

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 data³ 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).

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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 studies³ 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 Hammett⁶ 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 phenylcyclopropanecarboxyl-

(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**, 4015 (1958).

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

ates 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	ρ -Ester hydrolysis	ρ -Acid ionization
<i>trans</i> -Cinnamic	1.329 ^a	0.466 ^a
<i>trans</i> -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	Melting point, °C.
<i>p</i> -NO ₂	6.40	50.4-51.0
<i>p</i> -Cl ^b	2.37	(87.5-88.0) ^c
<i>p</i> -H	1.38	37.5-38.4
<i>p</i> -CH ₃ O	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_D^{20} 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).

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RETRACTION OF CHOLINE METHYL GROUP BIOSYNTHESIS

Sir:

Further study of the enzyme preparation reported to synthesize methyl groups of choline from formaldehyde¹ has indicated that choline is not synthesized by this preparation. It appears that the homogenate contains both the formaldehyde dehydrogenase of Strittmatter and Ball² 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) 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).