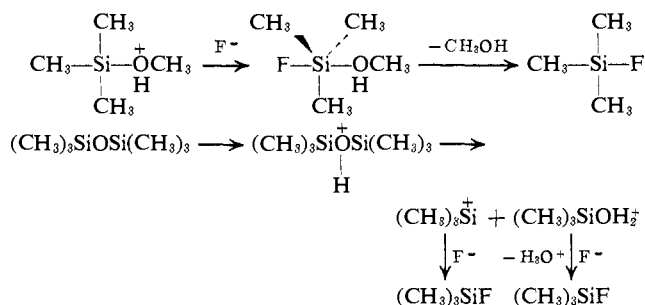


at silicon prior to the loss of methanol (direct displacement or Si(V) mechanism path<sup>20</sup>).



No electron-deficient deshielded species (siliconium ions) were observed in the nmr studies; instead only the derived fluorosilanes were present.

We share Sommer's views<sup>20</sup> as to the difficulties to find an accessible pathway to trivalent siliconium ion intermediates and the present work has not succeeded to provide such. We are, however, continuing our efforts out of conviction shared with Sommer that trialkyl (triaryl) silicon cations  $\text{R}_3\text{Si}^+$  and the corresponding carbonium ions,  $\text{R}_3\text{C}^+$  may in certain circumstances be of comparable stability relative to their precursors. It is thus not a question of inherent instability, but lack of sufficient imagination which prevented thus far to find a pathway to trivalent siliconium ions, avoiding the much

(20) L. H. Sommer and G. A. Baughman, *J. Amer. Chem. Soc.*, **83**, 3346 (1961).

more accessible direct displacement reactions involving Si(V) intermediates.

### Experimental Section

**Materials.** Hexamethyldisiloxane, trimethyltriphenyldisiloxane, hexaphenyldisiloxane, dimethyldiethoxysilane, triethoxysilane, methyltrimethoxysilane, and tetramethoxysilane were commercially available materials and were distilled (or recrystallized) prior to use. Trimethylmethoxysilane, triethylmethoxysilane, phenyldimethylmethoxysilane, and phenylmethylmethoxysilane were synthesized by the addition of an equimolar solution of methanol and pyridine to the corresponding chlorosilane or dichlorosilane and purified by distillation.

Trimethylfluorosilane was synthesized by the reaction of boron-trifluoride etherate with hexamethyldisiloxane. Triphenyltrimethylsiloxane was prepared by the reaction of sodium triphenylsilylanolate with trimethylchlorosilane in ether according to the method of Gilman, Benedict, and Hartzfield.<sup>21</sup>

**Nmr Spectra.** A Varian Associates Model A56/60A spectrometer equipped with a variable-temperature probe was used for all spectra.

**Sample Preparation.** Samples were prepared by dissolving approximately 1.5 ml of  $\text{HSO}_3\text{F}-\text{SbF}_6$  (4:1 to 8:1 mol:mol) in an equal volume of sulfur dioxide and cooling to  $-76^\circ$ . Approximately 0.2 ml of the alkoxy silane was dissolved in 1 ml of sulfur dioxide, cooled to  $-76^\circ$ , and added to the acid solution with vigorous agitation. The acid was always in large excess as indicated by the acid peak at about  $\delta$  10.9 in the nmr spectra. For simplicity this peak was deleted from the figures.

**Acknowledgment.** Support of this work through a grant of the National Science Foundation is gratefully acknowledged.

(21) H. Gilman, H. N. Benedict, and H. Hartzfield, *J. Org. Chem.*, **19**, 419 (1954).

## 1,3-Bisdiazopropane. Preparation and Cyclization to Pyrazole

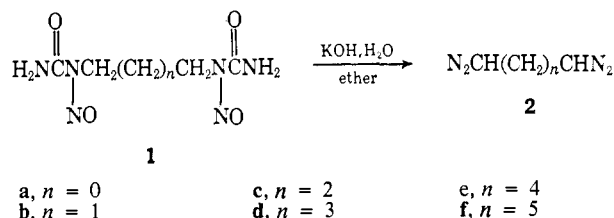
Harold Hart and James L. Brewbaker<sup>1</sup>

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Received September 9, 1968

**Abstract:** 1,3-Bisdiazopropane was prepared by treatment of crystalline potassium propane-1,3-bisdiazotate, which is thermally stable to  $168^\circ$ , with protonic solvents. In cyclohexene solution, 1,3-bisdiazopropane slowly decomposed at room temperature to nitrogen and pyrazole. Kinetic studies showed that 3-diazopropene was not an intermediate, although it also cyclizes to pyrazole. The possible mechanisms are discussed.

Bisdiazoalkanes have not been extensively studied. In 1949 Lettre and Brose<sup>2</sup> prepared the series of bisdiazalkanes **2c-2e** by treating ethereal solutions of the corresponding N,N'-dinitrosoureas (**1c-1e**) with aqueous potassium hydroxide. When they tried to prepare 1,3-bisdiazopropane (**2b**) by this procedure, numerous side reactions occurred and only a small amount of the yellow bisdiaz compound was extracted into the ether layer. Lieser and Beck<sup>3</sup> also reported

the preparation of this series of compounds (**2a-2f**) using essentially the same procedure. They noted that  $\alpha,\omega$ -bisdiazalkanes are highly unstable and that their stability decreases as the number of carbon atoms between the two diazo groups decreases.

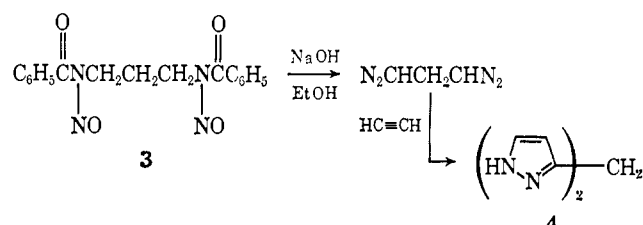


(1) Michigan State University Graduate Council Fellow, 1965-1966; National Science Foundation Predoctoral Fellow, 1966-1967.

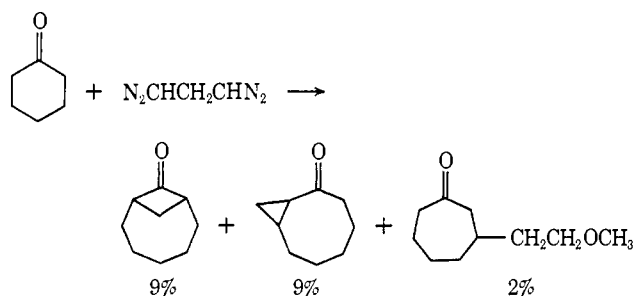
(2) H. Lettre and U. Brose, *Naturwissenschaften*, **36**, 57 (1949).

(3) T. Lieser and G. Beck, *Chem. Ber.*, **83**, 137 (1950).

Reimlinger<sup>4</sup> prepared 1,3-bisdiazopropane from *N,N'*-trimethylenebis(*N*-nitrosobenzamide) (**3**) in a mixed solvent of ethanol and ether by adding ethanolic sodium hydroxide. The yield was not reported but the author did state that 1,3-bisdiazopropane and acetylene react to form bis(pyrazolyl)-3-methane (**4**) in a yield of 85%.



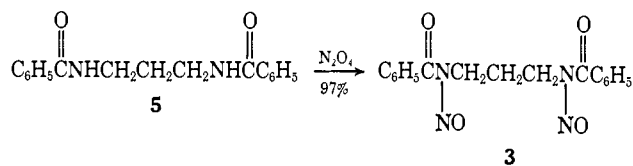
1,3-Bisdiazopropane has been converted, by reaction with aromatic acids or phenol, to the corresponding esters or ether of 1,3-propanediol.<sup>3</sup> It also has been generated in the presence of cyclohexanone, with which it reacts to form the products shown.<sup>5</sup>



It was the purpose of the present work to develop a reliable synthesis of 1,3-bisdiazopropane and to further explore its chemistry. During the work, it was noted that solutions of 1,3-bisdiazopropane slowly decompose to nitrogen and pyrazole, and we report here some studies on the mechanism of that reaction.

## Results

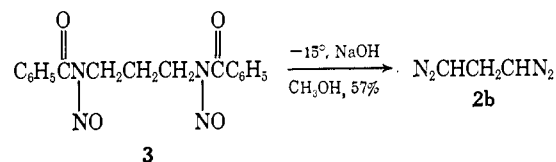
**Preparation of 1,3-Bisdiazopropane.** Solutions of 1,3-bisdiazopropane were prepared by two methods. The precursor was *N,N'*-trimethylenebis(*N*-nitrosobenzamide) (**3**), a stable, yellow solid which was prepared in high yield by adding dinitrogen tetroxide to a cold solution of *N,N'*-trimethylenebisbenzamide (**5**) in



1:1 acetic acid-acetic anhydride. Compound **3** was stored in a refrigerator for a year without noticeable

change although at room temperature and in room light some decomposition occurred after 2 months.

A clear, yellow solution of 1,3-bisdiazopropane in cyclohexene<sup>6</sup> was prepared by stirring a solution of **3** in cyclohexene with methanolic sodium hydroxide for 4 hr at  $-15^\circ$ . The yield of 1,3-bisdiazopropane was 57%. Dry solutions of **2b** in cyclohexene are stable



at  $-15^\circ$ ; at  $0^\circ$  gas slowly evolves, and at  $25^\circ$  the compound has a half-life of about 2 hr. Because of the potential danger in handling pure 1,3-bisdiazopropane,<sup>4</sup> our work was done with dilute solutions. No explosions occurred.

The infrared spectra of solutions of 1,3-bisdiazopropane prepared as described above showed intense bands at 2065 and  $1721\text{ cm}^{-1}$ . The former band is characteristic of the diazo group<sup>7</sup> and the latter is due to methyl benzoate. Methyl benzoate was produced by attack of methoxide ion on the carbonyl carbon of *N,N'*-trimethylenebis(*N*-nitrosobenzamide) and is a coproduct of the reaction. Because the presence of this ester in the solution can complicate the isolation of reaction products of 1,3-bisdiazopropane, an alternative synthesis was sought.

The production of diazo compounds by treatment of *N*-nitrosoamides with alkoxide involves initial attack of the alkoxide anion on the carbonyl carbon of the nitrosoamide,<sup>8,9</sup> to form a diazotate. Diazotates may be isolated as thermally stable, white salts which, however, are very sensitive to moisture. Until recently, only a few such compounds have been reported in the literature. Hantzsch and Lehmann<sup>10</sup> prepared both potassium methyl diazotate<sup>11</sup> and potassium benzyldiazotate by treating the corresponding ethyl alkylnitroso-carbamate with very concentrated aqueous potassium hydroxide solutions. Recently several other diazotates have been reported.<sup>12,13</sup>

We found that when a solution of *N,N'*-trimethylenebis(*N*-nitrosobenzamide) in anhydrous ether was added to a solution of potassium ethoxide in ether, a white solid considered to be potassium propane-1,3-bisdiazotate (**6**) immediately precipitated. Ethyl benzoate, the other reaction product, was isolated in over 82% yield.

(6) The reaction mixture is a two-phase system; **2b** formed in the methanolic phase is extracted by the cyclohexene. The choice of cyclohexene was made originally so that the photolysis of **2b** in cyclohexene could be studied. It proved to be a convenient solvent, though other hydrocarbons which freeze below  $-15^\circ$  might also be used. However, they must be sufficiently polar to extract the diazoalkane from methanol; hexane, for example, does not work well.

(7) L. J. Bellamy, "Infrared Spectra of Complex Molecules," 2nd ed, John Wiley & Sons, New York, N. Y., 1958, p 273.

(8) R. Huisgen and J. Reinsertshofer, *Ann.*, **575**, 174 (1952).

(9) C. D. Gutsche and I. Y. C. Tao, *J. Org. Chem.*, **28**, 883 (1963).

(10) A. Hantzsch and M. Lehman, *Chem. Ber.*, **35**, 897 (1902).

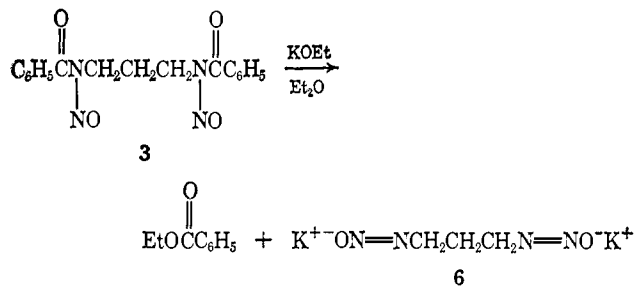
(11) E. Muller, H. Haiss, and W. Rundel, *ibid.*, **93**, 1541 (1960).

(12) R. Moss, *J. Org. Chem.*, **31**, 1082 (1966).

(13) T. K. Tandy and W. M. Jones, *ibid.*, **30**, 4257 (1965).

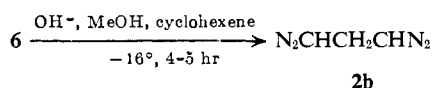
(4) H. Reimlinger, *Chem. Ber.*, **92**, 970 (1959).

(5) C. D. Gutsche and T. D. Smith, *J. Am. Chem. Soc.*, **82**, 406 (1960).

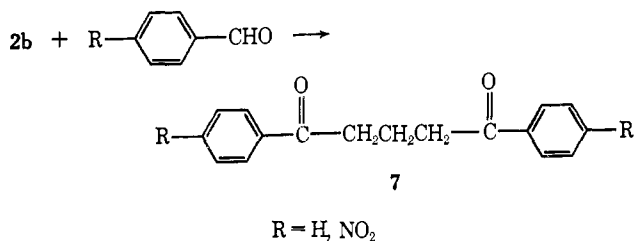


The white solid was insoluble in common organic solvents and was stable at room temperature when stored under dry nitrogen; when heated, it exploded at 168°. It decomposed, evolving nitrogen, when brought into contact with protic solvents such as water or methyl alcohol. The rate of gas evolution depended markedly on the acidity of the medium, being very slow in 50% aqueous potassium hydroxide solution but exceedingly rapid, almost violent, in 1 *N* aqueous sulfuric acid. The diazotate as formed was not pure, since only 84% of the theoretical amount of nitrogen was evolved when the crude material was decomposed with 1 *N* acid. Small amounts of benzoic acid were isolated from the aqueous solutions in which the diazotate had been decomposed, indicating that the contaminant was potassium benzoate.

The strongest evidence for the identity of this solid was the fact that 1,3-bisdiazopropane could be prepared from it. When potassium propane-1,3-bisdiazotate was stirred in the dark at -16° for several hours with cyclohexene and methanolic sodium hydroxide, 1,3-bisdiazopropane was produced and extracted into the cyclohexene phase (49% yield). This solution was free from contamination by methyl benzoate.



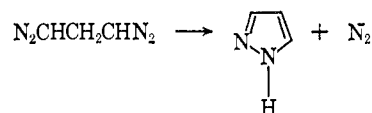
The infrared spectrum of the yellow cyclohexene solutions showed a very intense band at 2065 cm<sup>-1</sup>, characteristic of the diazo group.<sup>7</sup> The solutions had a λ<sub>max</sub> at 462 mμ (ε 27). The yellow color was rapidly discharged, and nitrogen was evolved when the solution was stirred with aqueous acid. Solid derivatives (7) were prepared by reaction with aromatic aldehydes.



The yield of 1,3-bisdiazopropane was determined by measuring the amount of gas liberated when a sample was decomposed in acid. The calculation assumed that all the gas evolved was derived from 1,3-bisdiazopropane. Whether or not this is true is not known for certain. Applequist and McGreer<sup>14</sup> and Moss<sup>12</sup> have

shown that diazoalkanes and solvolysis products are formed simultaneously from reactions that go through a diazotate intermediate. Thus, we might have expected that compounds such as 1-diazo-3-methoxypropane and 3-diazopropene would have been formed during our preparations of 1,3-diazopropane. 3-Diazopropene is red (λ<sub>max</sub> 486 mμ (ε 19)) and absorbs visible light much more strongly at 540 mμ than does 1,3-bisdiazopropane. It was calculated that if 3-diazopropene was present at all, it must have been in an amount less than 4% of total diazo compound. No products which could have arisen from 1-diazo-3-methoxypropane were isolated from reactions of these solutions. Thus, 1,3-bisdiazopropane was certainly the major diazo compound produced by our method.

**Cyclization to Pyrazole.** 1,3-Bisdiazopropane slowly decomposed at 25° in the dark. Nitrogen bubbled from clear, yellow solutions of this compound in cyclohexene and the yellow color slowly faded. The major decomposition product, pyrazole, was produced in 63% yield. In addition to pyrazole, a small amount of



polymeric material was formed. The kinetics were measured by analyzing the amount of pyrazole formed with time, using a vpc method. The first-order rate constant at 25° was 9.8 ± 0.4 × 10<sup>-5</sup> sec<sup>-1</sup> (t<sub>1/2</sub> ≅ 2 hr).

It was reported some time ago<sup>15,16</sup> that 3-diazopropene cyclizes thermally to pyrazole. Since it was possible that 3-diazopropene was an intermediate in the conversion of 1,3-bisdiazopropane to pyrazole, the rate of that reaction was also measured.<sup>17</sup> The reaction, which was quantitative, was followed spectrophotometrically, using the decrease in absorption at 486 mμ. The first-order rate constant in cyclohexene at 25° was 6.03 ± 0.03 × 10<sup>-5</sup> sec<sup>-1</sup> (cf. 2.3 × 10<sup>-4</sup> sec<sup>-1</sup> in tetrahydrofuran at 25°).<sup>18</sup>

## Discussion

The synthetic procedure described herein makes 1,3-bisdiazopropane a readily available material in solution. Potassium 1,3-bisdiazotate, its immediate precursor, is easily prepared in sizable quantities and can be stored indefinitely as long as it is well protected from moisture. It can be converted at will to bisdiazopropane solutions which are essentially free of contaminants. These solutions, however, must be kept and used at low temperatures, for at room temperatures, 1,3-bisdiazopropane decomposes thermally with a half-life of about 2 hr (25°) to pyrazole.

At least three reasonable mechanisms can be suggested for this conversion to pyrazole (A-C).

In mechanism A, loss of 1 mol of nitrogen gives a diazocarbene which rearranges to 3-diazopropene. The latter is known to cyclize to pyrazole,<sup>15-18</sup> although the rate of this reaction was not known in cyclohexene.

(15) D. W. Adamson and J. Kenner, *J. Chem. Soc.*, **286**, (1935).

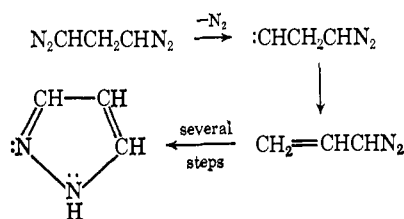
(16) C. D. Hurd and S. C. Lui, *J. Am. Chem. Soc.*, **57**, 2656 (1935).

(17) See also J. Brewbaker and H. Hart, *ibid.*, **91**, 711 (1969).

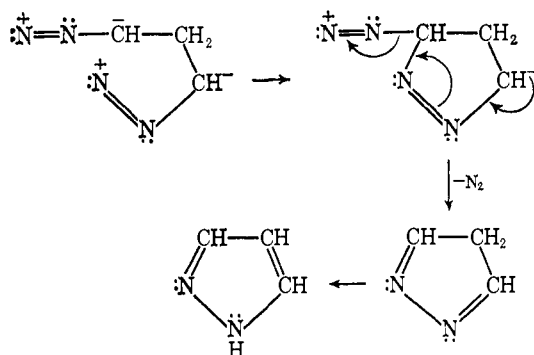
(18) A. Ledwith and D. Parry, *J. Chem. Soc.*, **B**, 41 (1967).

(14) D. E. Applequist and D. E. McGreer, *J. Am. Chem. Soc.*, **82**, 1965 (1960).

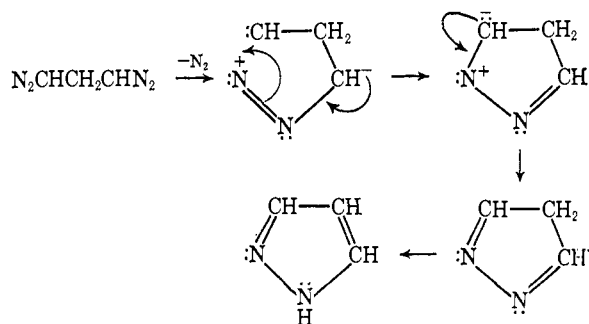
## Mechanism A



## Mechanism B



## Mechanism C



To test this mechanism, we prepared 3-diazopropene and measured its rate of isomerization to pyrazole. Under identical conditions, 1,3-bisdiazopropane rearranged to pyrazole with a comparable but somewhat larger rate constant than did 3-diazopropene. No buildup of 3-diazopropene (red) was detected in decomposing solutions of 1,3-bisdiazopropane (yellow). From these data, mechanism A can be ruled out.

Mechanisms B and C both lead to a cyclic azine which then isomerizes by prototropic rearrangement to pyrazole, the driving force for the final step being the formation of an aromatic system. The formation of an azine from 1,3-bisdiazopropane is perhaps not surprising, since the thermal decomposition of diazoalkanes nearly always gives some azine.<sup>19</sup> The amount varies. It is often large for aryldiazomethanes but is usually very small for alkyl diazomethanes. For example, Parham and Hasek have reported that when a solution of diphenyldiazomethane in benzene was refluxed for 5 days, the azine of benzophenone was produced in 79% yield.<sup>20</sup> However, the thermal decom-

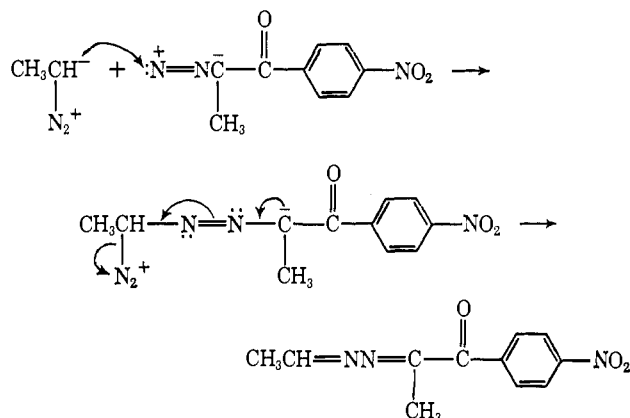
position of diazocyclohexane gave no azine; cyclohexene was the sole product.<sup>19</sup>

Mechanisms similar to B and C have been proposed for the formation of azines from diazoalkanes. One involves initial decomposition of the diazoalkanes to a carbene and nitrogen. The carbene attacks the terminal nitrogen of a second diazoalkane molecule, forming the azine. This mechanism is an intermolecular



version of mechanism C. Evidence has been presented that diazo compounds decompose unimolecularly to a carbene and nitrogen in the rate-determining step.<sup>21,22</sup> The carbene then reacts with a nucleophile in the product-determining step. If the nucleophile is another diazoalkane molecule, attack may occur at carbon or nitrogen, the latter being favored as the bulk of the carbene and/or diazo compound increase.<sup>23</sup>

There is, however, good evidence that other diazoalkanes react to form azines by a path similar to B. For example, Yates, Farnum, and Wiley reported<sup>24</sup> that diazoethane and  $\alpha$ -diazopropiophenone reacted to form an azine under conditions where each was stable in the absence of the other. This observation precludes a unimolecular decomposition of either diazo compound into a carbene and suggests the bimolecular mechanism shown, for which additional evidence was presented.



Apparently, diazoalkanes react to form azines by either of two mechanisms, one which involves a carbene and another which involves a nucleophilic attack of one molecule on the terminal nitrogen of a second molecule. Which of the mechanisms operates appears to depend on the nature of the groups attached to the diazo function. The bimolecular mechanism is most likely to occur when one diazo component is nucleophilic and the other strongly electrophilic. Since the two diazo functions in 1,3-bisdiazopropane are identical, one might be tempted to exclude mechanism B, although the fact that the reaction is intramolecular may offer

(21) H. Reimlinger, *Chem. Ber.*, **97**, 339 (1964).

(22) D. Bethell, D. Whittaker, and D. Callister, *J. Chem. Soc.*, 2466 (1965).

(23) H. Reimlinger, *Chem. Ber.*, **97**, 3503 (1964).

(24) P. Yates, D. G. Farnum, and D. W. Wiley, *Tetrahedron*, **18**, 881 (1962).

(19) P. A. S. Smith, "Open Chain Nitrogen Compounds," Vol. 2, W. A. Benjamin, Inc., New York, N. Y., 1966, p 223.

(20) W. E. Parham and W. R. Hasek, *J. Am. Chem. Soc.*, **76**, 935 (1954).

some entropy advantage over the bimolecular counterpart of B. Nevertheless we are inclined to favor mechanism C. The more rapid loss of nitrogen from one diazo function of 1,3-bisdiazopropane as compared with ordinary diazoalkanes may be the result of an electron-releasing inductive effect of the second diazo group.

### Experimental Section

All microanalyses were performed by the Spang Microanalytical Laboratory, Ann Arbor, Mich. Melting points are uncorrected. Spectrometers used were the Varian A-60 (nmr), Unicam SP200 (ir), and Unicam SP800 or Beckman DB (uv, visible). All spectra were calibrated against standard references.

**N,N'-Trimethylenebisbenzamide.** Benzoyl chloride (140 g, 1.0 mol) was slowly added dropwise to a well-stirred solution of 29.6 g (0.40 mol) of 1,3-diaminopropane and 60 g (1.5 mol) of sodium hydroxide in 600 ml of water at 10°. The slurry was stirred for 1 hr, then was filtered. The white crystalline product was washed with water, air dried, and recrystallized from hot 1:1 ethanol-benzene. The purified product (95.5 g, yield 85%) had mp 146.0–147.5° (lit.<sup>25</sup> mp 147–148°).

**N,N'-Trimethylenebis(N-nitrosobenzamide).** A cold solution of dinitrogen tetroxide<sup>26</sup> (100 mmol) in 50 ml of 1:1 acetic acid-acetic anhydride was slowly added to a stirred solution of 14.1 g (50 mmol) of N,N'-trimethylenebisbenzamide in 100 ml of 1:1 acetic acid-acetic anhydride at 5°. After being stirred at 5° for 20 min, the yellow solution was poured into 600 ml of ice water. A yellow oil separated and quickly crystallized. The yellow solid, 16.2 g (95%) was washed with water and air dried, mp 78° dec (lit.<sup>4</sup> mp 83–84.5° dec). The nmr spectrum showed a quintet at  $\tau$  8.32 (2 H) and a triplet at 6.06 (4 H),  $J = 7.1$  Hz, and a complex multiplet from 2.24 to 2.61 (10 H).

**Potassium Propane-1,3-bisdiazotate.** Potassium (0.80 g, 0.020 g-atom) was dissolved in 3.68 g (0.080 mol) of absolute ethanol and 20 ml of anhydrous ether under a nitrogen atmosphere. Anhydrous ether (50 ml) was added, followed by dropwise addition of a solution of 1.70 g (5.0 mmol) of N,N'-trimethylenebis(N-nitrosobenzamide) in 60 ml of anhydrous ether. Immediately a white precipitate formed. The slurry was forced through a fine glass frit filter by 6 psig nitrogen pressure. The white solid was washed twice (N<sub>2</sub> atmosphere) with anhydrous ether and dried at 0.1 mm pressure for 20 min at room temperature (yield 1.28 g).

The white solid was stable under a dry nitrogen atmosphere up to 168° where it decomposed explosively. It rapidly decomposed in water evolving a gas (84% of theoretical amount) and leaving a basic solution. From titration of this solution with standard hydrochloric acid a neutralization equivalent of 136 g of product per mole of base was calculated (theoretical neut equiv, 104). Small amounts of benzoic acid were isolated from this aqueous solution indicating that the diazotate was contaminated with potassium benzoate. The infrared spectrum of the crude product (fluorolube mull) showed bands at 2908 (s), 2878 (s), 1603 (s), 1571 (s), and 1385 (s) cm<sup>-1</sup> and (Nujol mull) 1603 (s), 1571 (s), 1162 (s), 1085 (s), 840 (s), and 800 (m) cm<sup>-1</sup>.

**1,3-Bisdiazopropane (2b).** From N,N'-Trimethylenebis(N-nitrosobenzamide). A slurry of 1.70 g (5.0 mmol) of N,N'-trimethylenebis(N-nitrosobenzamide) (3) in 40 ml of cyclohexene was cooled to -15° under nitrogen and a solution of 20 mmol of sodium hydroxide in 7 ml of methanol was added. After being stirred at 15° for 4 hr, the solution was allowed to warm to 0° and quickly extracted with cold 10% aqueous sodium hydroxide solution (two 40-ml portions). The yellow cyclohexene phase was dried over potassium hydroxide pellets at -15° for 30 min. The volume of gas evolved when a sample of this solution was decomposed with acid showed that 1,3-bisdiazopropane was produced in 57% yield. The solution showed strong ir bands at 2065 (diazo group) and 1720 cm<sup>-1</sup> (methyl benzoate) and its visible spectrum had a  $\lambda_{\max}$  (cyclohexene) at 462 m $\mu$  ( $\epsilon$  27).

**From Potassium Propane-1,3-Bisdiazotate.** Potassium propane-1,3-bisdiazotate (1.18 g of crude product prepared from 5.0 mmol of N,N'-trimethylenebis(N-nitrosobenzamide)) was crushed into a

fine powder under the surface of 40 ml of cyclohexene. The slurry was stirred at -16° in the dark for 4.75 hr with 7 ml of methanol containing 10 mmol of sodium hydroxide. The reaction mixture was quickly warmed to 0°, washed with cold 10% aqueous sodium hydroxide solution (two 40-ml portions), and dried for 1 hr over potassium hydroxide pellets at -30°. The infrared spectrum of this clear yellow solution showed a sharp intense band at 2065 cm<sup>-1</sup> (diazo group). The yield of 1,3-bisdiazopropane was 49%, as determined by N<sub>2</sub> evolution with dilute acid.

**Reaction of 1,3-Bisdiazopropane with Benzaldehyde.** A solution of 2.1 g (20 mmol) of freshly distilled benzaldehyde in 10 ml of cyclohexene was added to a solution of 3.6 mmol of 1,3-bisdiazopropane in 36 ml of cyclohexene at -22°. The solution was stirred for 16 hr with the temperature gradually being increased to +5°. The solvent was removed and the residue was distilled through a short-path column. The excess benzaldehyde was removed at atmospheric pressure and the product, 0.35 g of 1,5-diphenyl-1,5-pentanedione, was collected at reduced pressure, bp 164° (0.1 mm). After being recrystallized from methanol-water, the product had a corrected melting point of 66.0–67.0° (lit.<sup>27</sup> mp 67.5°). The dioxime of this diketone precipitated from methanol as white crystals, corrected mp 164–165° (lit.<sup>27</sup> mp 165–166°).

The same product was obtained in better yield by generating the 1,3-bisdiazopropane in the presence of benzaldehyde. Potassium propane-1,3-bisdiazotate (1.13 g) was quickly powdered in air and stirred under nitrogen with 40 ml of cyclohexene, 2.12 g (0.020 mol) of freshly distilled benzaldehyde, and 7.0 ml of methanol containing 0.010 mol of sodium hydroxide. The slurry was stirred for 16 hr starting at -22°. The temperature was slowly increased to +12°. Water (30 ml) was added and the two phases were separated. The aqueous phase was extracted with ether and the extracts were combined with the cyclohexene phase. The combined organic phase was washed with 5% hydrochloric acid, 5% sodium bicarbonate, and water. After being dried (MgSO<sub>4</sub>), the liquid was distilled through a short-path head. 1,5-Diphenyl-1,5-pentanedione (0.61 g, bp 171–189° (0.3 mm)) was collected as an oily white solid which, after recrystallization from methanol, had mp 65.5–66.0°. The yield based on the bisdiazotate was 52%.

**1,5-Di-(p-nitrophenyl)-1,5-pentanedione.** A solution of 0.88 g (5.8 mmol) of *p*-nitrobenzaldehyde in 10 ml of dry tetrahydrofuran was added to a solution of 2.7 mmol of 1,3-bisdiazopropane in 28 ml of cyclohexene at -21°. The solution was stirred for 9 hr. The temperature gradually increased to 12°. A cream-colored solid separated. The solvent was removed and the oily solid which remained was slurried with 3 ml of ether and filtered. The solid was recrystallized from hot benzene; 0.35 g of product having the following properties was collected: cream-colored crystals, mp 151.5–152.0°; ir (KBr) 3075 (w), 2920 (w), 1695 (s), 1685 (s), 1603 (m), 1526 (s), 1351 (s), 864 (m), 850 (m), and 735 (m) cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>)  $\tau$  7.57 (2 H, quintet,  $J = 6.8$  Hz), 6.67 (4 H, triplet,  $J = 6.8$  Hz), and 1.78 (8 H, AB quartet).

*Anal.* Calcd for C<sub>17</sub>H<sub>14</sub>N<sub>2</sub>O<sub>6</sub>: C, 59.55; H, 4.12; N, 8.18. Found: C, 59.53; H, 4.23; N, 8.16.

**Pyrazole from 1,3-Bisdiazopropane.** A clear yellow solution of 19 mmol of 1,3-bisdiazopropane in 310 ml of cyclohexene was allowed to stand in the dark for 48 hr. A gas evolved and the color faded. The solution was filtered to remove 0.21 g of a polymeric solid. After the filtrate was concentrated, the residue was distilled through a short-path column. Crude pyrazole (0.51 g, bp 170–190°) distilled as a colorless liquid which solidified. Recrystallization from hexane and sublimation at 65° (90 mm) gave white needles, mp 66–67° (lit.<sup>28</sup> mp 70°). The infrared and nmr spectra of this solid were identical with those of an authentic sample of pyrazole. A viscous brown oily residue (0.59 g) remained. The yield of pyrazole (61%) was determined by glpc analysis of a sample of the original reaction solution on a 5-ft column packed with 20% Carbowax 20M on Chromosorb W. The analysis was carried out at 232° with a helium flow rate of 40 cc/min using hexamethylbenzene as an internal standard.

**3-Diazopropene.** A cold solution of 11.0 g (120 mmol) of dinitrogen tetroxide<sup>28</sup> in 60 ml of anhydrous ether was added to a solution of 15.5 g (120 mmol) of ethyl allylcarbamate<sup>29</sup> in 60 ml of anhydrous ether at -50°. The blue solution was stirred (N<sub>2</sub>) and allowed to warm to 10°. The resulting yellow solution was

(25) J. R. Pollock and R. Stevens, "Dictionary of Organic Compounds," 4th ed, Vol. 2, Oxford University Press, New York, N. Y., 1965, p 877.

(26) A. Pedler and F. H. Pollard, *Inorg. Syn.*, **5**, 87 (1957).

(27) See ref 25, p 1288.

(28) C. D. Hodgman, "Handbook of Chemistry and Physics," 36th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1954, p 1126.

(29) S. Nirdlinger and S. F. Acree, *Am. Chem. J.*, **43**, 358 (1910).

washed with 5%  $\text{Na}_2\text{CO}_3$  and water and dried ( $\text{MgSO}_4$ ) and the ether was removed under reduced pressure. The faintly yellow liquid which remained was ethyl allylnitrosocarbamate (17.1 g, 91%); nmr (neat):  $\tau$  8.66 (3 H, methyl, t,  $J = 7$  Hz), 5.47 (2 H, ester methylene, q,  $J = 7$  Hz), 5.63 (2 H, N-methylene), and 4.00–5.17 (3 H, vinyl protons, m).

A solution of 10 mmol of the ethyl allylnitrosocarbamate in 20 ml of cyclohexene was added (5 min) to a mixture of 30 ml of cyclohexene and 10 ml of 3 *N* methanolic sodium methoxide solution (30 mmol). The mixture was stirred in the dark under nitrogen at  $+4^\circ$  (ice bath) for 90 min, then extracted with cold 10% aqueous sodium hydroxide (two 50-ml portions) and the clear, red solution of diazo compound in cyclohexene was dried over potassium hydroxide pellets for 10 min at  $4^\circ$ . The yield, determined by the amount of  $\text{N}_2$  evolved on treatment with acid, was 65%. The solution had a  $\lambda_{\text{max}}$  at 486  $m\mu$  ( $\epsilon$  19.4). A quantitative yield of pyrazole (mp ir, nmr) was obtained when a solution of 3-diazopropene in cyclohexane was allowed to stand in the dark at room temperature for 48 hr.

**Rate of Pyrazole Formation from 1,3-Bisdiazopropene.** Hexamethylbenzene (0.1228 g) was dissolved in 40 ml of a cyclohexene solution of 1,3-bisdiazopropene which had been prepared from 1.18 g of crude potassium propane-1,3-bisdiazotate. The solution was poured into a black bottle which was placed in a constant-tem-

perature bath at  $25.0^\circ$ . At various time intervals a 1.00-ml aliquot of the yellow solution was removed and added to a vial containing one drop of acetic acid. The acid destroyed any diazo compound present. The samples were analyzed for pyrazole by glpc using hexamethylbenzene as an internal standard. A 5-ft column packed with 10% Carbowax 20M on Fluoropak 80 was used at  $215^\circ$  with a helium flow rate of 20 cc/min. At the time the first sample was withdrawn there was 2.69 mmol of 1,3-bisdiazopropene in the solution (40.5 ml). This figure was obtained by measuring the absorbance of the solution at 462  $m\mu$  ( $\epsilon$  27.4). The rate constant for pyrazole formation at  $25^\circ$  was  $9.8 \pm 0.4 \times 10^{-6} \text{ sec}^{-1}$ .

**Rate of Pyrazole Formation from 3-Diazopropene.** The rate of disappearance of diazoalkene was followed through the decrease of absorbance at 486  $m\mu$ . A cyclohexene solution of the diazoalkene in a black bottle was placed in a constant-temperature bath at  $25.0^\circ$ . Samples were removed periodically and the absorbance was measured quickly. Plots of  $\log(A - A_\infty)$  vs. time were linear. Three measurements gave  $k_1 = 6.03 \pm 0.03 \times 10^{-6} \text{ sec}^{-1}$ .

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## The Cyclization of 3-Diazoalkenes to Pyrazoles

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**Abstract:** Eight 3-diazoalkenes have been prepared from the related ethyl alkenylnitrosocarbamates and methanolic sodium methoxide. All of these unsaturated diazo compounds spontaneously cyclized at room temperature to form pyrazoles in essentially quantitative yields. The cyclizations were cleanly unimolecular. The first-order rate constants for the reactions of four substituted *trans*-3-diazo-1-phenylpropenes fit the Hammett equation ( $\rho = -0.40$ ). The relative insensitivity of the cyclization rates to the electronic nature of substituents suggests that the reaction is an intramolecular 1,3-dipolar cycloaddition.

In 1935 it was briefly reported that 3-diazopropene slowly decomposed at room temperature to give pyrazole.<sup>2,3</sup> Adamson and Kenner<sup>2</sup> also noted that the decomposition was unimolecular and accelerated by light. Recently, Ledwith and Parry reported the results of a more detailed investigation of the relatively modest effect of light on the rate at which 3-diazopropene cyclizes.<sup>4</sup> Adamson and Kenner also observed that the red color of an ethereal solution of *trans*-1-diazo-2-butene slowly faded at room temperature. The product of this decomposition was not identified; later, Curtin and Gerber<sup>5</sup> showed that it was 3(5)-methylpyrazole.

The present report describes the cyclization of these and six additional 3-diazoalkenes. The rates at which these compounds thermally isomerize to pyrazoles were measured. The effect of substituents on these rates contributes to an understanding of the reaction mechanism.

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(2) D. W. Adamson and J. Kenner, *J. Chem. Soc.*, 286 (1935).

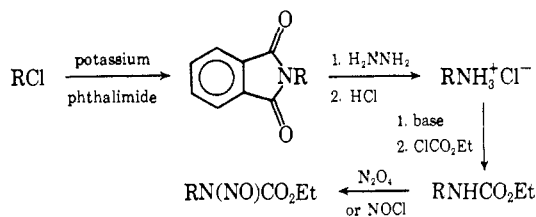
(3) C. D. Hurd and S. C. Lui, *J. Am. Chem. Soc.*, 57, 2656 (1935).

(4) A. Ledwith and D. Parry, *J. Chem. Soc., B*, 41 (1967).

(5) D. Y. Curtin and S. M. Gerber, *J. Am. Chem. Soc.*, 74, 4052 (1952).

## Results

Ethyl alkenylnitrosocarbamates, the precursors of the 3-diazoalkenes, were prepared using the synthetic sequence shown. In the final step, either of two reagents was used to nitrosate the ethyl alkenylcarbamate. Di-



nitrogen tetroxide reacted cleanly with all the carbamates not containing an aromatic ring to give the corresponding N-nitroso analogs in nearly quantitative yield. The aryl-substituted alkenylcarbamates, however, were only partially converted to the corresponding alkenylnitrosocarbamates by an equimolar amount of dinitrogen tetroxide even though all of the dinitrogen tetroxide was consumed. Evidently a portion of the reagent was lost in side reactions, possibly electrophilic