(D_2^3d). Space group $P\bar{4}2_1$ does not permit a tetrahedral arrangement of atoms around the phosphorus atom. Since the structure appeared to be isotypic with tetramethylammonium dichloroiodide[4] and since the Patterson projection could be explained on the basis of this structure, the structure based on $P\bar{4}2_1m$ was chosen.

Crystal Structure.—Using ($hk0$) data, a Patterson projection was made on ($00l$) and the approximate x- and y-parameters determined. From these parameters the signs of the $F(hk0)_{\text{obsd}}$ were calculated and used in a Fourier projection on ($00l$). The x- and y-parameters were refined as much as possible by a repetition of this Fourier projection. The z-parameters were obtained from a Patterson projection on (110). In order to obtain better agreement between the calculated and observed F values, an empirical temperature correction factor of the form $e^{-1.51 \sin^2\theta}$ was applied to the calculated F values. It was felt by the authors that the usual scheme of computing R_1 does not make sufficient allowance for reflections, which, while not zero, are not sufficiently strong to record on film with ordinary exposures. Accordingly, a slightly modified method of calculating the R_1 values, consisting of assigning each absent or unobserved reflection an F value which was calculated as follows, was used. The minimum intensity observable was corrected by the angle factors corresponding to each of the unobserved reflections. Taking one-half of the square roots of the quantities thus obtained yielded F values which were arbitrarily assigned to the absent reflections for the purpose of calculating R_1. The R_1 calculated in this manner is defined as R_1^*. Using the parameters chosen an R_1^* value of 0.27 was obtained.

The compound proved to be isostructural with tetramethylammonium dichloroiodide,[4] with the following atoms at the following positions of space group D_2^3d-$P\bar{4}\,2_1m$: 2 P at (b) ($0\ 0\ ^1/_2$), ($^1/_2\ ^1/_2\ ^1/_2$); 2 I at (c) ($0\ ^1/_2\ z$), ($^1/_2\ 0\ \bar{z}$) with $z = 0.161$; 4 Cl at (e) $x,\ ^1/_2 + x,\ z;\ \bar{x},\ ^1/_2 - x,\ z;\ ^1/_2 + x,\ \bar{x},\ \bar{z};\ \ ^1/_2 - x,\ x,\ \bar{z}$ with $x = 0.18_n$, $z = 0.16_1$; 8 Cl at (f) $xyz;\ ^1/_2 - x,\ ^1/_2 + y,\ \bar{z};\ \bar{x}\bar{y}z;\ ^1/_2\ .\ x,\ ^1/_2 - y,\ \bar{z};\ \bar{y}x\bar{z};\ ^1/_2 + y,\ ^1/_2 + x,\ z;\ y\bar{x}\bar{z};\ ^1/_2 - y,\ ^1/\ \cdot x,\ z$ with $x = 0.15_5$, $y = 0.07_9$, $z = 0.29_8$.

This structure consists of regularly tetrahedral PCl_4^+ ions, and linear $ClICl^-$ ions with the interatomic distances in ångström units are

P–8-fold Cl	1.98
I–4-fold Cl	2.36
8-fold Cl–8-fold Cl (within PCl_4^+ tetrahedra)	3.23
8-fold Cl–8-fold Cl (from one PCl_4^+ to the next)	3.50
4-fold Cl–8-fold Cl	3.56

Extensive calculations of intensities based on selected chlorine positions near those given above showed that the positions of chlorine atoms could be changed considerably without affecting the R_1^* value. For example

x for 4 (e)	0.16	0.17	0.18	0.19	0.20
R_1^*	.285	.271	.270	.272	.277

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[4] R. C. L. Mooney, *Z. Krist.*, [A] **100**, 519 (1939).

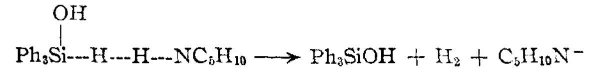
COMMUNICATIONS TO THE EDITOR

HYDROGEN ISOTOPE EFFECT IN THE HYDROLYSIS OF TRIPHENYLSILANE

Sir:

Recently, Gilman, Dunn and Hammond reported[1] that triphenylsilane-*d* was hydrolyzed in moist piperidine "almost six times faster than its protium analog." They attributed this unusual isotope effect to the displacement of a hydride ion in such a manner that a hydrogen–hydrogen bond of considerable strength is present in the transition state of the reaction. This picture of the reaction path might be formulated as

$$OH^- + Ph_3SiH + HNC_5H_{10} \longrightarrow$$



$$\overset{OH}{Ph_3Si}\text{---}H\text{---}H\text{---}NC_5H_{10} \longrightarrow Ph_3SiOH + H_2 + C_5H_{10}N^-$$

Because of the unusual effect reported for this reaction, we have examined several similar reactions which involve the formation of hydrogen, presumably by abstraction of a hydride ion. To enhance any isotope effects, tritium, rather than deuterium, was used in competitive measurements of k_T/k_H, the ratio of the isotopic reaction rates.

The alkaline alcoholic hydrolysis[2] of tripropylsilane-*t* was found to be about 0.7 as fast as that of its protium analog. The alcoholysis of lithium aluminum hydride-*t*[3] and of lithium borohydride-*t*[4] did not give consistent values of k_T/k_H, possibly because of changes in the reacting species; the observed values fell between 1.2 and 0.8.

In view of these results we have reinvestigated the hydrolysis of triphenylsilane in moist piperidine. Tritium-labeled triphenylsilane was prepared[5] by the reduction of triphenylchlorosilane with lithium aluminum hydride-*t*.[3] The triphenyl-silane-*t* was dissolved in a 1.0 *M* solution of water in piperidine, in a previously evacuated system, and permitted to react at 25°. At intervals, the reaction was stopped by cooling to −80°, and the evolved hydrogen was collected. The volume of each fraction was measured manometrically and its tritium content was determined in an ion chamber with a vibrating reed electrometer. The total volume and tritium content of the fractions agreed with those expected from analysis[5] of the triphenylsilane-*t* by hydrolysis with moist piperidine and potassium hydroxide. The experimental results are given in Table I. The ratio of the rate constants is calculated for each gas fraction from the expression

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[1] H. Gilman, G. E. Dunn and G. S. Hammond, THIS JOURNAL, **73**, 4499 (1951).

[2] F. P. Price, *ibid.*, **69**, 2600 (1947).

[3] K. E. Wilzbach and L. Kaplan, *ibid.*, **72**, 5795 (1950).

[4] W. G. Brown, L. Kaplan and K. E. Wilzbach, *ibid.*, **74**, 1343 (1952).

[5] H. Gilman and G. E. Dunn, *ibid.*, **73**, 3404 (1951).

$$\frac{k_{\rm T}}{k_{\rm H}} = \frac{d({\rm HT})}{d({\rm H_2})} \times \frac{({\rm Ph_3SiH})}{({\rm Ph_3SiT})} = \log \frac{({\rm HT})_\infty - ({\rm HT})_2}{({\rm HT})_\infty - ({\rm HT})_1} \Big/ \log \frac{({\rm H_2})_\infty - ({\rm H_2})_2}{({\rm H_2})_\infty - ({\rm H_2})_1}$$

where $({\rm HT})_t$ refers to the amount of tritium and $({\rm H_2})_t$ to the volume of gas collected up to time *t*. The average value of $k_{\rm T}/k_{\rm H}$, over the course of more than 40% reaction is 0.796 ± 0.004.

This result is in good agreement with a theoretical value of 0.8 calculated[6,7] considering only the stretching frequencies of the Si–H and H–H bonds in the proposed model. The corresponding theoretical value of $k_{\rm D}/k_{\rm H}$ is 0.9.

TABLE I

HYDROLYSIS OF TRIPHENYLSILANE-*t*

Fraction	Reaction cumulative %	H_2, mmole	HT, μcuries	HT/H_2, μcuries/ mmole	$k_{\rm T}k_{\rm H}$
1	16.2	0.286	20.9	73.1	0.803
2	24.8	0.151	11.2	74.2	0.792
3	40.6	0.279	21.5	77.1	0.794
4	100.0	1.046	104.0	99.4	
Total		1.762	157.6	89.4	

(6) J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949).

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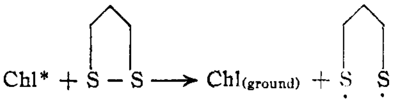
KENNETH E. WILZBACH

RECEIVED OCTOBER 1, 1952

A POSSIBLE PRIMARY QUANTUM CONVERSION ACT OF PHOTOSYNTHESIS[1,2]

Sir:

To account for the observation[3,4,5] that illumination prevents the appearance of newly assimilated carbon in the compounds of the tricarboxylic acid cycle, it was suggested[5] that the light shifts the steady-state condition of the thioctic acid-containing coenzyme[6,7] (protogen, lipoic acid, thioctic acid, P.O.F.) toward the reduced (dithiol) form, in which condition it is incapable of oxidatively decarboxylating pyruvic acid,[8,9] newly formed from CO_2, to give rise to the acetyl-CoA[10,11,12] required to bring this carbon into the compounds of the Krebs cycle. We are here reporting some observations leading to the further suggestion that this shift toward the dithiol form is the *direct* result of the light action and that a biradical formed by dissociation of the disulfide bond in a strained five-membered disulfide containing ring (as in 6,8-thioctic acid and trimethylenedisulfide) is the species in which the quantum absorbed by the plant pigments and stored as electronic excitation in chlorophyll[13] appears first as chemical bond potential energy; *i.e.*, that a possible primary quantum conversion act of photosynthesis is represented by the equation



(I)

Subsequent abstraction of H atoms[14,15] from a suitable donor by the thiyl free radicals would lead to the dithiol which would be reoxidized ultimately by CO_2. The residual oxidation product of the H donor would lead in the end to molecular oxygen. It is obvious that on both the reductant and oxidant sides the chemical products of the conversion of several quanta will be required to accomplish the reduction of each CO_2 molecule and the generation of each O_2 molecule.

These subsequent reactions, being strictly chemical, may lead to diverse energy rearrangements. For example, the chemical potential of reduced carbon might be converted by oxidative phosphorylation reactions into the energy of phosphoric anhydrides which, in turn, could raise the potential energy of intermediates in the reaction sequences leading to the evolution of molecular oxygen and to the reduction of CO_2.[16,17]

A value of the dissociation energy for this particular disulfide link lying in the region of 30–40 kcal. would constitute not only permissive evidence for reaction (I) but positive evidence in its support, since hitherto it has been difficult to suggest any likely primary chemical step capable of usefully absorbing the greater part of the ≃ 30–40 kcal. quantum of electronic excitation available for photosynthesis. Estimates of D(RS-SR) from simple open chain compounds range from 50[18] to 70[19] kcal. However, the fact that 5,8-thioctic acid is colorless, while 6,8-thioctic acid is yellow,[20] suggested that the incorporation of the S—S bond into a 5-membered ring might indeed introduce sufficient strain into it so as to reduce the S—S dissociation energy by as much as 25–30 kcal., thus bringing it down into the required range. A number of experiments have been performed using the product of the reaction of Na_2S_2 with $(CH_2)_3Br_2$ (trimethylenedisulfide) as a model substance. Its

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(1) The work described in this paper was sponsored by the U. S. Atomic Energy Commission.

(2) J. A. Barltrop, Rockefeller Fellow, 1952–1953, while on leave from Brasenose College and the Dyson Perrins Laboratory, Oxford University, England.

(3) A. A. Benson and M. Calvin, *J. Exptl. Bot.*, **1**, 63 (1950).

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(13) L. N. M. Duysens, *Nature*, **168**, 548 (1951).

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(15) E. F. P. Harris and W. A. Waters, *ibid.*, **170**, 212 (1952).

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(17) M. Calvin, J. A. Bassham, A. A. Benson and P. Massini, *Ann. Rev. Phys. Chem.*, **3**, 215 (1952).

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(20) Several milligrams of each of these synthetic[21] products were obtained through the courtesy of Dr. T. H. Jukes of Lederle Laboratories.

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absorption spectrum together with that of the two thioctic acids and *n*-propyl disulfide is shown in Figure 1. A light-induced fading of diphenylpicrylhydrazyl[22] at room temperature and dependent upon the presence of the disulfide was demonstrated. A photochemical polymerization of the disulfide by light of wave length greater than 4,000 Å. was sensitized by Zn tetraphenylporphin. These results may be taken to indicate that the dissociation energy of the disulfide bond in this compound is something less than 50 kcal. and that this dissociation may be brought about by energy transfer from some other molecule in a suitably excited state.

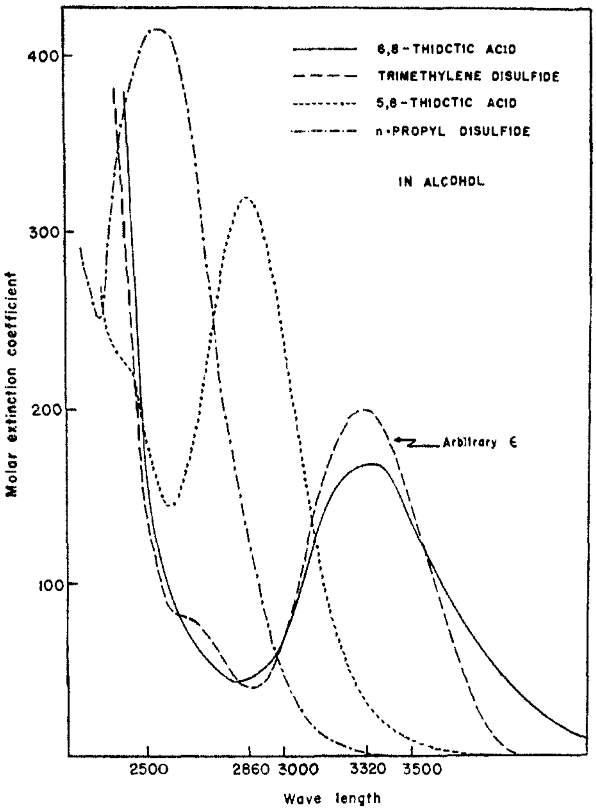

Fig. 1.—Absorption spectra of several disulfides.[33]

That such energy transfers may take place, and especially efficiently in condensed systems, has been amply demonstrated.[23,24,25,26,27] Since the grana have the optical properties of a condensed chlorophyll phase,[28,29,30,31] a quantum absorbed anywhere within that phase is very rapidly transferred among the identical molecules of that phase at the singlet or the triplet levels. Concomitant with this, there occurs a decrease in the probability of emission as fluorescence[23,24,25,32] and hence an increase in the availability of the quantum for chemical transformation (disulfide fission). In such a sytem, the high efficiency of energy conversion may be retained even though the ratio of chlorophyll to disulfide molecules be large (10^2–10^3).

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[32] D. McClure, private communication.

[33] We are indebted to Mr. Paul Hayes for the determination of these absorption spectra.

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RECEIVED NOVEMBER 17, 1952

ELECTROCHROMATOGRAPHIC SEPARATIONS OF RARE EARTHS

Sir:

Differential electrical migration in moist filter paper,[1,2,3] which has provided continuous[3] and discontinuous[2] separations of many ions, has now been applied to the separation of rare earths. These applications have incorporated many of the desirable physical and sorptive features of paper chromatography, and they have also utilized the principles of complex formation previously employed for the ion-exchange chromatography of rare earths.[4] They have yielded the resolved ions in a readily detectable and recoverable form.

For one-way, discontinuous migrations, filter paper (Eaton–Dikeman, Grade 301, 0.03 inch thick)[1] 3 to 6 feet by 20 inches was moistened with the electrolytic solution. About 50 μl. of the radioactive mixtures (about 0.3 μc. per component) and separate reference solutions of the components were added near the center.[1] The paper was encased in a polyethylene sheet, and the ends were dipped into separate portions of the electrolytic solution (8 l.) After electrolysis (5 v. per cm.,

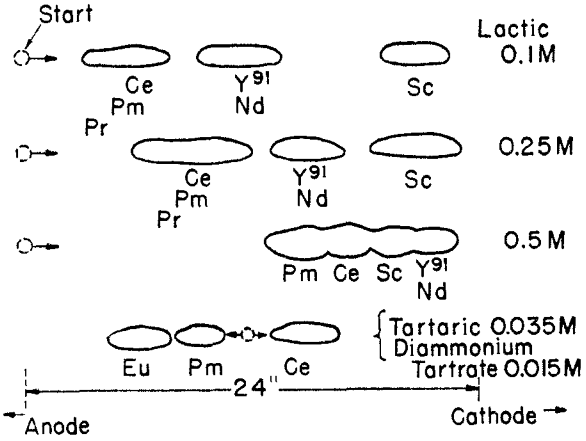

Fig. 1.—Migration of rare earths in lactic acid (24 hr.) and in tartrate solution (48 hr.).

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[1] H. H. Strain, *Anal. Chem.*, **24**, 356 (1952).

[2] H. H. Strain and G. W. Murphy, *ibid.*, **24**, 50 (1952).

[3] T. R. Sato, W. P. Norris and H. H. Strain, *ibid.*, **24**, 776 (1952).

[4] Ion Exchange, Plutonium Project Reports, THIS JOURNAL, **69**, 2769-2881 (1947).

1 to 2 days),[5] the paper was dried, and the ions were located photographically.[3]

As indicated in Fig. 1, the separability of rare earths increased with decreasing concentration of the supporting electrolyte, lactic acid. Although the mobility was great in about 1.5 *M* acid, Sc trailed the unseparated rare earths. In acid less than 0.1 *M*, electromigration produced slowly migrating, elongated zones. This migration behavior and the separability of the zones depended upon the selective sorbability of the ions by the paper. Separate chromatographic experiments showed that the sorbability of the ions increased with decreasing concentration of the lactic acid as has been found with Ca.[5]

In 0.1 *M* lactic acid, the rate of separation of Y from Ce increased during the electrolysis. Various cations separated in the following sequence (decreasing mobility): Cs + Rb, Sr, Ca, Co, Zn, Cu, Sc, Y^{90} + Y^{91} + Nd, Ce + Pr + Pm + Eu, Hg + Zr + Nb. The Hg + Zr + Nb did not migrate, but if stabilized with oxalate Zr + Nb migrated to the anode.

With diammonium tartrate (0.015 *M*) plus tartaric acid (0.035 *M*), Ce(III) migrated as a cation, Eu and Pm as anions (Fig. 1). The separability and the sign of the ionic charge depended upon tartrate concentration and *p*H. Separability was not due to sorbability by the paper.

As determined by photography,[5] separation of many binary and ternary mixtures was complete. These mixtures included parents and daughters as Nd–Pm, Ce–Pr, Ba–La, and Sr–Y.

Combination of electrical migration with transverse flow of solvent, as previously described,[3] has now provided continuous separation of alkalies and alkaline earths from the rare earths. It has also yielded continuous separations of Y from Ce and of the rare earths from anions such as $PO_4^{\equiv}$.

---

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RECEIVED SEPTEMBER 29, 1952

THE PEROXIDE AND LIGHT INDUCED REACTIONS OF AMINES WITH OLEFINS: A ONE-STEP SYNTHESIS OF *d,l*-CONIINE

Sir:

A reaction of considerable potential usefulness in organic synthesis, the addition of alkyl amines to olefins, has been observed. In the presence of a peroxide, a condensation occurs between the α-carbon atom of the amine and the olefin (the terminal carbon atom of 1-olefins) by what is probably a free-radical, chain reaction. For example, the reaction of piperidine with octene-1 in the presence of *t*-butyl peroxide gives 2-*n*-octylpiperidine, and *d,l*-coniine is obtained by the similar reaction of piperidine with propylene.

Under a pressure of nitrogen (25 lb./in.^{2}), a reaction mixture containing piperidine (382. g., 4.50 moles, b.p. 105–106°, $n^{20}D$ 1.4529), octene-1 (40 g., 0.36 mole, b.p. 120°, $n^{20}D$ 1.4090), and *t*-butyl peroxide (3 g.) was held at 120° for 50 hours. Additional peroxide (2 g. after 6 hours, 2 g. after 12 hours) was added. Distillation of the reaction mixture gave *t*-butyl alcohol (6.3 g., b.p. 80–82°), unreacted piperidine (359.5 g., b.p. 103–105°), octene-1 (9.5 g., b.p. 118–120°), and a product shown to be 2-*n*-octylpiperidine (31.7 g., b.p. 89° at 1 mm., $n^{20}D$ 1.4589).

Anal. Calcd. for $C_{13}H_{27}N$: C, 79.11; H, 13.79; N, 7.10; mol. wt., 197. Found: C, 79.34; H, 13.81; N, 7.17; mol. wt., 190.

This product was identified by a comparison of its chemical and physical properties with 2-*n*-octylpiperidine (b.p. 89° at 1 mm., $n^{20}D$ 1.4587) prepared (95% yield) by the dehydrogenation (over Adams catalyst in acetic acid solution) of 2-*n*-octylpyridine (prepared, 65% yield, by the reaction of α-picoline, 111 g., 1.2 moles, with *n*-heptyl bromide, 71.6 g., 0.40 mole, and sodamide, 54 g., 1.39 moles).[1] The product gave a hydrochloride (m.p. 155–156°; m.p. of mixture with authentic sample, 155–156°).

Anal. Calcd. for $C_{13}H_{28}NCl$: C, 66.67; H, 12.07; N, 5.99. Found: C, 66.53; H, 12.16; N, 5.99.

Its reaction with phenyl isothiocyanate gave a thiourea derivative (m.p. 95°; m.p. of mixture with authentic sample, 95°). *Anal.* Calcd. for $C_{20}H_{32}N_2S$: C, 72.23; H, 9.70; N, 8.42. Found: C, 71.92; H, 9.56; N, 8.45.

A picrate (m.p. 78–80°) was also obtained. *Anal.* Calcd. for $C_{19}H_{30}N_4O_7$: N, 13.12. Found: N, 13.07.

The high boiling residue was distilled to give a fraction (b.p. 145–155° at 1 mm., $n^{20}D$ 1.4683; 5.8 g., mol. wt. 299) presumed to have resulted from the condensation of one molecule of piperidine with two of octene-1. A residue (4.5 g., mol. wt. 448) remained. 2-*n*-Octylpiperidine (1 g.) was obtained in small yield when a solution containing piperidine (207 g., 2.44 moles) and octene-1 (20.5 g., 0.183 mole) was internally illuminated for 168 hours with a mercury discharge tube.

Piperidine (87. g., 1.03 mole) containing *t*-butyl peroxide (1.2 g.) was held at 125° for 12 hours under a pressure of propylene (30–40 lb./sq. in.). Additional peroxide (1.8 g.) was added as the reaction progressed. Distillation of the reaction mixture gave *d,l*-coniine (4 g., $n^{23}D$ 1.4513, b.p. 93° at 70 mm.).[2,3] This product was identified by its hydrochloride (m.p. 211–212° uncor.) and its platinichloride (m.p. 155–157° uncor.). Work to determine the scope and mechanism of this reaction is continuing.

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RECEIVED NOVEMBER 1, 1952

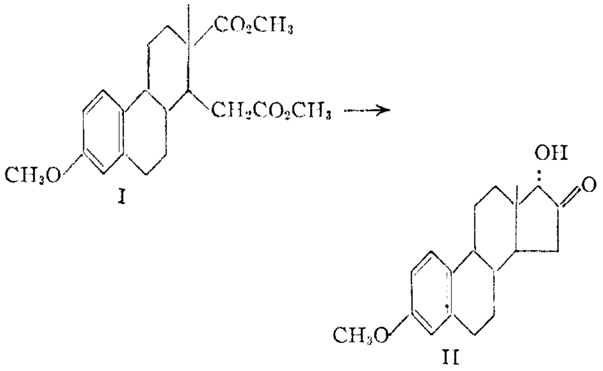
STEROID RING CLOSURES USING THE ACYLOIN CONDENSATION

Sir:

We have found that the acyloin condensation in a homogeneous liquid ammonia-ether solution is an efficient method of forming five- and six-membered rings. Sodium in liquid ammonia has not previously been considered to lead to practical yields of acyloins from esters.[1]

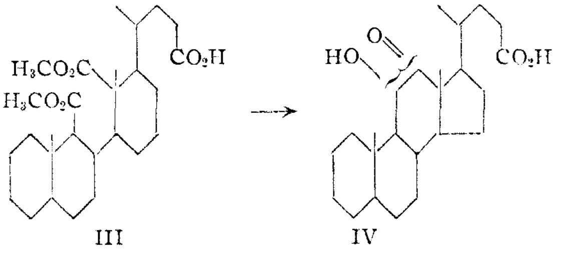
To a solution of 0.8 g. of sodium in 325 ml. of anhydrous ammonia and 225 ml. of ether (under pre-purified nitrogen) was added in one hour 1.8 g. of dimethyl marrianolate methyl ether (I)[2,3] dissolved in 225 ml. of ether. After complete removal of the ammonia by evaporation, the mixture was acidified with hydrochloric acid. Purification afforded 0.890 g. (60%) of 16-keto-α-estradiol-3-methyl ether (II), m.p. 162.0–162.4°, $[\alpha]^{31}\text{D}$ $-88°$ (c = 1.0, 95% ethanol). *Anal.* Calcd. for $C_{19}H_{24}O_3$: C, 75.97; H, 8.05. Found: C, 75.79; H, 8.09. Conventional heterogeneous acyloin reaction conditions (*e.g.*, finely dispersed sodium in refluxing xylene) did not yield detectable quantities of acyloin product from I.

The acyloin II and II acetate showed a depression of m.p. on admixture with 16-keto-β-estradiol-3-methyl ether[4] and the corresponding acetate, respectively. Reduction of II acetate by the ethanedithiol-Raney nickel method,[5] followed by saponification and chromic acid oxidation, afforded estrone methyl ether, identified by comparison with an authentic sample.



I

II



III

IV

By the same technique, 11,12-seco-cholane-24-acid-11,12 dimethyl ester (III) was cyclized in 75–80% yield to an 11,12-acyloin (m.p. 142–143°), identical with the lower melting ketol prepared by Reichstein's procedure[6] (bromination of 12-ketocholanic acid and subsequent alkaline hydrolysis). The non-crystalline diester III was obtained by nitric acid oxidation of 12-hydroxycholanic acid or by chromic acid oxidation of an 11,12-acyloin mixture to 11,12-seco-cholane-11,12,24-triacid[7,8] (m.p. 259–261°), followed by esterification with diazomethane and selective saponification. *Anal.* Calcd. for $C_{26}H_{42}O_6$: C, 69.30; H, 9.40; neut. equiv., 450. Found: C, 69.28; H, 9.25; neut. equiv., 446.

In other experiments employing a ratio of four equivalents of sodium to one of the diesters, the consumption of sodium appeared to be instantaneous. In each series only one of the four possible isomeric acyloins was obtained.

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(1) E. Chablay, *Ann. chim.*, (9) **8**, 205 (1917), was unable to isolate any acyloin material from such a reaction, and M. S. Kharasch, E. Sternfield and F. R. Mayo, *J. Org. Chem.*, **5**, 362 (1940), found the yield of linear acyloin to be much lower than in the case of the heterogeneous reaction.

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CRYSTAL STRUCTURE OF CYANURIC ACID

Sir:

The infrared spectra of cyanuric acid and deuterocyanuric acid, which were recently published in THIS JOURNAL, by Newman and Badger,[1] create doubts concerning the values of the interatomic distances found in an early X-ray structure determination by Moerman and Wiebenga.[2]

The crystal structure of cyanuric acid was reinvestigated in our laboratory by G. A. Croes, A. J. van Gent, R. P. van Oosten and D. W. Smits about two years ago. They started from new accurate measurements of the intensities of all X-ray reflections and refined the atomic coördinates by three dimensional Fourier syntheses. This work is not yet published, because we still want to study certain details of the electron density distribution. In connection with Newman and Badger's work, however, it may be interesting to report here the new values for the bond lengths. These are subject to a standard deviation of approximately 0.02 Å., which means that the probability that a given bond length is in error by more than 0.04 Å., or a bond angle by more than 3° is approximately 5%.

The molecules are all planar and situated almost exactly in parallel sheets (101). The old and new interatomic distances and bond angles are shown in Fig. 1 and Fig. 2, respectively, which show one molecule and its connections to others in the same layer.

The deviation from a trigonal symmetry of the central ring (Fig. 1) has disappeared (Fig. 2); the C–N bond lengths in the ring have practically not changed and are still all essentially identical.

On the other hand, a striking difference is observed between the new C=O distances and those previously reported. In the previous structure determination, which was based on estimated intensities and the use of the trial and error method only, we found two different C=O distances (1.24 Å. and 1.31 Å.), each with an estimated probable error of 0.06 Å., so that the difference was not

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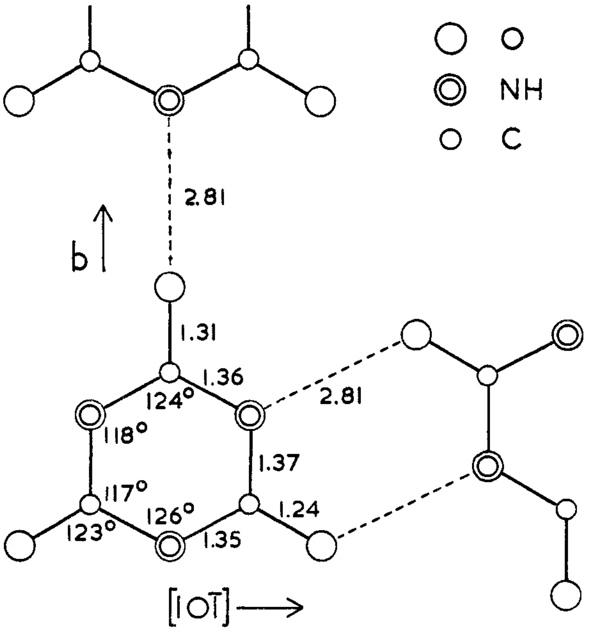

Fig. 1.—Part of crystal structure of cyanuric acid. Hydrogen bonds are indicated by dashed lines; atomic coördinates 1938.[2]

considered to be significant. The recent investigation proves that the two bonds have essentially the same lengths (1.21 Å. and 1.21_5 Å., respectively), which is in agreement with Newman and Badger's prediction on the basis of the infrared spectra. The new bond length, however, is much smaller than the mean value (1.28 Å.) of those previously observed. It is significantly smaller than the value (1.29 Å.) which is expected from mesomerism between the usually accepted resonating structures, with standard lengths 1.47, 1.26_5, 1.43 and 1.21_5 Å. for the pure C–N, C=N, C–O and C=O bond, respectively. It may be remarked, that small values for the length of a resonating C=O bond are also observed in other carefully investigated structures, namely, 1.19 Å. in N-acetylglycine[3] and 1.21 Å. in *dl*-alanine[4].

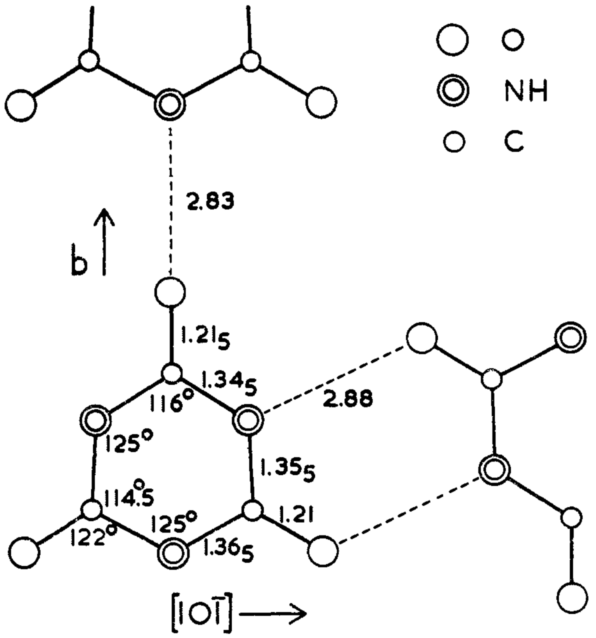

Fig. 2.—As Fig. 1, but with the atomic coördinates taken from a reinvestigation (1950) of the structure.

Two kinds of hydrogen bonds NH....O connect a molecule with others in the same plane. The first type, designated as class A by Newman and Badger, is directed parallel to the *b*-axis of the crystal; the second, class B, connects the molecules in the [101] direction. In class A the NH bond is directed exactly toward the hydrogen-bonded oxygen, in class B this is almost exactly the case. In our opinion, however, it is not possible to predict with certainty which of the two bonds is the shorter, without taking into account the complicated interaction of a molecule with all neighboring atoms. As is seen from Fig. 2 we find that hydrogen bond A is smaller than 2.85 Å. and possibly significantly shorter than bond B. This would be in disagreement with Newman and Badger's interpretation of the infrared spectra.

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