use of the usual alkaline regenerating agents has appeared in the literature, although it has been mentioned[1,2] that some hydrolysis occurs.

In the course of investigations on the sodium hydroxide regeneration of Amberlite IR-4B, in which the resin was exhausted with hydrochloric acid, then rinsed and backwashed with a total of 24 volumes of water, it was found that the hydrolysis was by no means negligible, amounting to 20% of the total capacity. This was therefore studied more closely.

Experimental

A sample of Amberlite IR-4B was freed of particles smaller than 30 mesh by wet screening, and placed in a $1/2$ in. o. d. pyrex tube, supported on a platinum screen. Regenerated, backwashed, settled and drained, the volume of resin was 105 ml. This had been exhausted with hydrochloric acid and regenerated with sodium hydroxide about 25 times before the test run.

Hydrochloric acid, 0.100 N, was run through the resin until the effluent concentration was also 0.100 N. Water was then run at 25 ml./min., the first 100 ml. being discarded as representing the volume of liquid in the column. The water was purified by ion exchange, and had a pH of 6.5. The effluent was collected in convenient increments, and titrated against 0.10 N sodium hydroxide, with phenolphthalein indicator. The run was continued until the titration values were found to approach that of the blank, 0.08 ml./100 ml.

This volume of water was not run without interruption. It was found, however, that standing overnight did not increase the acid concentration measurably, if this concentration was below 0.01 N. This indicates that under the conditions used, the approach to equilibrium was very close, and interruption of the flow would cause no significant error (compare Kunin,[3] Fig. 6).

The results are summarized in Table I. The total capacity of the 105 ml. of resin was found to be 0.270 equivalents in other experiments in which the resin, completely regenerated by 0.25 N sodium hydroxide, was exhausted with 0.10 N hydrochloric acid.

TABLE I

HYDROLYSIS OF ANION EXCHANGE RESIN HYDROCHLORIDE

Volume water, liters	Σ HCl removed, equivs.	Σ HCl calcd. Equation 1, equivs.	Σ HCl calcd. Freundlich, equivs.
2	0.053	0.052	0.019
5	.075	.078	.069
10	.095	.100	.100
20	.118	.121	.126
50	.145	.149	.155
100	.168	.170	.173
200	.189	.191	.188

Discussion

Table I gives the total volume of water used, V, in column 1, and the amount of hydrochloric acid removed from the resin, Σ HCl, in column 2. The third column was calculated from the empirical equation

$$\Sigma HCl = 0.07 \log V + 0.03 \tag{1}$$

Column 4 was calculated from the Freundlich adsorption isotherm. The result agrees with the conclusion of Kunin and Myers in their study of

(1) R. Kunin and R. J. Myers, THIS JOURNAL, 69, 2874 (1947).

(2) P. Smit, U. S. Patent Application No. 359,575 (Oct. 3, 1940).

(3) R. Kunin and R. J. Myers, J. Phys. Chem., 51, 1111 (1947).

acid adsorption[1,3] that the Freundlich equation can be applied at acid concentrations below 0.01 N. The data of Table I cannot be described in terms of the Donnan equilibrium, lending support to the hypothesis that the mechanism of acid removal by this resin is one of adsorption, and not of ion exchange.

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Dimercaptols of Dehydroisoandrosterone

By ROBERT H. LEVIN AND J. L. THOMPSON

A recent publication[1] reports the reaction of dehydroisoandrosterone acetate (I) with benzylmercaptan and ethylmercaptan to give the corresponding dimercaptols (II, III). Saponification of II led to the hydroxy compound IV.
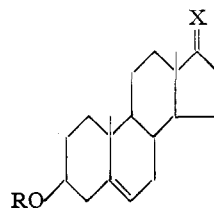
I	R = CH₃CO,	X = O
II	R = CH₃CO,	X = (SCH₂C₆H₅)₂
III	R = CH₃CO,	X = (SCH₂CH₃)₂
IV	R = H,	X = (SCH₂C₆H₅)₂
V	R = H,	X = (SCH₂CO₂H)₂

We had independently prepared the dibenzylmercaptol (IV) in 65% yield by directly condensing dehydroisoandrosterone with benzylmercaptan in the presence of zinc chloride and sodium acetate. Acetylation with acetic anhydride in pyridine at room temperature gave the acetate (II) of dehydroisoandrosterone dibenzylmercaptol in 94% yield.

In the same manner dehydroisoandrosterone has been condensed with thioglycolic acid to give the dimercaptol (V) in 73% yield. The sodium salt of this interesting compound is water soluble.

Experimental

Dibenzylmercaptol of Dehydroisoandrosterone (IV).— To a mixture of 2.8 g. of freshly fused and pulverized zinc chloride, 5 g. of anhydrous sodium sulfate, and 2.88 g. (0.01 mole) of dehydroisoandrosterone was added 25 ml. of benzyl mercaptan. After standing at room temperature for fifteen minutes the mixture was placed in the refrigerator for twenty hours, then allowed to warm up to room temperature and poured into 500 ml. of ice-water. The mixture was extracted with three 125-ml. portions of ether and the ether washed with 5% sodium hydroxide solution and with water and dried over anhydrous sodium sulfate. The ether solution was concentrated on the steam-bath and the excess benzyl mercaptan distilled at 1–5 mm. The residue was crystallized from hexane, giving 4.09 g. (79%) of product, m. p. 150–154°. which, after several recrystallizations from hexane, melted at 184–186°. The yield of pure material was 65% of the theoretical.

(1) Norymberska, Norymberski and Olalde, THIS JOURNAL, 70, 1256 (1948).

Anal. Calcd. for $C_{33}H_{42}OS_2$: C, 76.40; H, 8.16; S, 12.4. Found: C, 76.18; H, 8.53; S, 12.5.

Acetylation of IV (1 g.) in 5 ml. of acetic anhydride and 10 ml. of pyridine at room temperature for twenty hours and crystallization from acetone–water gave 1.02 g. (94%) of colorless needles, m. p. 150–152°, of the dibenzylmercaptol of dehydroisoandrosterone acetate.

Anal. Calcd. for $C_{35}H_{44}O_2S$: S, 11.4. Found: S, 11.4.

Dimercaptol of Dehydroisoandrosterone and Thioglycolic Acid (V).—In an analogous manner 2.88 g. (0.01 mole) of dehydroisoandrosterone, 2.8 g. of zinc chloride, and 5 g. of sodium sulfate were mixed and treated with 10 ml. of thioglycolic acid. The reaction mixture was poured into 500 ml. of water, giving a precipitate which was separated by filtration. Crystallization of the dimercaptol (V) from 100 ml. of acetone and 10 ml. of water gave 3.35 g. (73%) of material, m. p. 130–155°. Several recrystallizations from ethyl acetate gave colorless needles, m. p. 177–179°.

Anal. Calcd. for $C_{23}H_{34}O_5S_2$: S, 14.1. Found: S, 14.3.

Hydrolysis of the dimercaptol (V) in refluxing aqueous alcoholic hydrochloric acid gave dehydroisoandrosterone, m. p. 140–142°.

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A General Relation Among the Various Additive–Constitutive Physical Properties

By Fausto W. Lima

There have been found linear relations among some physical properties, like the one of R. T. Lagemann[1] between molecular refraction and Souder's viscosity constant, the numerical coefficients of which are obtained by the method of least squares.

Lagemann and Dunbar[2] showed also that molecular refraction, parachor, Souder's viscosity constant, van der Waals' *b* and molecular magnetic rotation are related to the molecular sound velocity[3] by linear relation; consequently, between any two of these properties there will also be linear relations.

We can show that there is a way of generalizing such relations and of obtaining new ones and, at the same time, of justifying them theoretically.

Let us consider the members of an homologous series of organic compounds; one can say that an additive–constitutive property *F* (like parachor, molecular refraction, Souder's viscosity constant, etc.) can be taken as *n* times the contributions of the CH_2 groups (where *n* are the number of CH_2 groups of the member of the homologous series) plus the contributions of any special characteristic of the series, like double bonds, triple bonds, carbonyls, carboxyls, or rings, etc.; one must include also the contributions of the hydrogen atoms that remain after putting CH_2 in evidence. We have then

$$F = nF_{CH_2} + F_1 \qquad (1)$$

where F_{CH_2} is the contribution of the group CH_2

and F_1 the contributions of the structural characteristic of the series plus the contribution of the hydrogen atoms that remain after putting CH_2 in evidence.

For another additive-constitutive property *G* one can write for the same series that

$$G = nG_{CH_2} + G_1 \qquad (2)$$

where the symbols have the same meaning as before but with regard to the *G* property.

By eliminating *n* between (1) and (2) we have

$$F = GF_{CH_2}/G_{CH_2} - G_1F_{CH_2}/G_{CH_2} + F_1 \qquad (3)$$

which is a linear relation

$$F = aG + b$$

The relation (3) shows why the slope F_{CH_2}/G_{CH_2} is the same for the components of any homologous series, as Lagemann[1] observed.

The equation (3) was tested for the relation Souder's viscosity constant (*I*)–parachor (*P*) and parachor (*P*)–molecular refraction (*R*) and the agreement between calculated and observed values was found to be less than 1%.

For the relation between *I* and *P*, $a = I_{CH_2}P_{CH_2} = 55.6/40 = 1.4$, and *b* for the series studied is

Paraffins	-37.7
Alkyl bromides	-36.5
Alkyl chlorides	-35.9
Alkyl iodides	-34.9
Monohydric alcohols	-3.8
Carboxyl acids (monobasics)	-19.7
Esters of acetic acid	-34.4
Esters of formic acid	-33.2
Esters of propionic acid	-39.8

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Triethylenetetranitramine

By G. N. R. Smart and George F Wright

The nitration of dialkylchloramines[1] and of monoalkyldichloramines[2] has recently been reported. It seemed of interest to inquire whether nitration would be successful in cases where these two types of chloramine linkage were incorporated into the same molecule. Triethylenetetramine was chosen as a type, and was N-chlorinated[3] to give N-hexachlorotriethylenetetramine, I.

We were unable to isolate the chloramine as a chemical individual. At best it decomposed slowly during evaporation of the solvent in which it was prepared; in the dry state it often decomposed explosively. However, a slight decomposition ought to be inconsequential since the more

(1) R. T. Lagemann, THIS JOURNAL, 67, 498 (1945).
(2) R. T. Lagemann and Dunbar, J. Phys. Chem., 49, 428 (1945).
(3) M. R. Rao, J. Chem. Phys., 9, 682 (1941).

(1) G. S. Myers and G. F Wright, Can. J. Res., 26B, 257 (1948).
(2) G. N. R. Smart and G. F Wright, ibid., 26B, 284 (1948).
(3) L. K. Jackson, G. N. R. Smart and G. F Wright. THIS JOURNAL, 69, 1539 (1947).