Conversion of 10 to 11. The deuterated derivative of 4-methoxybicyclo[2.2.2]octane-1-carboxylic acid (4 g, 0.022 mol) was treated with 48% aqueous hydrobromic acid in the manner previously indicated by Adcock and Kok[28] for the corresponding hydrogen analogue. After a similar workup, sublimation followed by recrystallization afforded colorless needles: 3.0 g (60%); mp 264-265 °C.

Conversion of 11 to a mixture of 1 + 1a. The bromo carboxylic acid (11, 2 g, 0.0085 mol) was treated with *tert*-butyl hypoiodite and then irradiated in the same manner as previously described for the preparation of 1-fluoro-4-iodobicyclo[2.2.2]octane from the corresponding acid.[5] A standard workup, followed by chromatography on alumina, afforded a mixture of 1-bromo-4-iodobicyclo[2.2.2]octane (1)[8] and its deuterium derivatives (1a) as a white solid after recrystallization: 2.0 g (74.6%); mp 224-226 °C; mass spectrum, m/z ($M^+ - Br$) (relative intensity) 187 (77.12), 188 (66.19), 189 (100), 190 (66.36), 191 (29.89), 192 (2.89). The results of the deuterium assay are given in the Results and Discussion section.

Acknowledgment. We are grateful to Dr. M. J. Thompson for carrying out the mass spectroscopic measurements.

(28) Adcock, W.; Kok, G. B. *J. Org. Chem.* **1985**, *50*, 1079.

Thermal Decomposition of Geminal Diazidomalonic Acid Derivatives. An Intermolecular Process

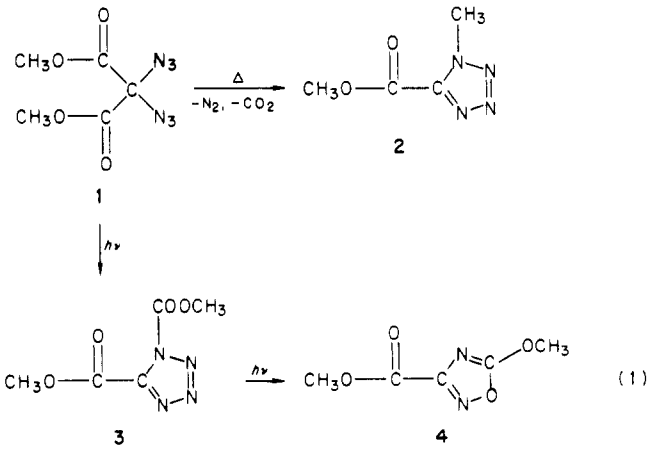
Robert M. Moriarty,*† B. R. Bailey III,† Indra Prakash,† and R. S. Miller‡

Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60680, and Department of Navy, Office of Naval Research, Arlington, Virginia 22217

Received February 25, 1985

Thermal decomposition of a 1:1 mixture of $(CH_3OCO)_2C(N_3)_2$ and $(CD_3OCO)_2C(N_3)_2$ to yield 1-methyl-5-carbomethoxytetrazole-d_x proceeds with crossover of the isotope label, indicating an intermolecular pathway for this reaction. A chain mechanism involving tetrazolium nucleophiles is proposed. The thermal decomposition of diazidomalonamide (**14**) and *N,N'*-dimethyldiazidomalonamide (**16**) occurs analogously yielding 5-carbamoyltetrazole (**15**) and 5-(methylcarbamoyl)tetrazole (**17**), respectively. In order to test the mechanistic possibility that a tetrazolium intermediate plays a role in these decompositions, lithio-5-carbomethoxytetrazole was added in 10% molar concentration to dimethyl diazidomalonate (1) in dodecane. A similar experiment was carried out with diazidomalonamide (**14**). In both cases the reaction occurred at lower temperatures, and in each case the same products were observed as those obtained in the normal thermolysis.

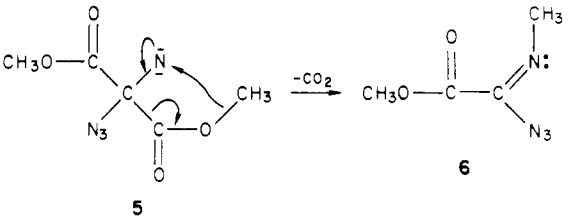
The thermal decomposition (140 °C, dodecane, 12 h) of dimethyl diazidomalonate (**1**) yields **2**.[1] The photochemical decomposition of **1** (1% benzene solution, high-pressure lamp 0.5-W, 2800 Å, room temperature) yields **3**.[2] Prolonged irradiation of **1** or separate irradiation of **3** yields **4** (eq 1).



(1)

The photochemical reaction is similar to that occurring in simpler systems, namely, loss of molecular dinitrogen upon irradiation and concomitant 1,2 group migration.[3] Whether a discrete nitrene intervenes is uncertain.[4a,b] Group migration could occur synchronously with loss of dinitrogen within the singlet manifold.[4] The ground-state triplet nitrene has been well characterized spectroscopically and is a discrete reaction intermediate.[5]

The thermal reaction **1** → **2** is obviously more complicated than simple group migration since a fragmentative loss of carbon dioxide must occur. The loss of CO_2 and methyl group transfer intramolecularly via the arrangement depicted in **5** → **6** corresponds to a 5-endo-tet process and is accordingly stereoelectronically unfavorable.[6]

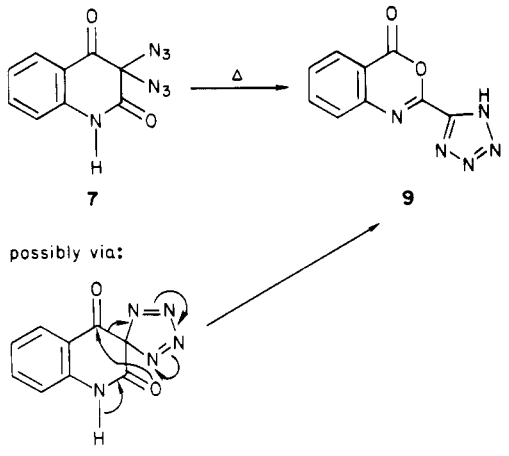


However, recently a mechanism for the decomposition of a geminal diazide appeared which pointed up the possibility of an alternative transfer. The specific example that was reported involved the rearrangement **7** → **8** → **9**.[7]

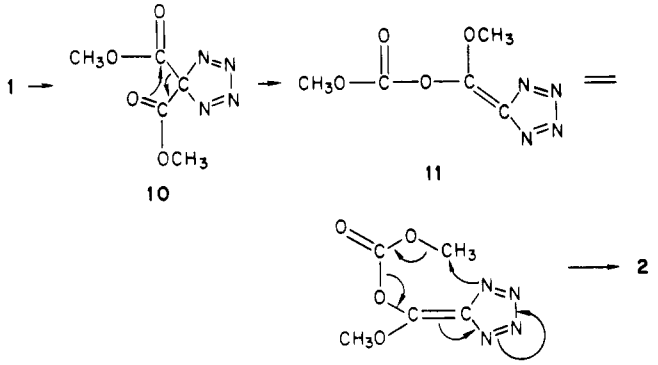
† Department of Chemistry.
‡ Department of Navy.

(1) Moriarty, R. M.; Serridge, P. *J. Am. Chem. Soc.* **1971**, *93*, 1534.
(2) Moriarty, R. M.; Kliegman, J. M.; Shovlin, C. *J. Am. Chem. Soc.* **1967**, *89*, 5958.
(3) (a) Lwowski, W. "Nitrenes"; Interscience: New York, 1970. (b) March, J. "Advanced Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1977; pp 178-186. (c) Carey, F. A.; Sundberg, R. J. "Advanced Organic Chemistry"; Plenum Press: New York, 1977; Part B, pp 301-321.
(4) (a) Moriarty, R. M.; Reardon, R. C. *Tetrahedron* **1970**, *26*, 1379. (b) Pritzkow, W.; Timm, D. *J. Prakt. Chem.* **1966**, *32*, 178. (c) Lewis, F. D.; Saunders, W. H. *J. Am. Chem. Soc.* **1971**, *93*, 47.
(5) Wasserman, E.; Smolinksy, G.; Yager, W. A. *J. Am. Chem. Soc.* **1964**, *86*, 3166.
(6) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734.

0022-3263/85/1950-3710$01.50/0

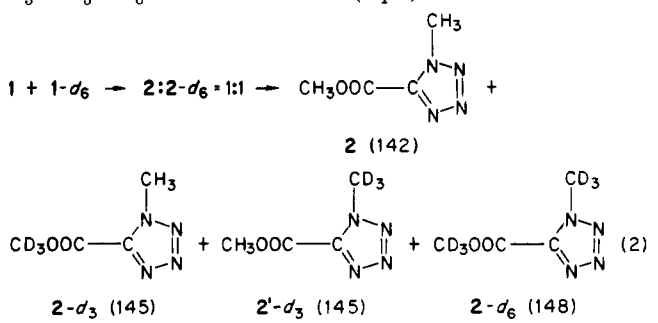


Applied to 1 an analogous thermal rearrangement process would be **10** → **11** → **2**.



The unfavorable 5-endo-tet process is now replaced by 7-endo-tet about which little is known with respect to its stereoelectronic likelihood. King and McGarrity have reported the first example of intramolecular methyl group transfer via a 9-endo-tet process.[8] In order to distinguish between the intramolecular and intermolecular pathways a labeling crossover experiment was carried out.

A sample of $(CD_3O_2C)_2C(N_3)_2$ (**1**-d_6), 99% deuterium incorporation, was synthesized from **1** by transesterification with CD_3OH. A 1:1 mixture of $(CH_3O_2C)_2C(N_3)_2$ (**1**) and $(CD_3O_2C)_2C(N_3)_2$ (**1**-d_6) was thermolyzed in dodecane at 140 °C for 7 h. If an intramolecular reaction were to occur the ratio of **2**:**2**-d_6 should be 1:1. If an intermolecular reaction were to occur, the ratio of **2**:**2**-d_3:**2**′-d_3:**2**-d_6 should be 1:1:1:1 (eq 2).



The analysis of the reaction product was carried out by means of mass spectrometry. For the intramolecular process the percentage relative abundance of **2** at 142 and **2**-d_6 at 148 should be in 1:1 ratio. Since the masses of **2**-d_3 and **2**′-d_3 are the same, namely, 145, the ratio of parent molecular ions as determined by mass spectrometry should be **2**:**2**-d_3 + **2**′-d_3:**2**-d_6 or 1:2:1 for the intermolecular process.

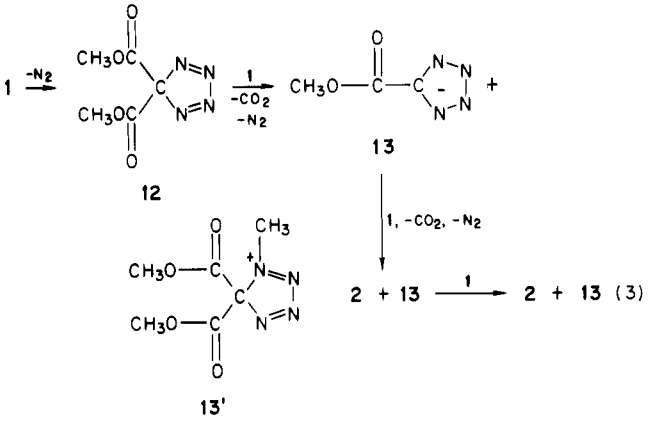
The parent molecular ions for the thermolysate were rather weak [m/z 142 (2.9), 145 (4.5), 148 (2.5)] but nonetheless close to the expected 1:2:1 ratio. However, P-28, which corresponds to loss of N_2, was an intense fragment. The observed ratios were m/z 114 (58), 117 (89) 120 (46). These correspond to **2**, **2**-d_3 + **2**′-d_3, and **2**-d_6 and are approximately the 1:2:1 ratio predicted for the *intermolecular mechanism*.

Furthermore, as would be predicted CH_3OCO [m/z 59 (92.7)] and CD_3OCO [m/z 62 [(96.8)] were approximately in 1:1 abundance ratio as were P − CH_3OCO [m/z 83 (37.7)] and P − CD_3OCO [m/z 86 (44.9)].

In a control experiment a 1:1 mixture of **2** and **2**-d_6 was subjected to the same mass spectrometric conditions as employed for the analysis of the thermolysis mixture, and the mass spectrum obtained was a composite of the spectra of either pure single component.

Any pathway for the intermolecular reaction must include *methyl group transfer between molecules or intermediates*. As a starting point we suspected that methyl radical, formed by homolytic fragmentation of diazide **1**, might play a role perhaps in effecting the decomposition of the azido group in a second molecule of **1**. However, acetyl peroxide decomposition in the presence of **1** did not initiate a reaction or cause any decomposition of **1** at a temperature lower than 140 °C. Similarly, other free-radical initiators such as azobis(isobutyronitrile) and azobis(propionitrile) were without effect on the thermal decomposition of **1**. Accordingly we were led to consider polar-type intermediates.

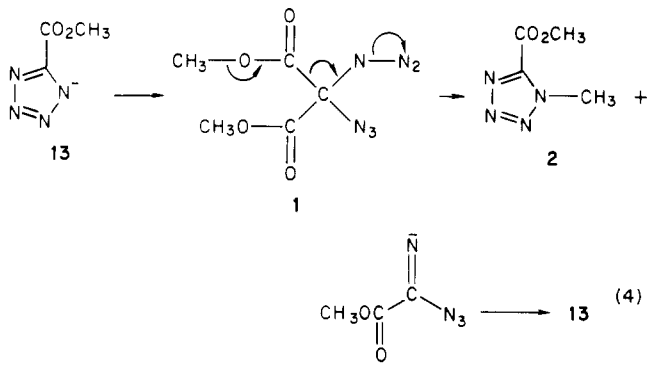
We propose that the methyl group transfer involves a nucleophilic alkylation process of the type in eq 3.



This reaction pathway possesses some of the characteristics of a chain reaction, and, could be viewed as an anionic chain reaction in which the tetrazolium anion **13** is the chain-carrying intermediate. The step that initiates the decomposition is thermal loss of molecular dinitrogen from **1** to yield tetrazole **12** analogous to the pathway suggested by Kappe et al.[7] Tetrazole **12** may undergo a trans methylation reaction with a molecule of **1** to yield **13**′ and **13** (via loss of CO_2 and N_2 from **1** to yield $CH_3O_2CC{=}N^-(N_3)$ which cyclizes to **13**) (eq 4). Tetrazolium anion **13** is the essential nucleophile which may react with a molecule of **1** to yield a molecule of product **2** with regeneration of **13** which continues the chain methyl transfer with loss of CO_2 and N_2 at each cycle.

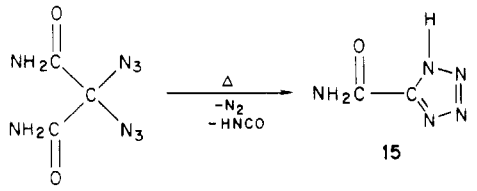
Tetrazolium anion **13** is resonance stabilized, being isoconjugate with the cyclopentadienyl anion. In addition it would be expected to be an excellent nucleophile. An analogous mechanism may operate in the case of the two

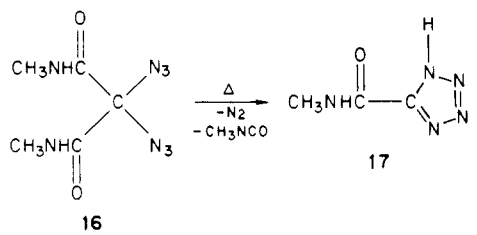
(7) Kappe, T.; Long, G.; Pongratz, E. *J. Chem. Soc., Chem. Commun.* **1984**, 338.
(8) King, J. F.; McGarrity, M. J. *J. Chem. Soc., Chem. Commun.* **1982**, 175.



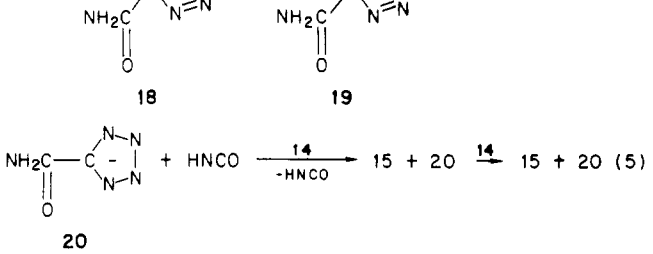
(4)

amido analogues 14 → 15 and 16 → 17.

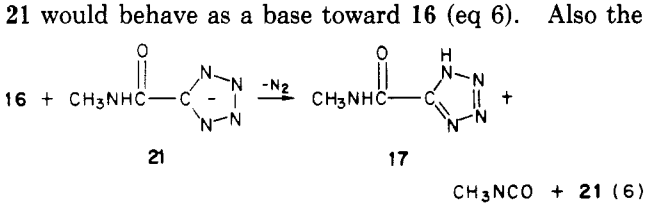




In the case of 14 the pathway analogous to the ester decomposition is as is in eq 5.



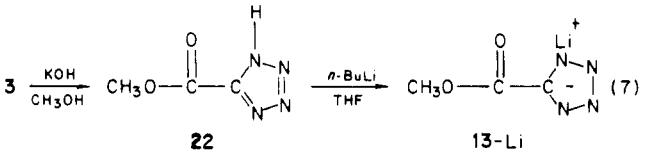
Reaction 16 → 17 follows the same pathway and, furthermore, lends support to the mechanism in the sense that, a priori, either the methyl group on nitrogen or the hydrogen atoms might be expected to migrate to an electron-deficient center as would occur in a nitrene mechanism. However, a tetrazolium anion intermediate such as 21 would behave as a base toward 16 (eq 6). Also the



(6)

yields of 15 and 17 are high, 89% and 90%, respectively, as would be expected for hydrogen transfer compared to alkyl group transfer as occurs in 1 → 2 (yield 9.2%).

The central feature of the above mechanisms is the decomposition of the geminal diazides triggered by anionic displacement and subsequent fragmentation. A test of this pathway is possible by synthesis of the tetrazolium anion. This was done as shown in eq 7.



(7)

A catalytic amount of 13-Li did not cause spontaneous decomposition of 1 at room temperature in dodecane. Decomposition of 1 occurred at 104–106 °C, 48 h, in dodecane in the presence of 13-Li in 10% molar concentration. In the absence of 13-Li the decomposition of 1 requires a temperature of 140 °C for 2 h. The result with diazidomalonamide (14) was more striking. Decomposition of 14 in dodecane occurred at 70–75 °C in the presence of 10% molar lithio-5-carbamoyltetrazole (14-Li) within 15 h relative to 140 °C for 2 h in the absence of 14-Li.

In summary we propose a novel anionic chain type mechanism to account for the intermolecular group transfer occurring in the fragmentative reaction of diazidomalonic acid derivatives.

Experimental Section

Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 727B spectrometer. ^{1}H NMR spectra were recorded on a Varian A-60 or Varian EM-360 spectrometer. Mass spectra were determined on a Hewlett-Packard GC–MS 5985A spectrometer. Microanalyses were performed by Microtech Labs, Skokie, IL.

Dimethyl Diazidomalonate (1). This compound was prepared in 70% yield by the method of Bretschneider and Karpitschka[9] and had bp 75–80 °C (0.25–0.1 mm).

Dimethyl Diazidomalonate-d_6 (1-d_6). A solution of dimethyl diazidomalonate (0.8 g, 3.7 mmol), CD_3OD (4.0 g, 110 mmol), and *p*-toluenesulfonic acid (0.1 g, 0.6 mmol) was refluxed for 50 h. After the mixture was cooled, methanol (deuterated) was removed under vacuum. The residue was treated with water (40 mL), and the resulting solution was extracted with ether (3 × 20 mL). The combined ether extracts were dried over anhyrous magnesium sulfate and filtered, and the filtrate was concentrated on a rotating evaporator at 24 °C (20 torr) to give 0.35 g (43%) of 99% deuterated diazido compound as determined by ^{1}H NMR and mass spectrometry.

Diazidomalonamide (14). This compound was prepared according to the procedure of Forster and Muller[10] and had mp 157–158 °C (lit.[10] mp 162 °C).

***N,N'*-Dimethyldiazidomalonamide (16).** This compound was prepared by the procedure of Forster and Muller,[10] and it had mp 104–105 °C.

Thermal Decomposition of Dimethyl Diazidomalonate (1). A solution of dimethyl diazidomalonate (1) (0.5 g, 2.3 mmol) in dodecane (2.0 g) was heated in an oil bath to 140 °C for 2 h. The reaction mixture was cooled to room temperature, and the dodecane was decanted from a black oil. The oil was washed with hexane (2 × 5 mL) and was then placed in a sublimation apparatus. The product was collected, 90 °C (0.03 mm): yield, 30 mg (9.2%) of 2; mp 108–109 °C (lit.[1] mp 108–109 °C); IR (KBr) 1745 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 4.1 (3 H, s, CH_3), 4.5 (3 H, s, CH_3); MS, *m/z* (relative intensity) 142 (M^+, 2), 114 (32), 111 (3), 102 (1), 101 (2), 88 (1), 86 (2), 84 (3), 83 (10), 69 (28), 59 (33), 42 (100).

Thermal Decomposition of a 1:1 Mixture of Dimethyl Diazidomalonate (1) and Dimethyl Diazidomalonate-d_6 (1-d_6). A solution of $(CH_3O_2C)_2C(N_3)_2$ (0.2568 g, 1.2 mmol), $(CD_3O_2C)_2C(N_3)_2$ (0.2640 g, 1.2 mmol), and dodecane (2 g) was heated to 140 °C for 24 h. The dodecane solvent was decanted, and the brown residue was washed with hexane (20 mL). The remaining brown oil was dissolved in chloroform (2 mL) and the solution was transfered to a sublimation apparatus. Solvent was removed under vacuum. The product was then sublimed at <0.005 mm

(9) Bretschneider, H.; Karpitschka, N. *Monatsh Chem.* **1953**, *84*, 1091.
(10) Forster, M. O.; Muller, R. *J. Chem. Soc.* **1910**, 126.

for 15 h, and the bath temperature was 80 °C. The crystalline product was washed with some hexane and dried. The product was analyzed by mass spectrometry at 20 and 70 eV.

Thermal Decomposition of Diazidomalonamide (14). A solution of diazidomalonamide (**14**) (100 mg, 0.5 mmol) in dodecane (1.0 g) was heated to 140–142 °C in an oil bath for 2 h. At the end of given time the reaction was cooled and the white solid separated, which was washed with hexane (5 mL) to give 50 mg (89%) of 5-carbamoyltetrazole (**15**): mp 230–232 °C (lit.[1] mp 231–232 °C); IR (Nujol) 1700 (C=O) cm^{-1}; NMR (Me_2SO-d_6) δ 4.5 (2 H, s, NH_2), 8.3 (1 H, s, NH); MS, *m/z* (relative intensity) 113 (M^+, 35), 86 (7), 85 (58), 71 (100), 70 (16), 69 (10), 60 (41), 57 (12), 44 (58), 42 (33).

Thermal Decomposition of *N,N'*-Dimethyldiazidomalonamide (16). *N,N'*-dimethyldiazidomalonamide (**16**) (150 mg, 0.7 mmol) in dodecane (1.0 g) was heated in an oil bath to 140–144 °C for 3 h. On cooling the reaction mixture, a white solid separated, which was filtered, washed with hexane (15 mL), and dried to give 80 mg (90%) of 5-(methylcarbamoyl)tetrazole (**17**): mp 233–235 °C (lit.[1] mp 235–236 °C); IR (Nujol) 1665 (C=O) cm^{-1}; NMR (Me_2SO-d_6) δ 2.4 (3 H, s, CH_3), 4.3 (1 H, s, $NHCH_3$), 8.3 (1 H, s, NH); MS, *m/z* (relative intensity) 127 (M^+, 20), 99 (18), 98 (4), 85 (16), 84 (8), 70 (16), 69 (12), 58 (100), 56 (38), 55 (10), 44 (15), 43 (44), 42 (30).

5-Carbomethoxytetrazole (22). Dimethyl tetrazole-1,5-dicarboxylate (**3**)[1] (372 mg, 2.0 mmol) was dissolved in 3% aqueous potassium hydroxide solution (5 mL) and methanol (10 mL), and the reaction mixture was stirred at room temperature for 6 h. It was diluted with water (20 mL), neutralized with acetic acid, and extracted with chloroform (3 × 10 mL). The combined chloroform extracts were washed with saturated sodium bicarbonate solution and then with water, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed in vacuo to give 75 mg of 5-carbomethoxytetrazole (**22**): mp 96–98 °C; IR (Nujol) 3405 (NH), 1740 ($COOCH_3$) cm^{-1}; NMR ($CDCl_3$) δ 4.16 (3 H, s, CH_3). Anal. Calcd for $C_3H_4N_4O_2$: C, 28.12; H, 3.12. Found: C, 28.43; H, 3.23.

Thermal Decomposition of Dimethyl Diazidomalonate (1) in the Presence of the Lithium Salt of 5-Carbomethoxytetrazole (13-Li). A solution of 5-carbomethoxytetrazole (**22**) (64 mg, 0.5 mmol) in dry tetrahydrofuran (5 mL) was cooled to −78 °C, and to this was added dropwise a solution of *n*-butyllithium (0.5 mL, 2.5 M) in dry tetrahydrofuran (5 mL) under nitrogen. The reaction mixture was stirred at −78 °C for 1 h, and then it was slowly brought to room temperature. After the mixture was stirred 0.5 h at room temperature, a solution of dimethyl diazidomalonate (**1**) (1.0 g, 4.6 mmol) in dodecane (2.0 g) was added at once, and the reaction mixture was heated in an oil bath to 104–106 °C for 2 days. The reaction mixture was cooled to room temperature, and the dodecane was decanted from a black oil. The oil was washed with hexane (2 × 5 mL): IR (Nujol) 1745 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 4.1 (3 H, s, CH_3), 4.51 (3 H, s, CH_3). The NMR of the crude product shows 10% of the 5-carbomethoxy-1-methyltetrazole.

Thermal Decomposition of Diazidomalonamide (14) in the Presence of the Lithium Salt of 5-Carbamoyltetrazole (15-Li). To a cold solution of 5-carbamoyltetrazole (**15**) (56.5 mg, 0.5 mmol)[1] in dry tetrahydrofuran (10 mL) at −78 °C was added dropwise a solution of *n*-butyllithium (1.5 mL, 2.5 M) in dry tetrahydrofuran (10 mL) under nitrogen. The reaction mixture was allowed to stir at −78 °C for 1 h, and then it was slowly brought to room temperature and was stirred for 2 h. To this was added a suspension of diazidomalonamide (**14**) (500 mg, 2.5 mmol) in dodecane (1 g), and the reaction mixture was heated at 70–75 °C for 15 h. The reaction mixture was cooled, and the solid was filtered, washed with water and then with hexane, and dried to give 200 mg (81%) of 5-carbamoyltetrazole (**15**): mp 240–242 °C; IR (KBr) 1700 (C=O) cm^{-1}.

Acknowledgment. We thank the Office of Naval Research for support of this work under N00014-83K-0306.

Registry No. **1**, 19132-24-2; **1**-d_6, 97763-82-1; **2**, 32366-17-9; **2**-d_3, 97752-03-9; **2'**-d_3, 97752-04-0; **2**-d_6, 97752-05-1; **3**, 16932-76-6; **13-Li**, 97752-06-2; **14**, 32366-18-0; **15**, 32366-22-6; **15-Li**, 97752-07-3; **16**, 32366-19-1; **17**, 32366-23-7; **22**, 97752-08-4.

Reaction of *gem*-Dibromocyclopropanes with Potassium Dimethyl Phosphite in Liquid Ammonia. A Highly Stereoselective Reduction

Gordon F. Meijs* and Ian R. Doyle

Department of Organic Chemistry, The University of Aldelaide, Adelaide, S.A. 5001, Australia

Received March 6, 1985

Although *gem*-dibromocyclopropanes undergo substitution with other $S_{RN}1$ nucleophiles in liquid ammonia solution stimulated by "350 nm" light, only reduction is observed with dimethyl phosphite ion. This reduction proceeds in the absence of light and involves nonradical intermediates. It gives high yields of the trans monobromides **4** with little or no contamination by the cis isomers **5** or the direduced products **6**. *gem*-Dichlorocyclopropanes are inert under the reaction conditions. The reaction is suited to preparative work.

It has recently been reported that *gem*-dibromocyclopropanes undergo a photostimulated reaction with certain nucleophiles to afford disubstituted products.[1] The reactions bear apparent similarity to the well-known $S_{RN}1$ reaction in that they are retarded by radical inhibitors and do not occur in the dark. Nucleophiles which have been shown to react with *gem*-dibromocyclopropanes,[1] such as thiophenoxide ion, pinacolone enolate, and cyanomethyl anion, are all effective $S_{RN}1$ nucleophiles on aromatic systems.[2,3]

However, diphenylphosphide ion, a very reactive nucleophile in aromatic $S_{RN}1$ chemistry,[4] undergoes a reaction with *gem*-dibromocyclopropanes in which the first step is *reduction* to the monobromide, followed by a substitution of the remaining bromine to form cyclopropyldiphenylphosphines.[5,6] We sought, therefore, to examine the behavior of other phosphorus nucleophiles under conditions believed to promote substitution.

Dialkyl phosphite ions are also effective aromatic $S_{RN}1$ nucleophiles,[7] although they are somewhat less reactive

(1) Meijs, G. F. *J. Org. Chem.* **1984**, *49*, 3863–65.
(2) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413–20.
(3) Rossi, R. A.; de Rossi, R. H. "Aromatic Substitution by the $S_{RN}1$ Mechanism"; American Chemical Society: Washington, D.C., 1983.
(4) Galli, C.; Bunnett, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 7140–47.
(5) Meijs, G. F. *Tetrahedron Lett.* **1985**, *26*, 105–6.
(6) See, also: Rossi, R. A.; Santiago, A. N.; Palacios, S. M. *J. Org. Chem.* **1984**, *49*, 3387–88.

0022-3263/85/1950-3713$01.50/0