

g. (0.17 mmole), 17% yield, reported²⁵ 72–73°. The infrared spectra of the two samples were identical, showing a strong carbon–bromine bond at 695 cm.⁻¹.

(2) A solution of compound I, 0.050 g. (0.212 mmole), and stilbene, 0.036 g. (0.212 mmole), in 1 ml. of ethylbenzene (b.p. 134–134.5°) was heated in vacuum at 100° for 50 minutes, concentrated to dryness in vacuum and treated with methanol. Stilbene was recovered; 0.014 g., 39% yield, m.p. and mixed m.p. 123–125°. The residue was an oil.

(3) A solution of I, 0.061 g. (0.26 mmole), and freshly sublimed quinone, m.p. 114–115°, 0.221 g. (2.0 mmoles), in 6 ml. of benzene was heated under nitrogen at 90° (bath tempera-

ture) for 42 hr. The solution was concentrated and sublimed in vacuum leading to recovery of quinone and separation of some black solid, 0.020 g. melting unsharply above 160°, presumably quinhydrone. The black residue, 0.145 g., was heated with a little ethanol, leading to compound IV, 0.003 g., 5% yield, m.p. and mixed m.p. 155–157°. The residue was chromatographed on alumina, leading to 3,6-diphenylpyridazine, 0.028 g., 47% yield, m.p. and mixed m.p. 219–220°.

Acknowledgment.—We are pleased to acknowledge generous support of this work by the National Science Foundation.

WALTHAM, MASS.

(25) R. Fittig and E. Erdmann, *Ann.*, **216**, 194 (1883).

[CONTRIBUTION NO. 403 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

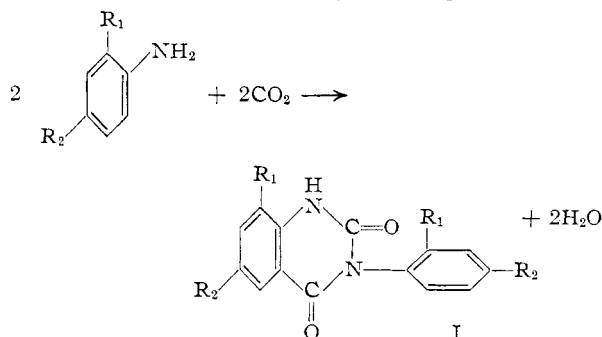
Quinazoliniones from Aromatic Amines and Carbon Dioxide

BY T. L. CAIRNS, D. D. COFFMAN AND W. W. GILBERT

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The reaction of carbon dioxide with certain primary aromatic amines at 8500 atm. and 200–250° has given high conversions to 3-aryl-2,4(1H,3H)-quinazoliniones (I). A sharp pressure threshold for the reaction was found at about 3300 atm.; the quinazoliniones were not formed at lower pressures, while conversions increased to 65–70% at the highest temperatures and pressures investigated.

Previous communications¹ from this Laboratory have described investigations of the effects of pressures of 6000 to 8500 atm. on chemical reactions. This paper reports a new reaction, the high pressure synthesis of 3-aryl-2,4(1H,3H)-quinazoliniones (I) from certain primary aromatic amines and carbon dioxide according to the equation²



This unusual transformation has been examined in terms of the effects of temperature, pressure, solvents, catalysts and substituents. Conversions of aniline to 3-phenyl-2,4(1H,3H)-quinazolinione (I, R₁ = R₂ = H) as high as 70% were obtained at temperatures above 200° at 8500 atm., but the conversion fell to zero at 150°. A sharp pressure threshold for the reaction was found at about 3300 atm. The quinazolinione was not formed at lower pressures, and the conversion increased rapidly with increased pressures above the threshold value. The reaction occurred in the presence of either alkaline or acidic catalysts, but with acidic catalysts the yield of quinazolinione was de-

creased by formation of unidentified by-products. In the uncatalyzed reaction, formation of the corresponding *sym*-diaryllurea was the chief competing reaction.

Quinazoliniones were also obtained from *o*-toluidine (15% conversion, R₁ = CH₃, R₂ = H) and from *p*-toluidine (50% conversion, R₁ = H, R₂ = CH₃). Quinazoliniones were not identified among the reaction products when the aromatic amine contained nitro, halogen or hydroxyl substituents or when the amine was α - or β -naphthylamine.

Primary aromatic diamines have given complex intractable products with carbon dioxide under these conditions. These products may have been low molecular weight polymeric quinazoliniones or polymeric ureas.

Experimental

Aniline and CO₂.—Aniline (4.08 g.) and carbon dioxide (2.39 g.) were charged into a stainless steel cylinder fitted with a movable piston.³ In some runs a small quantity of nitrogen (*ca.* 0.3 g.) was used to ensure return of the piston to its original position when the external pressure on it was released at the end of the experiment. The cylinder was placed in a Bridgman-type pressure apparatus,⁴ and its contents were subjected to an initial pressure of 8500 atm. at room temperature. The entire high-pressure system was then heated to 200°. After 14 hr. the apparatus was cooled to room temperature. The final pressure was about 7900 atm. The pressure was released and the cylinder removed and vented. The reaction product was washed from the vessel with ether and collected on a filter to give 3.37 g. of crude solid, m.p. 267–268°. It was purified by recrystallization from a mixture of ethanol and benzene or by sublimation under reduced pressure to give white crystals, m.p. 275–280°.

Anal. Calcd. for C₁₄H₁₀N₂O₂: C, 70.57; H, 4.23; N, 11.76. Found: C, 70.76; H, 4.43; N, 11.60, 11.65.

The product was identified as 3-phenyl-2,4(1H,3H)-quinazolinione by hydrolysis to aniline and anthranilic

(3) Cf. reference 1a, p. 3986; 1d, p. 749.

(4) P. W. Bridgman, "The Physics of High Pressure," G. Bell and Sons, London, 1949, pp. 30–59.

(1) (a) T. L. Cairns, G. L. Evans, A. W. Larchar and B. C. McKusick, *THIS JOURNAL*, **74**, 3982 (1952); (b) T. L. Cairns, A. W. Larchar and B. C. McKusick, *ibid.*, **74**, 5633 (1952); (c) *J. Org. Chem.*, **17**, 1497 (1952); (d) **18**, 748 (1953); (e) T. L. Cairns, D. D. Coffman, Richard Cramer, A. W. Larchar and B. C. McKusick, *THIS JOURNAL*, **76**, 3024 (1954).

(2) W. W. Gilbert, U. S. Patent 2,680,741, June 8, 1954.

acid and by comparison of its m.p., mixed m.p., infrared spectrum and X-ray diffraction pattern with authentic material prepared by cyclization of the N-phenylurea of anthranilic acid.⁵

TABLE I

REACTION OF ANILINE WITH CARBON DIOXIDE: EFFECT OF TEMPERATURE, PRESSURE AND CATALYSTS ON SYNTHESIS OF 3-PHENYL-2,4(1H,3H)-QUINAZOLINEDIONE

Reactions of possible intermediates		Quinazoline-dione, g.
Charge, g.	Conditions ^a	
Aniline, 4.08	200°	3.37
CO ₂ , 2.39	8500-7900	
Aniline, 71.5	250° ^b	0 ^c
CO ₂	3000	
Aniline, 71.5	320° ^d	0 ^e
CO ₂	3000	
Aniline, 4.03	250°	0 ^f
CO ₂ , 1.75	1500-1150	
Aniline, 4.23	250°	0.05 ^g
CO ₂ , 2.52; N ₂ , 0.32	3300-2600	
Aniline, 4.00	250°	0.74
CO ₂ , 2.14	4300-3600	
Aniline, 1.05	250°	0.05
CO ₂ , 1.79	5300	
Aniline, 4.33	250°	1.68 ^h
CO ₂ , 3.65; N ₂ , 0.20	6000-5600	
Aniline, 4.00	150°	0 ⁱ
CO ₂ , 2.56	8500-7700	
Aniline, 4.16	200°	2.51
CO ₂ , 3.97	8500-8100	
Aniline, 2.02	100°	0 ^j
CO ₂ , 2.07; H ₂ O, 4.00	8500-7900	
Aniline, 4.06; H ₂ O, 0.75	250°	3.72
CO ₂ , 3.27; Na ₂ CO ₃ , 1.00	8500-7700	
Aniline, 3.14; AlCl ₃ , 1.00	200°	1.55 ⁱ
CO ₂ , 4.00; N ₂ , 0.24	8500-7700	
Aniline, 2.00; AlCl ₃ , 3.00	250°	0.05 ^j
CO ₂ , 3.06; N ₂ , 0.40	8500-7100	
Aniline, 2.09; CO ₂ , 3.07	250°	0.16 ^k
Aniline·HCl, 2.00; N ₂ , 0.28	7300-3200 ^k	
Aniline, 1.86; CO ₂ , 4.02	150°	0 ^m
Aniline·HCl, 2.00; N ₂ , 0.19	8500-7900	
Aniline, 2.07; CO ₂ , 2.95	200°	0.67 ⁿ
Aniline·HCl, 2.00; N ₂ , 0.33	8500-7900	
Aniline, 4.10; CO ₂ , 2.63	250°	2.15
Concd. HCl, 0.02; N ₂ , 0.39	8500-7900	
Aniline, 4.11; CO ₂ , 2.56	200°	1.62
Powd. NaOH, 0.50; N ₂ , 0.30	8500-7700	
Aniline, 4.06; CO ₂ , 3.48	150°	0 ^h
K ₂ CO ₃ , 0.50; N ₂ , 0.30	8500-7300	
Aniline, 4.25; N ₂ , 0.23	250°	2.25 ^h
CO ₂ , 3.73	8500-7900	
Phenyldimethylphosphine, 0.10		
Aniline, 3.99; N ₂ , 0.23	150°	0 ^o
CO ₂ , 4.14	8500-7900	
Phenyldimethylphosphine, 0.10		
<i>sym</i> -Diphenylurea, 2.00	250°	0
CO ₂ , 2.82; N ₂ , 0.15	8500-7900	
Ether, 2.56		

(5) C. Paal, *Ber.*, **27**, 977 (1894).

<i>sym</i> -Diphenylurea, 3.00	200°	0.15 ^p
CO ₂ , 3.61; N ₂ , 0.35	8500-6600	
Triethylamine, 0.56		
Anthranilic acid, 3.04	250°	0.02 ^q
Ether, 4.98	8500-8900	
Anthranilic acid, 3.26	250°	1.67 ^{r,p}
CO ₂ , 3.20; N ₂ , 0.46	8500-8100	
Phenyl isocyanate, 10.54	250°	0 ^r
	8500-7100	

^a Reaction time 12-15 hr. unless otherwise specified. Pressures are initial and final pressures in atm. ^b Reaction time, 3 hr. ^c Small amount of *sym*-diphenylurea formed. ^d Reaction time, 2 hr. ^e *sym*-Diphenylurea, 0.16 g. ^f No *sym*-diphenylurea detected. ^g *sym*-Diphenylurea, 0.12 g. ^h *sym*-Diphenylurea, 0.02 g. ⁱ Neutral fraction, 0.43 g., m.p. 43-47°. ^j Neutral fraction, 0.32 g., m.p. 36-41°. ^k Slow leak in reactor. ^l Neutral fraction, 1.20 g., m.p. 44-46°. ^m Neutral fraction, 0.10 g., m.p. 50-53°. ⁿ Neutral fraction, 0.85 g., m.p. 30-40°. ^o *sym*-Diphenylurea, 0.29 g. ^p Some aniline recovered. ^q CO₂ formed. ^r Quantitative conversion to triphenyl isocyanurate.

In most of this work the crude reaction product was purified by suspension in ether and extraction first with 2 *N* hydrochloric acid and then with 5% sodium hydroxide solution. The 3-aryl-2,4-(1H,3H)-quinazolinediones were recovered by saturating the sodium hydroxide solution with carbon dioxide. The small neutral fraction which was sparingly soluble in ether was recrystallized from ethanol to give the *sym*-diarylyurea. From aniline and carbon dioxide this urea was *sym*-diphenylurea, long white needles, m.p. 244-246°. The mixed m.p. with authentic *sym*-diphenylurea, m.p. 245-247°, was not depressed.

Examples in the table illustrate the effects of temperature, pressure, solvents, catalysts and substituents on the reactions of representative primary aromatic amines with carbon dioxide. The relative proportions of 3-aryl-2,4-(1H,3H)-quinazolinediones and *sym*-diarylyureas are also indicated.^{6,7,8}

Discussion

The formation of 3-aryl-2,4-(1H,3H)-quinazolinediones from aromatic primary amines and carbon dioxide has not been described previously. A British patent⁹ claims the preparation of *sym*-diarylyureas from aniline or ethylaniline in the presence of a molar deficiency of aluminum chloride under 50-70 atm. of carbon dioxide pressure at 105-150°. In the present investigation, however, it was found that aluminum chloride or hydrogen chloride (added as aniline hydrochloride) decreased the yield of 3-phenyl-2,4-(1H,3H)-quinazolinedione without giving isolable quantities of *sym*-diphenylurea. This effect was accompanied by an increased formation of unidentified, low-melting, neutral, ether-soluble side-reaction products.

It does not appear that *sym*-diphenylurea was formed first and that subsequently it underwent reaction with more carbon dioxide to give the quinazolinedione. However, the experiments to demonstrate this point are not unequivocal, since phenomena involving contact of carbon dioxide with massive crystals of *sym*-diphenylurea *vs.*

(6) A. F. Kizber and A. J. Glagoleva, *Doklady Akad. Nauk, S.S.S.R.*, **83**, 89 (1952); *C. A.*, **47**, 4343 (1953). The m.p. of 3-*p*-tolyl-6-methyl-2,4(1H,3H)-quinazolinedione was reported to be 285-286° and that of 3-(1-naphthyl)benzo[h]quinazoline-2,4(1H,3H)-dione to be 333-334°.

(7) G. V. Jadhav, *J. Indian Chem. Soc.*, **10**, 391 (1933), reported *sym*-di- α -naphthylurea, m.p. 296°, and *sym*-di- β -naphthylurea, m.p. 310°.

(8) P. Pierron, *Ann. chim. phys.*, [8] **15**, 194 (1908), reported benzimidazolone platelets, m.p. 310° (sublimes above 270°).

(9) G. T. Morgan and D. D. Pratt, British Patent 353,464 (to Imperial Chemical Industries, Ltd.), July 20, 1931.

TABLE II

REACTIONS OF OTHER AROMATIC PRIMARY AMINES WITH CARBON DIOXIDE

Reaction temperature 250° unless otherwise specified; reaction time 12–14 hr.

Charge, g.	Pressure, atm.	Quinazoline-dione, g.
<i>o</i> -Toluidine, 3.96 CO ₂ , 2.88	7500–7100	Some ^a
<i>o</i> -Toluidine, 4.00 CO ₂ , 3.33; N ₂ , 0.36	8500–7900	0.76 ^b
<i>p</i> -Toluidine, 3.73 CO ₂ , 2.92; N ₂ , 0.78	8500–7900	2.33
<i>p</i> -Toluidine, 8.00 ^c CO ₂ , 8.03; N ₂ , 0.35	8500–7700	5.09 ^{d,e}
2,6-Dimethylaniline, 3.82 CO ₂ , 4.34; N ₂ , 0.27	8500–7500	0 ^f
α -Naphthylamine, 3.00 CO ₂ , 3.03; Ether, 2.16; N ₂ , 0.14	8500–8300 ^g	.. ^h
α -Naphthylamine, 3.00 CO ₂ , 4.48; N ₂ , 0.13	8500–8300	..
β -Naphthylamine, 2.00 CO ₂ , 2.26; Ether, 2.53; N ₂ , 0.18	8500–8100	0 ⁱ
<i>p</i> -Phenylenediamine, 3.05 CO ₂ , 4.69; N ₂ , 0.13	8300–8100	.. ^k
2,4-Diaminotoluene, 2.80 CO ₂ , 3.16; N ₂ , 0.53	8500–8100	.. ^l
<i>o</i> -Phenylenediamine, 3.03 CO ₂ , 4.89; N ₂ , 0.28	8500–7300	.. ^m
Benzidine, 2.95 CO ₂ , 4.39; N ₂ , 0.19	8100–7300	.. ⁿ

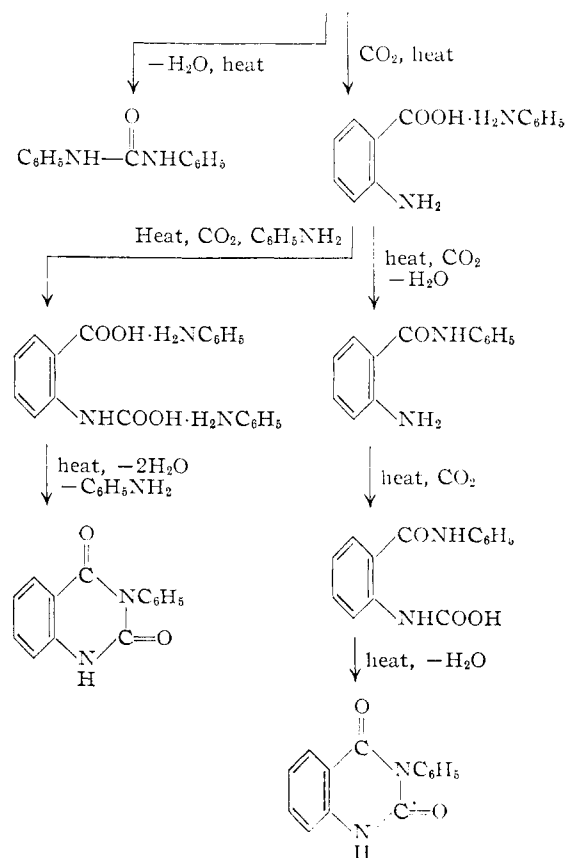
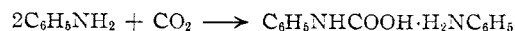
^a Recovered 0.46 g. of *sym*-di-*o*-tolylurea, m.p. and mixed m.p. with authentic *sym*-di-*o*-tolylurea, 257–258°. ^b M.p. 224–225° from methanol–benzene. *Anal.* Calcd. for C₁₆H₁₄N₂O₂: C, 72.18; H, 5.30; N, 10.52. Found: C, 72.30; H, 5.48; N, 10.57, 10.53. Some *sym*-di-*o*-tolylurea formed. ^c Two runs combined. ^d M.p. 288–290° from methanol–benzene. A. F. Kizber and A. J. Glagoleva⁶ reported m.p. 285–286° for 3-*p*-tolyl-6-methyl-2,4(1H,3H)-quinazolinedione. *Anal.* Calcd. for C₁₈H₁₄N₂O₂: C, 72.18; H, 5.30; N, 10.52. Found: C, 71.89; H, 5.37; N, 10.44, 10.47. ^e Also recovered *sym*-di-*p*-tolylurea, 0.05 g., m.p. and mixed m.p. with authentic sample, 271–272°. ^f Recovered 1.41 g. of *sym*-di-2,6-dimethylphenylurea, m.p. above 325° (sublimation). *Anal.* Calcd. for C₁₇H₂₀N₂O: C, 76.09; H, 7.51; N, 10.44. Found: C, 76.46; H, 7.65; N, 10.42, 10.38. ^g 200°. ^h Recovered 1.71 g. of di- α -naphthylurea, m.p. 310–312°. *Anal.* Calcd. for C₂₁H₁₆N₂O: C, 80.74; H, 5.16; N, 8.97. Found: C, 80.97; H, 5.85; N, 8.94, 8.96. G. V. Jadhav⁷ reported *sym*-di- α -naphthylurea, m.p. 296°. ⁱ An alkali-soluble solid, m.p. 345° (0.68 g. from methanol–benzene), that was precipitated from alkaline solutions by carbon dioxide, gave no satisfactory analytical results for a quinazolinedione. 3-(1-Naphthyl)-benzo[h]quinazoline-2,4(1H,3H)-dione, m.p. 333–334°, was reported by A. F. Kizber and A. J. Glagoleva.⁶ ^j Recovered 0.30 g. of di- β -naphthylamine and 0.17 g. of *sym*-di- β -naphthylurea, m.p. 310–315°. ^k *Anal.* Calcd. for C₂₁H₁₆N₂O: C, 80.74; H, 5.16; N, 8.97. Found: C, 80.37; H, 5.18; N, 9.75, 9.76. ^l Recovered 3.52 g. of black solid, m.p. above 350°. Intractable solid Soxhlet extracted with ether without appreciable weight loss. *Anal.* Calcd. for (C₈H₄N₂O₂)₂ (polymeric quinazolinedione): C, 60.00; H, 2.51; N, 17.51. Found: C, 60.51; H, 4.44; N, 17.57, 17.49. ^m Recovered 3.17 g. of brown solid which darkened at 240–250°. Intractable solid Soxhlet extracted with ether. *Anal.* Calcd. for (C₈H₄N₂O₂)₂ (polymeric quinazolinedione): C, 62.07; H, 3.47; N, 16.09. Found: C, 61.60; H, 4.96; N, 15.53, 15.60. ⁿ Recovered 1.27 g. of cyclic urea benzimidazolone, m.p. 320°. P. Pierron⁸ reported benzimidazolone, m.p. 310°. *Anal.* Calcd. for C₇H₆N₂O: C, 62.67; H, 4.51; N, 20.89. Found: C, 62.36; H, 4.57; N, 20.59, 20.64. ^o Recovered 2.96 g. of gray

solid. Soxhlet extraction with ether, methanol, acetone and dimethylformamide gave no appreciable loss in weight of solid. *Anal.* Calcd. for (C₁₃H₁₀N₂O)₂ (polymeric urea): C, 74.27; H, 4.80; N, 13.33. Found: C, 73.10; H, 4.95; N, 13.54, 13.63.

finely divided urea crystals formed *in situ* from aniline and carbon dioxide might lead to entirely different rates of reaction. In the presence of a small amount of triethylamine to give a basic environment, *sym*-diphenylurea did give a detectable quantity of the quinazolinedione, but the reaction was complicated by gross amounts of unidentified by-products.

Recent work by Kizber and Glagoleva⁶ indicated that *sym*-diphenylurea when heated with potassium carbonate for 5 hr. at 250–260° under 50–55 atm. carbon dioxide pressure underwent modest conversions to *p*-aminobenzoic acid, anthranilic acid and 3-phenyl-2,4(1H,3H)-quinazolinedione. Further the potassium salt of anthranilic acid was converted to the quinazolinedione by heating in a sealed tube at 230–240° for 8 hr. *sym*-Diphenylurea was also cleaved by potassium carbonate and carbon dioxide in 8 hr. at 160–170°, giving 80–85% of the potassium salt of phenylcarbamic acid. The latter on heating above 180° in carbon dioxide was converted to potassium salts of *p*-aminobenzoic and anthranilic acids.

Conditions in the present reaction system do not favor the formation of phenyl isocyanate, which, incidentally, at 250° and 8500 atm. was quantitatively trimerized to triphenyl isocyanurate, m.p.



265–270°. The aniline salt of phenylcarbamic acid, $C_6H_5NHCOOH \cdot H_2NC_6H_5$, might be stable even in the presence of water under carbon dioxide pressure. This salt might be capable of rearranging under the combined agencies of heat and carbon dioxide pressure to give the aniline salt of anthranilic acid in analogy to the reported results with the potassium salt. This mechanism appears consistent with the observed lower conversions in the presence of aluminum chloride and aniline hydro-

(10) N. W. Hofmann, *Ber.*, **18**, 764 (1885). Triphenyl isocyanurate, m.p. 275°, was prepared by heating phenyl isocyanate (5 moles) with potassium acetate (1 mole) at 100°.

chloride. Other possible intermediates in the transformation to the quinazolinone are indicated in the diagram.

Acknowledgments.—The authors are pleased to acknowledge the assistance given by Dr. N. E. Searle who supplied known samples of *sym*-di-*o*-tolyl- and di-*p*-tolylurea. We would like to thank Drs. W. W. Prichard, E. L. Jenner, J. R. Roland and A. L. Barney, and Messrs. A. W. Larchar, H. S. Young and P. J. Rennolds for stimulating discussions and helpful suggestions.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE STERLING-WINTHROP RESEARCH INSTITUTE]

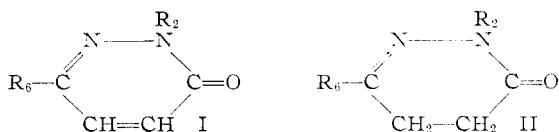
Absorption Spectra of Heterocyclic Compounds. VII.¹ Some 3(2H)-Pyridazones

BY EDGAR A. STECK AND FREDERICK C. NACHOD

RECEIVED MARCH 2, 1957

The absorption spectra of a series of 3-pyridazones have been reported and interpreted.

Pyridazine derivatives may be considered to contain a potential hydrazine unit in the 1,2-diazine ring and hence are not readily obtainable from biochemical transformations involving nitrogen. In fact, this ring system has not been found to occur in natural products, a sharp distinction from the other diazines. This heterocyclic type has not been investigated as thoroughly as the pyrimidines and pyrazines, and relatively few reports of physicochemical studies on pyridazines have appeared in the literature.^{2–14} Some work has been done^{3,9,13} on the absorption spectra of 3(2H)-pyridazones, which are cyclic hydrazones. Our interest in the 6-substituted 3(2H)-pyridazones as chemotherapeutic agents^{15,16} and intermediates for the preparation of other potential pharmaceuticals has led us to study the absorption spectra of this type (I) and also the related 4,5-dihydro compounds II.



(1) Previous contribution: E. A. Steck, F. C. Nachod and G. W. Ewing, *THIS JOURNAL*, **71**, 2334 (1949).

(2) M. G. Korshun and C. Roll, *Bull. soc. chim.*, [4] **39**, 1223 (1926).

(3) D. Biquard and P. Grammaticakis, *ibid.*, [5] **7**, 766 (1940).

(4) W. Hückel and W. Jahnentz, *Ber.*, **74**, 652 (1941); **75**, 1438 (1942).

(5) R. C. Evans and F. Y. Wiselogle, *THIS JOURNAL*, **67**, 60 (1945).

(6) W. C. Schneider, *ibid.*, **70**, 627 (1948).

(7) A. Macoll, *J. Chem. Soc.*, 670 (1946).

(8) A. Albert, R. Goldacre and J. Phillips, *ibid.*, 2240 (1948).

(9) H. Gregory, J. Hills and L. F. Wiggins, *ibid.*, 1248 (1949).

(10) S. Dixon and L. F. Wiggins, *ibid.*, 3236 (1950).

(11) O. Chalvet and C. Sandorfy, *Compt. rend.*, **228**, 566 (1949).

(12) F. Halverson and R. C. Hirt, *J. Chem. Phys.*, **17**, 1165 (1949).

(13) K. Eichenberger, R. Rometsch and J. Druey, *Helv. Chim. Acta*, **37**, 1298 (1954).

(14) R. H. Horning and E. D. Amstutz, *J. Org. Chem.*, **20**, 1069 (1955).

(15) E. A. Steck, U. S. Patent 2,624,730.

(16) E. A. Steck, R. P. Brundage and L. T. Fletcher, (a) *THIS JOURNAL*, **75**, 1117 (1953); (b) to be published.

The range of structures which may be chosen for 3(2H)-pyridazones and related dihydro compounds is limited sharply by the non-equivalence of the two formulas possible for pyridazine.^{5,7} Thus, comparison of the absorption spectra of 6-phenyl-3(2H)-pyridazine (I, $R_2 = H$, $R_6 = C_6H_5$) with those of 2-methyl-6-phenyl-3-pyridazine (I, $R_2 = CH_3$; $R_6 = C_6H_5$) and 3-methoxy-6-phenylpyridazine (III) clearly substantiates the formulation of the first-mentioned compound as (I). The spectra of the three compounds in 95% ethanol are shown in Fig. 1.



Absorption spectra of 6-(2-thienyl)-3(2H)-pyridazine and the related 4,5-dihydro compound in 95% ethanol, 0.01 *N* sodium hydroxide and 0.01 *N* hydrochloride are presented in Fig. 2. 4,5-Dihydro-6-(2-thienyl)-3(2H)-pyridazine shows little difference in pattern of spectra in the three solvents. While the spectra of 6-(2-thienyl)-3(2H)-pyridazine in ethanol and acid are identical, the absorption in basic solutions is more closely related in effect to those obtained with the dihydro compound. This indicates that the sodium enolate, which may be formed through keto-enol tautomerism in this type of the pyridazine, is more or less closely related to the dihydropyridazine (*cf.* ref. 13). However, the behavior in neutral or acid solution shows that 6-(2-thienyl)-3(2H)-pyridazine may not exist in keto form (in those solvents) as evident by comparison of Fig. 2 with Fig. 1.

In Table I, the comparison of spectral absorption of 6-substituted 3(2H)-pyridazines in neutral, alkali and acid solutions is presented. A chlorine in the *p*-position of the phenyl group produced a slight batho- and hyperchromic effect, this being more pronounced when ethanol was the solvent. This behavior is not unexpected, nor was a similar one in the case of the 6-(2-thienyl)-3(2)-pyridazine