NMR ($CDCl_3$) δ 7.57–7.51 (m, 2 H), 7.49–7.41 (m, 1 H), 7.33–7.25 (m, 2 H), 7.12 (s, 5 H), 4.15–3.50 (m, 7 H), 1.30 (t, J = 7.0 Hz, 3 H), 1.03 (t, J = 7.0 Hz, 3 H).

Diethyl (2-Phenylethyl)phosphonate.[25] $PhCH_2CH_2P$ was prepared from the reaction of styrene and potassium diethyl phosphite. Styrene (1 mmol) was added to the solution of diethyl phosphite ion (10 mmol) generated by t-BuOK in Me_2SO (10 mL) under a nitrogen atmosphere. The mixture was stirred in the dark at 50 °C for 22 h, poured into water, and extracted with ether. The ether extract was washed twice with water, dried over anhydrous sodium sulfate, and concentrated under vacuum. GLC analysis of the mixture showed a 68% yield of the phosphonate and 21% of the unreacted styrene. The phosphonate, $PhCH_2CH_2P$, was also obtained from the reaction of (*E*)-(2-phenylethenyl)mercury chloride and potassium diethyl phosphite under photolysis or in the dark but in lower yield as shown in Table V. In a number of experiments where potassium *tert*-butoxide contaminated with potassium hydroxide was used to generate the diethyl phosphite ion, the photoreactions gave diethyl (*E*)-(2-phenylethenyl)phosphonate (**1j**) instead of the saturated product. $PhCH_2CH_2P$: GCMS m/z (relative intensity) 242 (M^+, 37), 138 (100), 111 (96), 110 (29), 105 (28), 104 (65), 91 (19), 83 (27), 82 (53), 77 (24); ^1H NMR ($CDCl_3$) δ 7.33–7.24 (m, 2 H), 7.23–7.14 (m, 3 H), 4.15–4.00 (m, 4 H), 2.98–2.83 (m, 2 H), 2.15–1.93 (m, 2 H), 1.31 (t, J = 7.0 Hz, 6 H).

Diethyl (*E*)-(2-Phenylethenyl)phosphonate (1j).[26-28] The β-styryl phosphonate was obtained from (*E*)-(2-phenylethenyl)-mercury chloride and potassium diethyl phosphite generated from potassium hydroxide. The phosphite anion was generated by stirring diethyl phosphite (1.0 mmol) and potassium hydroxide (1.0 mmol) in Me_2SO (10 mL) in a Pyrex tube equipped with a rubber septum. After the mixture was stirred for 5 min, the mercurial (0.5 mmol) was added, and the mixture was deoxygenated for 5 min with a stream of nitrogen. The mixture was irradiated with a 275-W sunlamp placed ca. 20 cm from the reaction vessel. After the photolysis, the mixture was decanted from the shiny mercury bead formed during the reaction, poured into water, and extracted with ether. The ether extract was washed twice with water, dried over anhydrous sodium sulfate, and concentrated under vacuum. The mixture consisted of the phosphonate in 70% yield, styrene in 8% yield, and $PhCH(P)CH_2P$ in 13% yield. The vinyl phosphonate had the following properties: GCMS m/z (relative intensity) 240 (M^+, 12), 167 (13), 147 (17), 131 (100), 104 (20), 103 (12), 102 (15), 77 (17); ^1H NMR ($CDCl_3$) δ 7.60–7.44 (m, 2 + 1 H), 7.43–7.26 (m, 3 H), 6.26 (t, J = 17.5 Hz, 1 H), 4.20–4.05 (m, 4 H), 1.35 (t, J = 7.0 Hz, 6 H).

Diethyl (1-Phenylethenyl)phosphonate (5).[28,29] The α-styryl phosphonate was prepared from the reaction of **4** and potassium *tert*-butoxide. To the solution of 0.5 mmol of **4** in 10 mL of dry Me_2SO was added 0.6 mmol of t-BuOK. The resulting yellow mixture was stirred at room temperature for 5 min and then poured into water. The product was extracted with ether, washed with water, dried over anhydrous sodium sulfate, and concentrated. The mixture contained 87% of **5**: GCMS m/z (relative intensity) 240 (M^+, 45), 212 (41), 196 (21), 168 (20), 131 (38), 130 (70), 129 (37), 104 (59), 103 (100), 102 (22), 77 (50); ^1H NMR ($CDCl_3$) δ 7.60–7.05 (m, 5 H), 6.33 (dd, $J_{HP(cis)}$ = 21.9 Hz, J_{HH} = 1.50 Hz, 1 H), 6.15 (dd, $J_{HP(trans)}$ = 45.7 Hz, J_{HH} = 1.50 Hz, 1 H), 4.20–3.98 (m, 4 H), 1.28 (t, J = 7.0 Hz, 6 H).

Diethyl (2-Oxo-2-phenylethyl)phosphonate.[30] The keto phosphonate was obtained from **6** (0.3 mmol) and t-BuOK (0.4 mmol) in 5 mL of dry Me_2SO. The mixture was stirred at room temperature for 30 min and worked up by the usual procedure to give a mixture that contained the keto phosphonate in 78% yield and unreacted starting material. The keto phosphonate had the following properties: GCMS m/z (relative intensity) 256 (M^+, 5), 146 (16), 120 (23), 105 (100), 77 (41); ^1H NMR ($CDCl_3$) δ 8.03–7.98 (m, 2 H), 7.60–7.40 (m, 3 H), 4.20–4.05 (m, 4 H), 3.62 (d, J = 22.6 Hz, 2 H), 1.27 (t, J = 7.0 Hz, 6 H).

Diethyl (2,2-Diphenylethenyl)phosphonate (2j). The reaction of $Ph_2C{=}CHHgBr$ with $[(EtO)_2P(O)]_2Hg$ to form **2j** was reported previously.[5]

Diethyl (Phenylethynyl)phosphonate (3j). The reaction of $(PhC{\equiv}C)_2Hg$ with $[(EtO)_2P(O)]HgCl$ to form **3j** was reported previously.[5]

Acknowledgment. The relative reactivities of the β-styryl chloride and bromide were determined by V. Rongkavilit and T. White.

Registry No. (*E*)-**1**, Q = t-Bu, 3846-66-0; (*Z*)-**1**, Q = t-Bu, 3740-05-4; (*E*)-**1a**, 36525-03-8; (*E*)-**1c**, 66680-88-4; (*E*)-**1d**, 16212-06-9; (*E*)-**1e**, 40110-66-5; (*E*)-**1f**, 7214-53-1; (*E*)-**1g**, 4110-77-4; (*E*)-**1h**, 588-72-7; (*E*)-**1i**, 42599-24-6; (*Z*)-**1i**, 57918-63-5; (*E*)-**1j**, 20408-33-7; **1j** dihydro derivative, 54553-21-8; **2**, Q = t-Bu, 23586-64-3; **2a**, 24522-19-8; **2b**, 67341-86-0; **2c**, 91083-76-0; **2d**, 26189-62-8; **2h**, 13249-58-6; **2i**, 19997-66-1; **2j**, 78462-91-6; **3**, Q = t-Bu, 4250-82-2; **3c**, 3757-88-8; **3d**, 5324-64-1; **3f**, 35460-31-2; **3i**, 932-88-7; **3j**, 3450-67-7; **4**, 119337-14-3; **5**, 25944-64-3; **6**, 2519-12-2; $PhCH(Bu\text{-}t)CH_2SO_2Ph$, 113303-16-5; $PhCH(Bu\text{-}t)CH_2SPh$, 113303-14-3; $PhC(Bu\text{-}t){=}CHSPh$, 113303-15-4; (*E*)-$PhC(Bu\text{-}t){=}CHSO_2Ph$, 119337-13-2; (*Z*)-$PhC(Bu\text{-}t){=}CHSO_2Ph$, 119337-15-4; $PhCH{=}CH_2$, 100-42-5; $(PhCH{=}CH)_2Hg$, 64984-50-5; $Ph_2C{=}CH_2$, 530-48-3; $PhCOCH_2P(O)(OEt)_2$, 3453-00-7.

(25) Coutrot, P.; Youssefi-Tabrizi, M.; Grison, C. *J. Organomet. Chem.* **1986**, *316*, 13.
(26) Hirao, T.; Masunaga, T.; Ohshiro, Y.; Agawa, T. *Tetrahedron Lett.* **1980**, *21*, 3595.
(27) Teulade, M.-P.; Savignac, P.; Aboujaude, E. E.; Lietge, S.; Collignon, N. *J. Organomet. Chem.* **1986**, *304*, 283.
(28) Tavs, P.; Weitkamp, H. *Tetrahedron* **1970**, *26*, 5529.
(29) Krueger, W. E.; MeLean, M. B.; Rizwaniuk, A.; Maloney, J. R.; Behelfer, G. L.; Boland, B. E. *J. Org. Chem.* **1978**, *43*, 2877.
(30) Mathey, F.; Savignac, P. H. *Tetrahedron* **1978**, *34*, 649.

Photolysis of 2-Alkoxy-Δ^3-1,3,4-oxadiazolines. A New Route to Diazoalkanes

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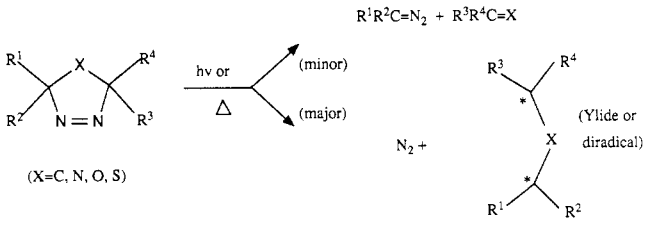
2-Alkoxy-2,5,5-trialkyl-Δ^3-1,3,4-oxadiazolines (**2**), when photolyzed in solution with 300-nm light, afford the appropriate diazoalkane (**3**) and ester (**4**) in high yield. The diazoalkanes undergo intermolecular reaction, giving rise to azines (**5**), or they can be trapped in situ with 1,3-dipolarophiles to afford cycloadducts (**7** or **11**), which can in turn be photolyzed to the corresponding cyclopropenes (**8**) and cyclopropanes (**12**), respectively.

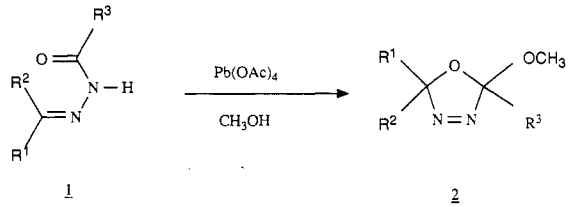
Diazo compounds are important reagents for organic synthesis.[1] Their major reactions include 1,3-dipolar cycloadditions,[2] Wolff rearrangements,[1,3] and carbene formation for cyclopropanations and single-bond insertions.[1,3]

0022-3263/89/1954-1842$01.50/0

Scheme I



Scheme II[a]



1 2

[a] **a**, $R^1 = R^2 = R^3 = CH_3$; **b**, $R^1 = R^3 = CH_3$, $R^2 = C_2H_5$; **c**, $R^1 = R^2 = C_2H_5$, $R^3 = CH_3$; **d**, $R^1 = CH(CH_3)_2$, $R^2 = R^3 = CH_3$; **e**, $R^1 = C(CH_3)_3$, $R^2 = R^3 = CH_3$; **f**, $R^1R^2 = (CH_2)_4$, $R^3 = CH_3$; **g**, $R^1R^2 = (CH_2)_5$, $R^3 = CH_3$; **h**, $R^1 = R^2 = CH_3$, R^3 = cyclopropyl; **i**, R^1 = cyclopropyl, $R^2 = R^3 = CH_3$; **j**, $R^1 = R^2 = CH_3$, $R^3 = C_6H_5$.

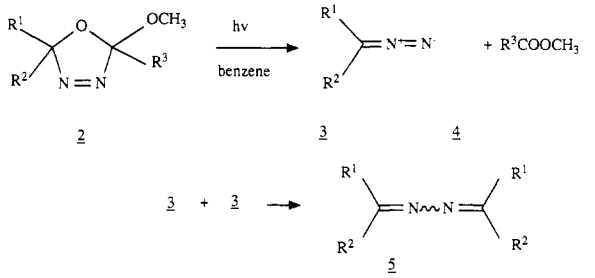
The most common methods for the preparation of diazoalkanes[4] involve either oxidation of the appropriate hydrazones or base-promoted cleavage of tosylhydrazones or of *N*-alkyl-*N*-nitroso compounds such as urethanes, ureas, or carboxamides.[4,5] Although a large number of diazo compounds have been synthesized by those or other[4,5] methods, very few dialkyl diazomethanes ($R^1R^2CN_2$) have been utilized, probably because of difficulty in purifying those of higher molecular weight safely, as for example, by codistillation with a solvent such as ether.[6]

Thermolysis or photolysis of pyrazolines or their analogues involves cycloreversion to N_2 as the major fragmentation pathway,[7] in general (Scheme I).

We now report that photolysis of the readily accessible[8] 2-alkoxy-2,5,5-trialkyl-Δ^3-1,3,4-oxadiazolines (**2**) leads to remarkably clean fragmentation to diazoalkanes ($R^1R^2CN_2$) and esters (R^3COOR^4), in sharp contrast to the N_2-forming photofragmentation[9] of other Δ^3-1,3,4-oxadiazolines.

Compounds **2**, prepared by oxidation of *N*-acylhydrazones of ketones (**1**) with $Pb(OAc)_4$ in methanol[8] (Scheme II), were nearly pure compounds (>95%), except for cis/trans isomerism in appropriate cases, as judged by

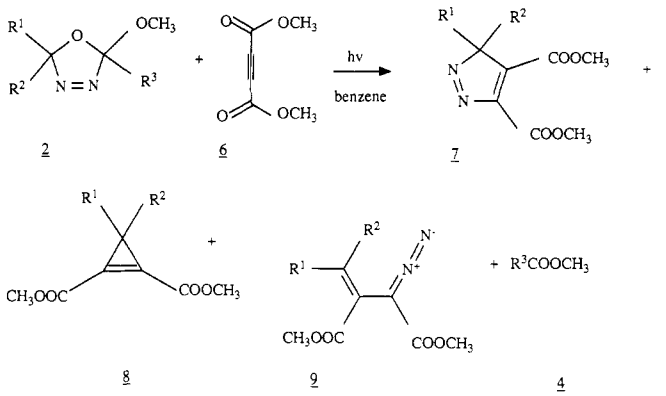
Scheme III



2 3 4

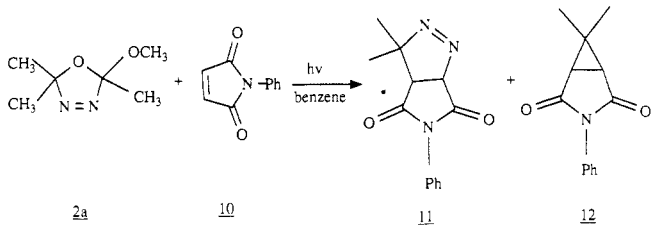
3 + 3 → 5

Scheme IV



2 6 7 8 9 4

Scheme V



2a 10 11 12

^{1}H NMR spectral data at 500 MHz. Those spectra, together with infrared scans for the detection of carbonyl groups, were particularly useful for establishing the low levels (<5%) of the most likely volatile impurity (the analogous 2-acetoxyoxadiazoline) in each case. Analysis (CHN) of a representative sample of **2b** (not purified beyond distillation) was satisfactory.

The identities of the oxidation products, as members of the family **2**, was confirmed by ^{1}H NMR and UV spectroscopy. All of them have two UV maxima, with λ_{max} (cyclohexane) between 218 and 230 nm ($\log \epsilon = 2.26 \pm 0.05$) assigned to the π–π^* transition and between 318 and 326 nm ($\log \epsilon = 2.33 \pm 0.15$) assigned to the n–$\pi^*$ transition. Mass spectrometric molecular weights could not be obtained for **2** because the molecular ion signal was indistinguishable from background.

Yields, isomer ratios, and ^{1}H NMR spectral data of the oxadiazolines (**2**) are given in the Experimental Section.

Photolysis of **2** in oxygen-free benzene with 300-nm light, in a Rayonet apparatus, resulted in rapid (15 min) development of the pink color of **3** and of a sharp band near 2020 cm^{-1} in the IR spectrum. The pink color was discharged on longer exposure (~5 h) or on standing in the dark.[10a] Products were the ester **4** and the appropriate

(1) Wulfman, D. S.; Linstrumelle, G.; Cooper, C. F. In *The Chemistry of Diazonium and Diazo Groups*; Patai, S., Ed.; Wiley: Chichester, 1978; Part 2, pp 821–976.

(2) (a) Regitz, M.; Heydt, H. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; pp 393–558. (b) Huisgen, R. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; pp 1–176.

(3) Whittaker, B. In *The Chemistry of Diazonium and Diazo Groups*; Patai, S., Ed.; Wiley: Chichester, 1978; Part 2, pp 593–644.

(4) Regitz, M. In *The Chemistry of Diazonium and Diazo Groups*; Patai, S., Ed.; Wiley: Chichester, 1978; Part 2, pp 659–708.

(5) Regitz, M.; Mass, G. In *Diazo Compounds. Properties and Synthesis*; Academic Press; Inc.: Orlando, 1986; Chapters 5–13.

(6) Codistillation with ether is generally used for the purification of diazoalkanes of low molecular weight. For an example, see: Andrews, S. D.; Day, A. C.; Raymond, P.; Whiting, M. C. *Org. Synth.* **1970**, *50*, 27–30.

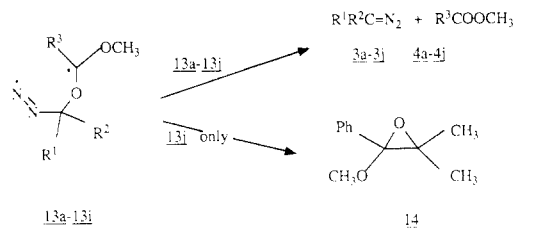
(7) (a) Maier, H.; Zeller, K.-P. *Angew, Chem., Int. Ed. Engl.* **1977**, *16*, 835–851. (b) Bianchi, G.; Micheli, C. D.; Gandolfi, R. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 721–738. (c) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99–150. See ref 7b and 7c for exceptions, many of them involving a bicyclic starting material.

(8) (a) Warkentin, *J. Synthesis* **1970**, 279–286. (b) Bēkhazi, M.; Warkentin, J. *J. Am. Chem. Soc.* **1981**, *103*, 2473–2474. (c) Bēkhazi, M.; Warkentin, J. *J. Am. Chem. Soc.* **1983**, *105*, 1289–1292.

(9) Hoffmann, R. W.; Luthardt, H. J. *Chem. Ber.* **1968**, *101*, 3861–3871.

(10) (a) Most of the bleaching is the result of the well-known thermal reaction, presumably, because the absorption maxima of diazoalkanes (λ_{max} ca. 220 and 440 nm) are well separated from lamps' maximum output. (b) A single azine from **2a**, **2c**, and **2e**. Three isomeric azines (by ^{1}H NMR and GC) from **2b** and **2d**, as expected. Authentic samples for comparison of gc retention times and ^{1}H NMR spectra were prepared.[11]

Scheme VI



azine **5**;[10] both were formed in essentially quantitative yields (NMR) (Scheme III). The oxadiazoline **2j** also afforded 3,3-dimethyl-2-methoxy-2-phenyloxirane (**14**) (vide infra), in ca. 5% yield.

Diazoalkane intermediates were demonstrated by photolysis of **2a–g** in benzene containing dimethyl acetylenedicarboxylate (**6**) in 20% excess. Esters **4** (>90%) and products of cycloaddition (**7**)[12] (50–70%) were obtained, together with cyclopropenes **8** and, in trace amounts, diazoesters **9**[13] (scheme IV).

Coproducts **8** and **9**, as well as excess **4**, were readily separated from **7** by centrifugal chromatography. Either prolonged photolysis of **2** and **6** or additional irradiation of pure **7** furnished **8** in ca. 70% yield. Similarly, photolysis of **2a** and *N*-phenylmaleimide (**10**) gave **11** and **12** in 1:1 ratio (80% yield). Further photolysis converted essentially all of the **11** to **12**[14] (Scheme V).

Neither trans piperylene (0.1 M) nor benzophenone (0.03 M) had any noticeable effect on the rate or on the products of photolysis of **2a** in C_6D_6. Presumably the oxadiazolines decompose from a singlet excited state, via diradical **13**.[15] The fact that **2h** afforded methyl cyclopropanecarboxylate cleanly indicates that β-scission of the diradical **13h** to form diazoalkane and ester is faster than β-scission to open the cyclopropane ring. The former β-scission must also be significantly faster than the loss of N_2, as the high yields of the ester indicate. Only in the case of **2j** was β-scission to the carbonyl ylide, the precursor of the oxirane **14** (5%), competitive (Scheme VI).

Compounds **2** are thus convenient precursors of diazoalkanes, which can be released safely and cleanly over a range of temperatures in a variety of solvents. They should be particularly useful for in situ reactions of diazoalkanes with substrates that are not strongly absorbing near 300 nm. Recent work directed toward the synthesis of *cis*-pyrethroids[16] or bicyclobutanes,[17] for example, but confined to diazomethane or diazopropane precursors, serves to bring the potential of the present source of diazoalkanes into focus.

Experimental Section

General. Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected. Proton NMR spectra were recorded on a Bruker AM-500 or a EM-390 spectrometer with TMS or residual CH signals on $CDCl_3$ or C_6D_6 as internal standards. ^{13}C NMR spectra were recorded with the Bruker AM-500 machine. Infrared spectra (IR), obtained with a Perkin-Elmer model 283 instrument, are reported in wavenumbers (cm^{-1}), calibrated against the 1601.4-cm^{-1} band of polystyrene. Centrifugal chromatography was carried out on silica (Merck Kieselgel $60PF_{254}$) coated plates (coating 2 mm thick) spinning in a Chromatotron Model 17924T apparatus. Plastic-backed, Merck Kieselgel $60F_{254}$, 0.2-mm silica plates were used for analytical thin-layer chromatography (TLC). Commercially available solvents and reagents were purified by standard procedures.

2-Acetylhydrazones of Ketones (1). Most of these were prepared by refluxing solutions of equimolar amounts of acetylhydrazine and of the appropriate ketone in benzene until all water was removed (Dean–Stark trap, 5–15 h). The solvent was removed under vacuum, and the residue was recrystallized. The acetyl hydrazone of pinacolone (**1e**) was obtained by refluxing a solution of acetylhydrazine in excess pinacolone for 20 h. Excess pinacolone was distilled off, and the residue was recrystallized. Although most of the acetylhydrazones were known compounds, the ^1H NMR spectral data of most of them had not been reported and are therefore included below.

1-Acetyl-2-(2-propylidene)hydrazine (1a): 75% yield; mp 139–141 °C (Et_2O) (lit.[18] mp 140 °C); ^1H NMR (90 MHz, $CDCl_3$) δ 9.20 (br s, 1 H, NH), 2.20 (s, 3 H, Ac), 1.97 (s, 3 H), 1.87 (s, 3 H).

1-Acetyl-2-(2-butylidene)hydrazine (1b): 72% yield; mp 82–83 °C (Et_2O) (lit.[18] mp 82 °C); ^1H NMR (90 MHz, $CDCl_3$) δ 9.30 (s, 1 H, NH), 2.32 (q, J = 7.5 Hz, 2 H), 2.30 (s, 3 H, Ac), 1.91 (s, 3 H), 1.13 (t, J = 7.5 Hz, 3 H).

1-Acetyl-2-(3-pentylidene)hydrazine (1c): 70% yield; mp 60–62 °C ($EtOH/Et_2O$) (lit.[18] mp 59 °C); ^1H NMR (90 MHz, $CDCl_3$) δ 9.05 (br s, 1 H, NH), 2.28 (s, 3 H, Ac), 2.28 (q, J = 7.5 Hz, 4 H), 1.12 (t, J = 7.5 Hz, 6 H).

1-Acetyl-2-(3-methyl-2-butylidene)hydrazine (1d): 63% yield; mp 49–50 °C ($MeOH/H_2O$); ^1H NMR (90 MHz, $CDCl_3$) δ 8.55 (br s, 1 H, NH), 2.46 (sept, J = 6.8 Hz, 1 H), 2.30 (s, 3 H, Ac), 1.87 (s, 3 H), 1.13 (d, J = 6.8 Hz, 6 H); MS (EI) m/e 142.1097 calcd for $C_7H_{14}N_2O$ 142.1103).

1-Acetyl-2-(3,3-dimethyl-2-butylidene)hydrazine (1e): 75% yield; mp 80–82 °C; ^1H NMR (90 MHz, $CDCl_3$) δ 8.90 (br s, 1 H, NH), 2.22 (s, 3 H, Ac), 1.78 (s, 3 H), 1.10 (s, 9 H); MS (EI) m/e 156.1273 (calcd for $C_8H_{16}N_2O$ 156.1259).

1-Acetyl-2-(1-cyclopentylidene)hydrazine (1f): 73% yield; mp 121–123 °C (lit.[19] mp 118–120 °C); ^1H NMR (90 MHz, $CDCl_3$) δ 8.73 (br s, 1 H, NH), 2.62–2.05 (m) with 2.30 (s) superimposed, total 7 H, 2.03–1.63 (m, 4 H).

1-Acetyl-2-(1-cyclohexylidene)hydrazine (1g): 75% yield; mp 120–122 °C (MeOH) (lit.[20] mp 123–124 °C).

1-(Cyclopropylcarbonyl)-2-(2-propylidene)hydrazine (1h): 70% yield; mp 120–122 °C ($Et_2O/EtOH$); ^1H NMR (90 MHz, $CDCl_3$) δ 8.80 (br s, 1 H, NH), 2.06 (s, 3 H), 1.92 (s, 3 H), 1.20–0.60 (m, 5 H); MS (EI) m/e 140.0957 (calcd for $C_7H_{12}N_2O$ 140.0947).

1-Acetyl-2-(1-cyclopropyl-1-ethylidene)hydrazine (1i): 72% yield; mp 110–112 °C; ^1H NMR (90 MHz, $CDCl_3$) δ 9.00 (br s, 1 H, NH), 2.24 (s, 3 H, Ac), 1.80 (s, 3 H), 1.85–1.50 (m, 1 H), 0.83–0.68 (m, 4 H); MS (EI) m/e 140.0944 (calcd for $C_7H_{12}N_2O$ 140.0947).

1-Benzoyl-2-(2-propylidene)hydrazine (1j): mp 127–129 °C (MeOH) (lit.[20] mp 128–131 °C).

2-Alkoxy-2,5,5-trialkyl-Δ^3-1,3,4-oxadiazolines (2). These compounds were obtained as described previously,[8c] with the exception that the temperature during addition of lead tetraacetate was kept at −10 °C. The products, which were purified by vacuum distillation, are listed below.

2-Methoxy-2,5,5-trimethyl-Δ^3-1,3,4-oxadiazoline (2a): 75% yield; bp 48–51 °C (15 mmHg).[8c]

(11) Arnal, E.; Elguero, J.; Jacquier, R.; Marzin, C.; Wylde, J. *Bull. Soc. Chim. Fr.* **1965**, 877–878.

(12) (a) Franck-Neumann, M.; Buchecker, C. *Tetrahedron Lett.* **1969**, 15–17. Franck-Neumann, M.; Miesch, M. *Tetrahedron* **1983**, *39*, 1247–1254.

(13) (a) The UV maxima of the pyrazoles (**7**) (λ_{max} ca. 245 and 380 nm (log ϵ = 2)) mean that their photolysis with 300-nm light is inefficient. Filters could presumably be used for complete protection of **7**. (b) The presence of **9** was inferred from strong infrared absorption near 2080 cm^{-1}. Palmer, G. E.; Bolton, J. R.; Arnold, D. R. *J. Am. Chem. Soc.* **1974**, *96*, 3708–3709.

(14) Corey, E. J.; Jautelat, M. *J. Am. Chem. Soc.* **1967**, *89*, 3912–3914.

(15) (a) Gassman, P. G.; Greenlee, W. J. *J. Am. Chem. Soc.* **1973**, *95*, 980–982. (b) Keppel, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 1350–1351.

(16) (a) Franck-Neumann, M.; Miesch, M.; Kempf, H. *Tetrahedron* **1987**, *43*, 845–852. (b) Franck-Neumann, M.; Miesch, M.; Kempf, H. *Tetrahedron* **1987**, *43*, 853–858.

(17) Baird, M. S.; Hussain, H. H. *Tetrahedron* **1987**, *43*, 215–224.

(18) Rohnert, H. *Z. Chem.* **1965**, *5*, 302–303.

(19) Lapidus, M.; Grant, N. H.; Alburn, H. E.; Clark, D. E.; Fletcher, H. Ger. Offen. 1,931,419 (Cl. C 07c, A 61k), 1970; *Chem. Abstr.* **1970**, *73*, 3538z.

(20) McGirk, R. H.; Cry, C. R.; Ellis, W. D.; White, E. H. *J. Org. Chem.* **1974**, *39*, 3851–3855.

5-Ethyl-2-methoxy-2,5-dimethyl-Δ^3-1,3,4-oxadiazoline (2b): 67% yield; cis:trans ratio = 1:1.8; bp 44–45 °C (1.3 mmHg); ^{1}H NMR of trans isomer (500 MHz, C_6D_6) δ 2.92 (s, 3 H, OMe), 1.64–1.51 and 1.47–1.38 (m, diasterotopic CH_2), 1.53 (s, 3 H), 1.28 (s, 3 H, C_5-Me), 0.75 (t, J = 7.5 Hz, 3 H); ^{1}H NMR of cis isomer (500 MHz, $CDCl_3$) δ 2.93 (s, 3 H, OMe), 1.82–1.71 and 1.64–1.51 (m, diastereotopic CH_2), 1.49 (s, 3 H), 1.13 (s, 3 H, C_5-Me), 0.89 (t, J = 7.5 Hz, 3 H). Chemical shifts of overlapping multiplets refer to the observed range for the mixture of isomers. The composite integral for overlapping signals was satisfactory. Anal. Calcd for $C_7H_{14}N_2O_2$: C, 53.14; H, 8.92; N, 17.71. Found: C, 53.44; H, 8.66; N, 18.19.

5,5-Diethyl-2-methoxy-2-methyl-Δ^3-1,3,4-oxadiazoline (2c): 75% yield; bp 50–52 °C (1.5 mmHg); ^{1}H NMR (90 MHz, $CDCl_3$) δ 3.30 (s, 3 H, OMe), 2.10–1.51 (m, 4 H, CH_2), 1.71 (s, 3 H), 1.10 (t, J = 7.5 Hz, 3 H), 0.92 (t, J = 7.5 Hz, 3 H).

2-Methoxy-2,5-dimethyl-5-(1-methylethyl)-Δ^3-1,3,4-oxadiazoline (2d): 75% yield; bp 54–56 °C (1.5 mmHg), cis:trans ratio = 1:2.2; ^{1}H NMR of trans isomer (500 MHz, C_6D_6) δ 2.95 (s, 3 H, OMe), 1.64 (sept, J = 6.8 Hz, 1 H), 1.55 (s, 3 H, C_2-Me), 1.24 (s, 3 H, C_5-Me), 0.95 (d, J = 6.8 Hz, 3 H), 0.78 (d, J = 6.8 Hz, 3 H); ^{1}H NMR of cis isomer (500 MHz, C_6D_6) δ 2.96 (s, 3 H, OMe), 1.71 (sept, J = 6.8 Hz, 1 H), 1.48 (s, 3 H, C_2-Me), 1.10 (d, J = 6.8 Hz, 3 H), 1.06 (s, 3 H, C_5-Me), 0.86 (d, J = 6.8 Hz, 3 H).

2-Methoxy-2,5-dimethyl-5-(2,2-dimethylethyl)-Δ^3-1,3,4-oxadiazoline (2e): 70% yield; bp 44–45 °C (0.3 mmHg); >95% trans; ^{1}H NMR (500 MHz, C_6D_6) δ 3.06 (s, 3 H, OMe), 1.57 (s, 3 H, C_2-Me), 1.28 (s, 3 H, C_5-Me), 0.92 (s, 9 H).

2-Methoxy-2-methyl-3,4-diaza-1-oxa[4.4]spironon-3-ene (2f): 70% yield; ^{1}H NMR (90 MHz, $CDCl_3$) δ 3.07 (s, 3 H, OMe), 2.40–1.65 (m, 8 H), 1.60 (s, 3 H).

2-Methoxy-2-methyl-3,4-diaza-1-oxa[4.5]spirodec-3-ene (2g): 65% yield; ^{1}H NMR (90 MHz, $CDCl_3$) δ 3.06 (s, 3 H, OMe), 2.10–1.17 (m, 10 H), 1.55 (s, 3 H).

2-Cyclopropyl-2-methoxy-5,5-dimethyl-Δ^3-1,3,4-oxadiazoline (2h): 67% yield; bp 52–53 °C (1.4 mmHg); ^{1}H NMR (90 MHz, $CDCl_3$) δ 3.19 (s, 3 H, OMe), 1.58 (s, 3 H), 1.50 (s, 3 H), 1.50–1.10 (m, 1 H), 0.70–0.30 (m, 4 H).

5-Cyclopropyl-2-methoxy-2,5-dimethyl-Δ^3-1,3,4-oxadiazoline (2i): 73% yield; bp 53–55 °C (1.4 mmHg); cis:trans ratio = 1:1.3; ^{1}H NMR of trans isomer (90 MHz, C_6D_6) δ 3.06 (s, 3 H, OMe), 1.51 (s, 3 H, C_2-Me), 1.35 (s, 3 H, C_5-Me), 1.27–0.82 (m, 1 H), 0.57–0.07 (m, 4 H); ^{1}H NMR of cis isomer (90 MHz, C_6D_6) δ 2.90 (s, 3 H, OMe), 1.44 (s, 3 H), 1.14 (s, 3 H, C_2-Me), 1.27–0.82 (m, 1 H), 0.57–0.07 (m, 4 H). The chemical shifts of overlapping multiplets refer to the observed range for the mixture of isomers. Composite integrals for overlapping peaks were satisfactory.

Diazoalkane Cycloadducts to Dimethyl Acetylenedicarboxylate (7) and *N*-Phenylmaleimide (11). Oxadiazoline **2** (1.0 mmol) and **6** or **10** (1.2 mmol) in benzene (2 mL) were irradiated at room temperature with 300-nm light (Rayonet apparatus) for 5 h. The reaction products were separated on silica gel by using centrifugal chromatography (Chromatotron). A 9:1 mixture of petroleum ether and ethyl acetate was used as the eluent. The cycloadducts are listed below.

3,4-Bis(methoxycarbonyl)-5,5-dimethylpyrazole (7a): 65% yield; lit.[12] ^{1}H NMR (90 MHz, $CDCl_3$) δ 4.01 (s, 3 H), 3.92 (s, 3 H), 1.55 (s, 6 H).

3,4-Bis(methoxycarbonyl)-5-ethyl-5-methylpyrazole (7b): 67% yield; ^{1}H NMR (90 MHz, $CDCl_3$) δ 4.04 (s, 3 H), 3.96 (s, 3 H), 2.53 (m, 6 lines, ^3J = 7.5 Hz, ^2J = 15 Hz, 1 H) 2.00 (m, ^3J = 7.5 Hz, ^2J = 15 Hz, 1 H), 1.60 (s, 3 H, Me), 0.61 (t, J = 7.5 Hz, 3 H, Me); MS (EI) m/e 227.1028 (M + H)$^+$ (calcd for $C_{10}H_{14}N_2O_4$ + H, 227.1028).

3,4-Bis(methoxycarbonyl)-5,5-diethylpyrazole (7c): 67% yield; ^{1}H NMR (90 MHz, $CDCl_3$) δ 4.03 (s, 3 H), 3.96 (s, 3 H), 2.56 (m, 6 lines, ^3J = 7.5 Hz, ^2J = 15 Hz, 2 H), 2.03 (m, 6 lines, ^3J = 7.5 Hz, ^2J = 15 Hz, 2 H), 0.60 (t, J = 7.5 Hz, 6 H); MS (CI, NH_3) m/e 241.1178 (M + H)$^+$ (calcd for $C_{11}H_{16}H_2O_4$ + H, 241.1184).

3,4-Bis(methoxycarbonyl)-5-methyl-5-(1-methylethyl)-pyrazole (7d): 65% yield; ^{1}H NMR (90 MHz, $CDCl_3$) δ 4.04 (s, 3 H), 3.97 (s, 3 H), 2.52 (sept, J = 6.8 Hz, 1 H), 1.60 (s, 3 H), 1.10 (d, J = 6.8 Hz, 3 H), 0.80 (d, J = 6.8 Hz, 3 H); MS (EI) m/e 240.1110 (calcd for $C_{11}H_{16}N_2O_4$ 240.1106).

3,4-Bis(methoxycarbonyl)-1,2-diazaspiro[4.4]nona-1,3-diene (7f): 56% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.94 (s, 3 H), 3.86 (s, 3 H), 2.34–2.23 and 2.19–2.09 and 2.08–1.96 (m, 8 H); MS (EI) m/e 238.0949 (calcd for $C_{11}H_{14}N_2O_4$ 238.0950).

3,4-Bis(methoxycarbonyl)-1,2-diazaspiro[4.5]deca-1,3-diene (7g): 64% yield; lit.[21] ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.98 (s, 3 H), 3.85 (s, 3 H), 2.21–2.10, 2.04–1.93, 1.90–1.81, 1.59–1.49, and 1.45–1.36 (m, 10 H).

3,4-Bis(methoxycarbonyl)-5-methyl-5-cyclopropylpyrazole (7i): 55% yield; ^{1}H NMR (90 MHz, $CDCl_3$) δ 4.01 (s, 3 H), 3.89 (s, 3 H), 1.62 (s, 3 H), 1.50 to –0.20 (m, 5 H); MS (CI, NH_3) m/e 239.1031 (M + H)$^+$ (calcd for $C_{11}H_{14}N_2O_4$ + H, 239.1028).

4,4-Dimethyl-7-phenyl-2,3,7-triazabicyclo[3.3.0]oct-2-ene-6,8-dione (11): 40% yield; mp 156–157 °C (ether); ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.62–7.19 (m, 5 H), 6.02 (d, J = 9.0 Hz, 1 H, C_5-H), 3.02 (d, J = 9.0 Hz, 1 H, C_5-H), 1.64 (s, 3 H), 1.58 (s, 3 H); MS (CI, NH_3) m/e 244.1094 (M + H)$^+$ calcd for $C_{13}H_{13}N_3O_2$ + H, 244.1083).

Products of Nitrogen Photoelimination (8 and 12). Fifty milligrams of pure **7** or 100 mg of **2** and **6** in benzene (2 mL) were irradiated with 300-nm light in a Rayonet apparatus for 5 and 12 h, respectively. The products were separated by using centrifugal chromatography on silica gel (Chromatotron). A 9:1 mixture of petroleum ether and ethyl acetate was used as eluent.

3,3-Dimethyl-1,2-bis(methoxycarbonyl)cycloprop-1-ene (8a): 70% yield; lit.[12] ^{1}H NMR (90 MHz, $CDCl_3$) δ 3.92 (s, 6 H), 1.49 (s, 6 H).

3-Ethyl-3-methyl-1,2-bis(methoxycarbonyl)cycloprop-1-ene (8b): 67% yield; ^{1}H NMR (90 MHz, C_6H_6) δ 3.30 (s, 6 H), 1.53 (q, J = 7.5 Hz, 2 H), 1.25 (s, 3 H), 0.62 (t, J = 7.5 Hz, 3 H).

3,3-Diethyl-1,2-bis(methoxycarbonyl)cycloprop-1-ene (8c): 65% yield; ^{1}H NMR (90 MHz, $CDCl_3$) δ 3.89 (s, 6 H), 1.73 (q, J = 7.5 Hz, 4 H), 0.78 (t, J = 7.5 Hz, 6 H); MS (CI, CH_4) m/e 213.1121 (M + H)$^+$ (calcd for $C_{11}H_{16}O_4$ + H, 213.1122).

3-Methyl-3-(1-methylethyl)-1,2-bis(methoxycarbonyl)-cycloprop-1-ene (8d): 58% yield; ^{1}H NMR (90 MHz, $CDCl_3$) δ 3.93 (s, 6 H), 1.93 (sept, J = 6.8 Hz, 1 H), 1.35 (s, 3 H), 0.89 (d, J = 6.8 Hz, 6 H); MS (CI, CH_4) m/e 213.1121 (calcd for $C_{11}H_{16}O_4$ + H, 213.1122).

3-Cyclopropyl-3-methyl-1,2-bis(methoxycarbonyl)cycloprop-1-ene (8i): 60% yield; ^{1}H NMR (90 MHz, $CDCl_3$) δ 3.90 (s, 6 H), 1.50 (s, 3 H), 1.50–1.04 (m, 1 H), 0.63 to –0.05 (m, 4 H); MS (CI, NH_3) m/e 211.0973 (M + H)$^+$ (calcd for $C_{11}H_{14}O_4$ + H, 211.0966).

6,6-Dimethyl-3-phenyl-3-azabicyclo[3.1.0]hexane-2,4-dione (12): 40% yield; mp 138–140 °C (petroleum ether/$CHCl_3$) (lit.[14] mp 142–143 °C); ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.40–7.10 (m, 5 H), 2.42 (s, 2 H), 1.40 (s, 3 H), 1.29 (s, 3 H).

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(21) Gstach, M.; Kisch, H. *Chem. Ber.* **1982**, *115*, 2586–2591.