

sodium hydride in dimethylformamide (DMF) or with dimethylsodium in dimethyl sulfoxide (DMSO) at room temperature, nitrogen (and H₂ in the case of the NaH reaction) was eliminated and a deep-red solution of the allyl anion **4** (configuration unknown) was obtained as its sodium salt. The solution was stable for several days if kept with the usual precautions for handling metalorganic compounds. Acidification was accompanied by immediate decolorization and gave >90% of dimethyl 1,1-diphenyl-1-butene-2,3-dicarboxylate⁶ (**5a**, mp 80.5–81.5°, ν_{CO} (KBr) 1701 and 1743 cm⁻¹). The Stobbe condensation of benzophenone and dimethyl methylsuccinate produced an ester acid (94%), which furnished **5a** with diazomethane.

Deuterium exchange experiments reveal the virtually quantitative formation of the allyl anion **4**. After treatment of the pyrazoline **1a** with an excess of dimethylsodium in DMSO and quenching of the allyl anion **4** after 45 min with CH₃-CO₂D + CH₃OD, we isolated 85% of the diester **5**, containing the H and D species, **5a** and **5b**, in the ratio 8:92. The analogous reaction of the deuterated pyrazoline **1b** with dimethylsodium and acidification by CH₃-CO₂H + CH₃OH after 3 min produced 69% of diester **5a** with no detectable amount of **5b**. The red color of **4** also disappeared when methyl bromide was introduced; the product of methylation, **6** (mp 101–103°; nmr (CDCl₃) τ 6.58 and 6.59 (2- and 3-CO₂CH₃, s), 8.64 (2-CCH₃, s)), was formed in 95% yield.

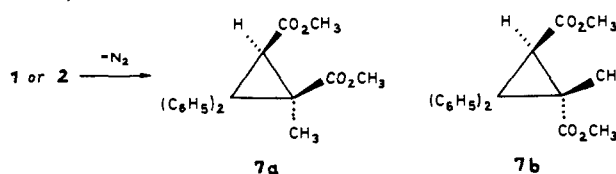
Corresponding experiments were carried out with **1a**, **1b**, and sodium hydride in DMF. Under these heterogenous conditions, H,D and D,H exchanges in the conversion **1** → **5** were less complete, i.e., deuteration after 45 min gave **5a** and **5b** in a 25:75 ratio (100% yield), whereas protonation yielded **5a** and **5b** in a 73:27 ratio. Evidently, the allyl anion **4** competes with NaH in the deprotonation of **1**. This phenomenon was further illustrated by treatment of **1a** with NaH in dioxane, which gave **5a** without generation of a red color. Here the NaH, which acts as a catalyst, produces the allyl anion **4** in a small stationary concentration and induces an anion chain reaction: **1a** + **4** → **3** + **5a**; **3** → N₂ + **4**.

Is the 1-pyrazolin-4-yl anion **3** an intermediate in the process **1** → **4** or does the loss of N₂ occur simultaneously with the deprotonation of **1**? Sodium methoxide in methanol established a 79:21 equilibrium of the *cis*-pyrazoline **1a** and the *trans* isomer **2** without any evolution of N₂. Also, H,D exchange in position 4 of the pyrazolines **1a** and **2** by NaOCH₃-CH₃OD occurred readily (90–98% D). As expected, protonation and deuteration of the anion **3** are faster than its cycloreversion. The assumption is plausible that **3** is also an intermediate in the nitrogen elimination in the aprotic solvents DMSO and DMF.

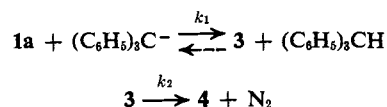
What makes it probable that the pyrazolin-4-yl anion **3** suffers a *one-step concerted* nitrogen loss to form the allyl anion **4** in a reaction that corresponds to a 1,3-dipolar cycloreversion? The anion **4** eliminates nitrogen >10¹² times faster than does the neutral pyrazoline **1a**. The thermolysis of the pyrazolines **1a** and **2** produced the *cis,trans* isomeric cyclopropanes **7** without admixture of the olefinic diester **5**; **7a** and **7b**

(6) All new compounds gave satisfactory elementary analyses and were spectroscopically characterized.

were obtained in a 32:68 ratio from **1a** and in a 3:97 ratio from **2** in benzonitrile at 120°. Kinetic measurements of N₂ evolution from **1a** at four temperatures led to $\Delta H^\ddagger = 29.2$ kcal mol⁻¹ and $\Delta S^\ddagger = +2$ eu. At -40°, ΔG^\ddagger would be 28.7 kcal mol⁻¹.



Sodium triphenylmethide in tetrahydrofuran induced N₂ evolution from **1a** at -40° in a pseudo-first-order reaction⁷ with $k_1 = 2.5 \times 10^{-4}$ sec⁻¹. Provisional rate comparison of the pyrazolines **1a** and **1b** revealed $k_{\text{H}}/k_{\text{D}} \approx 6$ at -20°. This isotope effect suggests the deprotonation of the pyrazoline to be rate determining.



The absence of an induction period in the nitrogen evolution allows the estimate $k_2 > 10k_1$. Thus, the process **3** → **4** must have an activation barrier $\Delta G^\ddagger < 16.3$ kcal mol⁻¹ at -40°. Therefore, the 1,3-cycloreversion of the pyrazolin-4-yl anion **3** to the allyl anion **4** + N₂ has an activation energy more than 12 kcal mol⁻¹ lower than that of the conversion of the pyrazoline **1a** to the cyclopropanes **7** via the trimethylene species.⁸ This marked difference is in agreement with a concerted N₂ elimination from **3** without formation of reactive intermediates. Rate differences for nitrogen elimination have been used earlier to distinguish between orbital symmetry-allowed and symmetry-forbidden processes.⁹

Do not solvation phenomena devalue the mechanistic significance of a rate comparison between the breakdown of the neutral pyrazoline and the fragmentation of its anion **4**? THF solvates anions less than cations. The anionic charge is more highly dispersed in the product **4** than in the reactant **3**. Therefore, an enhancement in solvation forces would probably retard the process **3** → **4** and decrease the $\Delta\Delta G^\ddagger$ of the two reactions.

(7) The zero order in base, which was used in nearly stoichiometric amount, shows its catalytic activity. That the allyl anion is as active as the triphenylmethide anion in the deprotonation of **1a** seems to offer the simplest explanation.

(8) R. J. Crawford and A. Mishra, *J. Amer. Chem. Soc.*, **88**, 3963 (1966).

(9) N. Rieber, J. Alberts, J. A. Lipsky, and D. M. Lemal, *ibid.*, **91**, 5668 (1969).

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Electrocyclic Ring Opening of a Cyclopropyl Anion to an Allyl Anion

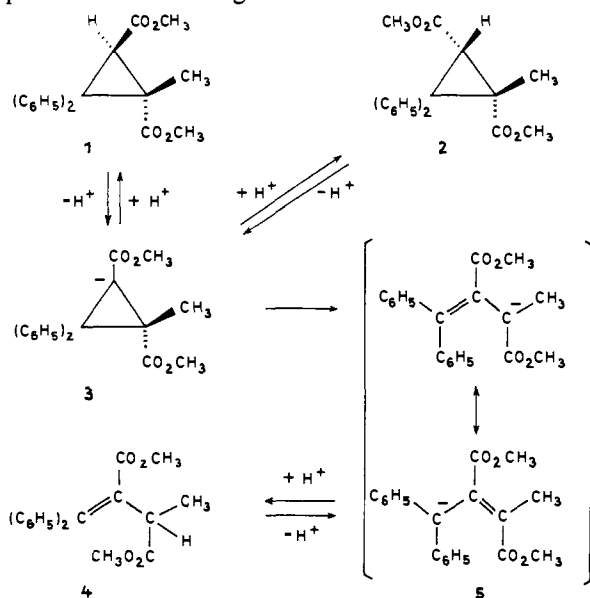
Sir:

Woodward and Hoffmann¹ predicted conrotation for the thermal ring opening of the cyclopropyl anion to the

(1) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965).

allyl anion. To the best of our knowledge no clear-cut example of this electrocyclic ring opening is known to date. The alkaline ring scission of 1-nitro-2-phenyl-3-benzoylcyclopropane and analogous compounds was interpreted by a cleavage of the 2,3 bond of the cyclopropyl anion.² However, HNO_2 elimination³ and nucleophilic attack on the three-membered ring⁴ have also been proposed as primary steps. Several ring openings of bicyclic cyclopropyl anions to aromatic anions have been described.^{5,6}

What structural prerequisites must be fulfilled for the cyclopropyl anion \rightarrow allyl anion conversion to take place? An electron-attracting substituent acidifies a cyclopropyl hydrogen and facilitates deprotonation to give a carbanion. Also, substituents that stabilize negative charge at the two remaining carbons, which become the terminal centers of the allyl anion, are expected to aid the ring scission.



On reaction of dimethyl 1-methyl-3,3-diphenylcyclopropane-1,2-*trans*-dicarboxylate⁷ (**1**) with sodium hydride in dimethylformamide (DMF) at 20°, 0.9 equiv of hydrogen was set free. The deep-red solution contained the allyl anion **5**⁸ (configuration unknown) and, on acidification with methanolic hydrogen chloride, gave the olefinic diester **4**⁸ in 70% yield. Treatment of **1** or **2** with sodium methoxide in methanol at 60° established a 98:2 equilibrium of these *trans*,*cis* isomers without formation of **4**. The cyclopropyl anion **3** is the logical intermediate in the *cis*,*trans* isomerization as well as in the electrocyclic ring opening.

In elegant stereochemical studies by Walborsky, *et al.*,⁹ no ring opening was observed for 1-methyl-2,2-diphenylcycloprop-1-yl lithium or -sodium and for the 1-cyano-2,2-diphenylcycloprop-1-yl anion. Thus, two

(2) L. I. Smith and V. A. Engelhardt, *J. Amer. Chem. Soc.*, **71**, 2676 (1949).

(3) E. P. Kohler and L. I. Smith, *ibid.*, **44**, 624 (1922).

(4) E. P. Kohler and J. B. Conant, *ibid.*, **39**, 1404 (1917).

(5) G. Wittig, V. Rautenstrauch, and F. Wingler, *Tetrahedron, Suppl.*, **7**, 189 (1966).

(6) G. Boche, D. Martens, and W. Danzer, *Angew. Chem.*, **81**, 1003 (1969).

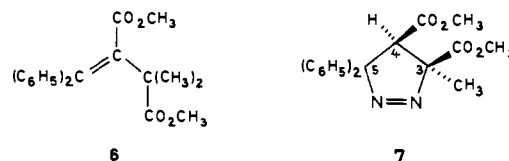
(7) W. M. Jones and W.-T. Tai, *J. Org. Chem.*, **27**, 1030 (1962).

(8) P. Eberhard and R. Huisgen, *J. Amer. Chem. Soc.*, **94**, 1345 (1972).

(9) H. M. Walborsky, F. J. Impastato, and A. E. Young, *ibid.*, **86**, 3283 (1964); J. B. Pierce and H. M. Walborsky, *J. Org. Chem.*, **33**, 1462 (1968); H. M. Walborsky and J. M. Motes, *J. Amer. Chem. Soc.*, **92**, 2445 (1970).

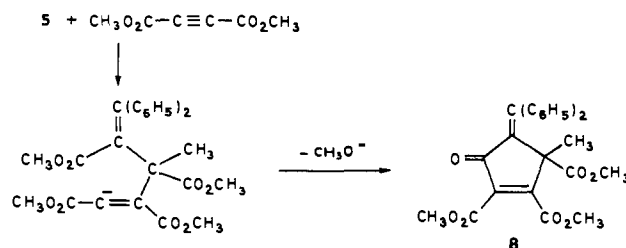
phenyl groups at one of the potentially terminal carbons of the allyl anion do not by themselves provide enough driving force for the ring opening.

As expected, the dimethyl 1,1-diphenyl-1-butene-2,3-dicarboxylate (**4**) also furnished the allyl anion **5** on treatment with NaH in DMF. Reaction of the red solution with methyl bromide produced **6**⁸ in 83% yield.

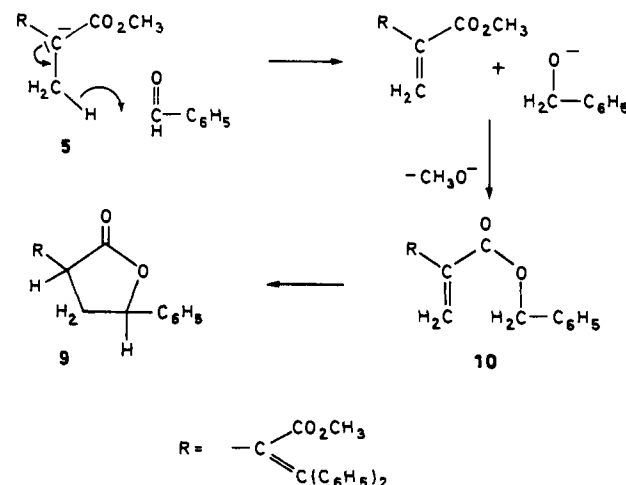


Is it conceivable that the observed formation of **5** from the **4** anion of the pyrazoline **7**⁸ takes place *via* the cyclopropane **1** or the olefinic diester **4**? Both pathways can be discarded. Though the heterogeneity of the system does not allow precise kinetic measurement, we subjected **7**, **4**, and **1** to identical treatment with NaH in DMF and followed the gas evolution ($\text{H}_2 + \text{N}_2$ for **7**, H_2 in the case of **1** and **4**) from the rapidly stirred mixture at 21°. The half-lives obtained (1.2, 9, and 17 min) correspond roughly to rate ratios of 14:2:1 for **7**, **4**, and **1**. Thus, neither the cyclopropane **1** nor the olefinic diester **4** can be an intermediate in the conversion of **7** into the allyl anion **5**.

Concerning the steric course of the cyclopropyl anion ring opening, the verification of the predicted conrotation still rests on experiments with the isoelectronic aziridine system.¹⁰



Allyl anions should undergo concerted cycloadditions of the type $\pi_4s + \pi_2s$ as do their zwitterionic heteroanalogous (1,3 dipoles).⁸ Interestingly, however, we found that the reaction of **5** with dimethyl acetylenedicarboxylate produced a compound $\text{C}_{25}\text{H}_{22}\text{O}_7$



(10) R. Huisgen, W. Scheer, and H. Huber, *ibid.*, **89**, 1753 (1967).

(30% yield) to which we assign the tentative structure **8**, and we also observed the reaction of **5** with benzaldehyde to give a substance $C_{26}H_{22}O_4$ (30%) believed to be **9**.¹¹ Reasonable pathways to these unexpected products are shown. The failure of **5** to undergo the concerted cycloaddition is attributed to its high nucleophilicity, which evidently exceeds that of 1,3 dipoles by far.

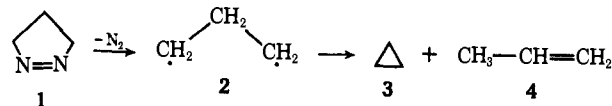
(11) Assignments are based on spectral and analytical data. Details are to be reported elsewhere.

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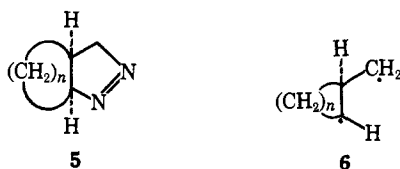
Formation of 1,4-Pentadiene and Vinylcyclopropane in the Thermal and Photochemical Decomposition of 2,3-Diazabicyclo[3.2.0]hept-2-ene

Sir:

Pyrazolines (e.g., **1**) normally undergo thermal¹ and photochemical² decomposition to form cyclopropanes (**3**) and olefins (**4**), presumably *via* the intermediacy of



“trimethylene” diradicals such as **2**. Although the detailed structure of **2** is still a matter of some discussion,³ the cyclopropane-olefin product pattern is observed in a large number of substituted systems. These include bicyclic pyrazolines such as **5** ($n = 3$) which probably⁴ react initially *via* intermediate **6**



However, data for the case of **5** ($n = 2$), which should generate diradical **17** (*vide infra*), are somewhat confusing. One substituted derivative, **7**, gave typical

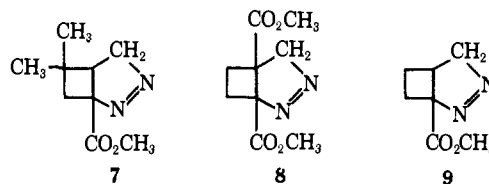
(1) (a) R. J. Crawford and A. Mishra, *J. Amer. Chem. Soc.*, **88**, 3963 (1966); (b) R. J. Crawford and D. Cameron, *ibid.*, **88**, 2589 (1966); (c) R. J. Crawford and G. L. Erickson, *ibid.*, **89**, 3907 (1967); (d) R. J. Crawford and L. J. Ali, *ibid.*, **89**, 3908 (1967); (e) A. Mishra and R. J. Crawford, *Can. J. Chem.*, **47**, 1515 (1969); (f) D. E. McGreer, R. S. McDaniel, and M. J. Vinje, *ibid.*, **43**, 1389 (1965); (g) D. E. McGreer, N. W. K. Chiu, M. G. Vinje, and K. C. K. Wong, *ibid.*, **43**, 1407 (1965); (h) D. E. McGreer, N. W. K. Chiu, and M. G. Vinje, *ibid.*, **43**, 1398 (1965); (i) D. E. McGreer and W.-S. Wu, *ibid.*, **45**, 461 (1967); (j) B. H. Al-Sader and R. J. Crawford, *ibid.*, **46**, 3301 (1968); (k) W. R. Roth and M. Martin, *Tetrahedron Lett.*, 3865 (1967); (l) A. L. Allred and R. L. Smith, *J. Amer. Chem. Soc.*, **89**, 7133 (1967); (m) W. R. Roth and M. Martin, *Tetrahedron Lett.*, 4695 (1967); see also, (n) *Justus Liebig's Ann. Chem.*, **702**, 1 (1967).

(2) (a) R. Moore, A. Mishra, and R. J. Crawford, *Can. J. Chem.*, **46**, 3305 (1968); (b) K. B. Wiberg and A. deMeijere, *Tetrahedron Lett.*, 59 (1969).

(3) See, for example, (a) R. G. Bergman and W. L. Carter, *J. Amer. Chem. Soc.*, **91**, 7411 (1969); (b) R. Hoffmann, *ibid.*, **90**, 1475 (1968); (c) L. Salem, *Accounts Chem. Res.*, **4**, 322 (1971); (d) L. Salem and C. Rowland, *Angew. Chem.*, in press; (e) K. Q. Siu, W. M. St. John, and E. F. Hayes, *J. Amer. Chem. Soc.*, **92**, 7249 (1970); (f) J. A. Horsley, Y. Jean, C. Moser, L. Salem, R. M. Stevens, and J. S. Wright, *ibid.*, **94**, 282 (1972).

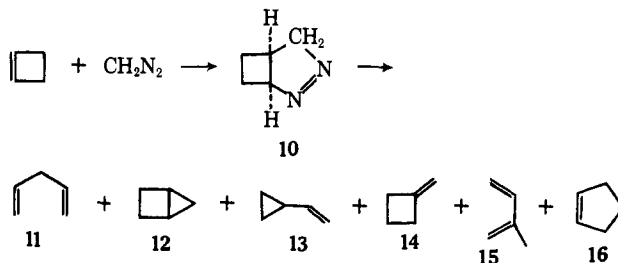
(4) (a) P. B. Condit and R. G. Bergman, *Chem. Commun.*, 4 (1971); (b) M. P. Schneider and R. J. Crawford, *Can. J. Chem.*, **48**, 628 (1970).

bicyclopentane and olefin products,⁵ although on photolysis it was reported to form a “complex product mixture.” Another system, **8**, decomposed to both bicyclopentane and substituted 1,4-pentadienes on irradiation; no thermal decomposition was reported.⁶ Compound **9** produced 1-carbomethoxybicyclo[2.1.0]-



pentane “and five other [unidentified] products” when heated.⁷ Addition of carbenes and carbenoids to substituted cyclobutenes (which might directly generate diradicals of general structure **6** ($n = 2$)) has been reported to give dienes, bicyclopentanes, and vinylcyclopropanes as well as other products.⁸ Because these systems appear to behave so differently, we felt that a careful study of the thermal and photochemical decomposition of the parent molecule **10** was warranted. We herein report the results of such a study.

Addition of diazomethane to cyclobutene in pentane solution at room temperature produced a 76% yield of 1,3-dipolar addition product **10** after 4 days. Compound **10** was purified by gas-liquid chromatography (glc); its properties and spectral data ($\nu_{\text{max}}^{\text{C-Cl}}$ 1540 cm^{-1} ; $\nu_{\text{max}}^{\text{MeOH}}$ 323 nm (ϵ 338); nmr δ (CCl_4) 1.0–3.0 (complex absorption, 5 H), 4.38 (mult, 2 H), 5.06 (mult, 1 H)) were consistent with the structure assigned by earlier workers.⁹ Gas-phase thermal decomposition in a quartz flow system or in the injector port of a glc instrument gave rise to six products (88% yield), **11–16**,



in the proportions listed in Table I. Somewhat surprisingly, direct irradiation of **10** (Pyrex vessels) in pentane solution increased the relative amount of bicyclopentane formed, and photosensitized decomposition resulted in an even larger proportion of **12**.

The formation of **11** as a major product in the thermal decomposition is unprecedented. Its presence, along with that of vinylcyclopropane (**13**), raises the possibility that diradical **17**, a potential initial intermediate, may be in equilibrium with an isomeric “di- π -methane” intermediate¹⁰ formally written here as diradical **18**.

(5) T. H. Kinstle, R. L. Welch, and R. W. Exley, *J. Amer. Chem. Soc.*, **89**, 3660 (1967).

(6) M. Franck-Neumann, *Tetrahedron Lett.*, 2979 (1968).

(7) P. G. Gassman and K. T. Mansfield, *J. Org. Chem.*, **32**, 915 (1967).

(8) (a) C. S. Elliott and H. M. Frey, *Trans. Faraday Soc.*, **64**, 2352 (1968); (b) H. M. Frey, *Chem. Commun.*, 260 (1965); (c) N. C. Yang and T. A. Marolewski, *J. Amer. Chem. Soc.*, **90**, 5644 (1968).

(9) H. Paul, I. Lange, and A. Kausmann, *Chem. Ber.*, **98**, 1789 (1965).

(10) (a) For references to a number of examples of the di- π -methane rearrangement, see H. E. Zimmerman and P. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969). For other examples and mechanistic studies, see (b) H. E. Zimmerman and A. A. Baum, *ibid.*, **93**, 3646 (1971); (c) H. E.