*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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[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).

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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

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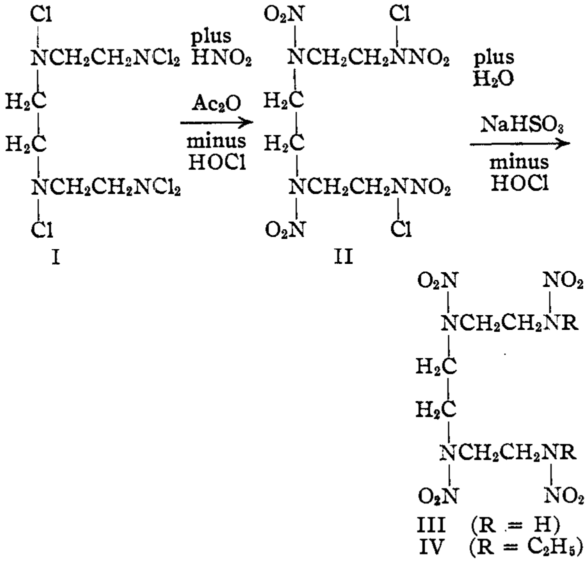
[1] G. S. Myers and G. F Wright, *Can. J. Res.*, **26B**, 257 (1948).

[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).

sensitive linkage (RNClR > $RNCl_2$) is known to decompose largely to the amine hydrochloride. The amine hydrochloride linkage has been found to revert to the chloramine in the presence of nitric acid in acetic anhydride.[1]

No attempt was made therefore to isolate the N-hexachlorotriethylenetetramine, I, from the chloroform solution in which it was prepared. Direct nitration in acetic anhydride solution yielded $N^1,N^4$-dichlorotriethylenetetranitramine, II, in fair yield, and this was converted readily to triethylenetetranitramine by means of aqueous sodium sulfite.



I II

III (R = H)
IV (R = $C_2H_5$)

The alkali soluble III was characterized by conversion to $N^1,N^4$-diethyltriethylenetetranitramine, IV, with diazoethane.

### Experimental[4]

**Chlorination of Triethylenetetramine.**—A solution of 49 g. (0.3 mole) of triethylenetetramine and 252 g. (3.0 moles) of sodium bicarbonate in 1500 cc. of water was combined with 100 cc. of chloroform and treated at 25° with a rapid stream of chlorine for ten hours. The chloroform layer was separated and dried with calcium chloride. This chloroform solution was used for the nitration described subsequently. Analysis showed that it contained five-sixths of the expected electropositive chlorine.

**Dichlorotetranitrotriethylenetetramine.**—One-half of the chloroform solution (assumed to be 0.15 mole of N-hexachlorotriethylenetetramine) was added proportionately with 36.3 ml. (0.9 mole) of 98% nitric acid to 143 ml. (1.5 mole) of acetic anhydride over one hour. The temperature was maintained at 40° during addition and subsequently for one hour. After the mixture was chilled to 0° for nine hours it was filtered to remove 25 g. of material melting roughly at 114–116°. This crude product when analyzed for electropositive chlorine seemed to be a mixture of $N^1$-chloro and $N^1,N^4$-dichlorotriethylenetetranitramine. If it were the latter compound the yield would be 42% of theoretical.

**Triethylenetetranitramine.**—When the crude reaction product (25 g.) was suspended in 250 cc. of cold stirred half-saturated sodium sulfite solution for nine hours the electropositive chlorine was consumed. The suspension was then filtered to remove 17.5 g. (36% yield from triethylenetetramine), melting at 159–160°. This material was dissolved in alkali (*p*H 8) and filtered. It was reprecipitated (m. p. 168°) by acidification to *p*H 4 with dilute hydrochloric acid. Final purification (m. p. 174.1°) was effected by two crystallizations from hot nitromethane (10 cc. per g.). The compound gave a positive Franchimont test for a nitramine. It formed an insoluble silver salt and a relatively insoluble pyridine salt.

*Anal.* Calcd. for $C_6H_{14}N_8O_8$: C, 22.1; H, 4.30; N, 34.4. Found: C, 22.4; H, 4.25; N, 33.9.

**$N^1,N^4$-Diethyltriethylenetetranitramine.**—A suspension of 0.5 g. of triethylenetetranitramine in an ether solution containing 0.25 g. of diazoethane evolved gas rapidly. Evaporation of the ether left a sirup which gradually solidified during four days. It was crystallized from ethanol to melt at 68–70° (yield 50% of theoretical). A recrystallization raised this melting point to 96.5–96.8°. The compound was insoluble in alkali, and it gave a positive Franchimont test for a nitramine.

*Anal.* Calcd. for $C_{10}H_{22}N_8O_8$: C, 31.5; H, 5.82; N, 29.3. Found: C, 31.9; H, 5.85; N, 29.1.

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[4] All melting points have been corrected against known standards.

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# The Rare Earth Metals and their Compounds. VIII. An Improved Method for the Synthesis of Some Rare Earth Acetylacetonates[1a]

BY JOSEPH G. STITES, C. N. MCCARTY AND LAURENCE L. QUILL

Methods reported in the literature[1-7] for the preparation of the acetylacetonates of the rare earths involve, for the most part, the addition of a solution of sodium or ammonium acetylacetonate to a dilute acid solution of the rare earth nitrate. The yields are either unreported or are low.

This study was undertaken to observe the effect of changing the acidity on the formation of the rare earth acetylacetonates since (a) acetylacetone is a weak acid and (b) completeness of precipitation of many rare earth compounds is *p*H dependent. Also, since acetylacetone is so easily oxidized it was thought that part of the lower yield resulting when the nitrates of the rare earths are used was due to an oxidation effect and, consequently, that the chlorides might give better results.

### Experimental

A weighed quantity of rare earth oxide was dissolved in the minimum amount of dilute hydrochloric acid and the *p*H of the solution adjusted by the addition of dilute ammonium hydroxide to a value of approximately 5.0 as measured by the glass electrode. A solution of ammonium acetylacetonate was prepared by adding concen-

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[1a] Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the Chicago meeting April 1948.

(1) W. Biltz, *Ann.*, **331**, 334 (1904).

(2) G. Jantsch and E. Meyer, *Ber.*, **53B**, 1577–1587 (1920).

(3) G. Urbain, *Bull. soc. chim.*, [3] **15**, 338–347 (1896).

(4) G. Urbain, *Ann. chim. phys.*, [7] **19**, 223 (1900).

(5) R. C. Young and J. Kovitz, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., New York, 1947, p. 123.

(6) R. A. Staniforth, L. L. Quill and J. P. McReynolds, Thesis, Ohio State University, 1943, unpublished.

(7) J. K. Marsh, *J. Chem. Soc.*, 1084 (1947).