apparatus equipped with a water trap. After removal of the water which had formed, the remainder of the benzene was distilled off and the residual oil poured into 500 ml. of ice-water and stirred vigorously. The crude solid (13.9 g., 53%, m. p. 74–77°), was recrystallized from *n*-hexane and then melted at 76–77°. Criegee and Stanger,[4] who prepared this substance from cyclohexene oxide and trichloroacetic acid, reported a melting point of 76–77°.

***trans*-1,2-Cyclohexanediol Trichloroacetate *p*-Toluenesulfonate.** (a) **Trichloroacetylation of the Mono-*p*-toluenesulfonate.**—*trans*-1,2-Cyclohexanediol *p*-toluenesulfonate (8.1 g., 0.03 mole) prepared in 84% yield (m. p. 97°) by a modification of the method of Criegee and Stanger[4] or Winstein, Hess and Buckles[5] and pyridine (5 ml., 0.06 mole) were mixed and the trichloroacetyl chloride[3] (3.4 ml., 0.03 mole) added slowly without cooling. The reaction mixture crystallized on standing overnight, and after 200 ml. of water had been stirred in, the crystalline suspension was refrigerated. The crude solid was removed, washed with water, and dried in air (10 g., 80%, m. p. 98–102°). It was recrystallized three times from absolute alcohol and once from *n*-hexane and then melted at 104.0–104.5°.

Anal. Calcd. for $C_{15}H_{17}O_5Cl_3S$: C, 43.27; H, 4.09; Cl, 25.70; S, 7.69. Found: C, 43.29; H, 4.08; Cl, 25.60; S, 7.79.

(b) **Tosylation of the Mono-trichloroacetate.**—*trans*-1,2-Cyclohexanediol trichloroacetate (15.7 g., 0.06 mole) and *p*-toluenesulfonyl chloride (11.4 g., 0.06 mole) were dissolved by warming with pyridine (19.3 ml., 0.24 mole) to 55°. After maintaining the mixture at this temperature for a few minutes, it was allowed to cool to room temperature and remain overnight. The solidified mixture was then stirred with cold water (500 ml.) and the residual solid removed, washed with water and dried in air (23.9 g., 96%, m. p. 103–104°). It was recrystallized from *n*-hexane (22.1 g., yield 89%) and then melted at 105°. The melting point of a mixture of the products from part (a) and part (b) was not lower than that of either product melted separately.

The reaction of this compound (0.1 *M*) with sodium acetate (0.1 *M*) in glacial acetic acid at 91° was followed by the method of Winstein and co-workers[1] and gave a first order reaction rate constant of approximately 6.7 ($k \times 10^4$ in hour^{-1}). The reaction products were not isolated.

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RECEIVED DECEMBER 28, 1949

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(4) Criegee and Stanger, *Ber.*, **69B**, 2753 (1936).

(5) Winstein, Hess and Buckles, THIS JOURNAL, **64**, 2798 (1942).

COMMUNICATIONS TO THE EDITOR

ACTIVATION OF THIONASE BY FOLIC ACID[1]

Sir:

It has been found that preparations of thionase (the enzyme responsible for the cleavage of cystathionine and cysteine[2]) may be inactivated by dialysis against dilute acetate buffer (0.01 *M*, *p*H 4.0). The activity of the enzyme was restored by the addition of folic acid. Adenylic acid, adenosinetriphosphate, diphosphopyridine nucleotide, vitamin B_{12} or aureomycin did not reactivate the inactive material.

A solution of enzyme in saline had an activity toward L-allocystathionine such that 1.2 mg. of homocysteine was produced from 4.4 mg. of substrate in 30 min. by 1 ml. of enzyme. This solution was dialyzed for 48 hr. against the acetate buffer. The material that precipitated was redissolved in the original volume of saline and was found to be without activity. Fifty γ folic acid per ml. of digest (total volume 10 ml., 0.02 *M* histidine buffer, *p*H 7.3) was added and the activity was found to be restored to the extent that 0.7 mg. of homocysteine was produced. The relationship of activity to concentration of folic acid was reasonably linear up to concentrations of folic acid of the order of 150 γ per ml.; at this level an activity of 1.0 mg. of homocysteine was found. Similar activations with other substrates and other methods of analyses were observed.

These results are difficult to interpret since the levels of folic acid required for reactivation are of a different order of magnitude than any possible concentration in the enzyme. The purified enzyme was found to have, aside from the protein component, peaks of absorption near 245, 285 and 350 mμ. These peaks disappeared during the dialysis. However, if it were assumed that certain of these peaks were due to a derivative of folic acid, less than 0.5 γ per ml. of digest was present in the fully-active preparation. Studies as to the nature of the activation by folic acid and the possibility of more active derivatives of folic acid are in progress.

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RECEIVED MAY 12, 1950

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(1) These studies were supported by grants from the U. S. Public Health Service.

(2) F. Binkley and D. Okeson, *J. Biol. Chem.*, **182**, 273 (1950).

THE ISOLATION OF A NEW THYMINE PENTOSIDE FROM SPONGES[1]

Sir:

When certain air-dried sponges, particularly those of the genus *Cryptotethia*, are extracted in a Soxhlet apparatus with acetone, a nicely crystal-

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(1) Contributions to the Study of Marine Products. XXVIII.

line material separates from the boiling solvent. This material has been identified as a mixture of nucleosides, all of which appear to have not previously been reported. One of them was readily obtained by repeated recrystallization from water in form of clear needles of a high degree of purity. It melted at 246–247°; $[\alpha]^{22}\mathrm{D}$ +80.0° (*c*, 1.1 in 8% sodium hydroxide), and $[\alpha]^{22}\mathrm{D}$ +92° (*c*, 0.88 in pyridine). *Anal.* Calcd. for $C_{10}H_{14}N_2O_6$: C, 46.50; H, 5.48; N, 10.85. Found: C, 46.84; H, 5.42; N, 11.09. In neutral aqueous solution, the absorption spectrum showed a single maximum at 2690 Å. (E_M 9,250). The failure of this compound to show a spectral response to a change in the *p*H is similar to that described in the case of thymine desoxyriboside.[2]

Vigorous hydrolysis of the nucleoside with boiling 10% sulfuric acid afforded thymine, m. p. 321°. *Anal.* Calcd. for $C_5H_6N_2O_2$: C, 47.62; H, 4.79; N, 22.21. Found: C, 47.29; H, 4.15; N, 22.09. Its absorption spectra determined in neutral and basic media were identical with those of an authentic sample of thymine. As yet the conventional methods for the isolation and identification of the carbohydrate fragment of the nucleoside have been unsuccessful. The following evidence, however, proves the compound to by a thymine pentofuranoside. Upon benzoylation by means of a modified Schotten-Baumann method a tribenzoate was obtained, m. p. 190–191°; $[\alpha]^{22}\mathrm{D}$ +78.3° (*c*, 0.28 in methanol). The tri-*p*-bromobenzoate similarly prepared melted at 223–224°. *Anal.* Calcd. for $C_{31}H_{23}O_9N_2Br_3$: Br, 29.70. Found: Br, 28.74. Titration of the nucleoside according to the method of Lythgoe and Todd[3] consumed one mole of periodate without the formation of formic acid. The high dextrorotatory power of the nucleoside suggests that it is a xylofuranoside rather than the as yet unknown thymine ribofuranoside. It is proposed to name this compound spongothymidine to indicate its origin and its relationship to thymidine.

(2) Stimson and Reuter, This Journal, **67**, 847 (1945).

(3) Lythgoe and Todd, *J. Chem. Soc.*, 592 (1944).

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RECEIVED MAY 4, 1950

METHYL ETHYL KETONE PHOTOCHEMICAL PROCESSES

Sir:

In view of the recent publication by Durham, Martin and Sutton,[1] of preliminary results on the ratio of ethyl radical to methyl radical formation in the photolysis of methyl ethyl ketone, it may be well to report certain of the results of our study[2] of the photolysis of this ketone at 3130 and 2654 Å.

Methyl ethyl ketone–iodine mixtures were irradiated in the vapor phase in a manner similar to that described by Gorin[3] and later extend by Blacet and co-workers.[4,5] Alkyl radicals formed in the primary reactions were "trapped" by iodine and the quantum yields of methyl and ethyl iodide formed in this fashion were obtained with the aid of a mass spectrometer. As a check, quantum yields of the total alkyl iodides were determined by a micro chemical procedure involving titration of the iodides. Analyses of the traces of products pumped off the condensed phase at −75° were carried out with the mass spectrometer and a micro gas analysis apparatus. Some of the significant results obtained are summarized in Table I.

TABLE I

QUANTUM YIELDS OF ORGANIC IODIDES FROM THE PHOTOLYSIS OF METHYL ETHYL KETONE–IODINE MIXTURES AT 3130 AND 2654 Å.

Wave length, Å.	2654	3130	3130
Temp., °C.	100	100	175
Φ CH_3I	0.08	0.01	0.02
Φ C_2H_5I	.44	.40	.43
Φ Total iodides	1.02	.68	.71

If one assumes that the quantum yields of methyl iodide and ethyl iodide are a valid measure of the reactions (A) and (B)

$$\mathrm{CH_3COC_2H_5} + h\nu \begin{array}{ll} \longrightarrow \mathrm{C_2H_5 + CH_3CO} & \text{(A)} \\ \longrightarrow \mathrm{CH_3 + C_2H_5CO} & \text{(B)} \end{array}$$

it is evident that at 3130 Å. and 100° process (A) is about forty times as probable as (B), but at 100° and 2654 Å. it is roughly six times as probable.

It was found that the quantum yield of carbon monoxide at 175° and 3130 Å. was only 0.11 compared to that of 0.43 for ethyl iodide. This fact seems good evidence that at this wave length the acetyl radicals are sufficiently stable, even at 175°, so that most of them do not spontaneously decompose on formation, but survive many collisions and react in some other manner. An intensive search utilizing chemical and mass spectrometric methods was made in an effort to detect acetyl iodide which might be expected to be a reaction product, however, no analytical evidence for this compound was found.

In addition to methyl and ethyl iodide, another iodide was found in relatively large amounts. Preliminary chemical and mass spectrometric evidence is indicative of the isopropyl iodide structure, but the results are not as yet conclusive. The quantum yield for "Total iodide" in Table I is the sum of the yields of the latter iodide and those of methyl and ethyl iodides. The quantum yield of the third iodide is apparently temper-

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(1) R. W. Durham, G. R. Martin and H. C. Sutton, *Nature*, **164**, 1052 (1949).

(2) J. N. Pitts, doctoral dissertation, University of California, Los Angeles, July, 1949.

(3) E. Gorin, *Acta Physicochimica U. R. S. S.*, **8**, 513 (1938); *J. Chem. Phys.*, **7**, 256 (1939).

(4) F. E. Blacet and J. D. Heldman, This Journal, **64**, 889 (1942).

(5) F. E. Blacet and D. E. Loeffler, *ibid.*, **64**, 893 (1942).