either may be too small in intensity to be seen or may be absent entirely. From this consideration it would seem that B_7H_{13} is a likely formula.

The possibility of a B_7 compound has been mentioned previously from mass spectral data[3] but no pattern or formula was reported because of the masking effect of higher boranes present.

After submission of this communication, our attention was called to a report of Professor Riley Schaeffer at the Boston meeting of the American Chemical Society (April 6–10, 1959) that he had evidence for a heptaborane. He reported mass peaks up to 91 with a minimum formula B_7H_{14} and, therefore, suggested that the hydride may be B_7H_{15}.

(3) R. E. Dickerson, P. J. Wheatley, P. A. Howell and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 200 (1957).

DEPARTMENT OF CHEMISTRY
RENSSELAER POLYTECHNIC INSTITUTE — ROBERT W. SCHAEFER, KENNETH H. LUDLUM, STEPHEN E. WIBERLEY
TROY, NEW YORK

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TRANSMISSION OF ELECTRONIC EFFECTS BY THE CYCLOPROPANE RING. RATES OF ALKALINE HYDROLYSIS OF SOME ETHYL *p*-SUBSTITUTED 2-PHENYLCYCLOPROPANECARBOXYLATES

Sir:

Considerable controversy exists over the ability of the cyclopropane ring to transmit conjugative effects. Spectral studies of the excited state often have indicated some "double bond character" of the three-membered ring,[1] although there is evidence that the ring does not transmit conjugative effects in certain cases.[2] Information on molecules in the ground state also is inconsistent. Dipole moment studies[3] suggest an electronic interaction of the cyclopropane ring (with an attached chlorine atom), as does the 1,6-addition of diethyl malonate anion to diethyl vinylcyclopropane-1,1-dicarboxylate.[4] In contrast is a recent evaluation of the relative transmission ability of the ethylenic unit (–CH=CH–), the saturated dimethylene group ($-CH_2CH_2-$), and the cyclopropane ring via a comparison of the ionization constants of *trans*-cinnamic acids, β-phenylpropionic acids, and *trans*-2-phenylcyclopropanecarboxylic acids.[5] Comparison of the Hammett[6] ρ value for the three series showed that the cyclopropane ring was about as good as the dimethylene group but inferior to the ethylenic group in transmitting electronic effects.

We wish to make a preliminary report of a corresponding comparison of the rates of hydrolysis of the ethyl esters in 87.8% ethanol at 30°. In this series the ethyl phenylcyclopropanecarboxylates have an intermediate ρ value (Table I) indicating that the cyclopropane ring is better than a dimethylene group but poorer than an ethylenic unit in transmitting electronic effects. This is in agreement with the dipole moment work but at variance with the data obtained from ionization constants.

In Table I the ρ values for the ionization of the acids and for the alkaline hydrolysis of the esters are compared. In Table II are the rate constants for four ethyl *trans*-2-phenylcyclopropanecarboxylates prepared from acids which have the same physical constants as those previously reported.[7]

TABLE I

COMPARISON OF REACTION CONSTANTS

Series	*p*-Ester hydrolysis	*p*-Acid ionization
trans-Cinnamic	1.329[a]	0.466[a]
trans-2-Phenylcyclopropane	0.789[b]	0.182[c]
β-Phenylpropionic	0.489[a]	0.212[a]

[a] Taken from the compilation by H. H. Jaffe, *Chem. Revs.*, **53**, 191 (1953). [b] This work. [c] Ref. 5.

TABLE II

RATES OF ALKALINE HYDROLYSIS OF ETHYL *trans*-2-(*p*-SUBSTITUTED-PHENYL)-CYCLOPROPANECARBOXYLATES IN 87.8% ETHANOL AT 30°

Substituent	$k \times 10^3$ l. mole^{-1} sec.$^{-1}$[a]	Melting point, °C.
p-NO_2	6.40	50.4–51.0
p-Cl[b]	2.37	(87.5–88.0)[c]
p-H	1.38	37.5–38.4
p-CH_3O	1.00	82.0–82.8

[a] Average of two determinations: initial (KOH) = 0.04 *M*, (RCOOEt) = 0.025 *M*; temperature, 30.00 ± 0.02°. [b] $n^{24}D$ 1.5331. [c] B p. at 0.3 mm.

Other *trans* esters and several *cis* acids and esters of this series also have been prepared. The properties and rates of hydrolysis will be the subject of a subsequent article.

(7) E. N. Trachtenberg and G. Odian, THIS JOURNAL, **80**, 4015 (1958).

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF TEXAS — RICHARD FUCHS
AUSTIN 12, TEXAS — JORDAN J. BLOOMFIELD

RECEIVED APRIL 4, 1959

RETRACTION OF CHOLINE METHYL GROUP BIOSYNTHESIS

Sir:

Further study of the enzyme preparation reported to synthesize methyl groups of choline from formaldehyde[1] has indicated that choline is not synthesized by this preparation. It appears that the homogenate contains both the formaldehyde dehydrogenase of Strittmatter and Ball[2] and the hydroxymethyl tetrahydrofolic acid dehydrogenase of Hatefi, *et al.*[3] Much of the radioactive formaldehyde incorporated is accounted for by these two enzyme systems. In addition there is some reaction between the formaldehyde and amino-

(1) See, for example, W. W. Robertson, J. F. Music and F. A. Matsen, THIS JOURNAL, **72**, 5260 (1950); G. W. Cannon, A. A. Santilli and P. Shenian, *ibid.*, **81**, 1660 (1959), and references therein.

(2) L. I. Smith and E. R. Rogier, *ibid.*, **73**, 3840 (1951); R. H. Eastman and S. K. Freeman, *ibid.*, **77**, 6642 (1955), and preceding papers.

(3) B. I. Spinrad, *ibid.*, **68**, 617 (1946); M. T. Rogers and J. D. Roberts, *ibid.*, **68**, 843 (1946).

(4) R. W. Kierstead, R. P. Linstead and B. C. L. Weedon, *J. Chem. Soc.*, 3616 (1952).

(5) E. N. Trachtenberg and G. Odian, THIS JOURNAL, **80**, 4018 (1958).

(6) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 186.

(1) R. Venkataraman and D. M. Greenberg, THIS JOURNAL, **80**, 2025 (1958).

(2) P. Strittmatter and E. G. Ball, *J. Biol. Chem.*, **213**, 1445 (1955).

(3) Y. Hatefi, M. J. Osborn, L. D. Kay and F. M. Huennekens, *ibid.*, **227**, 637 (1957).

ethanol or dimethylaminoethanol to form products that are not the result of methylation.

The radioactive products are co-precipitated with carrier choline reineckate, but more careful recrystallization procedures reveal the loss of radioactivity with continued recrystallizations. The tetrahydrofolic acid effect probably resulted from the hydroxymethyltetrahydrofolic acid dehydrogenase present. In a similar way the effect of diphosphopyridine nucleotide could be explained by the presence of the formaldehyde dehydrogenase which uses DPN in oxidizing formaldehyde to formic acid.

With aminoethanol and formaldehyde as substrates, paper chromatography indicated the formation of N-formylaminoethanol which had an R_f value similar to that of choline. This probably is not the product of an enzymatic reaction.

DEPARTMENT OF BIOCHEMISTRY
UNIVERSITY OF CALIFORNIA D. M. GREENBERG
SCHOOL OF MEDICINE P. FIGARD
SAN FRANCISCO, CALIFORNIA

RECEIVED APRIL 30, 1959

BROMINOLYSIS OF PHOSPHATIDES IN ORGANIC SOLVENTS[1]

Sir:

In a previous communication[2] the oxidation of lysolecithin by permanganate was reported. A search for another oxidant led to the finding that bromine in buffered aqueous solution was also capable of oxidizing lysolecithin.[2,3] In organic solvents, however, a novel reaction takes place. When lysolecithin (mixture of alpha and beta isomers) is treated with bromine in either chloroform or methanol, brominolysis occurs at room temperature to yield choline and lysophosphatidic acids (alpha and beta isomers). Oxidation does not occur to any appreciable extent.

Lecithin[4] and phosphatidylethanolamine[4] also undergo brominolysis but at a much slower rate than does lysolecithin. With these diester phosphatides the reaction requires 24–48 hours or longer (in contrast to 3–8 hours for lysolecithin) and there are produced phosphatidic acids and either choline or ethanolamine, respectively. Smaller amounts of phosphorylcholine and phosphorylethanolamine also may be formed.

In order to facilitate this study P^{32}-lysolecithin was used and was prepared biosynthetically from rat liver as described previously.[2] The time course of the reaction in chloroform is given in Fig. 1. At the time intervals indicated, appropriate aliquots of the reaction mixture were removed for paper chromatographic analysis and the radioactivity in the lysophosphatidic acid and in the lysolecithin was determined. Chromatography was carried out on silicic acid impregnated paper as described previously.[5] The R_f values of choline, lysolecithin and lysophosphatidic acid were 0.02, 0.21 and 0.64, respectively. The lysophosphatidic acid spot consisted of two overlapping components. Free choline also was identified by paper chromatography in other solvent systems.[6]

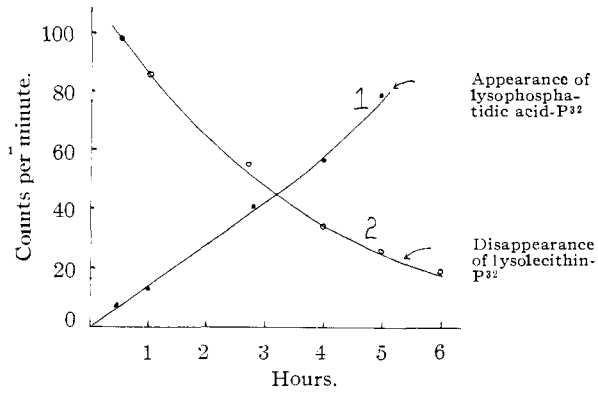

Fig. 1.—Brominolysis of P^{32}-lysolecithin in chloroform: five milligrams of P^{32}-lysolecithin was dissolved in 1.0 ml. of chloroform (Mallinckrodt, "Analytical Reagent"). To the solution was added 5 microliters of pure liquid bromine. The solution was mixed, stoppered and let stand at room temperature. At the time intervals indicated 10-microliter aliquots were removed for paper chromatographic analysis.[5] The lysolecithin and lysophosphatidic spots were cut from the chromatograms and the radioactivity in each was determined. Curve 1 shows the rate of appearance of the radioactive lysophosphatidic acid; curve 2 the rate of disappearance of the starting lysolecithin.

Brominolysis of lysolecithin in methanol occurs readily but the lysophosphatidic acids which are formed are hydrolyzed rapidly during the reaction. The maximum yield of lysophosphatidic acids in methanol is about 35% and is attained after 2-3 hours. The yield of lysophosphatidic acids in chloroform is 80–95% and is attained after 6–8 hours.

The reaction in chloroform was carried out on a larger scale using myristoyl-lysolecithin which was prepared from a synthetic dimyristoyllecithin[4] by snake venom hydrolysis.[2] The choline bromide precipitates out of solution in chloroform (but not in methanol) as the reaction proceeds and can be isolated easily. The lysophosphatidic acids were purified by column chromatography on silicic acid[5] and by converison to the barium salt. The free lysophosphatidic acids were found to contain 13.05% bromine.[7]

The brominolysis reaction allows for the preparation of lysophosphatidic acids and phosphatidic acids and complements the diazometholysis reaction[8] as a tool for establishing the stereochemical configuration of the phosphatides.

(1) This work was supported in part by funds from a Grant (No. H-2063) from the National Heart Institute, United States Public Health Service.

(2) G. V. Marinetti, J. Erbland and E. Stotz, *Biochim. et Biophys. Acta*, **33**, 403 (1959).

(3) G. V. Marinetti and K. Temple, *Fed. Proceedings*, **18**, 281 (1959).

(4) Synthetic samples from Dr. E. Baer, University of Toronto, Toronto, Canada.

(5) G. V. Marinetti, J. Erbland and J. Kochen, *Fed. Proc.*, **16**, 837 (1957).

(6) G. V. Marinetti, D. Scaramuzzino and E. Stotz, *J. Biol. Chem.*, **224**, 819 (1957).

(7) The analysis for bromine was done by the Schwartzkopf Microanalytical Laboratory, Woodside, N. Y. The theoretical content for bromine varies depending on the nature of the product. The analysis indicates that a mixture of the brominated and non-brominated forms is present and could explain the finding that two components are seen on paper chromatograms.

(8) E. Baer and J. Maurukas, *J. Biol. Chem.*, **212**, 39 (1955).

DEPARTMENT OF BIOCHEMISTRY
UNIVERSITY OF ROCHESTER G. V. MARINETTI
SCHOOL OF MEDICINE AND DENTISTRY K. TEMPLE
ROCHESTER, NEW YORK ELMER STOTZ

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