in the condensation of dicyclohexylamine with ethylene oxide. When Gilman and Clark[7] could not condense isopropyllithium with tri-isopropylsilane, they attributed this to the sterically hindered nature of the isopropyl group.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY BROOKLYN COLLEGE BROOKLYN 10, NEW YORK

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RECEIVED JANUARY 24, 1949

(7) Gilman and Clark, *ibid.*, **69**, 1499 (1947).

(8) Present address: Northport Veterans' Hospital, Northport, N. Y.

4-*n*-Butyl-2,6-di-*t*-butylphenol

Following the method of Stevens,[1] isobutylene was bubbled into 9.2 g. of 4-*n*-butylphenol[2] containing 0.25 ml. of concentrated sulfuric acid until the gain in weight of the reaction mixture showed that slightly more than the theoretical amount (6.9 g.) had been added, then the excess isobutylene was swept out with natural gas. The reaction mixture was washed free from acid with successive 5% sodium carbonate washes, dried by adding benzene and distilling, and the product vacuum distilled. The main fraction of 11 g. (68%) boiled at 154–157° (10.5 mm.), and on refractionation gave a clear, colorless, rather viscous product, b. p. 144–144.5° (6 mm.), $n^{20}D$ 1.5019, d^{20}_4 0.920.

Anal. Calcd. for $C_{18}H_{30}O$: C, 82.38; H, 11.52. Found: C, 82.30; H, 11.52.

(1) D. R. Stevens, *Ind. Eng. Chem.*, **35**, 655–660 (1943).

(2) R. V. Rice and W. C. Harden, *J. Am. Pharm. Assoc.*, **25**, 7-9 (1936).

GEOCHEMICAL SECTION
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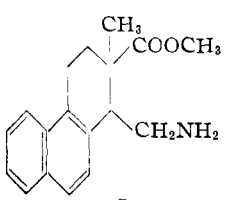
RECEIVED MARCH 7, 1949

COMMUNICATIONS TO THE EDITOR

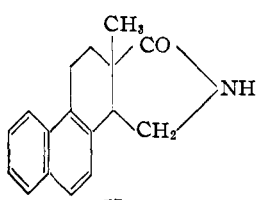
THE LACTAMS OF *cis*- AND *trans*-1-AMINOMETHYL-2-CARBOMETHOXY-2-METHYL-1,2,3,4-TETRAHYDROPHENANTHRENE

Sir:

In order to secure more information concerning the configuration of the steroids at the C/D ring juncture, we have prepared the diastereoisomeric (*cis* and *trans*) amino esters (I) which correspond in configuration to desoxyequilenin and desoxyisoequilenin and have studied their tendency to form γ-lactams (II). It was hoped that their



I



II

behavior in this respect would indicate which amino ester had the *cis* and which the *trans* configuration. It was found that both amino esters yielded lactams, one of which must be the *cis* lactam and the other the *trans* lactam. However, the lactam from the amino ester related to desoxyisoequilenin formed more rapidly than the lactam from the amino ester related to desoxyequilenin. Thus, when an aqueous solution of the amine ester hydrochloride corresponding to desoxyequilenin was treated with one equivalent of alkali and the liberated product was extracted immediately into ether (total time, ten minutes), only the free amino ester was formed. Under identical conditions the amino ester corresponding to desoxyisoequilenin gave a 60% yield of the γ-lactam (II) (m. p. 205–206°. *Anal.* Calcd. for $C_{17}H_{17}NO$: C, 81.24; H, 6.77; N, 5.58. Found: C, 81.11; H, 6.86; N, 5.46). The lactam (m. p. 234–236°. *Anal.* Found: C, 81.20; H, 6.83; N, 5.33) of the desoxyequilenin series was obtained when an excess of alkali was employed and the ether solution of the amino ester was allowed to stand for a longer period of time.

The more rapid formation of the lactam from the amino ester corresponding to desoxyisoequilenin may be indicative of the *cis* configuration which is currently assigned to desoxyisoequilenin. Further evidence is being sought in experiments in progress on the preparation of the corresponding 2-methyl-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic acids and a study of their ability to form anhydrides.

The amino esters were prepared by Curtius degradation of the acetic acid side chain of the two diastereoisomeric (*cis* and *trans*) 2-carbomethoxy-2-methyl-1,2,3,4-tetrahydrophenanthrene-1-acetic acids.[1] The degradation was accomplished by treatment of the acid chloride with sodium azide,[2] followed by rearrangement of the resulting azide to the isocyanate, which was hydrolyzed by concentrated hydrochloric acid to the amine ester hydrochloride in good yield; m. p.: normal (desoxyequilenin) form, 241–242°; iso form, 212–213°. *Anal.* Calcd. for $C_{18}H_{22}ClNO_2$:

(1) Bachmann and Wilds, THIS JOURNAL, **62**, 2084 (1940). The α acid has been shown to have the configuration of desoxyisoequilenin; the β acid corresponds to desoxyequilenin. The results of these experiments will be published soon.

(2) After our work had been completed, Billeter and Miescher, *Helv. Chim. Acta*, **31**, 1302 (1948), reported that the acid chloride of the 7-methoxy derivative of the acid did not react with sodium azide.

C, 67.59; H, 6.93; Cl, 11.08; N, 4.38. Found: (normal form) C, 67.55; H, 6.94; Cl, 11.44; N, 4.27; (iso form) C, 67.50; H, 6.93; Cl, 11.07; N, 4.31.

DEPARTMENT OF CHEMISTRY
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RECEIVED APRIL 25, 1949

A MATERIAL IN BOVINE STOMACHS RELATED TO BLOOD GROUP B SUBSTANCE[1]

Sir:

Blood group A substances in cattle have been studied[2,3] and the possible presence of blood group B substance noted.[4] Our findings using hemagglutination-inhibition indicate that substances with either blood group A, B, O, AO, BO, or with negligible activity can be obtained by an identical procedure[5] from different individual bovine stomachs (abomasus). The purified[6,7] substances were analyzed: N, 5.0–7.2%; reducing sugar as glucose (after hydrolysis) 51–60%; hexosamine (after hydrolysis) 23–34%; methylpentose 1.5–5.2%. Analytical data of hog[6] and human[7] substances are similar, except that their methylpentose contents are higher.[8]

Four of nine preparations showed only blood group B activity, which was 1–5% the activity of B substances from human saliva or horse stomach as determined by hemagglutination-inhibition.

TABLE I

ANTIBODY N PRECIPITATED FROM 2.0 ML. SERUM OF A HUMAN OF BLOOD GROUP A IMMUNIZED WITH HORSE B SUBSTANCE

Bovine substance added, μg	Antibody N precipitated, μg	Vol. of supernatant giving detectable agglutination of human B cells,[a] ml.	Antibody N precipitable from supernatant by horse B, μg	Total antibody N, μg
25	24.6	0.05	11.0	35.6
50	29.0	.1	4.9	33.9
100	24.5	.2	1.2	25.7
250	19.6	.2	1.6	21.2
500	10.4	.2	2.1	12.5
Horse B				
60	32.5[b]			

[a] 0.003 ml. of original serum is capable of agglutinating the quantity of B cells used. [b] Point of maximum precipitation. No agglutinins for human B cells are detectable in the supernatant.

(1) Aided by grants from the United States Public Health Service and the William J. Matheson Commission.

(2) G. Hartmann, *Det. Kgl. Videnskab. Selskab Biol. Medd.*, Copenhagen, **15**, No. 10 (1941).

(3) E. Jorpes and T. Thaning, *J. Immunol.*, **51**, 215, 221 (1945).

(4) K. Landsteiner and M. W. Chase, *J. Exp. Med.*, **63**, 813 (1936).

(5) W. T. J. Morgan and H. K. King, *Biochem. J.*, **37**, 640 (1943).

(6) A. Bendich, E. A. Kabat and A. E. Bezer, *J. Exp. Med.*, **83**, 485 (1946).

(7) E. A. Kabat, A. Bendich, A. E. Bezer and S. M. Beiser, *ibid.*, **85**, 685 (1947).

(8) H. Baer, Z. Dische and E. A. Kabat, *ibid.*, **88**, 59 (1948).

However, the bovine B substances cross reacted extensively but not completely with anti-horse B and showed a much higher capacity to precipitate anti-B per unit weight than would have been expected from the hemagglutination-inhibition test.

The table shows the anti-horse B nitrogen precipitable from 2.0 ml. serum by various quantities of bovine B, as compared with horse B. The cow B precipitates anti-B as evidenced in the supernatant by the reduction in anti-B agglutinins and in antibody N precipitable by homologous horse B substance. Excess bovine B inhibits precipitation and reduces the quantity of antibody precipitable from the supernatant by horse B.

DEPARTMENTS OF BACTERIOLOGY AND NEUROLOGY
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RECEIVED APRIL 5, 1949

(9) American Academy of Allergy Fellow, 1948, 1949.

INSECTICIDAL ACTIVITY OF 1,1,4,4-TETRA-(*p*-CHLOROPHENYL)-2,2,3,3-TETRACHLOROBUTANE

Sir:

The recent communication by Fleck[1] prompts me to report that 1,1,4,4,tetra-(*p*-chlorophenyl)-2,2,3,3-tetrachlorobutane (II), closely related to the compound III which is shown by the above author to be produced in the ultraviolet irradiation of DDT (I), has been found to possess decided insecticidal activity.

R_2CHCCl_3 (I) R = *p*-ClC_6H_4-
$R_2CHCCl_2CCl_2CHCR_2$ (II)
$R_2CHCCl{=}CClCHR_2$ (III)

Although I have been aware of this fact for a year, only preliminary tests are at hand, because much time has been consumed in various attempts to obtain a more satisfactory procedure for the preparation of II than the method of Brand and Bausch.[2a] However, recently, a test was performed by Prof. E. Delvaux (Agronomic Institute, Louvain) which gave evidence that II is as toxic as DDT to *Drosophila melanogaster* Meig., though slightly weaker in knock-down activity.

The insecticidal power of II suggests that it may contribute possibly to some extent to the well-known high residual effect of DDT, because it is not objectionable at all to assume that II is an intermediate product in the formation of III,[2b] which is provisionally considered as being much less effective than II, by analogy with the strong decrease in activity which accompanies the conversion of DDT into the corresponding ethylenic derivative.

Besides, in connection with the problem of the relation between insecticidal activity and chemical constitution an extensive review of the litera-

(1) Fleck, THIS JOURNAL, **71**, 1034 (1949).

(2) (a) Brand and Bausch, *J. prakt. Chem.*, **127**, 232 (1930); (b) **127**, 233 (1930).