

dimethoxyethane was treated with 0.0937 g. of potassium. A dark green color appeared on the surface of the metal almost immediately. At the end of 3 hr. the solution was almost black and a small piece of potassium remained. The small piece of potassium was still in evidence after an additional 14 hr., when it was removed, wt. 0.012 g. A solution of 0.0612 g. of water in 10 ml. of 1,2-dimethoxyethane was added dropwise. The green color became orange. The reaction mixture was shaken with a mixture of water and pentane. The pentane layer was washed with water, dried, filtered and evaporated to an oil. Gas chromatography on a 20% silicone gum column using a Loenco gas chromatograph preparative column produced two components in approximately equal yields, the first being starting material. The second was demonstrated to be neither 1-ethylnaphthalene nor tetrahydroacenaphthalene by infrared analysis.

**Vapor Phase Chromatographic Analysis.**—Pure samples of 1-ethylnaphthalene (see above), acenaphthene, 2-phenylpentane<sup>17</sup> and 3-phenylpentane<sup>17</sup> were used as standards. The mixture of 2-phenylpentenes and of 3-phenylpentenes obtained by treatment of 2-phenyl-3-pentyl *p*-toluenesulfonate<sup>3</sup> and 3-phenyl-2-pentyl *p*-toluenesulfonate<sup>3</sup> with sodium hydroxide were used as olefin standards.

(17) D. J. Cram, *J. Am. Chem. Soc.*, **74**, 2152 (1952).

For analysis of the products of reduction of methanesulfonates I and III and of ether II, the following techniques were employed. Analyses were carried out using a Perkin-Elmer model 154 vapor fractometer. Neat liquids (1  $\mu$ l.) were injected onto a 6 ft. by 0.25 in. column of 33% polyethylene glycol on firebrick. At a column temperature of 125° and 15 p.s.i. of helium the retention time of 2-phenylpentane is 12.3 min. and that of 3-phenylpentane is 13.4 min.

For analysis of the products of reduction of ether V, the following techniques were used. The neat liquid (1  $\mu$ l.) was injected onto a 6 ft. by 0.25 in. column of 33% polyethylene glycol on firebrick. At a column temperature of 200° and 25 p.s.i. of helium the retention time of 1-ethylnaphthalene is 5.2 minutes.

**Spectral Analysis.**—The n.m.r. spectra were taken on a Varian Associates Model A60 n.m.r. spectrometer. The absorption bands of the compounds useful in this investigation are reported in Table I.

The infrared spectra of the deuterated and non-deuterated 1-ethylnaphthalenes and naphthylethanols differed somewhat, and were used to corroborate the conclusions derived from the n.m.r. data. The spectra were taken on 10% solutions by weight in methylene dichloride with sodium chloride optics and cells on a Perkin-Elmer model IR-5 infrared spectrophotometer. The data are in Table II.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES, LOS ANGELES 24, CALIF.]

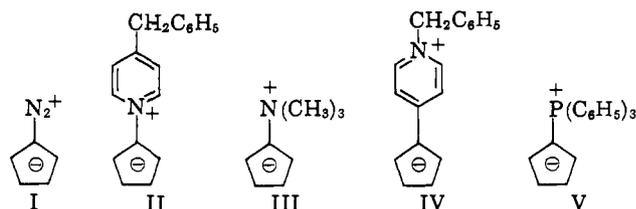
## Electrophilic Substitution and Other Reactions of Diazocyclopentadiene<sup>1</sup>

BY DONALD J. CRAM AND RICHARD D. PARTOS

RECEIVED NOVEMBER 19, 1962

Diazocyclopentadiene (I) has been found to undergo five electrophilic substitution reactions without destruction of the ylide  $\pi$ -electron system. Nitration produced two monosubstituted derivatives, the 2- predominating over the 3-isomer by a factor of two. Benzenediazonium tetrafluoroborate gave the 2-substitution product, whereas bromination gave tetrabromodiazocyclopentadiene. Mercuration resulted in formation of a highly unstable 2,5-diiodomercuri derivative, which was readily converted to 2,5-diiododiazocyclopentadiene. Diazocyclopentadiene added 1,2 to tetracyanoethylene to give an unstable acid which readily lost the elements of hydrogen cyanide to produce 2-(tricyanoethylene)-diazocyclopentadiene. No evidence of a Diels-Alder reaction was obtained. The tricyanovinyl group underwent nucleophilic substitution reactions typical of that function without loss of the diazocyclopentadiene nucleus. With dimethyl acetylenedicarboxylate, diazocyclopentadiene underwent a 1,4-dipolar addition reaction to produce a fused 5- to 6-membered ring system (XVII). The acidity of the substance is attributed partially to the presence of 10  $\pi$ -electrons in its conjugate base.

Aside from the molecular sandwich derivatives of which ferrocene is the prototype, five ylides of cyclopentadiene have been prepared; systems I,<sup>2</sup> II,<sup>3</sup> III,<sup>4</sup> IV<sup>5</sup> and V.<sup>6</sup>



The aromatic character of V was demonstrated by its coupling reaction with phenyldiazonium chloride,<sup>7</sup> which occurred in the 2-position.

Reactions of diazocyclopentadiene (I) have been confined to its catalytic reduction to cyclopentanone hydrazone,<sup>2</sup> its coupling reaction with triphenylphosphine to give a phosphazine,<sup>7</sup> its photolysis to give fulvalene,<sup>8</sup> and its reaction with organolithium reagents

to produce salts which in turn gave azoferrocene derivatives when treated with ferrous chloride.<sup>9</sup>

The present investigation is concerned with the electrophilic substitution and cycloaddition reactions of diazocyclopentadiene. From the outset, the work was directed toward answering the following questions. (1) Would the nucleus of I undergo electrophilic substitution without disruption of the diazo linkage? (2) Which position is the most subject to substitution? (3) How reactive is the ring system compared to other aromatic systems? (4) Could the substance be induced to undergo cycloaddition reactions?

**Electrophilic Substitution.**—Diazocyclopentadiene (I) underwent a number of electrophilic substitution reactions, which are discussed in turn in the following sections. In each case, the derivatives themselves serve as focal points for discussion of synthesis, structural assignments, reactions and physical properties.

**Nitration.**—Nitration of I in acetonitrile at 0° with benzoil nitrate gave a mixture of two mononitrodiazocyclopentadienes, chromatography of which on silica gel gave each component in a pure crystalline state. The dominant isomer (factor of two) preceded the other off the column, and exhibited the lower melting point (32° vs. 90°). These properties suggested the dominant isomer to have structure VI, since this structure should be associated with the less polar of the two isomers VI and VII. This provisional identification was confirmed by both direct chemical evidence and nuclear magnetic resonance (n.m.r.) spectral analysis.

Hydrogenation of the lower melting isomer followed by treatment of the product VIII with 2,4-dinitro-

(9) G. R. Knox, *Proc. Chem. Soc.*, 56 (1959).

(1) The authors wish to thank the U. S. Army Research Office (Durham) for a grant used in support of this work.

(2) W. von E. Doering and C. H. DePuy, *J. Am. Chem. Soc.*, **75**, 5955 (1953).

(3) (a) D. Lloyd and J. S. Sneezum, *Chem. Ind. (London)*, 1221 (1955); *Tetrahedron*, **3**, 334 (1958); (b) D. N. Kursanov and N. K. Baranetskaya, *Izv. Akad. Nauk S. S. R., Old. Khim. Nauk*, 362 (1958).

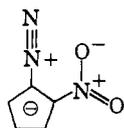
(4) W. W. Spooner, *Diss. Abstr.*, **16**, 458 (1956).

(5) D. N. Kursanov, N. K. Baranetskaya and Y. N. Setkina, *Dokl. Akad. Nauk S. S. R.*, **113**, 116 (1957).

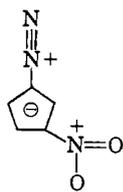
(6) F. Ramirez and S. Levy, *J. Am. Chem. Soc.*, **79**, 67, 6167 (1957).

(7) F. Ramirez and S. Levy, *J. Org. Chem.*, **23**, 2036 (1958).

(8) W. B. De More, H. O. Pritchard and N. Davidson, *J. Am. Chem. Soc.*, **81**, 5874 (1959).



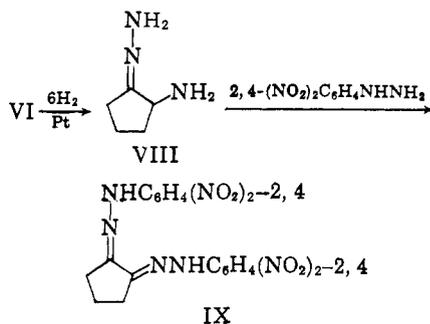
VI, m.p. 32°



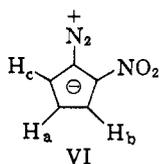
VII, m.p. 90°

phenylhydrazine gave osazone IX,<sup>10</sup> which was also prepared from 2-bromocyclopentadiene<sup>10</sup> with the same reagent. The two preparations of IX exhibited identical ultraviolet spectra and melting points, and did not depress one another's melting point.

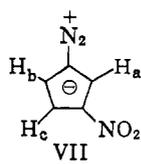
The n.m.r. spectrum of diazocyclopentadiene (I) exhibits two multiplets of equal area centered at 3.3 and 4.2  $\tau$ . The electron-withdrawing  $N_2^+$  group undoubtedly exerts a stronger deshielding effect on the 2,5-positions than on the 3,4-, and therefore the 4.2  $\tau$



bands are assigned to the 3,4-hydrogens and the 3.3  $\tau$  bands to the 2,5-hydrogens. The cyclopentadienide anion, which carries a full negative charge in the ring, absorbs at 4.5  $\tau$ ,<sup>11</sup> not far from the 3,4-hydrogens of I. The n.m.r. spectrum of VI contains three groups of peaks of equal areas, two quadruplets centered at 2.8 and 3.1  $\tau$ . This triplet is assigned to proton a, which has the most symmetrical environment and is the most shielded. Protons b and c are both adjacent to strongly electron-withdrawing groups, and give rise to the two quadruplets. Since the  $N_2^+$  group is probably more electron



$H_a$ , 4.0  $\tau$  ( $J_{ab}$  4.8,  
 $J_{ac}$  3.7 c.p.s.)  
 $H_b$ , 3.1  $\tau$  ( $J_{bc}$  2.2 c.p.s.)  
 $H_c$ , 2.8  $\tau$



$H_a$ , 2.3  $\tau$  ( $J_{ac}$  2.3 c.p.s.,  
 $J_{ab}$  2.5 c.p.s.)  
 $H_b$ , 3.2  $\tau$  ( $J_{bc}$  5.1 c.p.s.)  
 $H_c$ , 3.6  $\tau$

withdrawing than the nitro group,  $H_c$  is tentatively assigned to 2.8  $\tau$  and  $H_b$  to 3.1  $\tau$ . Coupling constants are assigned on the usual basis (see formulation), the transannular constant ( $J_{bc}$ ) being lower valued than the other two. The n.m.r. spectrum of VII contains a triplet at 2.3  $\tau$  and two quadruplets (3.2 and 3.6  $\tau$ ) all of equal area. The triplet is assigned to proton a, which is the most symmetrically located and deshielded of the three. Proton c should be more shielded than b, and accordingly c is assigned 3.6  $\tau$  and b 3.2  $\tau$ . The coupling constants are assigned on the usual basis (see formulation), again the transannular constants ( $J_{ab}$  and  $J_{ac}$ ) being lower valued than that associated with adjacent hydrogens. Structural assignments could have been made on the basis of coupling constants alone, since structure VI contains two sets of adjacent

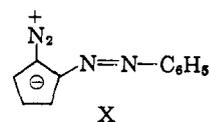
(10) F. Ramirez and R. J. Bellet, *J. Am. Chem. Soc.*, **76**, 491 (1954).

(11) G. Fraenkel, *ibid.*, **82**, 5846 (1960).

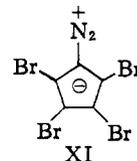
hydrogens and should have two relatively high valued coupling constants, whereas VII contains only one set of adjacent hydrogens, and should have only one high valued coupling constant.

Both VI and VII exhibit intense absorption at about 4.75  $\mu$  in the infrared, which demonstrates the presence of the diazo linkage. Both compounds are yellow, are extremely light sensitive, and darken rapidly unless protected from the light.

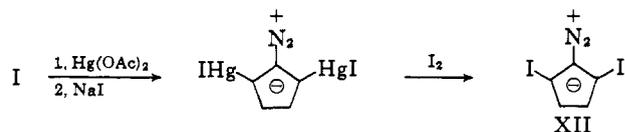
**Diazonium Coupling Reaction.**<sup>12</sup>—Treatment of diazocyclopentadiene with phenyldiazonium tetrafluoroborate gave 2-phenylazodiazocyclopentadiene (X) as deep violet needles. Unlike the other derivatives, X is not light sensitive. An attempt to confirm the position of substitution through n.m.r. analysis failed. The phenyl group complicated and obscured the absorptions of the other hydrogens. The structural assignment is made on the basis of analogy with the behavior of V toward diazo coupling, and I toward other electrophiles. The infrared spectrum of X contains the usual diazo absorption at 4.8  $\mu$ .



**Bromination.**—When treated with N-bromosuccinimide in acetonitrile, tetrabromodiazocyclopentadiene (XI) was produced. This light sensitive, brown crystalline solid decomposed when heated, and exhibited the usual intense diazo absorption at 4.8  $\mu$  in the infrared.



**Mercuration.**—Diazocyclopentadiene was converted to its 2,5-diiodomercuri derivative when mixed with mercuric acetate in dimethyl sulfoxide, followed by addition of a solution of sodium iodide in aqueous ethanol. The mercuri derivative is an extremely insoluble and unstable yellow solid. An explosion occurred when a small amount of the substance was ground with potassium bromide preparatory to spectral measurements. Hence the substance was converted to 2,5-diiododiazocyclopentadiene (XII) with iodine in chloroform. The compound is a light-sensitive, orange crystalline solid, whose infrared spectrum shows the



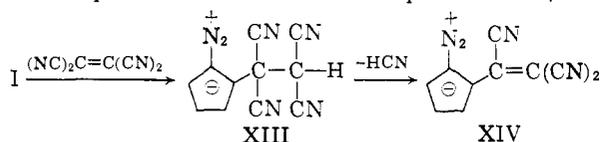
usual diazo absorption at 4.8  $\mu$ . The positions of substitution in XII were determined by n.m.r. analysis. The spectrum contains only one singlet, at 3.9  $\tau$ , and therefore the two hydrogens are in identical environments. The position of the singlet is only consistent with the presence of hydrogens in the 3,4-positions of the diiodo compound. The 3,4-hydrogens of diazocyclopentadiene absorb at 4.2  $\tau$ . The electronegative iodo groups deshield the hydrogens slightly and should move their absorption downfield. If the diiodo compound had hydrogens substituted in the 2,5-positions, their  $\tau$  values would have been somewhat less than 3.3.

(12) The authors wish to thank Dr. B. C. McKusick for suggesting this reaction.

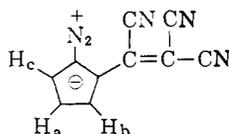
**Tricyanovinylolation.**—Tetracyanoethylene is an unusually reactive dienophile,<sup>13a</sup> as well as a weak electrophile capable of substituting highly reactive aromatic systems such as dimethylaniline, phenanthrene and azulene.<sup>13b,c</sup> Diazocyclopentadiene is potentially either a diene or an aromatic system subject to electrophilic substitution. It was therefore of interest to determine the role played by each reactant in response to the other.

Treatment of diazocyclopentadiene with tetracyanoethylene in anhydrous tetrahydrofuran gave 2-tetracyanoethyldiazocyclopentadiene. No evidence was obtained for a Diels–Alder reaction. The color changes during the reaction (an immediately formed purple color disappeared slowly) suggest that an intermediate  $\pi$ - $\pi$ -complex was formed, possibly as an immediate precursor of the  $\sigma$ -complex which is the usual intermediate of electrophilic substitution at unsaturated carbon.

Tetracyanoethyl compound XIII is a light-sensitive yellow crystalline solid whose infrared spectrum possesses the diazo absorption at 4.8  $\mu$ . The ultraviolet absorption spectrum of XIII is almost identical with that of diazocyclopentadiene (see later section). In the presence of water, XIII eliminated hydrogen cyanide to give 2-tricyanovinylidiazocyclopentadiene (XIV) as a light-sensitive, orange crystalline solid. Again the infrared spectrum contains the diazo peak at 4.73  $\mu$ .

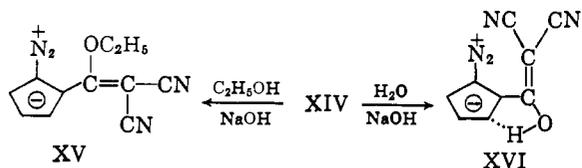


The position of substitution in XIV is demonstrated by its n.m.r. spectrum, which exhibits a triplet at 3.6  $\tau$  and two quartets at 2.3 and 2.6  $\tau$ . The spectrum is similar to that of 2-nitrodiazocyclopentadiene (VI) except that the more electron-withdrawing tricyano group (more than the nitro group) shifts the peak centers downfield by about 0.4–0.5  $\tau$  unit. The triplet is assigned to proton a, and the quadruplets are assigned to protons b and c for the same kinds of reasons outlined for VI. In the assignment of chemical shifts to protons b and c, it is assumed that the  $N_2^+$  group is more deshielding than the tricyanoethylene group.



$H_a$ , 3.6  $\tau$  ( $J_{ab}$  3.5,  $J_{ac}$  4.2 c.p.s.)  
 $H_b$ , 2.6  $\tau$  ( $J_{bc}$  2.0 c.p.s.);  $H_c$ , 2.3  $\tau$

Compound XIV underwent both hydrolysis and ethanolysis typical of tricyanoethylene aromatic compounds<sup>13b,14</sup> (see formulas). It is assumed that the positions of solvolysis are similar to those for the analogous benzene substituted compound.<sup>13b,14</sup> Compound XV exists as amber needles, whereas XVI is a yellow crystalline solid that decomposes when heated.

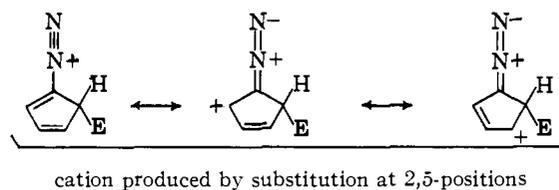


(13) (a) W. J. Middleton, R. E. Heckert, E. L. Little and C. G. Krespan, *J. Am. Chem. Soc.*, **80**, 2783 (1958); (b) B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman and H. F. Mower, *ibid.*, **80**, 2806 (1958); (c) J. R. Roland and B. C. McKusick, *ibid.*, **83**, 1652 (1961).

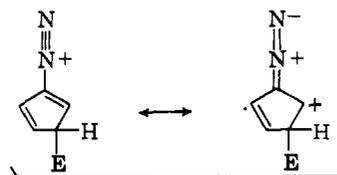
(14) G. N. Sausen, V. A. Engelhardt and W. J. Middleton, *ibid.*, **80**, 2815 (1958).

Both substances are light sensitive, and exhibit the diazo band at about 4.75  $\mu$  in the infrared spectra. The infrared spectrum of hydroxy compound XVI does not contain a free OH stretching absorption, but instead provides a broad but weak absorption at 3.32  $\mu$ . This peak, typical of strongly hydrogen bonded hydroxyl groups,<sup>15</sup> is undoubtedly due to intramolecular hydrogen bonding between the hydroxyl group and the negatively charged ring.

**Position of Electrophilic Substitution.**—The above data indicate a preference for electrophilic attack on the 2,5-positions over the 3,4-positions of diazocyclopentadiene. These substitution reactions probably involve cations as intermediates, which serve as models for the rate-determining transition state. The main contributing resonance structures for both types of cations are formulated. The cation that corresponds to substitution at the 2,5-positions is "through conjugated" and has three important contributors to the resonance hybrid. The cation which reflects substitution at the 3,4-positions is "cross conjugated," and has only two important contributors to the resonance hybrid. Thus the transition state for 2,5-positions should be the more stable, as is observed.



cation produced by substitution at 2,5-positions



cation produced by substitution at 3,4-positions

**Ultraviolet Absorption Spectra.**—The ultraviolet and visible absorption spectra of diazocyclopentadiene and its substitution products were taken, and the data are recorded in Table I. As with other aromatic compounds, substitution of conjugating substituents on the diazocyclopentadiene ring system results in shifts of the absorption bands to longer wave lengths. The two mononitro compounds VI and VII provide the only basis of assessing the difference in effect of substitution in the 2- vs. the 3-position. The two long wave length bands occur at 40 to 60  $m\mu$  longer wave lengths and at lower intensities in the spectrum of the 2-substituted compound as compared to the 3-derivative. Some analogy is found in the fact that the longest wave length band of *o*-nitroaniline absorbs 54  $m\mu$  higher wave length than that of *m*-nitroaniline.<sup>16</sup>

**1,4-Cycloaddition.**—In contrast to the behavior of tetracyanoethylene, dimethylacetylene dicarboxylate added 1,4- to diazocyclopentadiene to give a maroon solid, tentatively identified as 3,4-dicarbomethoxy-2H-cyclopenta[*c*]pyridazine (XVII). The compound is neither light nor heat sensitive. The infrared spectrum does not exhibit diazo absorption, but indicates the presence of an NH group. Apparently the initial adduct underwent a tautomeric proton shift from carbon to nitrogen. The structure written for compound XVII is one of two in which the proton is on nitrogen. Possibly the substance is a mixture of tautomers.

(15) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 103.

(16) L. Doub and J. M. Vandenberg, *J. Am. Chem. Soc.*, **69**, 2714 (1947); **71**, 2414 (1949).

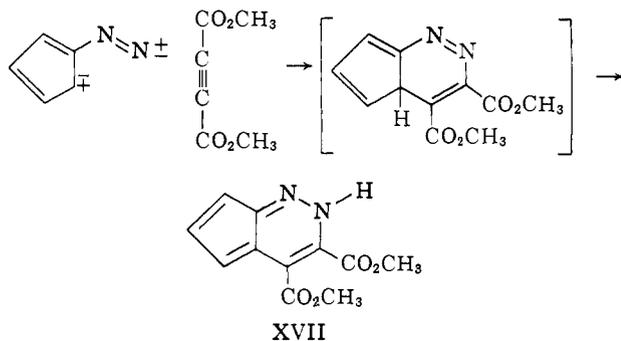
TABLE I  
 ULTRAVIOLET ABSORPTION SPECTRAL DATA<sup>a</sup> OF DIAZOCYCLOPENTADIENE AND DERIVATIVES

DCP = diazocyclopentadiene, TCNE = tetracyanoethyl, TRCV = tricyanovinyl, DCEV = dicyanoethoxyvinyl, DCHV = dicyano-hydroxyvinyl

Compound	$\lambda_{\max}$ , m $\mu$	$\epsilon$	$\lambda_{\max}$ , m $\mu$	$\epsilon$	$\lambda_{\max}$ , m $\mu$	$\epsilon$	$\lambda_{\max}$ , m $\mu$	$\epsilon$
DCP (I)	298	15,500	~340 <sup>b</sup>	~1,000	..	....	..	....
2-NO <sub>2</sub> DCP (VI)	252	13,000	330	7,000	385	6,000	..	....
3-NO <sub>2</sub> DCP (VII)	260	10,000	290	9,000	325	17,000	..	....
Osazone IX <sup>c</sup>	352	30,200	399	23,100	451	22,300	..	....
2-C <sub>6</sub> H <sub>5</sub> N <sub>2</sub> DCP (X)	240 <sup>d</sup>	9,800	272 <sup>d</sup>	15,800	304	20,000	~364 <sup>d</sup>	~5,000
(Br) <sub>4</sub> DCP (XI)	465	1,200	..	..	..	..	..	..
310	16,000	365 <sup>b</sup>	1,500	..	..	..	..	..
2,5-(I) <sub>2</sub> DCP (XII)	300	11,200	375	2,700	..	..	..	..
2-TCNE-DCP (XIII) <sup>e</sup>	301	17,300	~340 <sup>b</sup>	~3,000	..	..	..	..
2-TRCV-DCP (XIV) <sup>f</sup>	268	14,100	~336 <sup>d</sup>	~2,700	473	16,800	~525 <sup>d</sup>	~7,500
2-DCEV-DCP (XV)	224	8,500	266	8,200	314	8,200	366	4,300
2-DCHV-DCP (XVI)	252	18,000	292	14,900	333	13,000	398	16,700
Pyridazine (XVII) <sup>g</sup>	270	16,700	~288 <sup>d</sup>	~10,700	372	4,200	~391 <sup>d</sup>	~3,800
485	4,000	..	..	..	..	..	..	..
Pyridazine (XVII) <sup>h</sup>	285	29,000	370	4,300	485	780	..	..

<sup>a</sup> Cary model 11 or Cary model 14 recording spectrophotometer; solvent 95% ethanol unless otherwise specified. <sup>b</sup> Broad shoulder. <sup>c</sup> Solvent, chloroform. <sup>d</sup> Shoulder. <sup>e</sup> Solvent, ether. <sup>f</sup> Solvent, acetonitrile. <sup>g</sup> Solvent, 95% ethanol or 95% ethanol-0.12 N in H<sub>2</sub>SO<sub>4</sub>. <sup>h</sup> Solvent, 95% ethanol-0.12 N in NaOH.

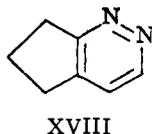
The substance is soluble in dilute sodium carbonate but not sodium bicarbonate, and is therefore a weak acid. The compound exhibits an apparent  $pK_a$  9.13.<sup>17</sup>



The compound is also a very weak base as shown by its solubility in 6 N hydrochloric acid. The acidity of the substance is possibly associated with the 10- $\pi$  electron system (isoelectronic with naphthalene) produced on deprotonation of XVII, as well as the presence of the two carbomethoxy groups.

The ultraviolet absorption spectrum of XVII was taken in neutral, acidic and basic 95% ethanol, and the results are recorded in Table I. The spectra in the first two media were almost identical, but marked changes occurred when the medium was made basic, as might be expected. The lack of difference between neutral and acidic medium suggests that XVII is not a strong enough base to be altered by the dilute acid of the spectral medium.

A search of the literature indicates that the dihydro derivative XVIII of this ring system is known,<sup>18</sup> but the fully unsaturated system is not reported.



### Experimental

**Spectra.**—All ultraviolet spectra were taken either on a Cary model 11 or Cary model 14 recording spectrophotometer. All infrared spectra were recorded on a Beckman model IR-5 spec-

(17) The authors are indebted to Professor E. Heilbronner for this determination [see W. Simon, E. Kovats, L. H. Chopard-dit-Jean and E. Heilbronner, *Helv. Chim. Acta*, **37**, 1872 (1954), and subsequent papers].

(18) R. H. Horning and E. D. Amstutz, *J. Org. Chem.*, **20**, 707 (1955).

trophotometer. All n.m.r. spectra were recorded with a Varian Associates model A-60 n.m.r. spectrometer in acetone, with hexamethyldisiloxane as an internal standard.

**Diazocyclopentadiene** was prepared<sup>2</sup> in 20-g. quantities in 43% yield, b.p. 45° (40 mm.),  $n_D^{20}$  1.6095. The material exhibited infrared absorption in chloroform at 3.36(w), 4.80(s), 7.09(m), 7.75(m), 9.45(m), 11.00(m)  $\mu$ . Care was taken to keep the material from contact with acid-washed glassware or polar surfaces.

**Nitration.**—To a cooled solution of 2.04 g. of silver nitrate in 25 ml. of acetonitrile was added 1.10 g. of diazocyclopentadiene. A cooled solution of 1.69 g. of benzoyl chloride in 10 ml. of acetonitrile was added slowly, the temperature being held below 5°. After 2 hr. at 0–5°, the reaction mixture was filtered, diluted with water and extracted twice with ether. The combined extracts were washed with water and dilute sodium bicarbonate, dried and evaporated. The residual oil was dissolved in a minimum amount of benzene and chromatographed on about 30 g. of silica gel, with benzene as the eluent. The 2-nitro isomer VI was eluted first (0.540 g., 33%, m.p. 29–31°) followed by the 3-nitro isomer VII (0.270 g., 17%, m.p. 82–90°). Recrystallization of VI from benzene–hexane gave yellow plates, m.p. 32–33°; infrared absorption in chloroform: 3.26(w), 3.37(w), 4.73(s), 6.73(s), 6.96(s), 7.23(m), 7.40(s), 7.48(s), 7.77(m), 7.90(s), 9.02(s), 9.51(m), 9.89(m), 11.82(m) and 12.39(m)  $\mu$ .

*Anal.* Calcd. for C<sub>8</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>: C, 43.80; H, 2.19. Found: C, 44.24; H, 2.43.

Isomer VII was recrystallized from chloroform–pentane to give yellow needles, m.p. 91–94°; infrared spectrum in chloroform: 3.22(w), 3.35(w), 4.74(s), 6.59(m), 6.73(m), 7.06(s), 7.25(m), 7.53(s), 7.85(s), 9.17(s), 9.44(m), 10.78(m), 12.30(m), 12.51(m)  $\mu$ .

*Anal.* Calcd. for C<sub>8</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>: C, 43.80; H, 2.19. Found: C, 44.01; H, 2.39.

**1,2-Cyclopentanedione Bis-2,4-dinitrophenylhydrazine (IX) from 2-Nitrodiazocyclopentadiene (VI).**—A solution of 0.049 g. of VI in 5 ml. of absolute ethanol was added to a pre-reduced slurry of 0.11 g. of platinum oxide in 10 ml. of 95% ethanol under an atmosphere of hydrogen. In 45 min., 50 ml. of hydrogen at 750 mm. (5.6 equivalents) was absorbed, and reaction stopped. The mixture was filtered, the filtrate was evaporated, and the residue was treated with 4 ml. of 2,4-dinitrophenylhydrazine in acidic ethanol. The mixture was heated for 1 minute at 90° and allowed to stand at 25°. The orange solid that separated (0.016 g., 10%, m.p. 225°) was collected, and recrystallized from first aqueous acetonitrile and then glacial acetic acid to give orange needles, m.p. 246–247°, undepressed upon admixture with authentic osazone IX. The ultraviolet spectrum of the substance was superimposable on that of authentic IX.

*Anal.* Calcd. for C<sub>17</sub>H<sub>14</sub>N<sub>6</sub>O<sub>8</sub>: C, 44.54; H, 3.06. Found: C, 44.68; H, 3.28.

**1,2-Cyclopentanedione Bis-2,4-dinitrophenylhydrazine (IX) from Cyclopentanone.**—Cyclopentanone was brominated<sup>10</sup> in 31% yield to give 2-bromocyclopentanone, b.p. 45° (1 mm.),  $n_D^{20}$  1.5083. This material was converted to osazone IX<sup>10</sup> in 56% yield, m.p. 246–248°. The ultraviolet absorption spectrum of this material in chloroform exhibited  $\lambda_{\max}$  at 352 m $\mu$  ( $\epsilon$  30,200), 399 m $\mu$  (23,100), 451 m $\mu$  (22,300).

*Anal.* Calcd. for  $C_{17}H_{14}N_8O_3$ : C, 44.54; H, 3.06. Found: C, 44.59; H, 3.30.

**2-Phenylazodiazocyclopentadiene (X).**—Phenyldiazonium boron tetrafluoride was prepared (46%).<sup>19</sup> To a solution of 1.05 g. of this material in 125 ml. of methanol containing 5 ml. of water at 0° was added a solution of 0.507 g. of diazocyclopentadiene in 5 ml. of methanol precooled to 0°. The mixture was stirred for 10 min. at 0°, poured into 375 ml. of water and extracted with ether. The extract was washed with water, dried and evaporated. The purple solid that separated was collected, wt. 0.250 g. (23%), and recrystallized from 50% ethanol; m.p. 92–94.5°. The infrared spectrum of the substance in chloroform exhibited bands at: 3.30(w), 3.37(m), 4.78(m), 6.31(m), 6.49(m), 6.76(s), 6.87(m), 7.08(s), 7.36(m), 7.50(m), 7.82(s), 8.83(s), 8.97(s), 9.59(m), 9.95(m), 10.22(m), 10.90(m)  $\mu$ .

*Anal.* Calcd. for  $C_{11}H_8N_4$ : C, 67.35; H, 4.08. Found: C, 67.35; H, 4.24.

**Tetrabromodiazocyclopentadiene (XI).**—To a solution of 0.20 g. of diazocyclopentadiene in 10 ml. of acetonitrile was added in small portions 1.0 g. of N-bromosuccinimide. The mixture was stirred for 5 min. at room temperature, diluted with water and extracted with ether. The ether extract was washed with water, dilute sodium bisulfite and again water. The solution was dried, evaporated, and the brown residual solid was recrystallized from aqueous ethanol to give 0.200 g. (35%) of brown needles, which decomposed slowly when heated. The infrared spectrum of the substance in carbon tetrachloride exhibited bands at: 4.76(s), 4.85(m), 6.72(w), 7.26(m), 8.10(s)  $\mu$ .

*Anal.* Calcd. for  $C_5Br_4N_2$ : C, 14.71; Br, 78.43. Found: C, 14.66; Br, 77.94.

**2,5-Diiododiazocyclopentadiene (XII).**—To a solution of 2.0 g. of mercuric acetate in 20 ml. of dimethyl sulfoxide was added 0.500 g. of diazocyclopentadiene. After standing at 25° for 20 min., the mixture was added to an ice-cold solution of 1.5 g. of sodium iodide in 25 ml. of 50% aqueous ethanol in a centrifuge tube. A yellow flocculent precipitate appeared immediately. The mixture was centrifuged, and the supernatant liquid decanted. The residual solid was washed 3 times with cold water and once with ethanol. The residue was suspended in 40 ml. of chloroform and treated portionwise with 1.4 g. of iodine. The mixture was stirred 1 additional hr. and filtered. The filtrate was washed with dilute sodium thiosulfate, dried and evaporated. The residue was chromatographed on 30 g. of silica gel with pentane as eluent. A yellow solid, 0.23 g. (21%), was collected, and was recrystallized from first pentane and then aqueous ethanol to give hard yellow crystals, m.p. 80–82.5°. The infrared spectrum of the substance XII in chloroform exhibited bands at: 3.39(w), 4.80(s), 7.42(s), 7.67(m), 7.85(s), 9.58(m), 11.78(m)  $\mu$ .

*Anal.* Calcd. for  $C_5H_2N_2I_2$ : C, 17.44; H, 0.58. Found: C, 17.39; H, 0.68.

**2-Tetracyanoethyldiazocyclopentadiene (XIII).**—To a solution of 0.417 g. of tetracyanoethylene in 5 ml. of tetrahydrofuran was added 0.300 g. of diazocyclopentadiene. The mixture was stirred for 30 min., the solvent was evaporated, and the residue was chromatographed on silica gel with benzene as developer. A yellow solid, 0.390 g. (55%), m.p. 87–96°, was eluted from the column. Recrystallization of the material from chloroform-pentane gave yellow needles, m.p. 95.5–97.5°. The infrared spectrum of the material in chloroform exhibited bands at: 3.35(w), 3.50(w), 4.80(s), 7.20(s), 7.44(m), 7.80(s)  $\mu$ .

(19) A. Roe, in R. Adams, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1949, Vol. 5, p. 202.

*Anal.* Calcd. for  $C_{11}H_4N_6$ : C, 60.00; H, 1.82. Found: C, 60.37; H, 2.02.

**2-Tricyanovinylidiazocyclopentadiene (XIV).**—To a solution of 2.8 g. of tetracyanoethylene in 75 ml. of tetrahydrofuran was added 2.2 g. of diazocyclopentadiene. The mixture was stirred for 15 min. and then slowly added to 2 liters of water with rapid stirring in a fume hood (hydrogen cyanide was evolved). The mixture was stirred for 20 min., and the brown solid that separated (4.1 g. or 97%) was collected. Recrystallization of this material from ethanol gave 1.9 g. (45%) of orange crystals. Further recrystallization of the material from acetone gave orange needles, which decomposed when heated to about 130°. The compound in chloroform solution exhibited bands in the infrared at: 3.32(w), 4.51(w), 4.73(s), 6.57(s), 7.20(s), 7.52(m), 7.70(s), 8.67(m)  $\mu$ .

*Anal.* Calcd. for  $C_{10}H_2N_6$ : C, 62.18; H, 1.55. Found: C, 62.48; H, 1.71.

To a solution of 0.060 g. of 2-tetracyanoethyldiazocyclopentadiene in 3 ml. of acetone was added 15 ml. of water. The mixture was stirred in a fume hood for 15 min. and filtered. The orange needles (0.040, 76%) that separated were collected and found to be identical in all respects with XIV obtained directly from I.

**2-(1-Ethoxydicyanovinyl)-diazocyclopentadiene (XV).**—A solution of 0.200 g. of XIV in 5 ml. of dimethylformamide was added dropwise to 250 ml. of ethanol containing 5 drops of 18 N sodium hydroxide. After 5 min. the mixture was neutralized with sulfuric acid and extracted with chloroform. The chloroform extract was washed with water, dried, evaporated, and the residue was crystallized from ether-pentane to give 0.150 g. (72%) of crude material, m.p. 87–92°. Recrystallization of the material from chloroform-pentane gave amber needles, m.p. 91.5–92.5°. The infrared absorption of the compound in chloroform exhibited bands at: 3.38(w), 4.54(m), 4.77(s), 6.55(s), 7.12(m), 7.50(s), 7.62(s), 7.87(m)  $\mu$ .

*Anal.* Calcd. for  $C_{11}H_8N_4O$ : C, 62.26; H, 3.77; N, 26.42. Found: C, 62.14; H, 3.93; N, 26.17.

**2-(1-Hydroxydicyanovinyl)-diazocyclopentadiene (XVI).**—To 5 ml. of 10% sodium hydroxide was added 0.500 g. of XIV. The mixture was stirred at 25° for 15 min., and about 0.25 g. of unreacted starting material was collected. The filtrate was neutralized with hydrochloric acid and extracted with ether. The ethereal solution was dried and evaporated to give 0.070 g. (15%) of a brown solid. Recrystallization of this material from ether-pentane gave a yellow crystalline solid, which decomposed slowly when heated. The material (XVI) exhibited bands in the infrared in chloroform solution at: 3.32(w), 3.45(w), 4.53(m), 4.74(s), 6.49(m), 7.48(m)  $\mu$ .

*Anal.* Calcd. for  $C_9H_4N_4O$ : C, 58.70; H, 2.17. Found: C, 58.41; H, 2.37.

**3,4-Dicarbomethoxy-2H-cyclopenta[c]pyridazine (XVII).**—A solution of 0.66 g. of diazocyclopentadiene in 2 ml. of tetrahydrofuran was added to 0.52 g. of dimethyl acetylenedicarboxylate. The mixture was held at reflux for 15 min. The solvent was evaporated at 25° and reduced pressure (an explosion occurs if the reaction mixture is heated in the absence of solvent!). The residue was dissolved in 5 ml. of ether and pentane was added. The precipitate that separated (0.100 g., 13%, of maroon solid) was recrystallized from ether-pentane to give a maroon crystalline solid, m.p. 97.5–98.5°. In chloroform, the substance XVII gave bands at: 2.99(w), 3.33(w), 3.40(w), 5.80(s), 6.96(m), 7.75(s), 8.32(s), 8.54(m)  $\mu$ .

*Anal.* Calcd. for  $C_{11}H_{10}N_2O_4$ : C, 56.41; H, 4.27; equiv. wt., 241. Found: C, 56.44; H, 4.48; equiv. wt., 247.