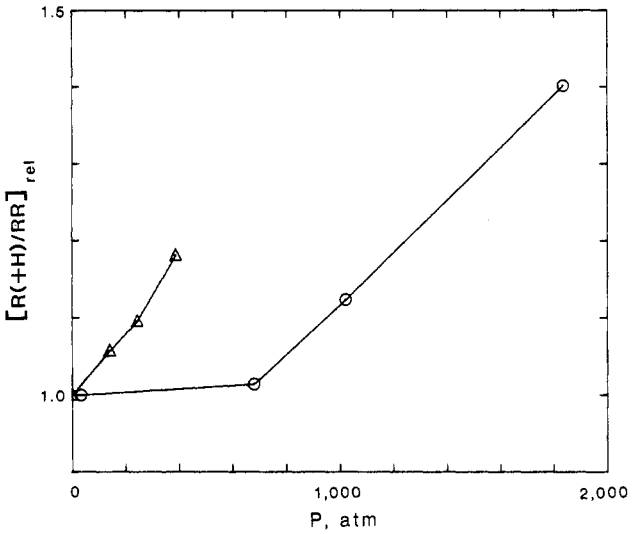


Figure 2. Pressure dependence of $[R(+H)/RR]_{rel}$ (see ref 7) from the pressure studies (Table I) (○) and from data of Schuh and Fischer (Table II) (△).

Fischer from Table II.[7] Similarly, these respective sets of normalized values of R(+H)/RR have been plotted as a function of pressure in Table II. In the first case (Figure 1), the viscosity values used for the pressure results are those shown in Table I. In the second case (Figure 2), the "pressure" values used for Schuh and Fischer's data in the *n*-alkane solvents are the values of ΔP_i given in Table II. In effect, we are normalizing all pressures to *n*-octane at 1-atm external pressure.[8]

We contend that the solvent variation data and pressure variation data correlate much better with viscosity (Figure 1) than with pressure (Figure 2). This provides support for the model developed to explain these results (Table II), which was based on the assumption that certain rotational motions of *tert*-butyl radicals would have significantly greater viscosity dependence than other rotational motions.[2a]

Experimental Section

Di-*tert*-Butyl Ketone (2,2,4,4-Tetramethyl-3-pentanone). This ketone was synthesized according to the procedures of Dubois and Bauer:[9] bp 83–84 °C (53 mm); NMR δ 1.27 (s); IR 1685 cm^{-1} (C=O) (lit.[9] bp 69.5 °C (48 mm); IR 1686.5 cm^{-1}). The IR spectrum of this ketone was identical with Sadtler IR spectrum no. 5681 of an authentic sample of this compound and with that of a commercial sample obtained from the Pfaltz and Bauer Co.

Product Studies. A 0.17 M solution of 2,2,4,4-tetramethyl-3-pentanone was prepared in *n*-octane (Aldrich Gold label; H_2SO_4 washed and distilled) containing a small amount of benzene (0.014 M) as an internal standard. The solution was vacuum degassed via several freeze–pump–thaw cycles and brought to atmospheric pressure with pure dinitrogen. The solution was stored in a sealed container at 5 °C between experiments. Samples were withdrawn from the storage vessel and placed in the high-pressure optical cell in a nitrogen purged glovebag. The cell was pressurized and irradiated with a medium-pressure Hanovia mercury lamp at room temperature. Details of the optical cell and the photolysis apparatus have been described by Berge.[10] Under our conditions the solutions were irradiated for slightly less than 1 h to achieve conversion of ca. 5%.

Immediately after photolysis, the cell was depressurized and refrigerated at −5 °C for ca. 15 min to minimize loss of the volatile reaction products when the cell was opened. After opening, 1-μL injections of the reaction mixture were analyzed with a Varian Aerograph Series 1400 flame-ionization GLC in conjunction with a 30 ft × $^1/_8$ in. column containing 20% SF-96 on 60/80 firebrick at 90 °C. Solutions of authentic samples of 2-methylpropane, 2-methylpropene, and 2,2,3,3-tetramethylbutane were used to calibrate the column and peak areas were measured with a disc integrator.

Acknowledgment. Support by the National Science Foundation and the award of a University of California, Riverside, minigrant to M.E.F. are gratefully acknowledged. We also thank Dr. H. Schuh for helpful discussions and Dr. C. Berge for experimental assistance.

Registry No. Di-*tert*-butyl ketone, 815-24-7; *tert*-butyl radical, 1605-73-8.

(7) From Table I we have calculated and plot $[R(+H)/RR]_P/[R(+H)/RR]_{34atm}$; from Table II we have calculated and plot $[R(+H)/RR]_{n\text{-alkane}}/[R(+H)/RR]_{n\text{-octane}}$.

(8) While the internal pressure of *n*-octane at atmospheric pressure is substantially greater than 1 atm, this solvent system is our reference point, and, thus, values of ΔP_i (Table II) are correctly plotted along with values of external pressure (Table I).

(9) Dubois, J. E.; Bauer, P. *J. Am. Chem. Soc.* **1976**, *98*, 6993.

(10) Berge, C. T. Ph.D. Dissertation, University of California, Riverside, CA, 1979.

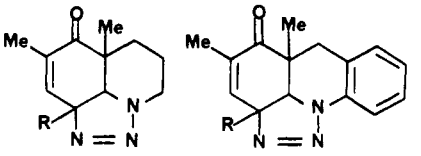
Photochemical Retro-Diels–Alder Reaction. Vinylketene Formation by Stereospecific Triazole Elimination

Arthur G. Schultz* and Sun Ok Myong

Department of Chemistry, Rensselaer Polytechnic Instutute, Troy, New York 12181

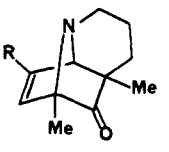
Received December 7, 1982

We have described the preparation of triazolines of type **1** and **2** by intramolecular azide–olefin cycloaddition from the appropriate 6-(3-azidopropyl)-2,4-cyclohexadien-1-one or 6-[*o*-azidobenzyl]-2,4-cyclohexadien-1-one. Triazolines **1a**, **1b**, and **2b** are excellent substrates for a new photochemical elimination–rearrangement to 2-azatricyclo-[4.4.0.0^{2,8}]decenones **3a**, **3b**, and **4b**, respectively. This two-step sequence provides a method for accomplishing the synthetic equivalence of an intramolecular cycloaddition between a diene and a nitrene.[1]

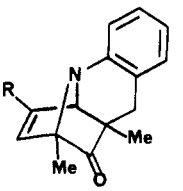


1a, R = Me
b, R = *t*-Bu

2a, R = Me
b, R = *t*-Bu



3a, R = Me
b, R = *t*-Bu



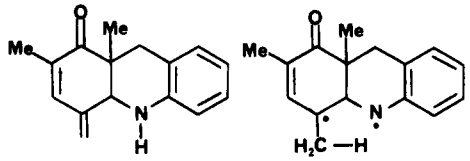
4a, R = Me
b, R = *t*-Bu

In marked contrast to **1a**, triazoline **2a** undergoes a different photorearrangement to give dienone **5** as the major reaction product.[1] Apparently diradical **6**, generated

(1) Schultz, A. G.; Dittami, J. P.; Myong, S. O.; Sha, C.-K. *J. Am. Chem. Soc.* **1983**, *105*, 3273.

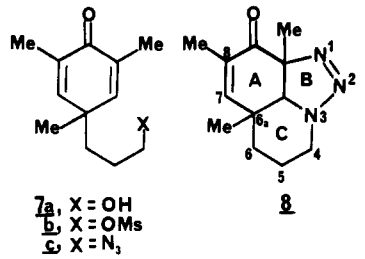
0022-3263/83/1948-2432$01.50/0

by photochemical elimination of molecular nitrogen from **2a**, undergoes preferential H-atom transfer from the C-(4)-methyl substituent to give **5**; radical recombination to give the azatricyclodecenone **4a** occurs to a minor extent.



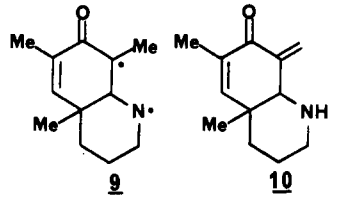
5 **6**

We wondered if the difference in photoreactivity between **1a** and **2a** is a consequence of the aromatic nucleus present in **2a**. To provide additional information regarding the mechanism of triazoline photorearrangements, we elected to prepare triazoline **8**. Photochemical elimination of N_2 from **8** would give diradical **9**, in which radical recombination of the type observed in the conversion of **1a** into **3a** is structurally impossible. We expected that hydrogen transfer in **9** would occur to give dienone **10**. The overall two-step conversion of azide **7c** to **10** could be of synthetic interest.



7a, X = OH
b, X = OMs
c, X = N_3

8



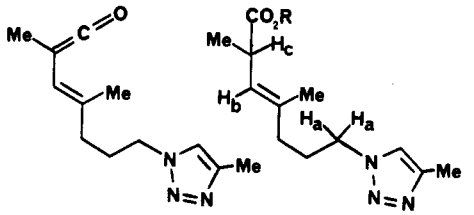
9 **10**

Results and Discussion

Triazoline **8** is prepared from 4-(3-hydroxypropyl)-2,4,6-trimethyl-2,5-cyclohexadien-1-one (**7a**)[2] by (a) conversion to mesylate **7b**, (b) treatment of **7b** with sodium azide in DMF to give **7c**, and (c) intramolecular azide–olefin cycloaddition by refluxing a solution of **7c** in benzene. Triazoline **8** is an easily purified crystalline material displaying a sharp melting range, a satisfactory elemental analysis of C, H, and N, and appropriate spectroscopic properties.

Brief irradiation of **8** in methanolic solution using a 366-nm light source gives triazole methyl ester **12a** in 80% isolated yield. The structure of **12a** was determined primarily by a high-resolution mass measurement (m/e 251.1649; calculated for $C_{13}H_{21}O_2N_2$ 251.1630), strong IR absorption at 1732 cm^{-1}, and a ^1H NMR spectrum compatible with the assigned structure. *E* stereochemistry for the olefinic bond in **12a** was revealed by a NOE experiment[3] (see Experimental Section).

Irradiation of **8** in benzene solution gives a mixture of products, which on chromatographic separation results in isolation of carboxylic acid **12b**. On the other hand, treatment of the photoreaction mixture with methanol produces methyl ester **12a**, which can be isolated in 33% yield. Complete characterization of photoreactions performed in aprotic solvents will require additional study.



11 **12a**, R = Me
b, R = H

Thus, the photochemistry of **8** is dominated by the cyclohexenone chromophore rather than reactions characteristic of triazolines. We presume that the photoexcited state of **8** experiences a retro-Diels–Alder reaction[4] to give vinylketene **11**. In benzene, the reactivity of **11** is complex, but in methanol, esterification occurs to give the well-characterized triazole methyl ester **12a**. The potential for formation of the stable triazole ring[5] may be a significant factor in directing the course of the primary photoreaction from molecular nitrogen extrusion (e.g., formation of diradical **9**) to ring fragmentation.

Exclusive formation of *E*-olefin stereochemistry in **12** is of mechanistic interest. Under the photolysis conditions (e.g., 366-nm light source), we assume that olefin stereochemistry is a direct result of the ring fragmentation process and is not due to photochemical olefin isomerization.[6] While definitive spectroscopic evidence for assignment of stereochemistry in triazoline **8** is not available at this time, we note that all cis stereochemistry is most compatible with the mechanistic requirements for intramolecular azide–olefin cycloadditions (e.g., **7c** → **8**).[1] All cis stereochemistry also has been proposed for the structurally related triazolines **1** and **2**.[1]

The cis AB ring fusion in **8** forces the A ring to adopt a boatlike conformation. For ring C to adopt a chair conformation,[7] the angular methyl group at the cis AC ring fusion must occupy a conformation pseudoaxial to ring A. Of course, if the AC ring fusion has trans stereochemistry, then the AC angular methyl group must necessarily occupy an axial environment. The crucial stereochemical observation is that *in both molecular models, the C(7)–C(8) bond is very nearly antiperiplanar to the C(6)–C(6a) bond.* Thus, *E*-olefin stereochemistry in **12** (and by inference, in ketene intermediate **11**) is in accord with the principle of least motion[8] in the transition state for conversion of **8** to

(2) Corey, E. J.; Trybulski, E. J.; Melvin, L. S.; Nicolaou, K. C.; Secrist, J. A.; Lett. R; Sheldrake, P. W.; Falck, J. R.; Brunelle, D. J.; Haslanger, M. F.; Kim, S.; Yoo, S. *J. Am. Chem. Soc.* **1978**, *100*, 4618.

(3) Ohtsuru, M.; Teraoka, M.; Tori, K.; Ken'ichi, T. *J. Chem. Soc.* **1967**, 1033.

(4) Ripoll, J. L.; Rouessac, A.; Rouessac, R. *Tetrahedron* **1978**, *34*, 19.

(5) Gilchrist, T. L.; Gymer, G. E. "Advances in Heterocyclic Chemistry"; Academic Press: New York, 1974; Vol. 16, pp 33–85.

(6) Quinkert, G. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 1072.

(7) Models of **8** have been constructed with sp^2 hybridization for N(3). In this way ring C can adopt a chair conformation analogous to cyclohexanone. With regard to this construction, we note the X-ray structural studies of Green, A. *Chem. Ber.* **1973**, *106*, 288, on 1-(4-methyl-1-pyrazolin-3-yl)-5,5-bis(trifluoromethyl)-Δ^2-1,2,3-triazoline, which indicate a near planar arrangement of the triazoline ring atoms and the substituent at the trisubstituted N atom. However, the triazoline ring in 1,4-dimethyl-5-ethyl-5-hydroxy-Δ^2-1,2,3-triazoline has been shown by X-ray analysis to be puckered with the hydroxyl group pseudoaxial and the *N*-methyl group pseudoequatorial; Kaas, K. *Acta Crystallogr., Sect. B* **1973**, *29*, 1458. This conformational preference has been ascribed to the anomeric effect: Olsen, E. *Acta. Chem. Scand., Ser. B* **1974**, *28*, 425. In the absence of additional information, the planar model for N(3) in **8** would seem the more reasonable.

(8) Hine, J. *J. Org. Chem.* **1966**, *31*, 1236. Tee, O. S.; Yates, K. *J. Am. Chem. Soc.* **1972**, *94*, 3074 and references cited in both of these papers.

11 by a retro-Diels–Alder process.

These discoveries help define the scope of triazolene photoreactivity and we intend to study the generality and utility of this process in related systems. Photochemical ketene formation of type 8 → 11 may have value in photoresist chemistry and photoaffinity labeling techniques.

Experimental Section

General Procedures. ^1H and ^{13}C NMR spectra were recorded on a Varian XL-200 spectrometer. IR spectra were obtained from either a Perkin-Elmer 137b or 298 spectrometer and UV spectra were obtained from a Perkin-Elmer 552 spectrometer. High-resolution mass measurements were performed at the University of California at Santa Barbara. Microanalyses were carried out by Spang Microanalytical Laboratory, Eagle Harbor, MI, and Galbraith Laboratories, Knoxville, TN.

4-[3-(Mesyloxy)propyl]-2,4,6-trimethyl-2,5-cyclohexadien-1-one (7b). The alcohol **7a** (0.22 g, 1.2 mmol) in dry methylene chloride (6 mL) was treated with triethylamine (0.25 mL, 1.8 mmol) and methanesulfonyl chloride (0.15 g, 1.3 mmol) at 0 °C for 15 min. Reaction workup as described by Crossland et al.[9] gave an oil (0.34 g) that was purified by flash chromatography (silica gel, 50% ether in hexane) to give mesylate **7b** (0.25 g, 78%): IR (film) 1670, 1640, 1355, 1180 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (s, 3 H), 1.38–1.75 (m, 4 H), 1.81 (s, 6 H), 3.00 (s, 3 H), 4.16 (t, 2 H, J = 6 Hz), 6.52 (s, 2 H).

4-(3-Azidopropyl)-2,4,6-trimethyl-2,5-cyclohexadien-1-one (7c). To a solution of the mesylate **7b** (0.23 g, 0.86 mmol) in DMF (5 mL) was added sodium azide (0.07 g, 1.0 mmol) and the reaction mixture was stirred at room temperature for 50 h. After filtration of the reaction mixture, the filtrate was concentrated in vacuo and the residue was dissolved in ether. The ether layer was washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo to afford **7c** (0.19 g, 95%). ^1H NMR analysis (200 MHz) indicated that **7c** was of sufficient purity to be used directly; an analytical sample of **7c** was prepared by flash chromatography (silica gel; 18% ethyl acetate in hexane), but an acceptable analysis could not be obtained. **7c**: IR (film) 2100, 1668, 1632 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.21 (s, 3 H), 1.20–1.50 (m, 2 H), 1.60–1.80 (m, 2 H), 1.90 (s, 6 H), 3.32 (t, 2 H, J = 6.5 Hz), 6.51 (s, 2 H).

5,6,6a,9,9a,9b-Hexahydro-9-oxo-6a,8,9a-trimethyl-4*H*-1,2,3-triazolo[4,5,1-*ij*]quinoline (8). A solution of azide **7c** (0.19 g, 0.87 mmol) in benzene (5 mL) was refluxed for 36 h. Evaporation of solvent gave an oil (0.18 g); chromatography of a portion of the oil (41 mg) on silica gel (80% ether in hexane) gave triazoline **8** (R_f 0.3, 27 mg, 66%) and azide **7c** (R_f 0.6, 7 mg, 17%). The triazoline **8** was recrystallized from ether: mp 105–106 °C; IR (film) 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.16 (s, 3 H), 1.72 (s, 3 H), 1.81 (d, 3 H, J = 1.4 Hz), 1.37–1.96 (m, 4 H), 3.11 (d, 1 H, J = 2.4 Hz), 3.29 (br d, 1 H, J = 12 Hz), 4.31 (br d, 1 H, J = 12 Hz), 6.34 (dd, 1 H, J = 2.4, 1.4 Hz); ^{13}C NMR ($CDCl_3$) δ 16.92 (q), 22.81 (q), 23.05 (q), 29.29 (t), 34.12 (s), 37.81 (t), 46.27 (t), 68.09 (d), 83.22 (s), 138.76 (s), 149.79 (d), 190.41 (s); UV (MeOH) λ_{max} 204 nm (23.99 × 10^3), 236 (1.13 × 10^4), 2.80 (2.21 × 10^3), 3.50 (4.77 × 10^2).

Anal. Calcd for $C_{12}H_{16}N_3O$: C, 66.03; H, 7.39; N, 19.25. Found: C, 65.90; H, 7.78; N, 19.06.

Photolysis of Triazoline 8. A solution of triazoline **8** (16 mg, 0.07 mmol) in methanol (10 mL) was irradiated under an argon atmosphere for 65 min. A water-cooled Hanovia 679A36 450-W mercury arc lamp fitted with Corning color filters 0-52 and 7-54 was employed as the 366-nm light source. The solution was concentrated in vacuo to give an oil (19 mg) that was purified by flash chromatography (silica gel, ether) to give triazole **12a** (14 mg, 80%): bp, 140 °C (0.6 mm); exact mass m/e 251.1649 (calcd for $C_{13}H_{21}O_2N_2$ 251.1630); IR (film) 3120, 1732, 1555, 1210, 1170, 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.21 (d, 3 H, J = 7.1 Hz), 1.66 (d, 3 H, J = 0.9 Hz), 1.96–2.08 (m, 4 H), 2.36 (s, 3 H), 3.26–3.48 (m, 1 H), 3.68 (s, 3 H), 4.38–4.16 (m, 2 H), 5.22 (d, 1 H, J = 9.1 Hz), 7.27 (q, 1 H, J = 0.9 Hz); UV (MeOH) λ_{max} 207 nm (ϵ 5.24 × 10^3).

A degassed sample of **12a** in $CDCl_3$ solution was subjected to a ^1H NMR double-resonance experiment; pulse angle = 60°, delay time = 10 s, acquisition time = 3 s, decoupler mode = YYN (gated decoupler off during data acquisition irradiation centered at δ 1.66 (vinyl methyl group) resulted in a 21% enhancement of the intensity of the resonance due to H_c and only a 2% enhancement of H_a and 6% enhancement of H_b. Furthermore, irradiation centered at δ 2.03 (vinyl methylene group) resulted in a 19% enhancement of H_b, a 4% enhancement of H_a, and no effect on H_c.

Photolysis of Triazoline 8 in Benzene Solution. A solution of triazoline **8** (77 mg, 0.35 mmol) in dry, spectrophotometric grade benzene (20 mL) was irradiated under an argon atmosphere with Pyrex-filtered light for 30 min. Evaporation of solvent and flash chromatography (silica gel, 50% ethyl acetate in hexane to pure ethyl acetate) gave **12b** as an oil (27 mg, 28%): IR (film) 3700–2200, 3120, 1720, 1555, 1215, 1067 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26 (d, 3 H, J = 7 Hz), 1.70 (d, 3 H, J = 1 Hz), 1.96–2.20 (m, 4 H), 2.36 (s, 3 H), 3.20–3.74 (m, 1 H), 4.00–4.70 (m, 2 H), 5.23 (d, 1 H, J = 10 Hz), 7.27 (q, 1 H, J = 1.0 Hz). This oil was soluble in 1 N sodium hydroxide solution. Treatment of **12b** (27 mg) with excess diazomethane in ether gave triazole methyl ester **12a** (27 mg).

In a separate experiment, triazoline **8** (14 mg) was irradiated in benzene (4 mL) as previously described. The resulting light-yellow solution was concentrated to one-third the original volume and an IR spectrum was recorded; IR (benzene) 1800, 1743 cm^{-1}. To this solution was added methanol (2 mL) and the resulting solution was stirred for 8 h at room temperature. Evaporation of solvent and chromatography (silica gel, 50% ethyl acetate in hexane) gave triazole methyl ester **12a** (5 mg, 33%).

Acknowledgment. This work was supported by the National Institute of General Medical Science (GM 26568). Assistance in the acquisition of NMR data by Dr. Herbert M. Schwartz is gratefully acknowledged. NMR spectra were recorded on a Varian XL-200 instrument purchased with funds provided, in part, by a National Science Foundation department instrumentation grant.

Registry No. **7a**, 67471-86-7; **7b**, 86013-52-7; **7c**, 86013-53-8; **8**, 86013-54-9; **11**, 86013-55-0; **12a**, 86013-56-1; **12b**, 86013-57-2.

(9) Crossland, R. K.; Servis, K. L. *J. Org. Chem.* **1970**, *35*, 3195.

Phosphoranylidenehydrazones as in Situ Sources of Diazo Compounds: A Facile Synthesis of Aryl-Substituted Benzoylcyclopropanes

Frank S. Guziec, Jr.*

Department of Chemistry, New Mexico State University, Las Cruces, New Mexico 88003

Frederick A. Luzzio[1]

Department of Chemistry, Tufts University, Medford, Massachusetts 02155

Received January 8, 1982

Diazo compounds are extremely important reagents in organic synthesis.[2] While a great variety of methods are currently available for the preparation of diazo compounds,[3] the instability of these materials and difficulties in handling them may limit their utility in a number of synthetic transformations. In the course of current synthetic work using acyl cyclopropanes as key intermediates we sought a method of generating diazo compounds in situ under neutral conditions. It appeared that one possible

(1) This work is taken in part from the Ph.D. dissertation of F.A.L., Tufts University, 1982.

(2) Wulfman, D. S.; Linstrumelle, G.; Copper, C. F. In "The Chemistry of Diazonium and Diazo Groups"; Patai, S., Ed.; Wiley: London, 1968; pp 821–956 and references therein.

(3) Regitz, M. In "The Chemistry of Diazonium and Diazo Groups"; Patai, S., Ed.; Wiley: London, 1968; pp 659–708 and references therein.

(4) Kosolapoff, G. M.; Maier, L. "Organophosphorus Compounds"; Wiley: New York, 1972; Vol. 3, pp 92–93 and references therein.

0022-3263/83/1948-2434$01.50/0