave a 90% yield. Perhaps silicon is not sufficiently electropositive to support a stable formate, although $Me_3Si(HCOO)$ might exist.

Exchange reactions such as that between $EtGe(C_2H_5COO)_3$ and Ph_2SiCl_2, which furnishes $EtGeCl_3$, indicate surprisingly mobile RCOO groups; such exchanges occur among compounds of germanium, phosphorus and silicon, or with a carbon compound containing an activated halogen. The elements germanium, silicon and phosphorus have comparable covalent single bond radii and probably the changes in entropy are finite but small.

Dimethylgermanium diacetate and 100% sulfuric acid liberated the expected quantity of anhydrous acetic acid, but the crystalline solid product was too difficultly soluble even in nitromethane to permit purification.

All three trimethylsilicon esters boil at lower temperatures than the corresponding free acids—*n*-butyric, chloroacetic and benzoic—which are partially associated.

Experimental

Starting Materials.—Professor Eugene G. Rochow of this Laboratory kindly furnished 100 g. of pure ethylgermanium trichloride (used as such herein) and 4 g. of a dimethylgermanium dihalide (converted into oxide before use), thus making this study possible.

Lead formate and each of the silver salts were precipitated from faintly acidic aqueous solutions using sodium salts of the acids, with careful washing and drying; however, silver trifluoroacetate was made from aqueous trifluoroacetic acid and silver oxide, with cautious evaporation and drying.

Ethylgermanium Triformate.—Ethylgermanium triiodide did not react with anhydrous sodium formate, despite 10 hours reflux in benzene. In contrast, 9.5 g. of $EtGeI_3$ and 22 g. of powdered lead formate in 60 ml. of benzene gave a yellow lead salt at once, although heating did not occur spontaneously. A half-hour of reflux removed the iodine nearly completely from the solution; thereupon followed filtration and washing of the solid with benzene, next distillation of solvent. Distillation of 6.5 g. of product furnished a center fraction as in Table I.

Ethylgermanium Triacetate, Tripropionate, Tri-*n*-butyrate, Tri-*n*-valerate.—Typically, 24 g. of $Ag(C_2H_5COO)$ and 6.55 g. of $EtGeCl_3$—an excess of 30% in silver salt—in 50 ml. of pure, dry benzene furnished a temperature rise of nearly 30°; after an hour of reflux on a steam-bath with shaking, there followed the usual filtration, with washing of silver salts, then distillation of benzene, and transfer of product to smaller equipment. Table I lists the distillation of the 9.6-g. product, a yield of 95%, under 2 mm. pressure. Ordinarily the triacetate, made from $EtGeI_3$, remained a supercooled liquid.

Dimethylgermanium Diacetate.—Two grams of $(Me_2GeO)_4$[6] and 3.5 g. of acetic anhydride were given 1.5 hr. of free reflux at 760 mm., and then the excess anhydride was distilled at 760 mm. Later the center fraction of the diacetate distilled at 94–95° under 25 mm., and practically no organogermanium oxide remained. This diacetate melts at 50°, but it can easily supercool 10–15° if not stirred or touched with a capillary tip. It would have proved instructive to use the silver acetate method also, if material had permitted.

Silicon Esters.—Twenty grams, an excess, of Me_3SiCl and 15 g. of $Ag(n\text{-}C_3H_7COO)$, suspended in 50 ml. of benzene reacted with warming; an hour of reflux and the usual subsequent treatment furnished a 10-g. yield of ester, or 80% of the theoretical. Table I lists the distillations of the various esters. Hydrolyzable chlorine was essentially absent from the pure monochloroacetate; some free benzoic acid that contaminated the benzoate was nearly all removed by centrifuging after several hours at room temperature. A 30% excess of silver salt was necessary for the diacetate and the bis-(trifluoroacetate), to ensure complete reaction.

Physical Properties and Analysis (see Table I).—Melting points are: ethylgermanium triformate, 13°; ethylger-

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[1] 1932 Commonwealth Ave., Auburndale 66, Mass.

[2] H. H. Anderson, THIS JOURNAL, **72**, 2089 (1950).

[3] H. A. Schuyten, J. W. Weaver and J. D. Reid, *ibid.*, **69**, 2110 (1947).

[4] C. Pape, *Ber.*, **14**, 1875 (1881), b.p. 212–216°.

[5] H. Schmidt, C. Blohm and G. Jander, *Angew. Chem.*, **A59**, 233 (1947).

[6] E. G. Rochow, THIS JOURNAL, **70**, 1801 (1948).

TABLE I

All compounds distilled at lowest pressure listed. Handling of $EtGe(CH_3COO)_3$ as a supercooled liquid.

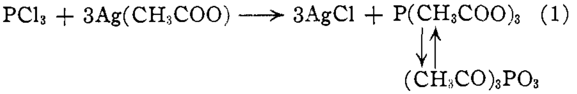
Compound	B.p. °C.	Mm.	d^{20}_4	n^{20}	R	Mol. wt. Calcd.	Mol. wt. Found	Neut. equiv., g. Calcd.	Neut. equiv., g. Found
$EtGe(HCOO)_3$	230 dec.	760	1.617	1.452	39.5	236.7	223	78.9	78.8, 80.1
	118	9							
$EtGe(CH_3COO)_3$	249	760	1.393	1.444	53.1	278.8	320	92.9	94.0
	99–101	1							
$EtGe(C_2H_5COO)_3$	256	760	1.271	1.443_4	67.0	320.9	230[a]	107.0	105.3, 105.3
	114–116	2							
$EtGe(n\text{-}C_3H_7COO)_3$	271 dec.	760	1.186	1.443_2	81.2	363.0	..	121.0	119.7, 119.5
	136–137	2							
$EtGe(n\text{-}C_4H_9COO)_3$	305	760	1.136	1.445_6	95.0	405.0	..	135.0	133, 133.5
	157–159	2							
$Me_2Ge(CH_3COO)_2$	188	760	...	....	..	220.8	205	110.4	109.5
	94–95	25							
$Me_3Si(n\text{-}C_3H_7COO)$	144	760	0.874	1.400_5	44.5	160.3	157	160.3	159.8, 159.4
$Me_3Si(C_6H_5COO)$	221	760	1.004	....	..	194.3	182	194.3	192.0, 192.7
$Me_3Si(CH_2ClCOO)$	159	760	1.057	1.423_1	40.2	166.7	173	166.7	168, 165
	70–71	30							
$Et_2Si(CF_3COO)_2$	155	760	1.270	....	..	312.2	306	156.1	154, 154
$(C_6H_5)_2Si(CH_3COO)_2$	176–178	3	...	....	..	300.4	...	150.2	149

[a] Low probably because of decomposition.

manium triacetate, 49°, supercooling easily; diethylgermanium diacetate, 50°, also supercooling easily; trimethylbenzoxysilane, about −15°; trimethyl-(monochloroacetoxy)-silane, −20°. Diphenyldiacetoxysilane was quite viscous at 25° and completely fluid at 100°. Ethylgermanium tributyrate was more viscous than carbon tetrachloride. All were colorless, and had odors weakly suggestive of the free acid. Ethanolic sodium hydroxide solution and micropipets were useful in titrations of available acidity. Molecular weights used camphor for liquids boiling above 200°, or vapor densities for lower-boiling liquids.

Unsuccessful Preparations.—These show decomposition as the main limitation: $EtGeCl_3$ (which did not react easily with Ag_3PO_4) and the appropriate silver salt yielded a crude benzoate decomposing at the b.p. of 220° under 1 mm., and a crude monochloroacetate of b.p. 195° under 2 mm. containing excessive available acidity, neut. equiv., 108. Crude $PhSi(CH_3COO)_3$ decomposed rapidly under distillation at 3 mm. Lead formate and $MeSiI_3$ gave a product decomposing vigorously when heated under 25 mm. pressure; lead formate and $n\text{-}Pr_2GeI_2$ did not react.

Phosphorus trichloride and silver acetate, 7.3 g. and 39 g., respectively, in 80 ml. of benzene, reacted with much evolution of heat; after an hour of reflux and filtering, washing and removal of solvent by distillation, 4 g. of product boiled at 56–57° under 37 mm. At 760 mm. the b.p. was 140°; also, d^{20}_4 1.081, and n^{20} 1.390_4. This information is consistent with data for acetic anhydride, and the reaction follows that found for phosphoryl chloride and thallous acetate.[5]



$$PCl_3 + 3Ag(CH_3COO) \longrightarrow 3AgCl + \underset{(CH_3CO)_3PO_3}{\underset{\downarrow\uparrow}{P(CH_3COO)_3}} \quad (1)$$

$$(CH_3CO)_3PO_3 + 3Ag(CH_3COO) \longrightarrow 3(CH_3CO)_2O + Ag_3PO_3 \quad (2)$$

These equations are similar to the previous ones,[6] in which the authors could have used silver acetate; phosphorus triacetate can plausibly isomerize into acetyl phosphite, which can react further with silver acetate to give acetic anhydride and silver phosphite. In this phosphorus is acidic and silver acetate is essentially basic. Other evidence, presented in the section on reactions of esters, indicates that phosphorus triacetate may be a stable compound, but should be made by an exchange reaction. In contrast, silicon and germanium are less acidic than phosphorus, and their acetates are more stable to silver acetates.

Germanium tetrachloride and acetic acid, even under 10 hours of free reflux, evolved very little hydrogen chloride, and thus germanium tetrachloride is unlike zirconium tetrachloride, which yields the tetraacetate with acetic acid on reflux.[7]

Bis-(trialkylsilicon) Sulfates by Silver Sulfate Method.—Silver sulfate converted trialkylchlorosilanes into the sulfates if nitromethane or nitrobenzene is used as solvent; this method is believed to be new. After 10 hours of reflux, 12 g. of Me_3SiCl and 24 g. of Ag_2SO_4 suspended in 20 ml. of nitromethane ultimately yielded 4.5 g. of crude $(Me_3Si)_2SO_4$, after filtration and washing of the silver salts. This yield of 30% is intermediate between that obtained with a salt like $Ag(CH_3COO)$ and failure to react with Ag_3PO_4. Benzene is not a good solvent for use with silver sulfate. A yield of 60% resulted when 21 g. of Et_3SiCl and 24 g. of Ag_2SO_4 in 40 ml. of nitrobenzene were given 5 hr. reflux with occasional shaking; 12 g. of product boiled at 279° with slight decomposition, had a refractive index of 1.443 at 20°, also reacted with water when shaken to give an organosilicon layer of low density. Perhaps the best way to make a trialkylsilicon sulfate would be to treat a trialkylacetoxysilane with a slight deficiency of sulfuric acid (100%). Previously bis-(trialkylsilicon) sulfates were prepared from concentrated sulfuric acid and hexamethyldisiloxane or hexaethyldisiloxane.[8]

Reactions of Esters.—Equations show the reactions.

$$2EtGe(CH_3COO)_3 + 3Ph_2SiCl_2 \longrightarrow 2EtGeCl_3\uparrow + 3Ph_2Si(CH_3COO)_2 \quad (1)$$

$$2EtGe(n\text{-}C_3H_7COO)_3 + 3Ph_2SiCl_2 \longrightarrow 2EtGeCl_3\uparrow + 3Ph_2Si(n\text{-}C_3H_7COO)_2 \quad (2)$$

$$2Me_2Ge(CH_3COO)_2 + 2H_2SO_4 \longrightarrow (Me_2GeSO_4)_2 + 4CH_3COOH\uparrow \quad (3)$$

$$3Me_3Si(CH_2ClCOO) + PBr_3 \longrightarrow 3Me_3SiBr\uparrow + P(CH_2ClCOO)_3 \quad (4)$$

$$Me_3Si(n\text{-}C_3H_7COO) + PhCOCl \longrightarrow Me_3SiCl\uparrow + n\text{-}C_3H_7COOPh \quad (5)$$

Upon gentle reflux the most volatile product (designated by ↑) escaped; this compound was identified by boiling point, refractive index and hydrolysis products. Typically, in equation 2, 6 g. of triester and 7.8 g. of Ph_2SiCl_2 yielded 3.4 g. of $EtGeCl_3$ in a 20-minute reflux under 43 mm.—b.p. 95°. Other reactions were at 760 mm. In equation 4 this is probably the appropriate method for making esters of phosphorus. The most volatile product boiled (760 mm.) at 139–142°, 142°, 119°, 82–83° and 57–60° in reactions 1 to 5, respectively. Equation 3 is a transesterification, while the others are exchanges. Space does not allow a discussion of the many known exchange reactions of silanes.

CHEMICAL LABORATORY OF HARVARD UNIVERSITY
CAMBRIDGE 38, MASS.

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(7) A. Rosenheim and J. Hertzmann, *Ber.*, **40**, 813 (1907).

(8) L. H. Sommer, E. W. Pietrusza, G. T. Kerr and F. C. Whitmore, THIS JOURNAL, **68**, 156 (1946); L. H. Sommer, G. T. Kerr and F. C. Whitmore, *ibid.*, **70**, 445 (1948).

Size Distribution of Spheres by Light Scattering[1]

BY F. BUECHE

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Several methods have been proposed during the past few years for determining the range of sizes of spherical particles in solution.[2] The purpose of this note is to outline another method which the author believes has some practical advantages over the others so far presented. This method makes use of the fact that for a solution of spheres of unequal size the position of the first angular intensity minimum does not yield the same sphere size for two different wave lengths. The method makes use of some relations derived by W. B. Dandliker[3] who apparently failed to notice the inherent simplicity of a method based upon them.

If one assumes that the Debye theory[4] may be applied to scattering by a solution of spheres, it may be shown that the condition which exists at the first minimum leads to the relation[3]

$$a_1{}^2G(y_1) = a_2{}^2G(y_2)$$

To obtain this relation one replaces the actual distribution of sizes by a rectangular distribution extending from radii of a_1 to a_2. The quantity y_1 is equal to

$$\frac{4\pi a_1}{\lambda} \sin\ ({}^1/{}_2\theta_m)$$

and similarly for y_2. The function $G(y)$, a function of y alone, is given in the table. Its algebraic form is given in reference 3.

y	$-G(y)$	y	$-G(y)$
1.5	0.06	5.0	3.50
2.5	1.21	5.5	1.60
3.5	4.70	6.0	1.37
4.0	5.95	6.5	3.79
4.5	5.50	7.0	7.39

The use of this result may be best illustrated by an example. Suppose one has measured the position of the angular minimum (for light plane polarized with plane perpendicular to the plane of observation) at two wave lengths λ and λ' to give the corresponding angles θ and θ'. Suppose further that $\lambda = 4000$, $\lambda' = 3000$, $\theta = 89°$ and $\theta' = 70°$.

From the definition of y and the values for λ and θ one may write $y = 0.0022\ a$. Since each y determines a value of $G(y)$ as shown in the table, one is able to plot curve 1 of the figure which shows a *vs.* $a^2/G(y)$. This curve does not uniquely determine either a_1 or a_2. However, to find unique values one need only plot a similar curve for the data obtained at λ'. This is curve 2 of the figure.

At the values of $a = a_1$ and $a = a_2$ both of these curves must satisfy equation 1. Therefore one must have

$$a_1{}^2G_1 = a_2{}^2G_2$$
$$a_1{}^2G_1{}^1 = a_2{}^2G_2{}^1$$

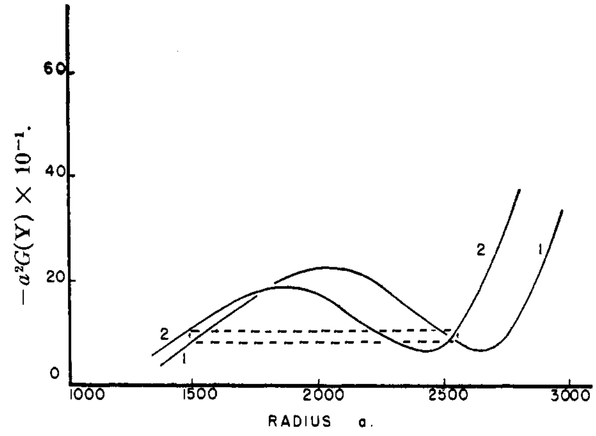

Fig. 1.

That is to say, the actual values of a_1 and a_2 will be such that at these two values the vertical coördinates of curve 1 equal each other and also the vertical coördinates of curve 2 equal each other. By inspection it is seen that this is true for $a_1 = 1500$ and $a_2 = 2600$. These tell us that the actual particle size distribution may be approximated by a rectangular distribution having limiting radii of 1500 and 2600.

It should be mentioned that when the distribution is very broad it may be necessary to use values $G(y)$ above $y = 8$. In that event the above treatment can only be considered as approximate since the simple Debye relations begin to fail in that region.

DEPARTMENT OF CHEMISTRY
CORNELL UNIVERSITY
ITHACA, NEW YORK

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[1] This work was carried out under a contract with the Office of Rubber Reserve, R. F. C., in connection with the U. S. Government's Synthetic Rubber Program.

[2] M. Kerker and V. K. LaMer, THIS JOURNAL, **72**, 3616 (1950); I. Johnson and V. K. LaMer, *ibid.*, **69**, 1184 (1947).

[3] W. B. Dandliker, *ibid.*, **72**, 5112 (1950).

[4] See for example the review article by G. Oster, *Chem. Rev.*, **43**, 336 (1948).

Dissociation Constants of N-Alkylethylenediamines[1,2]

BY FRED BASOLO AND R. KENT MURMANN

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The acid–base dissociation constants of ethylenediamine,[3] diethylenetriamine and triethylenetetramine[4] have been determined. In the course of investigating steric effects on the binding of metal ions with N-alkylethylenediamines, it was necessary to determine the acid–base dissociation constants or "hydrolysis" constants of the amines. Since the N-alkylethylenediamines form an interesting series of compounds, this paper reports the acid–base dissociation constants of five such diamines. The constants were determined in the presence of 0.05 M $Ba(NO_3)_2$ and 0.50 M KNO_3 by the method of Bjerrum.[3]

Experimental

Reagents.—N-Methyl- and N-ethylenediamine were each prepared by two methods which gave identical products with

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[1] Abstracted in part from a thesis by R. Kent Murmann, presented to the Graduate Faculty of Northwestern University, in partial fulfillment of the requirements for the degree of Master of Science in chemistry, August, 1951.

[2] This investigation was supported by a grant-in-aid from the National Institutes of Health—Grant No. G-3239.

[3] J. Bjerrum and P. Anderson, *K. Danske Vidensk. Selsk. Mathfys. Medd.*, **22**, No. 7 (1945).

[4] H. B. Jonassen, R. B. LeBlanc, A. W. Meibohm and R. M. Rogan, THIS JOURNAL, **72**, 2430 (1950).

derivatives melting at the same point. In general the method of O'Gee and Woodburn[5] was superior to that of Aspinall.[6]

N-Isopropyl- and N-*n*-butylethylenediamine were prepared by the method of O'Gee except that the free amines were dried with sodium before distillation.

N-*n*-propylethylenediamine was obtained by the courtesy of Dr. H. M. Woodburn at the University of Buffalo. It was redistilled over sodium.

The amines were fractionated through an eleven-inch column packed with stainless steel spiral and had the following boiling ranges

N-Alkylethylenediamines ($RNHCH_2CH_2NH_2$) R	B.p., °C.
Me	114–115
Et	125–126
i-Pr	137–138
n-Pr	152–153
n-Bu	75–77 (20 mm.)

These agree well with those reported by O'Gee and Woodburn.[5]

Preparation of Solutions and Titrations.—The amines were diluted with distilled water until they were 3 to 5 molar and then standardized against standard acid by means of conductometric titrations. The primary standard for all acid–base titrations was a sample of 99.96% potassium hydrogen phthalate obtained from the Bureau of Standards.

The constant ionic strength nitric acid solution containing barium nitrate was made by preparing a solution approximately 0.1 *N* in boiled nitric acid and adding reagent grade chemicals to make the solution 0.50 *M* in KNO_3 and 0.05 *M* in $Ba(NO_3)_2$. The nitric acid was then titrated against standard base using phenolphthalein as the indicator.

A Beckman *p*H meter model G was standardized against Beckman standard buffers at a *p*H of 4.00 and 9.00 before each run. A Beckman 1190–90 glass electrode was used which is accurate to *p*H's of 11 without corrections in the absence of sodium ion. The solutions were maintained at a constant temperature by means of a constant temperature bath at 25 ± 0.1° and by an intimate mixture of ice and water at 0 ± 0.1°.

The titration of the standard nitric acid solution with standard amine was accomplished by means of a microburet capable of being read to ± 0.001 ml. The hydrogen ion was followed by means of a *p*H meter which could be read to ± 0.02 *p*H unit.

A sample titration at the appropriate regions of *p*H along with calculated values of pK_1 and pK_2 are indicated in Table I. One notices the good agreement of the various *pK* values. In each case these values were checked by determining the respective *p*H's of two separate solutions which fall in the first dissociation constant range and in the second dissociation constant range. The constants calculated from these solutions agreed with those obtained from the titration within ±0.01 *pK* unit.

The dissociation constants at 0 and 25° along with the heats of neutralization are summarized in Table II. A graphic representation of these *pK* values is shown in Fig. 1. Although these compounds have comparable dissociation constants, it does appear that with the straight chain alkyls there is a gradual change in going from methyl to butyl with a slight maximum in the region of N-ethylethylenediamine. It is likewise noteworthy that although one may expect a more marked change in case of the pK_2 values as compared to changes in pK_1, this was not observed.

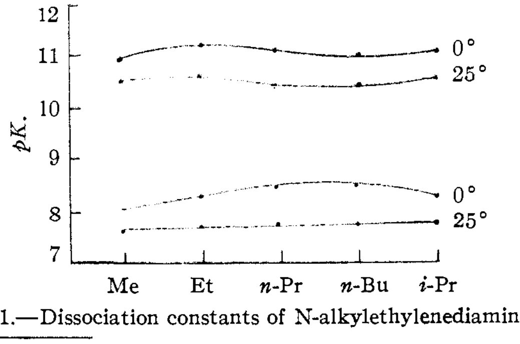

Fig. 1.—Dissociation constants of N-alkylethylenediamines.

TABLE I

DISSOCIATION CONSTANTS OF N-ETHYLETHYLENEDIAMINE AT 0°

Diamine, ml.	*p*H	C_{En}	C_{H}	pK_1
1.002	7.91	0.06223	0.10254	8.16
1.039	8.00	.06449	.10247	8.16
1.077	8.10	.06679	.10239	8.16
1.111	8.19	.06886	.10232	8.16
1.150	8.28	.07123	.10224	8.17
1.187	8.36	.07346	.10217	8.17
1.220	8.43	.07545	.10210	8.17
1.252	8.50	.07739	.10204	8.17
1.291	8.57	.07974	.10196	8.16
1.328	8.65	.08197	.10189	8.16
			Av.	8.16
				pK_2
2.050	10.50	0.12477	0.10048	11.12
2.085	10.53	.12681	.10041	11.11
2.120	10.55	.12885	.10034	11.10
2.160	10.59	.13110	.10026	11.11
2.191	10.62	.13300	.10006	11.11
2.337	10.72	.14146	.09992	11.10
2.413	10.77	.14585	.09978	11.11
2.481	10.80	.14976	.09965	11.10
2.594	10.85	.15624	.09944	11.10
2.709	10.90	.16282	.09922	11.08
			Av.	11.11

TABLE II

DISSOCIATION CONSTANTS AND HEATS OF NEUTRALIZATION OF N-ALKYLETHYLENEDIAMINES

$RNHCH_2$-CH_2NH_2 —R—	pK_1 0°	pK_1 25°	pK_2 0°	pK_2 25°	Δ*H*, kcal. pK_1	Δ*H*, kcal. pK_2
Me	8.00	7.56	10.83	10.40	− 6.55	− 6.30
Et	8.16	7.63	11.11	10.56	− 7.90	− 8.20
n-Pr	8.24	7.54	11.04	10.34	−10.4	−10.4
n-Bu	8.11	7.53	10.93	10.30	− 8.65	− 9.40
i-Pr	8.30	7.70	11.15	10.62	− 8.95	− 7.90

DEPARTMENT OF CHEMISTRY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

Chromatographic Investigations Related to Photographic Theory, II, Adsorption of Developing Agents and Sodium Sulfite[1]

BY T. H. JAMES AND W. VANSELOW

RECEIVED JANUARY 12, 1952

In a preceding paper,[2] the technique of elution chromatography was used to show that the photographic developing agents, *p*-phenylenediamine and hydrazine, are adsorbed by silver bromide. These agents displaced the adsorbed dyes, phenosafranin and 3,3′-diethyloxacarbocyanine, from the silver bromide surface. Hydroquinone and catechol, on the other hand, caused the dyes to be held even more tightly, and this suggested a coöperative adsorption of the negatively-charged developing agent

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[5] R. C. O'Gee and H. M. Woodburn, THIS JOURNAL, **73**, 1370 (1951).

[6] S. R. Aspinall, *ibid.*, **63**, 852 (1941).

(1) Communication No. 1473 from the Kodak Research Laboratories.

(2) T. H. James and W. Vanselow, THIS JOURNAL, **73**, 5617 (1951).

and the positively-charged dye. In these experiments, therefore, no evidence was obtained that hydroquinone or catechol is adsorbed by silver bromide in the absence of the positively-charged dye molecules.

The investigation has now been extended to include dyes which do not have a positive charge and hence would not attract the negatively-charged developer ions. The results obtained show that hydroquinone, catechol and hydroxylamine displace some adsorbed dyes from the silver bromide surface and hence must themselves become adsorbed by that surface.

Experimental Procedure

The preparation of the silver bromide columns and the general technique of charging and developing the columns were the same as those described in the preceding paper. The length of the silver bromide column was standardized at 20 cm. When aqueous solutions of developers were to be used, the columns were charged with dye in aqueous solution, and the charging and developing operations were carried out in the absence of oxygen in the apparatus described in the preceding paper.

The merocyanine dye, 4-[3-ethyl-2(3H)-benzothiazolylidene)-ethylidene]-3-methyl-1-(*p*-sulfophenyl)-5-pyrazolone (sodium salt), was used in most of the experiments. Each tube was charged with 2 cc. of 10^{-4} *M* dye solution. The eluate was collected in acetic acid solution to prevent oxidation of the developing agent on contact with air.

Results

Hydroquinone in 0.01 *M* aqueous solution could be used as a chromatographic developer at *p*H 8.0 and below without causing reduction of the silver bromide. When a solution of *p*H 9.0 was used, a slight amount of reduced silver formed toward the end of the experiment. Hydroquinone displaced the merocyanine dye, and its effectiveness increased with increasing *p*H of the solution. Some data are given in Fig. 1, where the amount of dye eluted in terms of the percentage of dye originally present in the column is plotted against the volume of eluate. It is seen that, even at *p*H 6, more dye was eluted by the hydroquinone solution than by an equal volume of water. The cause of the breaks observed in the curves representing *p*H 8 and 9 is not clear, but may be associated with the existence of two types of surface of somewhat different adsorptive properties. The break is not specific for hydroquinone, but has been obtained with other chromatographic developers (*e.g.*, dilute potassium bromide solutions), where the ratio of displaced dye to eluate volume is about the same. No breaks were observed when this ratio was either considerably larger or considerably smaller. Displacement of other dyes by hydroquinone has been observed, *e.g.*, eosin.

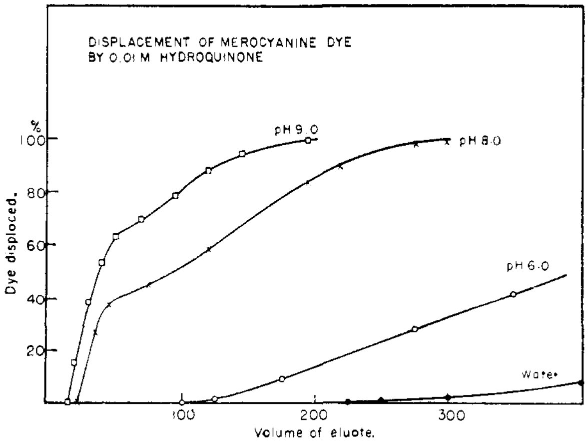

Fig. 1.—Displacement of merocyanine by 0.01 *M* hydroquinone at various *p*H values.

Figure 2 illustrates results obtained with catechol, hydroxylamine and resorcinol, A hydroquinone curve is included for comparison. The displacement of the merocyanine dye by catechol at *p*H 6.0 (not shown) was only slightly greater than that by hydroquinone at the same *p*H. The displacement by catechol at *p*H 8.0 was about the same as that by hydroquinone at *p*H 9.0. A break was not observed in the catechol curve for *p*H 8.0, but some reduction of silver bromide occurred in the later stages of the experiment, and the presence of a break may have been obscured by the appearance of developer oxidation product. Hydroxylamine was less effective than hydroquinone in displacing the dye, but its action was greater at *p*H 10 than at 8, showing that a *p*H-dependency exists for this agent as well. The displacement by water alone showed little or no dependency upon *p*H. Resorcinol was much less effective as a chromatographic developer than hydroquinone or catechol. A solution at *p*H 8 was no more effective than water, and a solution at *p*H 10 was less effective than one of hydroquinone at *p*H 8.

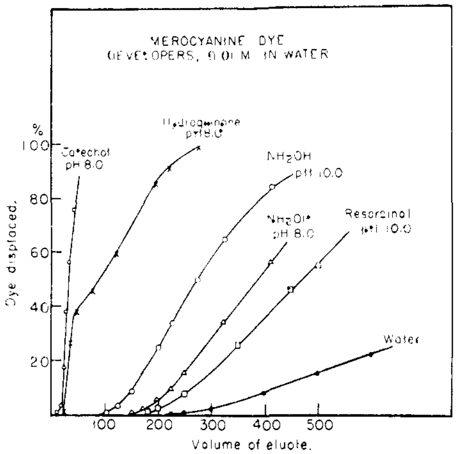

Fig. 2.—Displacement of merocyanine by various developing agents.

Sodium sulfite, which showed some coöperative adsorption with the positively-charged dyes, displaced the merocyanine, but was less effective than the photographic developing agents. Some data are given in Fig. 3. A sodium sulfate solution, on the other hand, was somewhat less effective than pure water in displacing the dye.

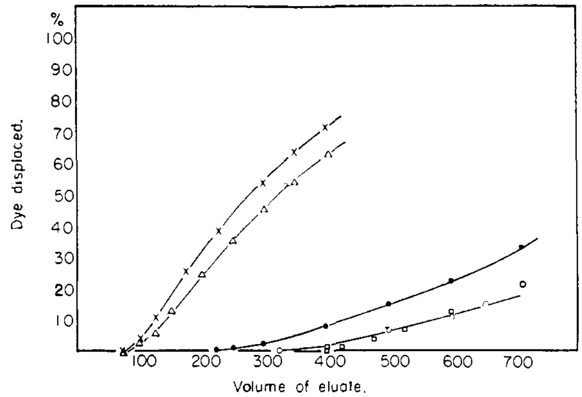

Fig. 3.—Displacement of merocyanine by sodium sulfite: -X-X-, 0.001 *M* Na_2SO_3; -Δ-Δ-, 0.01 *M* Na_2SO_3; -O-O-, 0.005 *M* Na_2SO_4; -□-□-, 0.0005 *M* Na_2SO_4; -●-●-, water.

It was shown previously that *p*-phenylenediamine in aqueous solution displaces phenosafranin and 3,3′-diethyloxacarbocyanine from the silver bromide surface. Some reduction of silver bromide occurred in the later stages of the elution, however. In an effort to avoid such reduction, solutions of *p*-phenylenediamine in acetone have been tried with success. In these experiments, the silver bromide tubes were first washed with three 5-cc. portions of acetone after the water had been expelled. The tubes were then charged with dye from acetone solution, and 2 cc. more of acetone used to rinse out the tube. Development by the p-phenylenediamine solution was then carried out in the usual manner. The dye in the eluate could be determined directly without the addition of acid.

The curves obtained with the p-phenylenediamine developer are regular in shape, resembling those of hydroxylamine in Fig. 2. A concentration series was run over a range of 100-fold. The dependence of elution upon concentration of p-phenylenediamine is illustrated in Fig. 4. Here, the logarithm of the maximum slope of the elution curve is plotted against the logarithm of the concentration of the p-phenylenediamine. A straight line of slope of 0.55 was obtained for each dye. If the maximum slope of the elution curve is a measure of the amount of p-phenylenediamine adsorbed, the straight lines in Fig. 4 would show that the adsorption is following the Freundlich isotherm. Similar results were obtained for the displacement of merocyanine dyes.

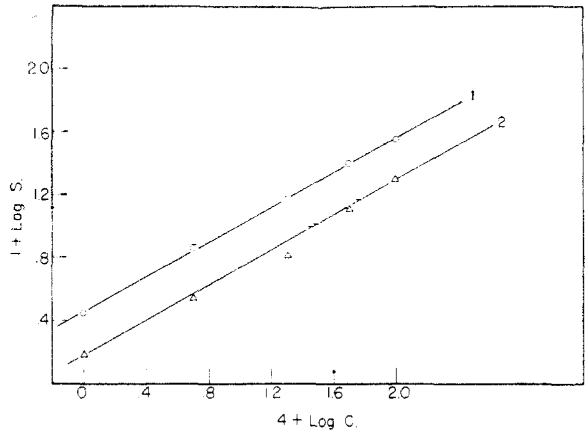

Fig. 4.—Dependence of displacement of dyes upon the concentration of p-phenylenediamine: curve 1, displacement of phenosafranin; curve 2, displacement of 3,3′-diethyloxacarbocyanine.

Some tests were made on the displacement of phenosafranin by 4-amino-3-methyl-N-ethyl-N-(β-methylsulfonamidoethyl)-aniline. The displacement curves obtained are similar in form to those obtained with p-phenylenediamine. The maximum slopes are 1.76 and 0.50 for developer concentrations of 0.01 and 0.001 M, respectively. If these data are plotted in the same way as the p-phenylenediamine data in Fig. 4, the slope of the straight line is 0.54, in excellent agreement with the value of 0.55 for the p-phenylenediamine. It is of interest to compare this concentration-dependence with that found by Fortmiller and James[3] for the development of liquid emulsions by derivatives of p-phenylenediamine. A log–log plot of their data yields a straight line of slope 0.54.

Discussion

The dye displacement experiments have demonstrated that hydroquinone, catechol, hydroxylamine, hydrazine, p-phenylenediamine and 4-amino-3-methyl-N-ethyl-N-(β-methylsulfonamidoethyl)-aniline are adsorbed by silver bromide. This supports the suggestion of Sheppard and Meyer[4] that adsorption of photographic developing agents by silver halide precedes the reduction of the silver salt in photographic development. The pH-dependence of displacement by hydroquinone and catechol indicates that these agents are adsorbed in the ionized form. Kinetic evidence indicates that the ionized forms of the developing agents likewise are involved in photographic development. Resorcinol is much less effective than hydroquinone and catechol, both in displacing the merocyanine dye and in photographic development. The low developer activity of the resorcinol can depend only in part on its lower adsorption, however, since the oxidation of this agent by silver ions from solution is much slower than the oxidation of hydroquinone and catechol.

ROCHESTER, N. Y.

[3] L. Fortmiller and T. H. James, *PSA Journal*, **17B**, 102 (1951).

[4] S. E. Sheppard and G. Meyer, THIS JOURNAL, **42**, 689 (1920).

Remarks on Spectra of Stilbene Derivatives

BY JOHN R. PLATT

Application of first-order perturbation theory[1] to the spectra of stilbene derivatives as given by Beale and Roe[2] leads to some important conclusions. For an allowed even–odd transition in a centrally symmetric molecule, such as the longest wave length transition in *trans*-stilbene, the oscillator strength is the square of a transition moment vector, M.[3] A small perturbation by a substituent, a, at a particular position introduces an additional perturbation vector, m_a. The total intensity becomes the square of the vector sum, $M + m_a$. If there is an angle, θ_a, between the vectors, the oscillator strength in suitable units is

$$f = (M + m_a \cos\theta_a)^2 + (m_a \sin\theta_a)^2$$
$$= M^2 + 2Mm_a \cos\theta_a + m_a^2$$

and the increment is

$$\Delta f = 2Mm_a \cos\theta_a$$

if m_a is relatively small.

For two substituents at opposite positions, the perturbation vectors will be parallel and the intensity increments will add linearly. (For an even–even transition, they would subtract. For a forbidden even–odd, where M is zero, the perturbation vectors would add linearly, but the intensity increments would go up as the square of the vector sum.[4]) For two substituents at any positions, the total intensity increment will be approximately the sum of the independent increments, in this first-order theory, as long as m_a and m_b are small compared to M.

Examination of Beale and Roe's f-values in the light of these remarks leads to the following conclusions.

(1) **The longest wave length singlet–singlet transition in *trans*-stilbene is necessarily even–odd** (in agreement with all theoretical predictions and with the high intensity. Reason: the 4-methylstilbene intensity is greater than that of stilbene; and the 4,4′-dimethyl intensity is greater still (in arithmetic progression) and not less.

(2) **The $N(CH_3)_2$ perturbation is larger than the** methyl (as noted by Beale and Roe) **and in addition it has the same sign.** Reason: the 4,4′-increments for these substituents add, and do not subtract. The same result has been found[5] for these substituents as they affect the benzene 2600 Å. bands; but the $N(CH_3)_2$ group had a relatively larger effect there.

[1] J. R. Platt, *J. Chem. Phys.*, **19**, 263 (1951).

[2] R. N. Beale and E. M. F. Roe, THIS JOURNAL, **74**, 2302 (1952).

[3] R. S. Mulliken and C. A. Rieke, *Rep. Prog. Phys.*, **8**, 231 (1941).

[4] J. R. Platt, *J. Chem. Phys.*, **19**, 263, 1484 (1951).

[5] J. R. Platt, unpublished.

(3) **The angle θ for position 3 is almost 90°.** Reason: a methyl group in this position produces little change in intensity,

The effect of substituents in the 2-positions, which probably produce steric hindrance, may be treated by the same perturbation theory, as long as the changes in intensity are relatively small. However, the perturbation vectors in this case are no longer necessarily coplanar with the perturbation vectors produced by substituents at other positions.

These general theoretical conclusions support and validate Beale and Roe's important experimental demonstration that *in a strong transition the intensity increments from substituents in particular positions are additive.*

Independent determination of m_a and θ_a at particular positions does not seem feasible for strong transitions (though it can be done for forbidden transitions[6]). If we assume m_a constant for a given substituent at all positions, θ_a can be approximately determined from the intensity increments except for an ambiguity of sign.

I am indebted to Drs. Beale and Roe for showing me their manuscript in advance of publication.

[6] J. R. Platt, "Electronic Structure and Excitation of Polyenes and Porphyrins," Chapter 4, Vol. 3 of "Radiation Biology," Ed., S. Hendricks, McGraw-Hill Book Co., Inc., New York, N. Y., 1952.

PHYSICS DEPARTMENT
UNIVERSITY OF CHICAGO
CHICAGO, ILL.
RECEIVED NOVEMBER 1, 1951

Autocatalyzed Hydrolysis of Sucrose by Acid

BY LAWRENCE J. HEIDT, F. WILLIAM SOUTHAM AND EDWARD A. SULLIVAN[1]

RECEIVED FEBRUARY 4, 1952

The rate of hydrolysis of sucrose by acid has been the subject of numerous investigations for over a century. Under the usual conditions in a given experiment at constant temperature, the effective concentration of the acid remains unchanged and the reaction is first order with respect to the concentration of the sucrose. We have found the reaction to be autocatalyzed as much as six-fold by a corresponding increase in the acidity under conditions where the increase in acidity on a mole basis corresponds to less than one-tenth per cent. of the sucrose hydrolyzed.

The reactions were carried out in sealed, clean, acid- and alkali-free, Kimble flasks placed in a bath whose temperature was controlled and recorded continuously to ±0.03°. Reaction was stopped by bringing the pH to 6 ± 0.2 by adding a solution of sodium bicarbonate to the reaction mixture in the bath. Loss of water from the reacting mixture or neutralized solution amounted to less than 1% in all cases.

The fraction of the sucrose hydrolyzed was determined in a manner previously described[2] from measurements of the reducing power of the solution toward a carbonate buffered cupritartrate reagent[3] at pH 8.7. The method eliminates any correction for mutarotation of the liberated sugars. The

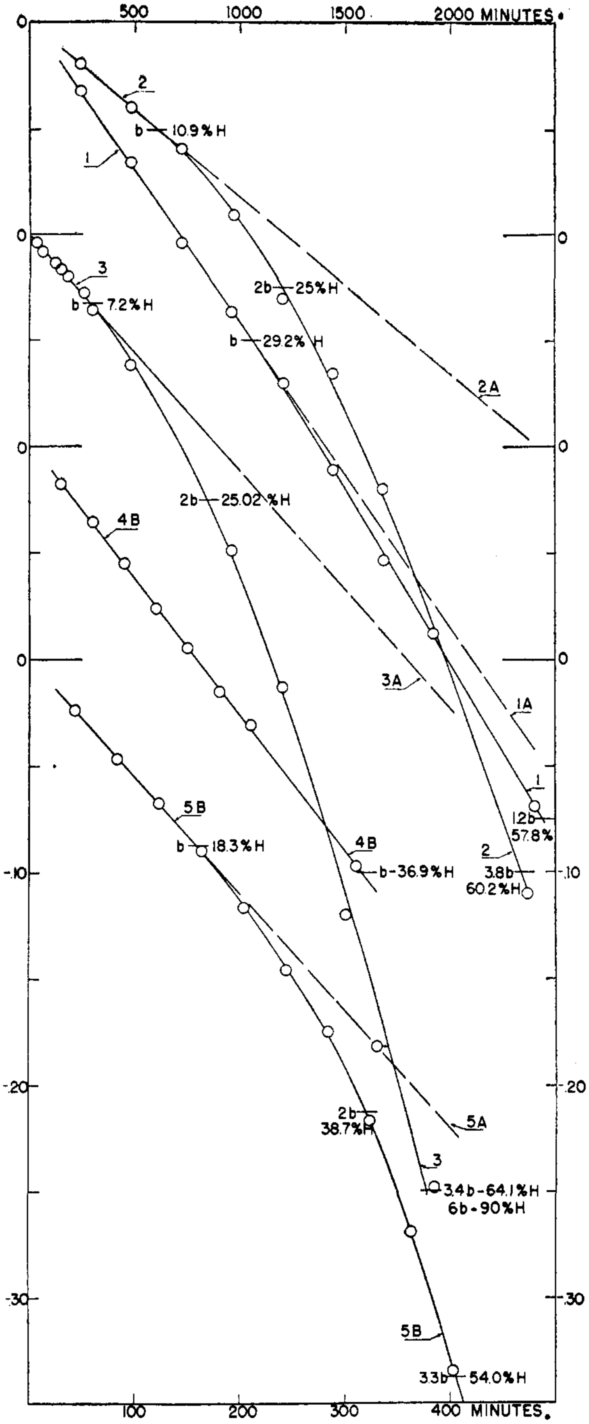

Fig. 1.—Evidence for autocatalysis in the hydrolysis of sucrose by acid. Common logarithms of one minus the fractional hydrolysis of sucrose are plotted as ordinates against the lengths of time the reaction has taken place under the conditions tabulated below. The curves would be straight lines if there were no measurable autocatalysis as is the case for curve 4B. The usual first-order rate constant equals −2.303b. The concentrations given below are the initial formal values at 0° in moles of acid per liter of solution and in g. sucrose (within 1 mg.) in the volume given in ml. (within 0.1 ml.). No color developed in any of the solutions. The % H in the fig. gives the % sucrose hydrolyzed.

Curve	Temp. °C.	10^4(HCl)	Sucrose	Time scale
1	75.10	1.05	2g./100 ml.	Upper
2	75.10	1.05	13g./55 ml.	Upper
3	75.10	2.7	80g./100 ml.	Upper
4B	75.10	5.4	80g./100 ml.	Lower
5B	95.10	1.05	13g./55 ml.	Lower

[1] The authors are indebted to the Sugar Research Foundation, Inc., for a grant-in-aid.

[2] L. J. Heidt and C. B. Purves, THIS JOURNAL, **66**, 1385 (1944).

maximum reducing power was determined in critical cases, such as represented by curve 3, Fig. 1, and was found to be within 3% of the value calculated for the conversion of all the sucrose into invert sugar.

The sucrose was a finely ground dry sample of Domino cane sugar, adant cut loaf, over 99.9 wt. % sucrose containing less than 0.018 wt. % invert sugar.[3] The water was triply distilled and was free of all impurities. The other materials were of analytical reagent or C.P. quality.[2]

The results are presented in Fig. 1. In the case of curve 3 autocatalysis increased the rate of the reaction sixfold (6b) by the time 90% of the sucrose had been hydrolyzed, and this was accompanied by a decrease in the *p*H of the reacting mixture. The increase in the acidity corresponded quantitatively to the increase in the rate. The *p*H values were measured with a glass electrode after the solutions had been cooled to 25°.

The extent of the autocatalysis was found to increase when there was an increase in (1) the per cent. sucrose hydrolyzed (curve 3), (2) the initial concentration of sucrose (*cf.* curves 1 and 2), (3) the temperature at which the hydrolysis was carried out (*cf.* curves 2 and 5B) and when there was (4) a decrease in the initial concentration of the acid (*cf.* curves 3 and 4B).

(3) L. J. Heidt and F. W. Southam, This Journal, **72**, 580 (1950).

Boron–Nitrogen Systems. II. Diethylaminoboron Dichloride[1]

By Robert C. Osthoff[2] and Charles A. Brown

Received January 5, 1952

The first paper of this series[3] was devoted to a discussion of the physical and chemical properties of dimethylaminoboron dichloride, in both its monomeric and dimeric forms. In this paper the properties of diethylaminoboron dichloride, $(CH_3CH_2)_2NBCl_2$, will be discussed.

Wiberg[4] has reported the preparation of diethylaminoboron dichloride by the action of boron trichloride upon diethylamine, but no yield data or experimental details were presented. Wiberg also found that diethylaminoboron dichloride formed no dimer, even after standing for one year at room temperature. This lack of dimer formation is in sharp contrast to the behavior of dimethylaminoboron dichloride which readily forms a rather stable dimer.[3] It was stated by Wiberg that diethylaminoboron dichloride reacts with hydrohalogen acids and with tertiary amines, but the properties of the resulting compounds have not been published.

Experimental

Preparation of $(CH_3CH_2)_2NBCl_2$.—Diethylaminoboron dichloride was obtained by fractionation of the reaction mixture which resulted from the action of excess boron trichloride (Matheson) upon diethylamine (Eastman Kodak Co. "White Label") used as supplied by the manufacturer without further purification, since none of the contaminants would give rise to products which would decrease the purity of the diethylaminoboron dichloride. The reactants were brought together at −196° *in vacuo*. By warming the reaction mixture slowly to room temperature (over about a 4-hour period) it was possible to fractionate the volatile products by passing them through traps at −20, −80 and −196°. Diethylaminoboron dichloride was collected in the trap which was held at −20° and further purified by bulb to bulb vacuum distillation. Based on the amount of diethylamine that was employed, the yield of product was 40%; the calculation of the yield was made by assuming that the preparative reaction may be formulated as

$$BCl_3 + 2HN(CH_2CH_3)_2 \longrightarrow (CH_3CH_2)_2NBCl_2 + (CH_3CH_2)_2NH\cdot HCl$$

A mole ratio of amine to boron trichloride of about 1.5 was used in the preparation of diethylaminoboron dichloride in order that none of the higher substitution products of boron trichloride (*i.e.*, bisdiethylaminoboron chloride and trisdiethylaminoboron) would be formed.

Characterization of Diethylaminoboron Dichloride.—In Table I are summarized the physical properties of diethylaminoboron dichloride which have been reported previously by Wiberg,[4] as well as the corresponding values which were observed by the authors.

The authors determined the melting point visually; the boiling point, the heat of vaporization, and the Trouton constant were evaluated by the authors from a study of the vapor pressure of the pure compound as will be described below. The experimental methods employed by Wiberg for the evaluation of these constants are not given in the literature.

Table I

Physical Properties of Diethylaminoboron Dichloride

Property	Reported by Wiberg[4]	Observed
M.p., °C.	−25.5	−23.0
B.p., °C.	150	148
Heat of vaporization, cal./mole	9560	9480
Trouton constant, cal./deg.	22.6	22.5

Measurements of vapor density at 22° by the authors gave an observed molecular weight of 151 (calcd. for $(CH_3CH_2)_2NBCl_2$, 153.9). It had been reported earlier by Wiberg[4] that this compound remained monomeric after standing at room temperature for one year. This was observed to be the case, since the authors found no evidence of dimer formation in samples which were stored for 18 months at room temperature in the absence of air and moisture. When sealed tubes of diethylaminoboron dichloride were heated to 190° in attempts to form a dimer, we observed only carbonization of the ethyl groups.

Liquid Density.—A dilatometric pycnometer was employed to evaluate the density of liquid diethylaminoboron dichloride in the temperature range of 5 to 95°. By application of the method of least squares to the observed data, the linear equation relating the density to the Centigrade temperature was found to be

$$d = 1.0796 - 0.001161\,t\ (\text{g./ml.})$$

Some of the observed and calculated values of the density are summarized in Table II. These values of the density were estimated to be accurate to about 0.05%.

Vapor Pressure.—By employment of isoteniscopes of the type described by Smith and Menzies,[5] the vapor pressure of diethylaminoboron dichloride was studied between 24 and 140°. In order to ensure the removal of adsorbed water from the isoteniscopes, the apparatus was repeatedly flamed in high vacuum. Above 80° each of the observed pressures was corrected by the subtraction of the vapor pressure of mercury at that temperature.

By application of the method of selected points to the vapor pressure data of two independent runs, the constants of the Antoine[6] equation were evaluated. Thus the vapor

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[1] Taken from Ph.D. thesis of Robert C. Osthoff, Harvard University, 1951.

[2] Procter and Gamble Fellow in Chemistry, Harvard University, 1951. Present address: Research Laboratory, General Electric Co., Schenectady, N. Y.

[3] C. A. Brown and R. C. Osthoff, This Journal, **74**, 2340 (1952).

[4] E. Wiberg, "Fiat Review of German Science," Vol. 23, Part I, pp. 217, *et seq.*

[5] A. Smith and A. W. C. Menzies, This Journal, **32**, 1412 (1910).

[6] G. W. Thomson, *Chem. Revs.*, **38**, 1 (1946).

TABLE II

CALCULATED AND OBSERVED VALUES OF THE DENSITY OF DIETHYLAMINOBORON DICHLORIDE AT VARIOUS TEMPERATURES

t, °C.	d, obsd.	d, calcd.
5.0	1.0744	1.0738
10.0	1.0680	1.0680
41.0	1.0313	1.0320
50.0	1.0211	1.0215
60.00	1.0100	1.010
70.0	0.9979	0.9983
80.0	.9857	.9863
90.0	.9746	.9741

pressure of liquid diethylaminoboron dichloride may be calculated at a given temperature by means of the equation

$$\log_{10} P_{\text{mm}} = 7.1825 - \frac{1618}{t + 230}$$

In Table III some of the observed and calculated values of the vapor tensions at various temperatures are presented.

TABLE III

CALCULATED AND OBSERVED VALUES OF THE VAPOR PRESSURES OF DIETHYLAMINOBORON DICHLORIDE

t, °C.	$P_{\text{mm.}}$ obsd.	$P_{\text{mm.}}$ calcd.
24.0	6.5	6.5
30.0	9.9	9.2
40.0	14.9	15.5
50.0	25.7	25.4
60.0	40.7	40.1
70.0	61.7	61.6
80.0	92.8	91.9
90.0	135.8	133.7
110.0	269.5	265.3
125.0	420.0	421.5

From the vapor pressure equation, the heat of vaporization was found to be 9480 g. cal. per mole, and the normal boiling point was found to be 148° by extrapolation. By combination of these values in the usual fashion, the Trouton constant was found to be 22.5 e.u.

Surface Tension.—By employment of the twin capillary method of Mills and Robinson,[7] the surface tension of diethylaminoboron dichloride was evaluated at various temperatures *in vacuo* (suitable precautions to prevent hydrolysis due to traces of moisture in the vacuum apparatus were observed).

The equation which relates the surface tension to the centigrade temperature is

$$\gamma(\text{vapor}) = 28.81 - 0.0984\, t \text{ (dynes per cm.)}.$$

Some calculated and observed values of the surface tension are given in Table IV.

TABLE IV

CALCULATED AND OBSERVED VALUES OF THE SURFACE TENSIONS OF DIMETHYLAMINOBORON DICHLORIDE

t, °C.	γ, obsd.	γ, calcd.
10.0	27.82	27.83
15.0	27.18	27.00
22.5	26.53	26.58
25.0	26.35	26.33
30.0	25.87	25.86
35.0	25.30	25.37
40.0	24.99	25.07
45.0	24.42	24.38
50.0	23.69	23.89
55.0	23.40	23.41
60.0	23.06	22.91

By application of the Eötvös equation to the surface tension data in the usual manner,[8] it was found that the surface energy may be expressed by means of the equation

$$\gamma(Mv)^{2/3} = 2.1(379 - t - 6) \text{ (ergs)}$$

where γ = the surface tension in dynes per cm., M = the molecular weight, v = the specific volume, and t = the centigrade temperatures.

Thus the Eötvös constant was found to be 2.1; this indicates that liquid diethylaminoboron dichloride is not appreciably associated. From this treatment it was possible to estimate the critical temperature as 279°.

From the surface tension data and the density data, the mean value of the parachor of diethylaminoboron dichloride in the temperature range of 10 to 60° was found to be 331.7 parachor units. In the first paper of this series[3] it was shown that a suitable value for the atomic parachor of boron in this type of compound is 20.3. By use of this value in conjunction with the atomic parachor values of Sugden,[9] the calculated value of the molar parachor of diethylaminoboron dichloride was found to be 331.9.

Reaction with Hydrogen Chloride.—Anhydrous hydrogen chloride (2.280×10^{-3} mole) was introduced into a vacuum chain by means of a compensating gas buret. Diethylaminoboron dichloride was then added in small amounts and the pressure of the system was determined at constant volume and constant temperature following each of the additions.[10] In this manner the graph of Fig. 1 was constructed in which the mole ratio $(CH_3CH_2)_2NBCl_2/HCl$ is plotted against the pressure. The nature of the curve of Fig. 1 is clearly indicative of the formation of the one-to-one addition compound of empirical formula, $(CH_3CH_2)_2NBCl_2 \cdot HCl$.

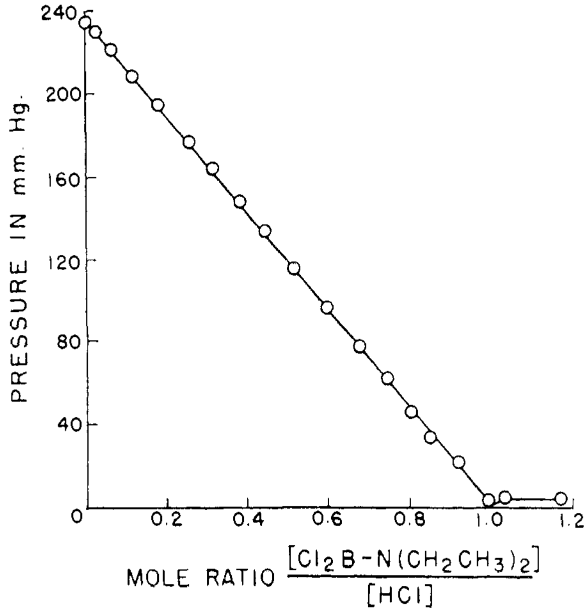

Fig. 1.—Pressure *vs.* mole ratio $[(CH_3CH_2)_2NBCl_2/HCl]$ for the reaction of diethylaminoboron dichloride with hydrogen chloride at 24.0°.

Anal. Calcd. for $(CH_3CH_2)_2NBCl_2 \cdot HCl$: C, 25.28; H, 5.78; N, 7.37; Cl, 55.93. Found: C, 25.20; H, 6.07; N, 7.18, Cl, 55.21.

$(CH_3CH_2)_2NBCl_2 \cdot HCl$ is somewhat soluble in anhydrous ethyl ether and may be purified by recrystallization from this solvent. The compound gives an instant precipitate of silver chloride when silver nitrate is added to its aqueous solution.

Reaction with Trimethylamine.—By the method described above, the the reaction of diethylaminoboron di-

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(7) H. Mills and P. L. Robinson, *J. Chem. Soc.*, 1823 (1927).

(8) S. Glasstone, "Textbook of Physical Chemistry," 2nd Ed., Chapter VII, D. Van Nostrand Co., Inc., New York, N. Y., 1946.

(9) S. Sugden, *J. Chem. Soc.*, **127**, 1540 (1925).

(10) R. C. Osthoff, C. A. Brown and F. H. Clarke, THIS JOURNAL, **73**, 4045 (1951).

chloride with trimethylamine was studied. Eastman Kodak Company White Label trimethylamine (vapor pressure at 0°, 676 mm.; calcd., 681 mm.[11]) was employed in the reaction. The course of this reaction, which was studied by means of a graph similar to that of Fig. 1, indicated that a one-to-one addition compound was formed. However, in the vicinity of a mole ratio of one, the straight line was rounded off and the pressure dropped only to about 20 mm. Inasmuch as this pressure is greater than the vapor pressure of diethylaminoboron dichloride, dissociation of the addition compound is indicated. The melting point of the trimethylamine adduct was observed to be about 20° with decomposition.

When the solid adduct was treated with water at about 10°, rapid hydrolysis took place, as indicated by the formation of an instant precipitate of silver chloride when the solution was treated with silver nitrate. Because of the low stability of the addition compound, it was impossible to obtain an elementary analysis for this substance.

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[11] A. Simon and J. Huter, *Z. Elektrochem.*, **41**, 28 (1935).

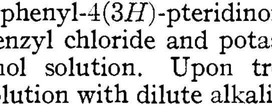
MALLINCKRODT CHEMICAL LABORATORIES
DEPARTMENT OF CHEMISTRY
HARVARD UNIVERSITY
CAMBRIDGE 38, MASSACHUSETTS

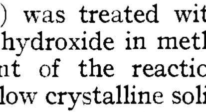
Pteridines, IX, Hydrolytic Ring Cleavage of 3-Benzyl-6,7-diphenyl-4(3*H*)-pteridinone

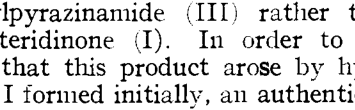
BY E. C. TAYLOR, JR.

RECEIVED NOVEMBER 23, 1951

A project at present under investigation in this Laboratory is the conversion of N-substituted amides of 3-aminopyrazinoic acids into 3-substituted 4(3*H*)-pteridinones. One compound of the latter type, 3-benzyl-6,7-diphenyl-4(3*H*)-pteridinone (I), has already been reported.[1] In an attempt to prepare I by an alternate route, 6,7-diphenyl-4(3*H*)-pteridinone (II) was treated with benzyl chloride and potassium hydroxide in methanol solution. Upon treatment of the reaction solution with dilute alkali, a yellow crystalline solid separated which proved to be 3-amino-N-benzyl-5,6-diphenylpyrazinamide (III) rather than the expected pteridinone (I). In order to test the hypothesis that this product arose by hydrolytic cleavage of I formed initially, an authentic sample of 3-benzyl-6,7-diphenyl-4(3*H*)-pteridinone (I) was treated with potassium hydroxide and 90% methanol. III was formed smoothly in 87.5% yield. If the reaction of 6,7-diphenyl-4(3*H*)-pteridinone (II) with benzyl chloride and potassium hydroxide in stock methanol was worked up after a shorter reaction period and the final addition of aqueous alkali was avoided, it was possible to isolate unreacted II, a small amount of I and some III from the reaction mixture. No III was formed under the same conditions when freshly prepared, absolute methanol was used as a solvent rather than stock methanol; under these conditions only a poor yield of pure I could be isolated from the reaction mixture. Attempts to synthesize I from 6,7-diphenyl-4(3*H*)-pteridinone (II) and benzyl chloride in the absence of alkali were unsuccessful, as were attempts to effect ring cleavage of II with dilute alkali alone.


I


II


III

The stability of II toward ring cleavage in dilute alkali is undoubtedly due to ready distribution of the negative charge of the anion over the pteridine ring system. Such a stabilization is impossible with I, as it cannot form a simple anion, and hydrolytic attack at C_2 followed by ring cleavage occurs with ease. A more general study of the hydrolytic cleavage of 3-substituted 4(3*H*)-pteridinones is under investigation.

These experiments support the generalization recently made by Albert, *et al.*,[2] that substituents on the pteridine nucleus are best introduced before ring closure.

Experimental[3]

6,7-Diphenyl-4(3*H*)-pteridinone (II).—A suspension of 15.0 g. (0.059 mole) of 5,6-diamino-4-hydroxy-2-mercaptopyrimidine sulfate[4] in 300 ml. of boiling water was treated with 20% sodium carbonate solution until all the suspended solid had dissolved. The *p*H was adjusted to 10 by the addition of dilute hydrochloric acid and 80 g. of wet Raney nickel added in small portions. After the violent evolution of gas had ceased, the mixture was heated under reflux for four hours. The reaction mixture was then allowed to cool, the nickel removed by filtration, and 12.4 g. (0.059 mole) of benzil dissolved in a mixture of 100 ml. of ethyl methyl ketone and 350 ml. of ethanol added to the filtrate. The resulting mixture was heated under reflux for eight hours. Acidification of the hot yellow solution and cooling caused the separation of colorless platelets which were collected by filtration and recrystallized from aqueous dimethylformamide; yield 13.2 g. (75%); m.p. (dec.) 297–298°.

Anal. Calcd. for $C_{18}H_{12}N_4O$: C, 72.0; H, 4.0; N, 18.7. Found: C, 72.0; H, 4.1; N, 18.6.

3-Amino-N-benzyl-5,6-diphenylpyrazinamide (III). **Method A.**—A mixture of 0.50 g. (0.00167 mole) of 6,7-diphenyl-4(3*H*)-pteridinone, 30 ml. of methanol, 0.2 ml. (0.00174 mole) of benzyl chloride and 0.16 g. (0.00286 mole) of potassium hydroxide was heated under reflux for two hours. Addition of 15 ml. of 2 *N* sodium hydroxide and warming caused the immediate separation of yellow needles. The reaction mixture was allowed to cool to room temperature, the crystals collected by filtration and recrystallized from ethanol; yield 0.483 g. (76%); m.p. 188.5–189°.

Method B.—To a solution of 75 mg. of 3-benzyl-6,7-diphenyl-4(3*H*)-pteridinone in 30 ml. of methanol was added 5 ml. of water containing 0.1 g. of potassium hydroxide and the solution heated under reflux for 10 minutes. The reaction mixture rapidly turned yellow with the simultaneous separation of yellow needles. Addition of 5 ml. of water and cooling gave 64 mg. (87.5%) of III in the form of long, yellow needles; m.p. 188.5–189°.

Mixed melting points of the products obtained by Methods A and B with an authentic sample of 3-amino-N-benzyl-5,6-diphenylpyrazinamide[1] showed no depression; infrared spectra of all three samples were identical.

3-Benzyl-6,7-diphenyl-4(3*H*)-pteridinone (I).—A mixture of 1.0 g. (0.00333 mole) of 6,7-diphenyl-4(3*H*)-pteridinone, 0.186 g. (0.00332 mole) of potassium hydroxide, 3.8 ml. (0.00332 mole) of benzyl chloride and 30 ml. of stock meth-

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[1] E. C. Taylor, Jr., THIS JOURNAL, **74**, 1651 (1952). It was prepared from 3-amino-N-benzyl-5,6-diphenylpyrazinamide (III) and formic acid in the presence of acetic anhydride.

[2] A. Albert, D. J. Brown and G. Cheeseman, *J. Chem. Soc.*, 474 (1951).

[3] All melting points are corrected.

[4] W. Traube, *Ann.*, **331**, 73 (1904).

anol was heated under reflux for one hour. Three milliliters of glacial acetic acid was added to the warm, yellow reaction solution, followed by sufficient hot water to induce crystallization. After cooling, the solution was filtered and the light yellow crystalline precipitate recrystallized from absolute ethanol. 3-Benzyl-6,7-diphenyl-4(3*H*)-pteridinone (I) (0.26 g., 25%) separated as colorless platelets from the warm ethanol; m.p. 248°. A mixed melting point with an authentic sample of I[1] showed no depression. Addition of a small amount of water to the ethanol filtrate and further cooling caused the separation of 0.19 g. of 3-amino-N-benzyl-5,6-diphenylpyrazinamide (III); m.p. 187°.

The mother liquor from the original reaction mixture above was diluted with an equal volume of water. A heavy, tacky yellow solid separated which was collected by filtration and extracted with 20 ml. of hot 1 *N* sodium hydroxide. Acidification of the filtrate precipitated 0.195 g. of unreacted 6,7-diphenyl-4(3*H*)-pteridinone (II), while repeated recrystallizations of the base-insoluble solid yielded an additional 0.11 g. (total yield 29%) of pure III.

In a second experiment, a mixture of 40 ml. of freshly prepared, anhydrous methanol, 0.793 g. (0.00264 mole) of 6,7-diphenyl-4(3*H*)-pteridinone, 0.301 ml. (0.00262 mole) of benzyl chloride and 0.148 g. (0.00264 mole) of potassium hydroxide was heated under reflux for 24 hours. By the end of this time, the reaction mixture was only faintly basic. Addition of a few drops of acetic acid to acidity followed by water caused the crystallization of light yellow crystals; yield 0.530 g.; m.p. 230–238°. Repeated recrystallizations from methanol gave 0.21 g. (20%) of pure I melting sharply at 248°.

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

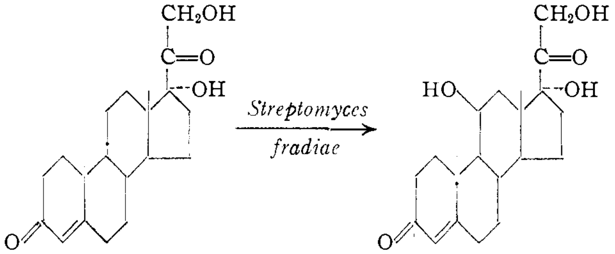
COMMUNICATIONS TO THE EDITOR

A PARTIAL MICROBIOLOGICAL SYNTHESIS OF ADRENAL CORTEX HORMONES

Sir:

It appears that either a hydroxyl group, having the *beta* configuration, or a ketone at the 11-position of the steroid nucleus is an obligatory structural requirement for the so-called carbohydrate-regulating hormone activity of the adrenal steroids, corticosterone, 11-dehydrocorticosterone, 17-hydroxycorticosterone and 11-dehydro-17-hydroxycorticosterone. Since both 11-desoxycorticosterone and 11-desoxy-17-hydroxycorticosterone are essentially devoid of this type of bioactivity, as measured by the Rat Liver Glycogen Deposition Assay,[1] it is possible to detect the introduction of an 11-β-hydroxyl group or an 11-keto group into these compounds by means of this assay.

We wish to report evidence for the microbiological oxygenation of these latter two steroids, with particular emphasis on the conversion of 11-desoxy-17-hydroxycorticosterone (Reichstein's compound S) (I) to 17-hydroxycorticosterone (Kendall's compound F, hydrocortisone) (II) by *Streptomyces fradiae*, Waksman's strain 3535.



I II

Several species of *Streptomyces* were incubated with 100-mg. quantities of 11-desoxycorticosterone and 11-desoxy-17-hydroxycorticosterone. The quantitative measurement of glycogen deposition activity in the resulting beers[2] and calculation of this bioactivity in terms of a theoretical conversion to corticosterone and 17-hydroxycorticosterone gave values which varied from 1.4 to 5.8%.

In an experiment of somewhat larger scale 5.0 g. of I was incubated with *Streptomyces fradiae*, strain 3535, for 7 hours at 24° in rotary shaker flasks, using a medium containing dextrose, soybean meal and distillers' solubles. The total volume of the beer was 15 liters. A neutral hormone concentrate which was obtained from the beer by a standard procedure,[3,4] weighed 4.86 g. and possessed total bioactivity equivalent to 140 mg. of 17-hydroxycorticosterone. Evaluation of this material by paper chromatography[5,6,7] indicated the presence of II, a trace of 11-dehydro-17-hydroxycorticosterone and unreacted I.

One-half of the neutral hormone concentrate (2.43 g.) was subjected to automatic partition column chromatography.[8] The three adrenal steroids mentioned above were found in individual bands in the resulting chromatogram. The "17-hydroxycorticosterone band" weighed 110 mg. First crop crystals from acetone (22.8 mg.) were identified as II. Evidence for this characterization was afforded by long-term paper chromatography in which fermentation product moved at a rate identical with authentic II. In addition, a mixture of the fermentation product and authentic II could not be resolved under any of several conditions. Furthermore, the data from infrared spectroscopy,[9] as shown in Fig. 1, provided additional evidence for the identification of the crystalline product from

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(1) M. L. Pabst, R. Sheppard and M. H. Kuizenga, *Endocrinology*, **41**, 55 (1947).

(2) We are indebted to Dr. K. J. Olson and his staff for the bioassays reported herein.

(3) M. H. Kuizenga, A. N. Wick, D. J. Ingle, J. W. Nelson and G. F. Cartland, *J. Biol. Chem.*, **147**, 561 (1943).

(4) W. J. Haines, R. H. Johnson, M. P. Goodwin and M. H. Kuizenga, *ibid.*, **174**, 925 (1948).

(5) A. Zaffaroni, R. B. Burton and E. H. Keutmann, *Science*, **111**, 6 (1950).

(6) R. B. Burton, A. Zaffaroni and E. H. Keutmann, *J. Biol. Chem.*, **188**, 763 (1951).

(7) W. J. Haines and N. A. Drake, *Fed. Proc.*, **9**, 180 (1950).

(8) W. J. Haines, N. A. Drake, C. D. Alway and M. P. Brunner, *Abstracts of Papers*, 118th Meeting Am. Chem. Soc., Chicago, Illinois, Sept. 1950, p. 11-M.

(9) We are indebted to Dr. J. L. Johnson and his staff for the infrared data reported herein.