in water, separated, heated to 80° with agitation with 5% sodium hydroxide, separated, washed neutral, and distilled. After the distillation of excess *m*-xylene the desired product was obtained in a fraction, b.p. 102–105° (2 mm.), amounting to 152 g. The residue amounting to 84 g. congealed. This was crystallized from methanol–benzene solution yielding 70 g. of a colorless compound, m.p. 106–107°. This product (XIIa) was the condensation product of two moles of *m*-xylene with one mole of 2,5-dichloro-2,5-dimethylhexane.

Anal. Calcd. for $C_{24}H_{34}$: C, 89.37; H, 10.63. Found: C, 89.25; H, 10.20.

The prior fraction, b.p. 102–105° (152 g.), congealed to a semicrystalline mass. It was dissolved in an equal weight of hot benzene, and methanol added until turbidity developed. Chilling with stirring gave 51 g. of crystals, m.p. 85–86°. Reworking the mother liquor yielded an additional 7 g. for a total yield of 58 g. (27%) of product, m.p. 85–86°, which was identical with the compound obtained earlier from *o*-xylene.

(c) Compound 18 from *p*-Xylene.—A solution of 183 g. of 2,5-dichloro-2,5-dimethylhexane in 183 g. of *p*-xylene was added with stirring to a mixture of 453 g. of *p*-xylene and 15 g. of aluminum chloride over a period of 1 hr. keeping the temperature at 17 to 21°. Strong evolution of hydrogen chloride was observed. The mixture was stirred for 3 hr. at 21–22°, quenched in water, and washed neutral. Upon vacuum distillation there was obtained, besides recovered *p*-xylene, a fraction, b.p. 101–109° (2.5–3.0 mm.), amounting to 153 g. and 52 g. of semicrystalline residue. The residue, crystallized from ethanol, gave 18 g. of product melting at 219–221° which proved to be identical with 1,1,4,4,5,5,8,8-octamethyl-1,2,3,4,5,6,7,8-octahydroanthracene[9] synthesized by the method of Bruson and Kroeger. The fraction, b.p. 101–109°, amounting to 153 g. was crystallized from an equal weight of ethanol to give 23 g. (10.5%) of colorless product, m.p. 85–86°, identical with the cyclialkylation product obtained from *o*-xylene.

Acetylation of Hydrocarbons.—The same general procedure was used for the preparation of all of these derivatives. A solution of 1 mole of the hydrocarbon and 1.1 moles of acetyl (propionyl or isobutyryl) chloride was added during the course of 30 to 60 min. to a suspension of 1.15 to 1.20 moles of ground (small granules) anhydrous aluminum chloride in 550 to 650 g. of ethylene dichloride with stirring throughout the reaction period and cooling to maintain a temperature of 20–25°. Stirring was usually continued for 1 hr. longer at 25°. The solution was quenched on ice and the resulting ethylene dichloride layer was washed with water to neutrality. The solvent was distilled and the remaining oil distilled *in vacuo*. The products which were found to be crystalline at room temperature were further purified by crystallizing from an equal weight of ethanol with chilling to 0 to 10°.

Formyl Derivatives.—The formyl derivative of hydrocarbon **7** was prepared by the oxidation of hydrocarbon **13**. The derivatives of hydrocarbons **5**, **13**, **19**, and **23**, were prepared by first chloromethylating and then oxidizing by the Sommelet method with hexamethylenetetramine. Procedures for this method are given in detail in U. S. Patent 2,800,511 (ref. 14).

6-Formyl-1,1,4,4-tetramethyltetralin.—A mixture of 96 g. of 1,1,4,4,6-pentamethyltetralin (hydrocarbon **13**), 50 g. of manganese dioxide, and 225 g. of 50% sulfuric acid was agitated at 60° for 30 hr. No apparent reaction occurred. Sufficient 93% sulfuric acid was added to bring the acid concentration to 60% and agitation was continued at 60° for another 30 hr. The cooled mixture was thinned with benzene and filtered. The benzene solution was washed with 5% sodium hydroxide then with water to neutrality and distilled. After recovery of 59 g. of unconverted hydrocarbon, b.p. 81–83° (2 mm.), there was obtained 22 g. of the desired aldehyde, a colorless liquid, b.p. 112–115° (2 mm.), which rapidly congealed. Crystallization, using 22 g. of ethanol, gave 16 g. of product, m.p. 53–54°, having a weak amber-like odor.

Anal. Calcd. for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.37; H, 9.09.

Dinitro Derivatives.—The following general procedure was used for all of the hydrocarbons which were nitrated. One mole of the hydrocarbon was added dropwise with agitation and cooling (15–25°) to a mixed acid composed of 6 moles of 98% nitric acid and 9.5 moles of 93% sulfuric acid. In some cases where the hydrocarbon was a solid, ethylene dichloride was added to the mixed acid and the hydrocarbon added in ethylene dichloride solution. The nitration mixture was quenched on ice, and the product taken up in benzene, washed with water, then with 5% sodium hydroxide until the washes were free of color, then with water to neutrality, and the solvent removed. When these derivatives were obtained as solids, they were purified by crystallizing from ethanol.

The prior procedure led to dinitration in all cases except one. Hydrocarbon **18** gave only a mononitro derivative. Nitration of hydrocarbon **25** resulted in removal of the isopropyl group producing a dinitro derivative identical with the one prepared from hydrocarbon **12**.

Acknowledgment.—The authors express appreciation to Dr. Max Luthy, The Givaudan Corporation, and to Professor J. L. E. Erickson, Louisiana State University, for their assistance and encouragement. We thank Mr. Harry Saunders of our perfumer staff for his help in odor evaluation of new musks. Thanks are due the Air Reduction Chemical and Carbide Company for generous samples of 2,5-dimethyl-2,5-hexanediol during the early stages of our work.

The Pyrolysis of Hexachlorocyclopentadiene[1]

E. T. McBee, Wendell L. Dilling,[2] and H. P. Braendlin

Department of Chemistry, Purdue University, West Lafayette, Indiana

Received November 13, 1963

Slow pyrolysis of hexachlorocyclopentadiene at *ca.* 250° gave octachloroindene, hexachlorobenzene, octachlorocyclopentane, dodecachlorodihydrotrindene, and a chlorocarbon, $C_{20}Cl_{14}$, of unknown structure.

The liquid phase pyrolysis of hexachlorocyclopentadiene (**1**) has been the subject of a brief study.[3] A closer examination of this reaction revealed the formation of not only octachlorocyclopentene (**2**) (11–22% conversion)[3b] and dodecachlorodihydrotrindene (**3**)[3a,4] (30%), but also octachloroindene (**4**) (9%), hexachlorobenzene (**5**) (0.8%), and a chlorocarbon, $C_{20}Cl_{14}$ (**6**) (1.2%), of unknown structure.

The products **4** and **5** were identified by comparison with known samples. A sample of authentic **4** was synthesized according to Eaton and co-workers[5] by the reaction of hexachloroindenone (**7**) with phosphorus pentachloride. Using the same conditions,[5] an appreciable amount of decachloroindan (**8**) was obtained in

---

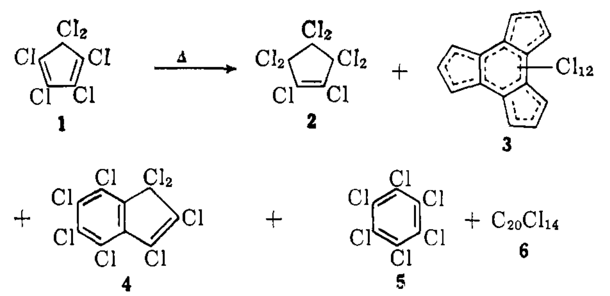
[1] This paper is based on a portion of a thesis submitted by Wendell L. Dilling to the Graduate School of Purdue University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Hooker Chemical Corporation Research Assistant, 1958–1959; National Science Foundation Cooperative Fellow, 1959–1962.

[3] (a) J. D. Idol, Jr., Ph.D. thesis, Purdue University, (1955); (b) R. H. Earle, Jr., Ph.D. thesis, Purdue University, (1957); (c) The gas phase pyrolysis of **1** recently has been reported by A. E. Ginsberg, R. Paatz, and F. Korte, *Tetrahedron Letters*, 779 (1962).

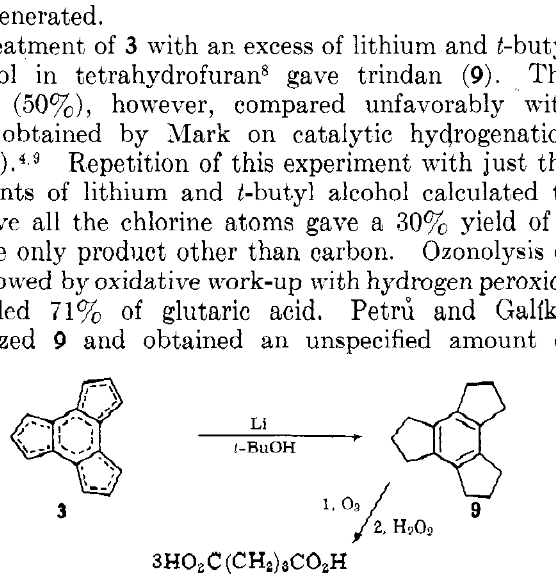
[4] V. Mark, *Tetrahedron Letters*, 333 (1961).

[5] P. Eaton, E. Carlson, P. Lombardo, and P. Yates, *J. Org. Chem.*, **25**, 1225 (1960).



addition to **4**.[6] **8** was not found in the reaction mixture from the pyrolysis of **1**, although it was one of the expected products, since **4** was isolated and chlorine was generated.

Treatment of **3** with an excess of lithium and *t*-butyl alcohol in tetrahydrofuran[8] gave trindan (**9**). The yield (50%), however, compared unfavorably with that obtained by Mark on catalytic hydrogenation (83%).[4,9] Repetition of this experiment with just the amounts of lithium and *t*-butyl alcohol calculated to remove all the chlorine atoms gave a 30% yield of **9** as the only product other than carbon. Ozonolysis of **9** followed by oxidative work-up with hydrogen peroxide afforded 71% of glutaric acid. Petrů and Galík[10] ozonized **9** and obtained an unspecified amount of glutaric acid; the ozonolysis of dodecahydrotriphenylene gave adipic acid in 14% yield.



Pyrolysis of decachlorobi-2,4-cylcopentadien-1-yl[11] (**10**) gave **3** (44%), **1** (22%), and **2** (13%).

Experimental[12]

Pyrolysis of 1.—Redistilled 1 (1400 g., 5.12 moles) was heated at reflux (*ca.* 240–250°) for 72 hr. The reaction mixture was cooled and diluted with hexane. The light yellow precipitate, 308 g., was recrystallized from benzene to give nearly white **3**, m.p. 345–347° (lit.[4,11b] m.p. 345–347°). The mother liquor was distilled to give 930 g. of a mixture of 1 and **2**, b.p. 53–89° (0.25–0.35 mm.) and 29.6 g. of a second fraction, b.p. 130–180° (0.75 mm.). The latter was chromatographed on alumina with hexane to give 8.5 g. of light yellow crystals which after vacuum subliming at 105° (0.45 mm.) melted at 131–132.5°, m.m.p. 132–133° with an authentic sample of **4**. The infrared and ultraviolet spectra of the two samples were identical.

Anal. Calcd. for C_9Cl_8: C, 27.59; H, 0.00; Cl, 72.41. Found: C, 27.29; H, 0.37; Cl, 72.30.

Continued elution with hexane gave 4.1 g. of white crystals, which after recrystallization from chloroform afforded **5**, m.p. 227–227.5°, m.m.p. 227–228° with an authentic sample. The infrared spectrum was identical with that of an authentic sample. The residue remaining from the distillation was chromatographed on alumina with hexane to give 11.0 g. of orange solid. Recrystallization from benzene–heptane gave bright orange crystals of **6**, m.p. 282–283° dec.; $\lambda_{max}^{CCl_4}$ 5.98 (w), 6.23 (m), 6.39 (s), 6.84 (s), 7.14 (m), 7.32 (w), 7.87 (m), 8.16 (s), 8.39 (s), 8.52 (m), 8.59 (s), 9.21 (w), 9.91 (s), 10.12 (s), 10.43 (w), 10.60 (m), 10.90 (s), 11.30 (s), 11.72 (w), 14.58 (m), 14.74 (m), 15.21 (m), 15.33 (s); $\lambda_{max}^{cyclohexane}$ (ϵ), 230 mμ (29,100), 313 mμ (57,500), 374 mμ (6500) 395 mμ (8200), 419 mμ (9300). The n.m.r. spectrum showed the absence of hydrogen protons.

Anal. Calcd. for $C_{20}Cl_{14}$: C, 32.61; H, 0.00; Cl, 67.39; mol. wt., 737. Found: C, 32.76; H, 0.23; Cl, 66.92; mol. wt., 728 (vapor pressure osmometry, benzene).

Pyrolysis of 10.—The reaction described by McBee, Idol, and Roberts[11a] was repeated. A sealed tube containing **10** (20.0 g., 0.0422 mole) was prepared and heated as described. The contents in the tube were slurried in pentane to give 7.5 g. (44%) of crude **3**. The mother liquor was distilled and 5.1 g. (22%) of **1**, b.p. 77–96° (0.7 mm.) and 3.7 g. (13%) of **2**, b.p. 96–125° (0.7, mm.) were obtained. An early cut of 1 (2.13 g., 0.0078 mole) was treated with maleic anhydride (0.77 g., 0.0078 mole), described by Kleiman,[14] to give 2.02 g. (70%) of 1,2,3,4,7,7-hexachlorobicyclo[2.2]-hept-2-one-5,6-dicarboxylic anhydride, which after vacuum sublimation, melted at 234–235°, m.m.p. 234–235° with an authentic sample. The infrared spectrum was identical with that of an authentic sample. A middle cut of **2**, after cooling, had a m.p. 38–39° and m.m.p. 38–39° with an authentic sample. The infrared spectrum was identical with that of the authentic sample.

Reaction of 7 with Phosphorus Pentachloride.—The reaction described by Eaton, Carlson, Lombardo, and Yates[5] was repeated using 5.6 g. (0.0166 mole) of **7**[5] and 10 g. (0.048 mole) of phosphorus pentachloride. The crude reaction mixture, 6.6 g., which gave an impure product on repeated crystallization from methanol, was chromatographed on acid-washed alumina with hexane and recrystallized from acetone–ethanol (95%) to give decachloroindan (**8**), 0.6 g. (8%), m.p. 136–137° (lit. m.p. ranged from 130° to 139°[5,7b,15]).

Anal. Calcd. for C_9Cl_{10}: C, 23.36; H, 0.00; Cl, 76.64. Found: C, 23.40; H, 0; Cl, 76.62.

The mother liquors were combined, evaporated to dryness, and recrystallized from methanol to give octachloroindene (**4**), 0.4 g. (6%), m.p. 133–133.5° (lit. m.p. ranged from 85° to 138.5°[5,7a,15b]); $\lambda_{max}^{CCl_4}$ 6.29 μ.

The crude yields of **4** and **8** were both estimated to be about 45–50% based on the infrared spectrum of the crude reaction mixture.

Reaction of 3 with Lithium and *t*-Butyl Alcohol.—Lithium (55.5 g., 8.0 g.-atoms) was added to a cooled suspension of **3** (161.5 g., 0.267 mole) and *t*-butyl alcohol (356.8 g., 4.80 moles) in 3 l. of dry tetrahydrofuran under nitrogen. After stirring at room temperature for 40 hr., the remaining lithium was destroyed by adding 2 l. of 20% hydrochloric acid. This mixture was extracted with ether and the extracts were washed well with water and dried. After removal of the ether, the residue was vacuum sublimed at 80° (0.25 mm.); yield, 26.4 g. (50%) of 9. Recrystallization from ethanol (95%) gave white needles, m.p.

---

[6] Zincke and co-workers[7] reported the synthesis of both **4** and **8** from **7** and phosphorus pentachloride, the only differences in the two preparations being the relative amounts of phosphorus pentachloride, the temperature, and the reaction time employed.

[7] (a) T. Zincke and H. Günther, *Ann.*, **272**, 243 (1893); (b) T. Zincke and K. H. Meyer, *ibid.*, **367**, 1 (1909).

[8] P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind.* (London), 405 (1960).

[9] V. Mark, 140th National Meeting of the American Chemical Society, Chicago, Ill., September, 1961, Abstracts of Papers, p. 7Q.

[10] F. Petrů and V. Galík, *Chem. Listy*, **51**, 2371 (1957); *Chem. Abstr.*, **52**, 6299 (1958).

[11] (a) E. T. McBee, J. D. Idol, Jr., and C. W. Roberts, *J. Am. Chem. Soc.*, **77**, 4375 (1955); (b) E. T. McBee, C. W. Roberts, and J. D. Idol, Jr., *ibid.*, **77**, 4942 (1955).

[12] Melting points were taken in capillary tubes and were uncorrected. Boiling points were uncorrected. Elemental microanalyses were determined by Dr. C. S. Yeh and Mrs. K. Keblys, Purdue University. Infrared spectra were recorded by Mrs. W. Dilling, Purdue University, on a Perkin-Elmer Model 21 or 221 spectrophotometer using sodium chloride optics, and the ultraviolet and visible spectra on a Bausch and Lomb Spectronic 505 spectrophotometer. Mr. W. E. Baitinger, Purdue University, obtained the n.m.r. spectrum with a Varian V-4311 spectrometer operating at a radio frequency of 60 Mc./sec. The spectrum was calibrated using the side-band technique.[13] The chemical shifts are reported as δ in p.p.m. from tetramethylsilane which was used as an internal reference. The areas under the peaks were measured with a planimeter.

[13] J. A. Pople, W. G. Schneider, and H. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw Hill Book Co., Inc., New York, N. Y., 1959, p. 74.

[14] M. Kleiman, U. S. Patent, 2,598,562 (1952); *Chem. Abstr.*, **46**, 7278 (1952).

[15] (a) H. Vollmann, U. S. Patent 2,734,927 (1956); *Chem. Abstr.*, **50**, 10782 (1956); (b) H. Vollmann, German Patent 844,143 (1952); *Chem Abstr.* **50**, 4227 (1956); (c) M. Ballester and J. Riera, *Anales Real Soc. Espan. Fis. Quim.* (Madrid), **56**, 897 (1960); (d) J. Bernimolin, *Chem. Ber.*, **87**, 640 (1954); (e) V. I. Shvemberger and V. M. Gordon, *J. Gen. Chem. USSR*, (Eng. Transl.), **8**, 1353 (1938).

96–96.5° (lit. m.p. ranged from 95 to 98°[4,10,16]); n.m.r. spectrum (CCl_4), a triplet (relative area 1.9) centered at −2.71, J = 6 c.p.s., and a quintuplet (relative area 1.0) centered at −2.06, J = 6 c.p.s. The infrared spectrum was identical with that given by Petrů and Galík.[10]

Anal. Calcd. for $C_{15}H_{16}$: C, 90.85; H, 9.15; Found: C, 90.62; H, 9.04.

Ozonolysis of 9.—Excess ozonized oxygen was passed through a solution of 9 (0.50 g., 0.0025 mole) in 50 ml. of methylene chloride at −78°. While the solution was still cold, 2 ml. of 30% aqueous hydrogen peroxide was added. The methylene chloride was evaporated leaving 0.71 g. (71%) of glutaric acid. Recrystallization from ether–hexane gave a material melting at 95–96°, which when mixed with an authentic sample melted at 95–96.5°. The infrared spectrum was identical with that of the authentic sample. According to the method of Shriner, Fuson, and Curtin,[17] the glutaric acid was converted to its di-*p*-bromophenacyl ester (81%) m.p. 137–138°, m.m.p. 137–138° with an authentic sample. The infrared spectra were identical.

Acknowledgment.—The financial assistance of the National Science Foundation and the Hooker Chemical Corporation is gratefully acknowledged.

---

(16) (a) O. Wallach, *Chem. Ber.*, **30**, 1094 (1897); (b) V. R. Skvarchenko, L. A. Chervoneva, J. I. Pastukhova, and R. Y. Levina, *Zh. Obshch. Khim.*, **29**, 2174 (1959); *Chem. Abstr.*, **54**, 10974 (1960); (c) W. H. Perkin and S. G. P. Plant, *J. Chem. Soc.*, **127**, 1138 (1925); (d) S. C. S. Gupta and A. Bhattacharjee, *Sci. Cult.* (Calcutta), **19**, 157 (1953); (e) S. C. S. Gupta and A. Bhattacharjee, *J. Indian Chem. Soc.*, **31**, 897 (1954); (f) J. Plevek, *Chem. Listy*, **50**, 246 (1956); *Collection Czech. Chem. Commun.*, **21**, 368 (1956); (g) R. Mayer, *Chem. Ber.*, **89**, 1443 (1956).

(17) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 200.

8-Amino-7-chloro-*s*-triazolo[4,3-*c*]pyrimidine and Related Compounds[1]

CARROLL TEMPLE, JR., ROBERT L. MCKEE, AND JOHN A. MONTGOMERY

Kettering-Meyer Laboratory, Southern Research Institute, Birmingham, Alabama, and the Venable Chemical Laboratory, University of North Carolina, Chapel Hill, North Carolina

Received March 8, 1963

The third possible heterocyclic ring system derivable from 5-amino-4-chloro-6-hydrazinopyrimidine has now been prepared by a remarkably facile ring closure with diethoxymethyl acetate. The surprising specificity of this and previously described ring closure procedures is discussed.

Previous investigators have found that treatment of 4-hydrazinopyrimidines with formic acid gives rise to the *s*-triazolo[4,3-*c*]pyrimidine ring system, if the 4-hydrazinopyrimidines contain a tautomeric group at C-2.[2] Otherwise the product is the 4-(2-formylhydrazinopyrimidine). Shiho, *et al.*, found that one such 4-(2-formylhydrazino)pyrimidine could be cyclized under forcing conditions (*i.e.*, refluxing phosphorus oxychloride) to a *s*-triazolo[4,3-*c*]pyrimidine.[3]

We have found that treatment of 5-amino-4-chloro-6-hydrazinopyrimidine (II) with formic acid resulted in the formation of 9-formamidohypoxanthine (IXa)[4] *via* 5-chloro-1,2-dihydropyrimido[5,4-*e*]-*as*-triazine (VIa).[5] That no *s*-triazolo[4,3-*c*]pyrimidine was formed in this reaction is in keeping with the results described earlier, since this pyrimidine contains no tautomeric group at C-2 and the alternative ring closures take place relatively easily. We now wish to report a remarkably facile synthesis of 8-amino-7-chloro-*s*-triazolo[4,3-*c*]pyrimidine by the reaction of II with diethoxymethyl acetate and the synthesis of some related compounds by other ring closure procedures. The facility with which this ring closure with diethoxymethyl acetate occurs is emphasized by two facts: (1) II contains no tautomeric group at C-2 and (2) neither of the two products previously obtained from II were formed in this reaction.[6] Further, this procedure and those developed previously by us now permit the preparation in excellent yield of all three of the heterocyclic ring systems derivable from a 5-amino-4-hydrazinopyrimidine.

Excess diethoxymethyl acetate reacted with II at room temperature to give 7-chloro-8-ethoxymethyleneamino-*s*-triazolo[4,3-*c*]pyrimidine (IVa) in 91% yield. The structure of IVa was established by microanalysis and by acid hydrolysis to 8-amino-7-chloro-*s*-triazolo[4,3-*c*]pyrimidine (VIIa). This compound was identified by the dissimilarity of its ultraviolet spectrum with those of its previously reported isomers VIa[5] and 9-amino-6-chloropurine (VIIIb)[4] (see Table I), which were obtained by the hydrochloric acid-catalyzed reaction of II with ethyl orthoformate. It is surprising

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA[a]

Compound	λ_{max} in mμ ($\epsilon \times 10^{-3}$)		
	0.1 *N* HCl	pH 7	0.1 *N* NaOH
VIIIb	263 (8.2)	264 (8.2)	262[b]
VIa	220[b]	222[b]	. . .
	335	330	
VIIa	221 (5.8)	222 (6.0)	276[b]
	278 (9.9)	277 (10.1)	303
	303 (8.4)	304 (7.9)	
VIIc	281 (9.85)	257 (8.7)	256[b]
	325 (8.30)	278 (10.1)	279
		319 (5.42)	320
VIIb	275 (11.0)	276 (10.9)	257 (10.1)
	320 (6.3)	320 (5.8)	281 (11.2)
			326 (4.04)

[a] The solutions used for these spectral determinations were prepared by dilution of aqueous VIIb, alcoholic VIIa, or *N*,*N*-dimethylformamide VIIc solutions with 0.1 *N* hydrochloric acid, 0.1 *N* sodium hydroxide, or pH 7 buffer. [b] Unstable.

---

(1) Part of this work was presented at the Southeastern Regional Meeting of the American Chemical Society, New Orleans, La., December 7, 1961. It was supported by funds from the C. F. Kettering Foundation and from the Cancer Chemotherapy National Service Center, National Cancer Institute, National Institutes of Health, contract no. SA-43-ph-1740.

(2) B. Camerino, G. Palamidessi, and R. Sciaky, *Gazz. chim. ital.*, **90**, 1830 (1960).

(3) D. Shiho, S. Tagami, N. Takahayashi, and R. Honda, *J. Pharm. Soc. Japan*, **76**, 804 (1956).

(4) J. A. Montgomery and C. Temple, Jr., *J. Am. Chem. Soc.*, **82**, 4592 1960).

(5) C. Temple, Jr., R. L. McKee, and J. A. Montgomery, *J. Org. Chem.*, **28**, 923 (1963).

(6) This statement is true although II is converted in high yield to 5-chloro-1,2-dihydropyrimido[5,4-*e*]-*as*-triazine (VIa) by treatment with ethyl orthoformate and mineral acid *at room temperature in less than an hour!*