Studies of "Formal" [1,5]-Sigmatropic Thermal Rearrangements of Dimethyl 3-Alkyl-3-methyl-3*H*-pyrazole-4,5-dicarboxylates and Dimethyl 4-Alkyl-5-methyl-4*H*-pyrazole-3,4-dicarboxylates

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Abstract: Studies of the thermal rearrangements of 3*H*-pyrazoles, **10a–e**, in benzene/toluene, chloroform, and methanol solvents are described. The mechanism for rearrangement appears to be two-step, involving discrete ion-pair intermediates. Large rate enhancements for these rearrangements in methanol and cation trapping by methanol are consistent with the proposed mechanism. Observed rate constants for the rearrangements of 3*H*-pyrazoles **10c**, **10d**, and **10e** in benzene-d_6 were determined. Insight into the sense of rearrangement by an ion-pair mechanism is also provided by analysis of the ^{1}H NMR spectra of the product mixtures. 3*H*-Pyrazoles **10b** and **10e** rearrange to afford 4*H*-pyrazoles **13b** and **13e**, respectively, and the thermal rearrangements of these pyrazoles in benzene-d_6 and methanol are described. Rate constants for the rearrangements of these more stable pyrazole isomers in benzene-d_6 were also determined. Cation-trapping experiments with methanol suggest that the 4*H*-pyrazoles also rearrange by a two-step mechanism, involving discrete ion-pair intermediates. Furthermore, it appears that different ion-pair intermediates are formed from the 3*H*-pyrazoles **10b** and **10e**, compared to the 4*H*-pyrazoles **13b** and **13e**, on the basis of cation-trapping experiments.

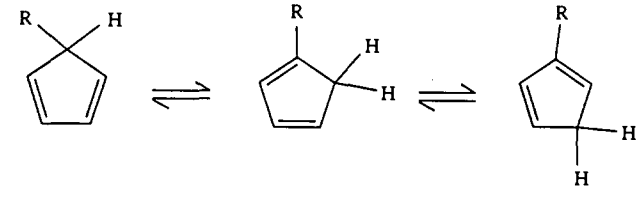
Introduction

Pericyclic reactions are processes characterized by concerted bonding changes taking place through reorganization of electron pairs within a closed loop of interacting orbitals. For a reaction to be classified as a pericycle reaction, the bonds breaking and forming must do so simultaneously rather than in two or more steps. Cycloadditions and sigmatropic reactions generally belong to the pericyclic category.[1]

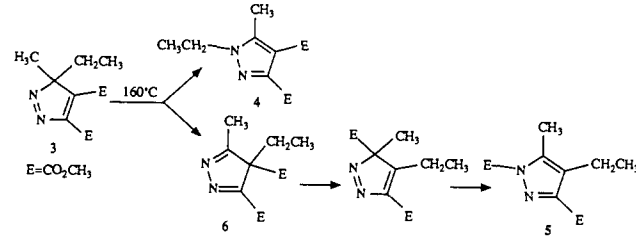
There are several examples of cycloaddition reactions which are known to occur by a stepwise mechanism rather than by a concerted process, either synchronous or asynchronous.[2] One type of cycloaddition reaction which has received much attention in the literature is the Diels–Alder reaction, a $2\pi + 4\pi$ cycloaddition process; stepwise Diels–Alder reactions have been discovered recently.[3]

Examples of "formal" sigmatropic rearrangements are more rare.[4] The [1,5]-sigmatropic rearrangements, belonging to the general class of sigmatropic reactions, are generally believed to occur by a one-step mechanism. Numerous experimental[1,5] and theoretical studies[6] in support of that mechanism have been published. In such a rearrangement an intramolecular shift of a group or atom from one position to another on the same face

Scheme I



Scheme II



of a π-system occurs, through a six-π-electron transition state. The migrating entity remains continuously and covalently bonded to the rest of the structure during its migration.

A familiar [1,5]-sigmatropic rearrangement is the migration of a hydrogen atom, on a cyclopentadiene ring, that rapidly interconverts 5-alkylcyclopentadienes with their 1-alkyl and 2-alkyl isomers[7a] (Scheme I). It has been suggested that the transition state for [1,5]-sigmatropic migration in cyclopentadiene is such that the migrating hydrogen is "protonic" while the underlying carbon skeleton resembles an "aromatic" cyclopentadienyl anion.[7] Only for the rearrangement of arylazo pentakis(methoxycarbonyl)cyclopentadienes has a mechanism involving discrete ion pairs been proposed.[8]

3*H*-Pyrazoles, as heterocyclic analogues of 1,3-cyclopentadienes, are also prone to [1,5]-sigmatropic rearrangement. Such thermal

(1) (a) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: London, 1976. (b) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781. (c) Gilchrist, T. L.; Storr, R. C. *Organic Reactions and Orbital Symmetry*; Cambridge University Press: London, 1972. (d) Spangler, C. W. *Chem. Rev.* **1976**, *76*, 187. (e) Mironov, V. A.; Fedorovich, A. D.; Akhrem, A. A. *Russ. Chem. Rev. (Engl. Transl.)* **1981**, *50*, 666.

(2) For several examples, see: Gompper, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 312 and references therein.

(3) (a) Jensen, F.; Foote, C. S. *J. Am. Chem. Soc.* **1987**, *109*, 6376. (b) Gupta, R. B.; Franck, R. W. *J. Am. Chem. Soc.* **1987**, *109*, 5393. (c) Baran, J.; Mayr, H.; Ruster, V.; Klärner, F.-G. *J. Org. Chem.* **1989**, *54*, 5016. (d) Gassman, P. G.; Singleton, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 6085. (e) Gassman, P. G.; Gorman, D. B. *J. Am. Chem. Soc.* **1990**, *112*, 8624.

(4) Gajewski, J. J.; Gortva, A. M.; Borden, W. T. *J. Am. Chem. Soc.* **1986**, *108*, 1083.

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(7) (a) McLean, S.; Haynes, P. *Tetrahedron* **1965**, *21*, 2329. (b) Schulman, E. M.; Merbach, A. E.; Turin, M.; Wedinger, R.; le Noble, W. J. *J. Am. Chem. Soc.* **1983**, *105*, 3988. (c) Replogle, K. L.; Carpenter, B. K. *J. Am. Chem. Soc.* **1984**, *106*, 5751. (d) Kahn, S. D.; Hehre, W. J.; Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 8291.

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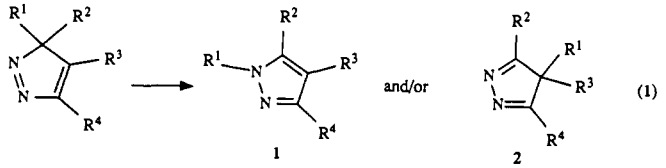
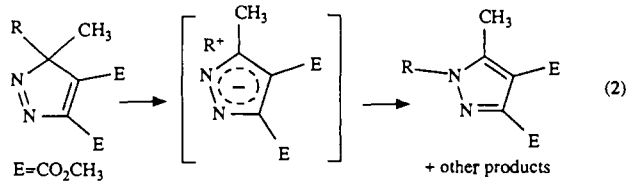
rearrangements are referred to as van Alphen–Hüttel rearrangements and are illustrated with eq 1.[9] A 1,5-anticlockwise migration of R^1 affords the 1*H*-pyrazole **1**, while a 1,5-clockwise migration of R^1 affords the 4*H*-pyrazole **2**. There are several examples of thermal concerted 3*H*-pyrazole rearrangements in the literature.[10] These rearrangements are characterized by low migratory aptitudes for saturated groups (e.g., alkyl) and high migratory aptitudes for unsaturated groups such as phenyl or ester.[10j]



(1)

An example of a 3*H*-pyrazole which undergoes "typical" [1,5]-sigmatropic rearrangement is given in Scheme II. 3-Ethyl-3-methyl-3*H*-pyrazole-4,5-dicarboxylic acid dimethyl ester (**3**) rearranges at 160 °C to give **4** (33%) and **5** (67%).[10m] A [1,5]-ethyl migration to nitrogen forms **4** while migration of ethyl to carbon forms intermediate **6**, which undergoes two consecutive anticlockwise [1,5]-ester migrations to give **5**.

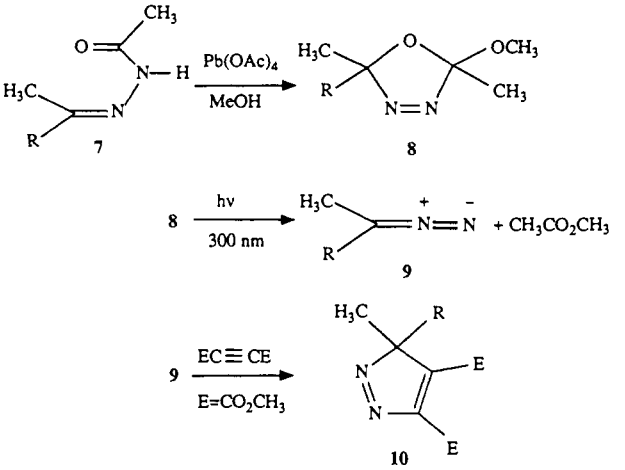
We recently discovered that some 3-alkyl-3-methyl-3*H*-pyrazole-4,5-dicarboxylic acid dimethyl esters undergo thermal rearrangement by an alternative mechanism,[11] although some of the products are those of "formal" [1,5]-sigmatropic processes. It appears that when the migrating group is relatively stable as a cation (R = CH_2OCH_3 or $C(Me)_3$), rearrangement takes place by a two-step mechanism involving an intermediate cation and pyrazole anion (eq 2). The enormous rate enhancements for these rearrangements combined with cation trapping by methanol provide strong support for such a mechanism. Such stepwise rearrangements probably represent part of a mechanistic continuum that runs from concerted, with very little charge separation, to the two-step, ion-pair extreme.



(2)

In this paper, we provide a more complete account of these rearrangements with additional examples of 3-alkyl-3-methyl-3*H*-pyrazole-4,5-dicarboxylic acid dimethyl esters which undergo rearrangement by a two-step mechanism and with observed rate constants for some of the rearrangements. Rearrangements of more stable isomers, the 4-alkyl-5-methyl-4*H*-pyrazole-3,4-dicarboxylic acid dimethyl esters, are included along with insight into the senses of rearrangement of both families by the ion-pair mechanism.

Scheme III[a]



[a] **a**: R = $CHPh_2$. **b**: R = CH_2OMe. **c**: R = $C(Me)_3$. **d**: R = 1-adamantyl. **e**: R = *p*-$CH_2C_6H_4OMe$.

Methods and Results

Preparation of 3*H*-Pyrazoles. The 3*H*-pyrazoles **10a–e** were generally prepared according to the method outlined in Scheme III. They could not be isolated as they rearranged in the media in which they were generated. Solvents used in the last step were benzene-d_6, toluene, chloroform or chloroform-*d*, and methanol or methanol-d_4. Therefore, the 3*H*-pyrazoles **10a–e** were obtained as solutions in those solvents.

The oxadiazolines **8a–e** were prepared by the oxidative cyclization of *N*-acylhydrazones of ketones (**7a–e**) with $Pb(OAc)_4$ in methanol solvent.[12,13] The preparation of **8c** was described previously.[13a]

Photolysis of the appropriate 5-alkyl-2-methoxy-2,5-dimethyl-Δ^3-1,3,4-oxadiazolines **8a–e** in a Rayonet apparatus gave diazoalkanes **9a–e** and methyl acetate.[13a] In situ cycloaddition of the appropriate diazoalkane to dimethyl acetylenedicarboxylate generated solutions of the unstable 3*H*-pyrazoles **10a–e**. By working quickly at low temperatures (see Experimental Section), we were able to observe 3*H*-pyrazoles **10c**, **10d**, and **10e** by ^1H NMR spectroscopy, but 3*H*-pyrazoles **10a** and **10b** could not be observed because they rearrange too rapidly.

Rearrangements of 3*H*-Pyrazoles. Scheme IV shows, in mechanistic terms, the types of products to be expected from rearrangements of **10a–e** in solution by an ion-pair pathway. An ion-pair intermediate could return to starting material or collapse in four alternative ways to form one or more of the isomers **11–14**. If the migrating cation has a β-hydrogen, proton transfer could generate **15** plus alkene. In a hydroxylic solvent such as methanol, the coproducts of **15** could include alkene as well as the appropriate ether, **16**. The distribution of products was found to be solvent dependent, and the results are arranged, in Table I, according to solvent. Inspection of Table I reveals the products formed from the rearrangement of 3*H*-pyrazoles **10a–e**, in benzene-d_6, $CHCl_3$ or $CDCl_3$, and CH_3OH or CD_3OD. The rearrangements led to very clean product solutions, and the numbers reported are percentages determined by ^1H NMR spectroscopy.

Rearrangements in Toluene/Benzene-d_6. 3*H*-Pyrazoles **10a** and **10b** rearranged too rapidly to be observed by ^1H NMR spectroscopy. Even when they were generated by the photolysis of **8a** and **8b**, respectively, in solutions of toluene-d_8 at −73 °C, followed by the addition of dimethyl acetylenedicarboxylate with the Rayonet bulbs switched off, quick warming to room temperature for ^1H NMR spectroscopy showed only products resulting from the rearrangement of **10a** and **10b**.

(9) (a) van Alphen, J. *Recl. Trav. Chim. Pays-Bas* **1943**, *62*, 485, 491. (b) Hüttel, R.; Riedl, J.; Martin, H.; Franke, K. *Chem. Ber.* **1960**, *93*, 1425. (c) Hüttel, R.; Franke, K.; Martin, H.; Riedl, J. *Chem. Ber.* **1960**, *93*, 1433. (d) Baumes, R.; Elguero, J.; Jacquier, R.; Tarrago, G. *Tetrahedron Lett.* **1973**, 3781.

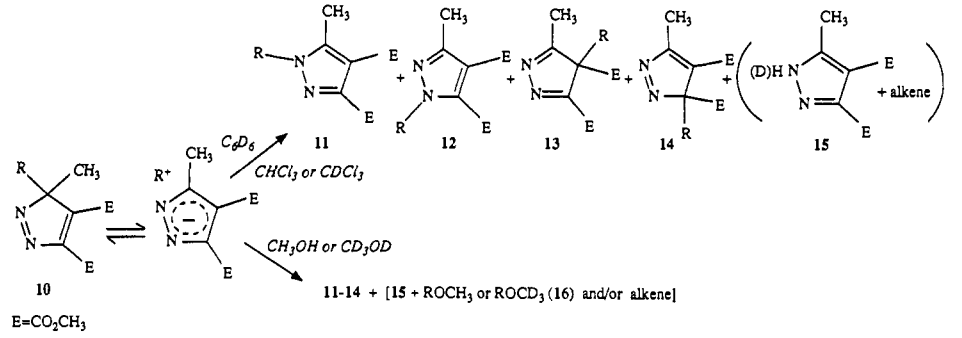
(10) For only a few examples, see: (a) Dürr, H.; Sergio, R. *Tetrahedron Lett.* **1972**, 3479. (b) Bernard, R. E.; Shechter, H. *Tetrahedron Lett.* **1972**, 4529. (c) Franck-Neumann, M.; Buchecker, C. *Tetrahedron Lett.* **1972**, 937. (d) Franck-Neumann, M.; Buchecker, C. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 240. (e) Franck-Neumann, M.; Dietrich-Buchecker, C. *Tetrahedron Lett.* **1976**, 2069. (f) Katner, A. S. *J. Org. Chem.* **1973**, *38*, 825. (g) Leigh, W. J.; Arnold, D. R. *Can. J. Chem.* **1979**, *57*, 1186. (h) Huisgen, R.; Reissig, H.-U.; Huber, H. *J. Am. Chem. Soc.* **1979**, *101*, 3647. (i) Huisgen, R.; Verderol, M. P. B.; Gieren, A.; Lamm, V. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 694. (j) Schiess, P.; Stalder, H. *Tetrahedron Lett.* **1980**, *21*, 1417. (k) Mataka, S.; Tashiro, M. *J. Org. Chem.* **1981**, *46*, 1929. (l) Mataka, S.; Ohshima, T.; Tashiro, M. *J. Org. Chem.* **1981**, *46*, 3960. (m) Frampton, C. S.; Majchrzak, M. W.; Warkentin, J. *Can. J. Chem.* **1991**, *69*, 373.

(11) Majchrzak, M. W.; Jefferson, E.; Warkentin, J. *J. Am. Chem. Soc.* **1990**, *112*, 2448.

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

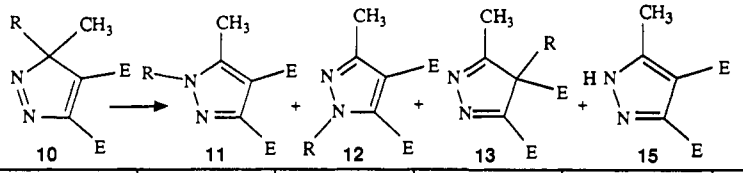
(13) (a) Majchrzak, M. W.; Bēkhazi, M.; Tse-Sheepy, I.; Warkentin, J. *J. Org. Chem.* **1989**, *54*, 1842. (b) Majchrzak, M. W.; Warkentin, J.; Woollard, J. M. R. *Struct. Chem.* **1991**, *2*, 137.

Scheme IV[a]



[a] **a**: R = $CHPh_2$. **b**: R = CH_2OMe. **c**: R = $C(Me)_3$. **d**: R = 1-adamantyl. **e**: R = *p*-$CH_2C_6H_4OMe$.

Table I. Products and Product Yields[a] from the Thermal Rearrangements of **10** at Ambient Temperature

Solvent	 10 11 12 13 15 + other					
Benzene-d_6	R=$CHPh_2$	91	9	nil	nil	
	R=CH_2OMe	77	nil	23	nil	
	R=$C(Me)_3$	39	nil	nil	61	60 alkene[b]
	R=1-Adamantyl	63[c]	nil	nil	nil	
	R=p-$CH_2C_6H_4OMe$	64	nil	36	nil	
Chloroform	R=$CHPh_2$	73	27	nil	nil	
	R=CH_2OMe	72	28	nil	nil	
	R=$C(Me)_3$[d]	28	5	nil	67	55 alkene[b]
	R=1-Adamantyl	69	31	nil	nil	
	R=p-$CH_2C_6H_4OMe$	56	11	32	nil	
Methanol	R=$CHPh_2$	26	22	nil	52	52 ether[f]
	R=CH_2OMe	25	nil	nil	75	61 ether[e]
	R=$C(Me)_3$	20	nil	nil	80	5 alkene[b] 72 ether[e]
	R=1-Adamantyl	54	17	nil	29	23 ether[f]
	R=p-$CH_2C_6H_4OMe$	45	4	nil	51	47 ether[f]

[a] At the level of detection afforded by ^1H NMR spectroscopy, the products listed were the only products from rearrangement and yield numbers reflect complete materials balance prior to opening of a tube, unless otherwise indicated. [b] Isobutene. [c] Yield of isolated product. The rearrangement appeared to proceed in quantitative yield. [d] Reaction solvent was $CDCl_3$. [e] $ROCD_3$ from reaction in CD_3OD. [f] $ROCH_3$ from reaction in CH_3OH.

Rearrangement of 3*H*-pyrazole **10a** in benzene-d_6 gave two 1*H*-pyrazoles, **11a** (91%) and **12a** (9%). These isomeric 1*H*-pyrazoles were identified on the basis of their ^1H and ^{13}C NMR spectra as well as their mass spectrometric molecular masses.

3*H*-Pyrazole **10b** rearranged to give **11b** (77%) and **13b** (23%), a 4*H*-pyrazole. The 4*H*-pyrazole could not be isolated as it was unstable under the conditions of centrifugal chromatography (silica gel), but its ^1H NMR spectrum could be obtained from the ^1H NMR spectrum of the mixture following the photolysis. Centrifugal chromatography (silica gel) of the photolysis residue gave **11b** (66%) and **15** (19%).

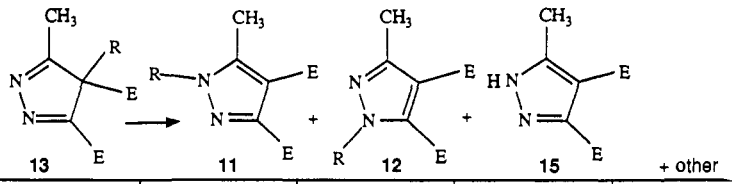
Unlike 3*H*-pyrazoles **10a** and **10b**, 3*H*-pyrazoles **10c**, **10d**, and **10e** could be observed by ^1H NMR spectroscopy. The diazoalkanes **9c–e** were generated at −73 °C in toluene, and dimethyl acetylenedicarboxylate was added with the Rayonet bulbs switched off. The mixture was warmed quickly to room temperature, and the toluene and volatiles were evaporated with a stream of dry N_2. The residue was dissolved in benzene-d_6, and NMR spectra were acquired immediately.

Observation of both the ^1H and ^{13}C NMR spectra of the photolysis mixture revealed that **10c** was formed in quantitative yield. The rearrangement of 3*H*-pyrazole **10c** in benzene-d_6 was not cleanly first-order, but good fits to first-order kinetics resulted from the addition of 2.5 equiv of triethylenediamine. Successive integrations of the ^1H NMR spectrum gave an observed rate constant of 6.2×10^{-5} s^{-1} at 35 °C.

3*H*-Pyrazole **10c** rearranged in benzene-d_6 to give **11c** (39%), **15** (61%), and 2-methylpropene (isobutene) (60%). The ratios of products formed in the presence of triethylenediamine were very similar. The presence of isobutene was confirmed by a ^1H NMR decoupling experiment on the reaction mixture following the rearrangement of **10c** (sealed NMR tube). Irradiation of the multiplet at 4.74 ppm (CH_2) caused the collapse of the triplet at 1.60 ppm (2 Me). 3*H*-Pyrazole **10d** was prepared by the same procedure as a solution in benzene-d_6. Observation of the ^1H and ^{13}C NMR spectra of the photolysis mixture revealed that **10d** was formed in quantitative yield. The observed rate constant, for the increase in the concentration of rearrangement product **11d** at 35 °C, was 5.6×10^{-5} s^{-1}. 3*H*-Pyrazole **10d** rearranged to give only **11d**.

The ^1H NMR spectrum of **10e** was obtained from a solution containing **11e** (25%), **13e** (10%), and **10e** (65%) in benzene-d_6. It was not possible to assign the ^{13}C NMR signals of **10e** from the spectrum of that solution. The observed rate constant for the disappearance of **10e** at 20 °C was 9.8×10^{-5} s^{-1}. It rearranged in benzene-d_6 to give **11e** (64%) and **13e** (36%). 4*H*-Pyrazole **13e**

Table II. Product and Product Yields[a] from Thermal Rearrangements of **13**

Solvent					
					
	13	**11**	**12**	**15**	+ other
Benzene-d_6	R=CH_2OMe[b,c]	57	43		
	R=p-$CH_2C_6H_4OMe_2$[d]	58	42		
Methanol	R=CH_2OMe[c,e,f]	nil	nil	100	100 $ROCD_3$
	R=p-$CH_2C_6H_4OMe$[e]	nil	nil	100	100 $ROCH_3$

[a] At the level of detection afforded by ^1H NMR spectroscopy, the products listed were the only products and the yield numbers reflect the percent yields determined by ^1H NMR spectroscopy. [b] Rearrangement at 90 °C. [c] Rearrangement of **13b** from solutions containing **13b** (23%) and **11b** (77%). [d] Rearrangement at 130 °C. [e] Rearrangement at ambient temperature. [f] Rearrangement in CD_3OD.

could be isolated by centrifugal chromatography (silica gel) as it was relatively stable.

Rearrangements in Chloroform or Chloroform-*d*. 3*H*-Pyrazole **10a** rearranged in chloroform solvent to give two isomeric 1*H*-pyrazoles, **11a** (73%) and **12a** (27%). 3*H*-Pyrazole **10b** also gave two isomeric 1*H*-pyrazoles, **11b** (72%) and **12b** (28%), but **10c** rearranged in chloroform-*d* solvent to give **11c** (28%), **12c** (5%), **15** (67%), and isobutene (55%). 3*H*-Pyrazole **10d** rearranged to afford two isomeric pyrazoles, **11d** (69%) and **12d** (31%), whereas **10e** rearranged to afford three isomeric pyrazoles, **11e** (56%), **12e** (11%), and **13e** (32%).

Rearrangements in Methanol or Methanol-d_4. Inspection of Table I reveals the products from the rearrangement of 3*H*-pyrazoles **10a–e** in methanol or methanol-d_4. Interception of the cationic migrating group with methanol competed with ion-pair collapse to 1*H*-pyrazole **11** and/or **12**. 3*H*-Pyrazoles **10b** and **10c**, both of which afforded a volatile methyl ether, were generated in deuterated solvent in order to determine the percentage of the methyl ether product conveniently by ^1H NMR spectroscopy. Rearrangement of 3*H*-pyrazole **10a** in methanol gave **11a** (26%), **12a** (22%), **15** (52%), and **16a** (52%). Similarly, 3*H*-pyrazole **10b** rearranged in methanol-d_4 to give **11b** (25%), **15** (as the D analogue, 75%), and **16b** (dimethoxymethane-d_3, 61%). Rearrangement of 3*H*-pyrazole **10c** in methanol-d_4 gave **11c** (20%), **15** (a mixture of H and D analogues, 80%), **16c** (*tert*-butyl methyl ether-d_3, 72%), and isobutene (5%). 3*H*-Pyrazole **10d** gave **11d** (54%), **12d** (17%), **15** (29%), and **16d** (23%) from rearrangement in methanol. Likewise, 3*H*-pyrazole **10e** gave **11e** (45%), **12e** (4%), **15** (51%), and **16e** (47%) from rearrangement in methanol.

The presence of dimethoxymethane-d_3 and *tert*-butyl methyl ether-d_3 from reaction of **10b** and **10c** in methanol-d_4 was confirmed by gas chromatography and ^1H NMR spectroscopy in spiking experiments with authentic samples of the nondeuterated analogues. The deuterated ethers, **16b** and **16c**, had ^1H NMR chemical shifts and gas chromatography retention times identical to those of nondeuterated analogues. The presence of benzhydryl methyl ether was confirmed by comparing spectroscopic data with those in the literature[14] while 1-adamantyl methyl ether and *p*-methoxybenzyl methyl ether were confirmed by comparing spectroscopic data with those of samples prepared by another route.[15a,b]

Rearrangement of 4*H*-Pyrazoles. Inspection of Table II reveals the products formed from the rearrangement of 4*H*-pyrazoles **13b** and **13e** in benzene-d_6 and methanol solvents. The rearrangements led to very clean product solutions, and the numbers reported are percentages determined by ^1H NMR spectroscopy.

Rearrangements in Benzene-d_6. As mentioned above, 4*H*-pyrazole **13b** could not be isolated. It was obtained as a solution, after the rearrangement of **10b** in benzene-d_6 solvent, which gave **11b** (77%) and **13b** (23%). The observed rate constant (1.1×10^{-4} s^{-1}) for the disappearance of **13b** at 90 °C was obtained from this crude reaction mixture. After the thermal rearrangement of **13b**, the mixture consisted of **11b** (90%) and **12b** (10%). Therefore, **13b** rearranges to give compounds **11b** and **12b** in the ratio 1.3:1.0. 4*H*-Pyrazole **13e** could be isolated, and its rearrangement in benzene-d_6 was followed by ^1H NMR spectroscopy. The increase in the concentrations of the rearrangement products **11e** and **12e** gave $k_{obsd} = 1.45 \times 10^{-4}$ s^{-1} at 130 °C. The products **11e** and **12e** were in the ratio 1.4:1.0.

Rearrangements in Methanol. The 4*H*-pyrazoles **13b** and **13e** were dissolved in methanol-d_4 and methanol, respectively, to determine if the migrating groups could be trapped. The photolysis mixture from the generation of 3*H*-pyrazole **10b** in benzene-d_6 and subsequent rearrangement to **11b** (79%) and **13b** (21%) was freed from volatiles, and the residue was dissolved in methanol-d_4. The ^1H NMR spectrum, taken immediately, revealed **11b** (79%), **15** (21%), and dimethoxymethane-d_3 (21%), indicating that 4*H*-pyrazole **13b** had dissociated to give only methanolysis products. Similarly, 4*H*-pyrazole **13e** was dissolved in methanol solvent, and after 10 min, the solvent was removed in vacuo and the residue was dissolved in $CDCl_3$. The ^1H NMR spectrum, taken immediately, revealed that *p*-methoxybenzyl methyl ether (100%) and **15** (100%) had been formed.

Discussion

Rearrangements of 3*H*-Pyrazoles. 3*H*-Pyrazoles **10a–e** contain migrating groups R which are known, from solvolysis of RX, to be relatively stable in cationic form.[16] It appears that these 3*H*-pyrazoles undergo stepwise rearrangement in benzene-d_6, chloroform, and methanol solvents.

The order of rates of rearrangement of the 3*H*-pyrazoles, from observed rate constants for rearrangement in benzene-d_6, was established as **10a** and **10b** > **10e** > **10c** ≈ **10d**. Rate constants for the fast rearrangements of 3*H*-pyrazoles **10a** and **10b** were not determined. These five 3*H*-pyrazoles rearrange with large rate enhancements (approximately 10^3 for the slowest) compared to 3*H*-pyrazoles **10** (where R = CH_3 or CH_2CH_3), which are known to rearrange at 160 °C.[10m]

The major rearrangement product of the 3*H*-pyrazoles in benzene-d_6 was the 1*H*-pyrazole **11**. The only exception was **10c**, where proton transfer between ions of the ion pair competed with ion-pair collapse to afford, as major products, **15** and isobutene. It is interesting that the rearrangement of 3*H*-pyrazoles **10b** and **10e** gave the 4*H*-pyrazole as the minor product. This observation is contrary to the reported rearrangements of other 3*H*-pyrazoles which include 4,5-diaryl-3,3-dimethyl-3*H*-pyrazoles,[10g] 3-alkyl-3,5-dimethyl-3*H*-pyrazoles[10j] (where alkyl = CH_3, CH_2CH_3, or CH_2Ph), and 3-alkyl-3-methyl-3*H*-pyrazole-4,5-dicarboxylic acid

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dimethyl esters (where alkyl = CH_3 or CH_2CH_3).[10m] Those rearrangements give primarily the kinetic product, the corresponding 4*H*-pyrazole, rather than the thermodynamically more stable aromatic counterpart, by what are believed to be "normal" [1,5]-sigmatropic migrations. Therefore, a different mechanism is required for the thermal rearrangement of 3*H*-pyrazoles **10b** and **10e**. 3*H*-Pyrazole **10e** rearranged to a larger percentage of the 4*H*-pyrazole (36%) compared to the rearrangement of 3*H*-pyrazole **10b**, which gave 23% of the 4*H*-pyrazole. This difference may be rationalized by assuming that rearrangement of **10e** is closer to the "normal" [1,5]-sigmatropic mechanism, where migration of a substituent to the adjacent carbon atom is favored, than rearrangement of **10b**. In equivalent language, the migration of *p*-$CH_2C_6H_4OMe$ in **10e** may occur through a "tighter" ion-pair intermediate compared to the migration of CH_2OMe in **10b**.

4*H*-Pyrazoles were not detected in the rearrangements of **10a**, **10c**, and **10d**. It appears that when the migrating group is large (i.e., R = $C(Me)_3$, $CHPh_2$, or 1-adamantyl), steric hindrance with the carbomethoxy substituent becomes an important product-determining factor. Either the 4*H*-pyrazole is not formed or the 4*H*-pyrazole is highly unstable and undergoes further rearrangement. We have not been able to distinguish between these options.

Only the rearrangement of **10a** in benzene-d_6 gave **12a** as the minor rearrangement product. Failure of the other ion pairs to form both of the possible aromatic end products, like **10a** does, implies that relatively "tight" ion pairs are formed during the rearrangement of **10b–e** in benzene-d_6. For **10a**, which affords the most stable cation of all the 3*H*-pyrazoles, the ion pair is likely to become more separated during its longer lifetime due to the increased stability of the cation. Therefore, collapse of the ion pair at N-2 occurs to form the other aromatic isomer also.

It is reasonable to assume that the ion-pair mechanism operates for the rearrangements of **10a–e** in benzene-d_6 solvent because of the large rate enhancements for rearrangement and because **10c** affords isobutene as a major product, probably from a *tert*-butyl cation intermediate. Radical intermediates leading to those products are most unlikely, in view of the large dependence of rates on the solvent. Moreover, the rearrangements of 3*H*-pyrazoles **10c–e** were observed by ^1H NMR spectroscopy and CIDNP was not observed. Although the absence of a CIDNP spectrum is not compelling evidence for the absence of radical-pair chemistry, a free radical mechanism is incompatible with the overall evidence.

Rearrangements of 3*H*-pyrazoles **10a–e** in chloroform solvent gave a mixture of two isomeric 1*H*-pyrazoles (**12** as the minor rearrangement product). The presence of **12** in all cases, when only **10a** gave **12a** in benzene, can probably be attributed to the following factor. An increase in solvent polarity, by increasing ion separations, causes an increased probability of ion-pair collapse at a site far away from the migration origin. This factor is also evident in the rearrangement of **10a**. The percentage of **12a** increased from 9 to 27% as a result of moving from benzene-d_6 to chloroform solvent.

The clean chemistry of **10a–e** in chloroform suggests that the ion-pair mechanism is again involved. Radical-pair chemistry in $CHCl_3$ would be expected to lead to some RH and to the formation of RD from reactions run in $CDCl_3$. There was no evidence for those products.

The generation of **10a–e** in methanol provides powerful evidence that an ion-pair mechanism operates in that solvent for the rearrangement of the 3*H*-pyrazoles. For 3*H*-pyrazoles **10a–e**, interception of R^+ with methanol competed with ion-pair collapse to give 1*H*-pyrazoles.[17]

Rearrangements of 4*H*-Pyrazoles. 4*H*-Pyrazoles are more stable than the 3*H*-pyrazole counterparts due to the presence of two relatively strong C=N double bonds, and consequently they have a higher barrier to ion-pair formation. 4*H*-Pyrazole **13b** could not be isolated while **13e** could be isolated by centrifugal chromatography. The difference in the rate constants (benzene) for **13b** (k_{obsd} = 1.1 × 10^{-4} s^{-1}, 90 °C) and **13e** (k_{obsd} = 1.5 × 10^{-4} s^{-1}, 130 °C) is a reflection of the relative stabilities of the different intermediate cations. Both **13b** and **13e** rearrange to give the isomeric 1*H*-pyrazoles **11** and **12** in about the same ratio (**11**:**12**=1.3–1.4:1). It would be expected that ion-pair formation from a 4*H*-pyrazole would lead to two isomeric 1*H*-pyrazoles in approximately the same ratio because the cation would have a similar probability of collapsing on each nitrogen site, given that the migration origin is equidistant from those nitrogen atoms.

It was found that both 4*H*-pyrazoles **13b** and **13e** undergo methanolysis at room temperature and that all the migrating cations are intercepted by methanol solvent in each case. The fact that, in methanol, a larger percentage of the migrating group is trapped by solvent if it originates from a 4*H*-pyrazole than if it originates from the isomeric 3*H*-pyrazole suggests that these isomeric pyrazoles lead to different ion pairs! Since those ion pairs must be identical once they have become well separated, the suggestion is that the ion pairs from the 4*H*-pyrazole are more "solvent separated" than the ion pairs from the 3*H*-pyrazole or that the former become solvent separated but the latter do not.

The different fates of isomeric 3*H*-pyrazoles and 4*H*-pyrazoles in methanol could also be explained in terms of competing stepwise and concerted mechanisms for the latter. We consider a common ion-pair mechanism more likely with differentiation arising out of small differences between the ion-pair geometries (memory effects or different degrees of separation) rather than an accidental matching of the activation free energies for concerted and stepwise mechanisms.

Conclusion

The 3*H*-pyrazoles **10a**, **10d**, and **10e** in addition to the 3*H*-pyrazoles previously reported (**10b** and **10c**) undergo rearrangement by a stepwise mechanism. The rearrangement of 3*H*-pyrazoles **10a–e** in benzene-d_6 affords primarily the 1*H*-pyrazoles **11a–e**. It appears that a relatively stable 4*H*-pyrazole is formed when the migrating group has low steric requirements (i.e., R = CH_2OCH_3 or *p*-$CH_2C_6H_4OMe$). When the migrating group is larger (i.e., R = $C(Me)_3$, $CHPh_2$, or 1-adamantyl), then either the 4*H*-pyrazole is not formed or the 4*H*-pyrazole is highly unstable and undergoes further rearrangement.

Evidence which supports a stepwise mechanism for the rearrangement of 3*H*-pyrazoles **10a–e** is in four parts. First, the 3*H*-pyrazoles **10a–e** rearrange with large rate enhancements compared to the rearrangements of 3*H*-pyrazoles **10** (where R = CH_3 or CH_2CH_3). Second, the 4*H*-pyrazole is not the major product in the rearrangement of 3*H*-pyrazoles **10b** and **10e** in benzene-d_6 solvent, contrary to all the rearrangements of 3*H*-pyrazoles where the sigmatropic mechanism is assumed. Third, the clean chemistry for the rearrangement of the 3*H*-pyrazoles in chloroform solvent suggests that a radical pair is not involved. Finally, methanol solvent intercepts the migrating groups during the rearrangement of the 3*H*-pyrazoles, diverting them to **15** and the appropriate methyl ether.

The 4*H*-pyrazoles **13b** and **13e** also rearrange by a two-step, ion-pair mechanism, at least in methanol solvent, because the migrating groups were completely intercepted. Whether or not these 4*H*-pyrazoles rearrange by the two-step mechanism in benzene-d_6, at the higher temperatures required, is still unclear.

Experimental Section

General. Melting points were determined on a Thomas-Hoover capillary melting point apparatus. Centrifugal chromatography was performed with silica gel (Merck Kieselgel 60 PF_{254}) coated plates (2 or 4 mm thick) spinning in a Chromatotron Model 7924T apparatus. Analytical thin-layer chromatography was performed with silica gel plates (E. Merck, D-Plastikfolien, Kieselgel 60 F_{254}). Proton nuclear magnetic resonance (^1H NMR) data were obtained on Varian EM-390, Bruker, AC-200, Bruker WM-250, or Bruker AM-500 spectrometers. Chemical shifts are reported in δ units (parts per million (ppm)) downfield from

(17) 3*H*-Pyrazole **10** (R = CH_2Ph) rearranges in methanol to 1-benzyl-5-methyl-1*H*-pyrazole-3,4-dicarboxylic acid dimethyl ester (42%) and 4-benzyl-5-methyl-4*H*-pyrazole-3,4-dicarboxylic acid dimethyl ester (58%). Benzyl methyl ether could not be detected. Therefore it appears that the benzyl substituent of **10** (R = CH_2Ph) is not sufficient to promote stepwise rearrangement.

tetramethylsilane, relative to the singlet at 7.24 ppm for chloroform or relative to the singlet at 7.15 ppm for benzene-d_5. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; bs, broad singlet. Coupling constants are reported in hertz (Hz). Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were obtained at 50 MHz on a Bruker AC-200 or at 125 MHz on a Bruker AM-500 spectrometer and are reported in ppm relative to the center line of a triplet at 77.0 ppm for chloroform-d_1 or a triplet at 128.0 ppm for benzene-d_6. High-resolution EI spectra were recorded on a VG ZAB-E double-focusing mass spectrometer. Samples were run at 70 eV, source temperature 200 °C, resolution 5000. Samples were introduced by direct insertion probe. Photolyses employed a Rayonet photochemical reactor fitted with 300-nm lamps.

Preparation of 2-Acetylhydrazones of Ketones (7). The following ketones were purchased from Aldrich Chemical Co. and were used as supplied: 1,1-diphenylacetone, methoxyacetone, pinacolone, 1-adamantyl methyl ketone, and (4-methoxyphenyl)acetone. Compounds **7a**, **7c**, and **7d** were prepared by refluxing equimolar amounts of acetylhydrazine and the appropriate ketone in ethanol for 24 h with 5 mol % of acetic acid. After the mixture was cooled to room temperature, crystals formed. For the preparation of **7b** and **7e**, solutions of equimolar amounts of acetylhydrazine and the appropriate ketone in benzene were refluxed until all the water was removed (Dean–Stark trap, 1 h for **7b** and 4 h for **7e**).

1-Acetyl-2-(1,1-diphenyl-2-propylidene)hydrazine (7a): 73% yield; mp 158–159 °C (EtOH); ^1H NMR (90 MHz, $CDCl_3$) δ 8.82 (bs, 1 H, NH), 7.45–7.18 (m, 10 H, 2 Ph), 5.02 (s, 1 H), 2.08 (s, 3 H, Ac), 1.87 (s, 3 H, Me); ^{13}C NMR (50 MHz, $CDCl_3$) δ 174.02, 151.73, 140.33 (2), 129.04 (4), 128.33 (4), 126.77 (2), 59.92, 20.34, 15.41; MS m/z (M^+) calcd for $C_{17}H_{18}N_2O$ 266.1419, found 266.1403.

1-Acetyl-2-(1-methoxy-2-propylidene)hydrazine (7b): 74% yield; mp 82–84 °C (EtOH); ^1H NMR (90 MHz, $CDCl_3$) δ 8.62 (bs, 1 H, NH), 4.00 (s, 2 H), 3.37 (s, 3 H, OMe), 2.28 (s, 3 H, Ac), 1.88 (s, 3 H, Me); ^{13}C NMR (50 MHz, $CDCl_3$) δ 174.15, 149.25, 75.97, 57.99, 20.28, 12.56; MS (CI, CH_4) m/z $(M + H)^+$ calcd for $C_6H_{12}N_2O_2$ + H 145.0977, found 145.0979.

1-Acetyl-2-(3,3-dimethyl-2-butylidene)hydrazine (7c): 75% yield; mp 82–83 °C (EtOH); (lit.[13a] mp 80–82 °C); the ^1H NMR spectrum was reported;[13a] ^{13}C NMR (50 MHz, $CDCl_3$) δ 174.01, 157.47, 38.52, 27.45 (3), 20.42, 11.12.

1-Acetyl-2-[1-(1-adamantyl)-1-ethylidene]hydrazine (7d): 75% yield; mp 169–170 °C (EtOH); ^1H NMR (200 MHz, $CDCl_3$) δ 8.50 (bs, 1 H, NH), 2.27 (s, 3 H, Ac), 2.05 (bs, 3 H, CH), 1.74 (bs, 15 H, Me + 6 CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 173.84, 157.38, 40.35, 39.77, 39.45 (2), 36.88, 36.75 (2), 28.36, 28.19 (2), 20.43, 10.05; MS m/z (M^+) calcd for $C_{14}H_{22}N_2O$ 234.1732, found 234.1736.

1-Acetyl-2-[1-(4-methoxyphenyl)-2-propylidene]hydrazine (7e): 90% yield; mp 122–124 °C (EtOAc); ^1H NMR (200 MHz, $CDCl_3$) δ 8.76 (bs, 1 H, NH), 7.19 (d, 2 H, J = 7.9 Hz), 6.85 (d, 2 H, J = 7.9 Hz), 3.79 (s, 3 H, OMe), 3.48 (s, 2 H), 2.28 (s, 3 H, Ac), 1.75 (s, 3 H, Me); ^{13}C NMR (50 MHz, $CDCl_3$) δ 173.79, 158.29, 151.45, 129.71 (2), 128.73, 113.78 (2), 54.96, 44.29, 20.27, 14.53; MS m/z (M^+) calcd for $C_{12}H_{16}N_2O_2$ 220.1212, found 220.1207.

Preparation of 5-Alkyl-2-methoxy-2,5-dimethyl-Δ^3-1,3,4-oxadiazolines (8). These compounds were obtained by a procedure similar to those described previously.[12c,13b] However, a few modifications were made, and therefore the complete procedure for their synthesis is reported. To a yellow solution of lead tetraacetate (16.5 mmol) in absolute methanol (65 mL) at −10 °C was added the acetylhydrazone **7** (15.0 mmol). The solution was stirred during the addition and thereafter. After 1 h, if the yellow color had not been discharged, the cold bath was removed. After the yellow color was eventually discharged, the reaction flask was once again cooled to −10 °C, and potassium hydroxide (pellets, 16.5 mmol, dissolved in 10 mL of absolute methanol) was added to the reaction flask to destroy the acetoxy–oxadiazoline coproduct. The solution was allowed to warm to room temperature slowly, and the reaction mixture was stirred overnight. Most of the solvent was removed in vacuo, water was added to the residue, and the aqueous solution was extracted with CH_2Cl_2. The organic layer was washed once with water before it was dried over magnesium sulfate. The solution was filtered, and the solvent was removed in vacuo. The residue was purified by centrifugal chromatography (silica gel, 19:1 hexane/ethyl acetate).

2-Methoxy-2,5-dimethyl-5-(1,1-diphenylmethyl)-Δ^3-1,3,4-oxadiazoline (8a): 63% yield; >98% trans (by ^1H NMR); ^1H NMR (200 MHz, $CDCl_3$) δ 7.47–7.14 (m, 10 H, 2 Ph) 4.74 (s, 1 H, CH), 3.21 (s, 3 H, OMe), 1.53 (s, 3 H, Me), 0.80 (s, 3 H, Me); ^{13}C NMR (50 MHz, $CDCl_3$) δ 138.63, 138.53, 133.83, 130.07 (4), 128.32 (2), 127.98 (2), 126.97, 126.91, 124.57, 59.46, 50.89, 23.78, 19.78; MS m/z ($M^+ - N_2$) calcd for $C_{18}H_{20}O_2$ 268.1463, found 268.1452.

2-Methoxy-5-(methoxymethyl)-2,5-dimethyl-Δ^3-1,3,4-oxadiazoline (8b): 45% yield; cis:trans ratio = 1.0:5.0; ^1H NMR of trans isomer (500 MHz, $CDCl_3$) δ 3.78 (d, 1 H, J = −10.8 Hz), 3.55 (d, 1 H, J = −10.8 Hz), 3.33 (s, 3 H, CH_2OMe), 3.12 (s, 3 H, OMe), 1.72 (s, 3 H, Me), 1.56 (s, 3 H, Me); ^1H NMR of cis isomer (500 MHz, $CDCl_3$) δ 3.72 (d, 1 H, J = −10.8 Hz), 3.69 (d, 1 H, J = −10.8 Hz), 3.41 (s, 3 H, CH_2OMe), 3.23 (s, 3 H, OMe), 1.63 (s, 3 H, Me), 1.45 (s, 3 H, Me); ^{13}C NMR of trans isomer (50 MHz, $CDCl_3$) δ 134.82, 121.28, 74.80, 59.39, 50.26, 22.38, 19.38; ^{13}C NMR of cis isomer (50 MHz, $CDCl_3$) δ 133.72, 120.42, 74.92, 59.52, 50.61, 23.52, 20.32; MS m/z (M^+ − OMe) calcd for $C_6H_{11}N_2O_2$ 143.0821, found 143.0804.

2-Methoxy-2,5-dimethyl-5-(2,2-dimethylethyl)-Δ^3-1,3,4-oxadiazoline (8c): 70% yield; the ^1H NMR spectrum was reported previously;[13a] ^{13}C NMR (50 MHz, $CDCl_3$) δ 131.05, 127.77, 50.80, 37.33, 25.31 (3), 19.17, 19.09.

5-(1-Adamantyl)-2-methoxy-2,5-dimethyl-Δ^3-1,3,4-oxadiazoline (8d): 81% yield; mp 54–57 °C; >94% trans (by ^1H NMR, 90 MHz); ^1H NMR (200 MHz, $CDCl_3$) δ 3.37 (s, 3 H, OMe), 2.09–1.48 (m, 15 H), 1.77 (s, 3 H, Me), 1.37 (s, 3 H, Me); composite integrals for overlapping signals were satisfactory; ^{13}C NMR (50 MHz, $CDCl_3$) δ 130.76, 127.62, 50.86, 39.11, 36.74 (3), 36.65 (3), 28.16 (3), 19.15, 18.03; MS m/z (M^+ − OMe) calcd for $C_{14}H_{21}N_2O$ 233.1654, found 233.1645.

2-Methoxy-5-(4-methoxybenzyl)-2,5-dimethyl-Δ^3-1,3,4-oxadiazoline (8e): 73% yield; cis:trans ratio = 1.0:2.7; ^1H NMR of trans isomer (500 MHz, $CDCl_3$) δ 7.07 (d, 2 H, J = 8.7 Hz), 6.80 (d, 2 H, J = 8.7 Hz), 3.77 (s, 3 H, p-C_6H_4OMe), 3.12 (s, 3 H, OMe), 3.18 (d, 1 H, J = −14.2 Hz), 3.04 (d, 1 H, J = −14.2 Hz), 1.56 (s, 3 H, Me), 1.21 (s, 3 H, Me); ^1H NMR of cis isomer (500 MHz, $CDCl_3$) δ 7.22 (d, 2 H, J = 8.7 Hz), 6.85 (d, 2 H, J = 8.7 Hz), 3.79 (s, 3 H, C_6H_4OMe), 3.23 (s, 1 H, J = −14.2 Hz), 3.13 (s, 3 H, OMe), 2.98 (d, 1 H, J = −14.2 Hz), 1.62 (s, 3 H, Me), 1.33 (s, 3 H, Me); composite integrals for overlapping peaks were satisfactory; ^{13}C NMR of trans isomer (50 MHz, $CDCl_3$) δ 158.54, 133.85, 131.51 (2), 126.28, 122.10, 113.30 (2), 54.87, 50.28, 43.28, 22.48, 21.79; ^{13}C NMR of cis isomer (50 MHz, $CDCl_3$) δ 158.54 (overlaps with trans isomer), 133.35, 131.23 (2), 126.62, 121.38, 113.52 (2), 54.87 (overlaps with trans isomer), 50.40, 42.57, 23.16, 22.12; MS m/z (M^+ − N_2) calcd for $C_{13}H_{18}O_3$ 222.1256, found 222.1269.

Rearrangement of 3*H*-Pyrazoles in Benzene-d_6 (General Method). Oxadiazoline **8** (0.25 mmol) and dimethyl acetylenedicarboxylate (DMAD) (0.30 mmol) in C_6D_6 (0.5 mL) were irradiated at room temperature with 300-nm light (Rayonet apparatus) for 6 h. A ^1H NMR spectrum was taken of the photolysis solution to determine the percentages of reaction products.

Rearrangement of 10a. The percentages of **11a** and **12a** determined by ^1H NMR spectroscopy (200 MHz) after photolysis of **8a** were 91 and 9, respectively. The volatiles were removed in vacuo, and centrifugal chromatography (silica gel, 4:1 hexane/ethyl acetate) gave **11a** (51%) and **12a** (8%).

5-Methyl-1-(1,1-diphenylmethyl)-1*H*-pyrazole-3,4-dicarboxylic acid dimethyl ester (11a): ^1H NMR (200 MHz, $CDCl_3$) δ 7.34–7.17 (m, 10 H, 2 Ph), 6.71 (s, 1 H), 3.87 (s, 3 H, OMe), 3.83 (s, 3 H, OMe), 2.45 (s, 3 H, Me); ^{13}C NMR (50 MHz, $CDCl_3$) δ 163.53, 163.21, 144.00, 143.50, 137.81 (2), 128.61 (4), 128.39 (4), 128.17 (2), 112.31, 67.00, 52.35, 51.67, 11.00; MS m/z (M^+) calcd for $C_{21}H_{20}N_2O_4$ 364.1423, found 364.1438.

3-Methyl-1-(1,1-diphenylmethyl)-1*H*-pyrazole-4,5-dicarboxylic acid dimethyl ester (12a): ^1H NMR (200 MHz, $CDCl_3$) δ 7.32–7.16 (m, 10 H, 2 Ph), 6.95 (s, 1 H), 3.79 (s, 3 H, COOMe), 3.78 (s, 3 H, COOMe), 2.38 (s, 3 H, Me); ^{13}C NMR (50 MHz, $CDCl_3$) δ 163.50, 161.46, 149.98, 138.46 (2), 137.15, 128.66 (4), 128.42 (4), 128.06 (2), 112.93, 67.53, 52.92, 51.61, 13.50; MS m/z (M^+) calcd for $C_{21}H_{20}N_2O_4$ 364.1423, found 364.1413.

Rearrangement of 10b. The percentages of **11b** and **13b** determined by ^1H NMR spectroscopy (200 MHz) after the photolysis of **8b** were 77 and 23, respectively. The volatiles were removed in vacuo, and the residue was purified by centrifugal chromatography (silica gel, 1:1 hexane/ethyl acetate) to give **11b** (66%) and **15** (19%). The spectroscopic data for **15** were identical to those previously reported.[15] 4*H*-Pyrazole **13b** could not be isolated without decomposition.

1-(Methoxymethyl)-5-methyl-1*H*-pyrazole-3,4-dicarboxylic acid dimethyl ester (11b): ^1H NMR (500 MHz, $CDCl_3$) δ 5.43 (s, 2 H), 3.93 (s, 3 H, COOMe), 3.85 (s, 3 H, COOMe), 3.33 (s, 3 H, OMe), 2.57 (s, 3 H, Me); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.23, 162.66, 144.55, 143.36, 113.50, 80.53, 56.80, 52.83, 51.74, 10.33; MS m/z (M^+) calcd for $C_{10}H_{14}N_2O_5$ 242.0903, found 242.0888.

4-(Methoxymethyl)-5-methyl-4*H*-pyrazole-3,4-dicarboxylic acid dimethyl ester (13b): ^1H NMR (200 MHz, C_6D_6) δ 4.28 (d, 1 H, J = −9.3 Hz), 3.92 (d, 1 H, J = −9.3 Hz), 3.38 (s, 3 H, COOMe), 3.09 (s, 3 H, COOMe), 2.76 (s, 3 H, OMe), 1.97 (s, 3 H, Me).

Rearrangement of 10c. The percentages of **11c**, **15**, and isobutene determined by ^1H NMR spectroscopy (90 MHz, sealed tube) were 39, 61, and 60, respectively. The solvent was removed in vacuo, and the

residue was separated by centrifugal chromatography (silica gel, 2:1 hexane/ethyl acetate) to give **11c** (24%) and **15** (38%).

1-*tert*-Butyl-5-methyl-1*H*-pyrazole-3,4-dicarboxylic acid dimethyl ester (11c): ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.91 (s, 3 H, COOMe), 3.83 (s, 3 H, COOMe), 2.65 (s, 3 H, Me), 1.67 (s, 9 H, $C(Me)_3$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 164.04, 163.43, 142.47, 140.82, 113.91, 61.87, 52.31, 51.65, 29.75, 13.15; MS m/z (M^+) calcd for $C_{12}H_{18}N_2O_4$ 254.1267, found 254.1266.

Rearrangement of 10d. The rearrangement of **10d** appeared to proceed in quantitative yield by observation of the ^{1}H NMR (200 MHz) spectrum. Centrifugal chromatography (silica gel, 4:1 hexane/ethyl acetate) gave **11d** (63%).

1-(1-Adamantyl)-5-methyl-1*H*-pyrazole-3,4-dicarboxylic acid dimethyl ester (11d): mp 141–143 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.90 (s, 3 H, OMe), 3.83 (s, 3 H, OMe), 2.69 (s, 3 H, Me), 2.31 (bs, 6 H, 3 CH_2), 2.24 (bs, 3 H, 3 CH), 1.75 (bs, 6 H, 3 CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 164.20, 163.46, 142.53, 141.06, 113.99, 63.24, 52.30, 51.66, 41.66 (3), 35.89 (3), 29.79 (3), 13.48; MS m/z (M^+) calcd for $C_{18}H_{24}N_2O_4$ 332.1736, found 332.1739.

Rearrangement of 10e. The percentages of **11e** and **13e** determined by ^{1}H NMR spectroscopy (200 MHz) were 64 and 36, respectively. The volatiles were removed in vacuo, and centrifugal chromatography (silica gel, 3:2 hexane/ethyl acetate) gave **11e** (37%) and **13e** (17%).

1-(4-Methoxybenzyl)-5-methyl-1*H*-pyrazole-3,4-dicarboxylic acid dimethyl ester (11e): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.09 (d, 2 H, CH, J = 8.4 Hz), 6.84 (d, 2 H, CH, J = 8.4 Hz), 5.29 (s, 2 H, CH_2), 3.94 (s, 3 H, COOMe), 3.83 (s, 3 H, COOMe), 3.78 (s, 3 H, OMe), 2.40 (s, 3 H, Me); ^{13}C NMR (50 MHz, $CDCl_3$) δ 163.34, 162.66, 159.40, 143.46, 142.77, 128.32 (2), 126.88, 114.22 (2), 112.83, 55.18, 53.52, 52.36, 51.61, 10.76; MS m/z (M^+) calcd for $C_{16}H_{18}N_2O_5$ 318.1216, found 318.1217.

4-(4-Methoxybenzyl)-5-methyl-4*H*-pyrazole-3,4-dicarboxylic acid dimethyl ester (13e): ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.81 (d, 2 H, CH, J = 8.7 Hz), 6.69 (d, 2 H, CH, J = 8.7 Hz), 3.97 (s, 3 H, COOMe), 3.80 (d, 1 H, CH, J = −14 Hz), 3.71 (s, 3 H, COOMe), 3.71 (s, 3 H, OMe), 3.45 (d, 1 H, CH, J = −14 Hz), 2.38 (s, 3 H, Me); ^{13}C NMR (50 MHz, $CDCl_3$) δ 176.52, 166.69, 165.27, 160.61, 159.08, 129.39 (2), 124.29, 114.86, 113.93 (2), 55.07, 53.65, 53.09, 36.77, 13.76; MS m/z (M^+) calcd for $C_{16}H_{18}N_2O_5$ 318.1216, found 318.1233.

Modified Preparative Procedure for the Observation of Some 3*H*-Pyrazoles. Oxadiazoline **8** (0.25 mmol) in toluene (0.5 mL) was irradiated at approximately −73 °C with 300-nm light (Rayonet apparatus) for 7 h. At −73 °C with the Rayonet bulbs switched off, DMAD (0.30 mmol) in 0.1 mL of toluene was added to the photolysis mixture. The mixture was warmed to room temperature, and the toluene and volatiles were evaporated at low temperature, with a stream of dry nitrogen gas. NMR spectral data was recorded immediately in benzene-d_6. 3*H*-Pyrazoles **10a** and **10b** could not be observed by ^{1}H NMR spectroscopy as the rearrangement of these 3*H*-pyrazoles had already taken place.

3-*tert*-Butyl-3-methyl-3*H*-pyrazole-4,5-dicarboxylic acid dimethyl ester (10c): quantitative yield; ^{1}H NMR (200 MHz, C_6D_6) δ 3.40 (s, 3 H, COOMe), 3.38 (s, 3 H, COOMe), 1.32 (s, 3 H, Me), 0.87 (s, 9 H, $C(Me)_3$); ^{13}C NMR (50 MHz, C_6D_6) δ 165.52, 160.67, 156.37, 145.19, 107.63, 52.40, 52.06, 37.94, 26.20, 16.32.

3-(1-Adamantyl)-3-methyl-3*H*-pyrazole-4,5-dicarboxylic acid dimethyl ester (10d): quantitative yield; ^{1}H NMR (200 MHz, C_6D_6) δ 3.45 (s, 3 H, COOMe), 3.43 (s, 3 H, COOMe), 1.87–1.45 (m, 15 H), 1.37 (s, 3 H, Me); ^{13}C NMR (50 MHz, C_6D_6) δ 165.68, 160.75, 156.30, 145.25, 108.20, 52.36, 52.04, 41.38, 37.98 (3), 36.73 (3), 29.06 (3), 15.04.

3-(4-Methoxybenzyl)-3-methyl-3*H*-pyrazole-4,5-dicarboxylic acid dimethyl ester (10e): ^{1}H NMR (200 MHz, C_6D_6) δ 6.99 (d, 2 H, J = 8.5 Hz), 6.57 (d, 2 H, J = 8.5 Hz), 3.44 (d, 1 H, J = −13.6 Hz), 3.35 (s, 3 H, COOMe), 3.26 (s, 3 H, COOMe), 3.15 (s, 3 H, OMe), 3.04 (d, 1 H, J = −13.6 Hz), 1.30 (s, 3 H, Me). Since 3*H*-pyrazole **10e** is unstable at room temperature, the ^{1}H NMR spectrum was obtained from solutions containing **11e** (25%), **13e** (10%), and **10e** (65%).

Determination of k_{obsd} for the Rearrangement of 3*H*-Pyrazoles 10c, 10d, and 10e. 3*H*-Pyrazoles **10c**, **10d**, and **10e** in benzene-d_6 solvent were generated by the method outlined above. To the solution containing **10c** was added triethylenediamine (2.5 equiv). Progress of the rearrangements of the 3*H*-pyrazoles was monitored by ^{1}H NMR spectroscopy at 250 MHz. Concentration vs time data (14 or more points) were obtained for the rearrangements of **10c** and **10e** to at least 2 half-lives by normalizing the integrated intensity of the methyl singlet of toluene (internal standard) against the integrated intensity of the methyl singlet at 1.32 ppm for each of the 3*H*-pyrazoles. Concentration vs time data (eight points) were obtained for the rearrangement of **10d** to 2 half-lives by normalizing the integrated intensity of the methyl singlet of residual DMAD against the increasing integrated intensity of the methyl singlet of 1*H*-pyrazole **11d** at 2.42 ppm. The resultant plots of ln [*I*] vs *t* gave the following observed rate constants: $k^{35°C}$(**10c**) = 6.2 × 10^{-5} s^{-1} (correlation coefficient = 0.9941), $k^{35°C}$(**10d**) = 5.6 × 10^{-5} s^{-1} (correlation coefficient = 0.9912), $k^{20°C}$(**10e**) = 9.8 × 10^{-5} s^{-1} (correlation coefficient = 0.9953).

Rearrangements in Chloroform (General Method). Oxadiazoline **8** (0.25 mmol) and DMAD (0.30 mmol) in 0.5 mL of $CHCl_3$ (**8c** was irradiated in $CDCl_3$) were irradiated at room temperature with 300-nm light (Rayonet apparatus) for 6 h. The volatiles from the photolysis mixture were removed (except solution containing the rearrangement products from **10c**) in vacuo, and the residue was dissolved in $CDCl_3$.

Rearrangement of 10a. The percentages of **11a** and **12a** by ^{1}H NMR spectroscopy (90 MHz) were 73 and 27, respectively. The volatiles were removed in vacuo, and the residue was purified by centrifugal chromatography (silica gel, 4:1 hexane/ethyl acetate) to give **11a** (50%) and **12a** (19%).

Rearrangement of 10b. The percentages of **11b** and **12b** by ^{1}H NMR spectroscopy (200 MHz) were 72 and 28, respectively. The volatiles were removed in vacuo, and the residue was separated by centrifugal chromatography (silica gel, 3:2 hexane/ethyl acetate) to give **11b** (56%) and **12b** (27%).

1-(Methoxymethyl)-3-methyl-1*H*-pyrazole-4,5-dicarboxylic acid dimethyl ester (12b): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.47 (s, 2 H), 3.92 (s, 3 H, COOMe), 3.81 (s, 3 H, COOMe), 3.29 (s, 3 H, OMe), 2.40 (s, 3 H, Me); ^{13}C NMR (50 MHz, $CDCl_3$) δ 163.05, 160.48, 149.70, 135.96, 114.27, 80.84, 56.82, 52.83, 51.56, 12.99; MS m/z (M^+) calcd for $C_{10}H_{14}N_2O_5$ 242.0903, found 242.0898.

Rearrangement of 10c. The percentages determined by ^{1}H NMR spectroscopy (200 MHz, sealed NMR tube) of **11c**, **15**, **12c**, and isobutene were 28, 67, 5, and 55. The volatiles were removed in vacuo, and the residue was purified by centrifugal chromatography (silica gel, 2:1 hexane/ethyl acetate) to give **11c** (20%), **15** (47%), and **12c** (4%).

1-*tert*-Butyl-3-methyl-1*H*-pyrazole-4,5-dicarboxylic acid dimethyl ester (12c): ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.95 (s, 3 H, COOMe), 3.79 (s, 3 H, COOMe), 2.42 (s, 3 H, Me), 1.59 (s, 9 H, $C(Me)_3$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 164.19, 163.34, 148.40, 137.17, 111.37, 62.11, 53.22, 51.39, 29.57 (3), 13.55; MS m/z (M^+) calcd for $C_{12}H_{18}N_2O_4$ 254.1267, found 254.1269.

Rearrangement of 10d. The percentages of **11d** and **12d** determined by ^{1}H NMR spectroscopy (200 MHz) were 69 and 31, respectively. The volatiles were removed in vacuo, and the residue was separated by centrifugal chromatography (silica gel, 4:1 hexane/ethyl acetate) to give **11d** (40%) and **12d** (19%).

1-(1-Adamantyl)-3-methyl-1*H*-pyrazole-4,5-dicarboxylic acid dimethyl ester (12d): ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.95 (s, 3 H, COOMe), 3.79 (s, 3 H, COOMe), 2.41 (s, 3 H, Me), 2.21 (bs, 9 H), 1.72 (bs, 6 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 164.33, 163.39, 148.39, 136.90, 111.12, 63.01, 53.24, 51.34, 41.93 (3), 35.85 (3), 29.74 (3), 13.60; MS m/z (M^+) calcd for $C_{18}H_{24}N_2O_4$ 332.1736, found 332.1739.

Rearrangement of 10e. The percentages of **11e**, **13e**, and **12e** determined by ^{1}H NMR spectroscopy (200 MHz) were 56, 32, and 11, respectively. The volatiles were removed in vacuo, and the residue was separated by centrifugal chromatography (silica gel, 1:1 hexane/ethyl acetate) to give **11e** (37%), **13e** (7%), and **12e** (7%).

1-(4-Methoxybenzyl)-3-methyl-1*H*-pyrazole-4,5-dicarboxylic acid dimethyl ester (12e): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.17 (d, 2 H, J = 8.7 Hz), 6.83 (d, 2 H, J = 8.7 Hz), 2.34 (s, 2 H, CH_2), 3.85 (s, 3 H, COOMe), 3.81 (s, 3 H, COOMe), 3.78 (s, 3 H, OMe), 2.41 (s, 3 H, Me); ^{13}C NMR (50 MHz, $CDCl_3$) δ 163.40, 161.12, 159.40, 149.70, 135.59, 130.31, 129.16 (2), 127.79, 114.00 (2), 55.22, 54.29, 52.85, 51.63, 13.25; MS m/z (M^+) calcd for $C_{16}H_{18}N_2O_5$ 318.1216, found 318.1225.

Rearrangements in Methanol (General Method). Oxadiazoline **8** (0.25 mmol) and DMAD (0.3 mmol) in CD_3OD or CH_3OH (0.5 mL) were irradiated at ambient temperature with 300-nm light (Rayonet apparatus) for 6 h.

Rearrangement of 10a in CH_3OH. The volatiles were removed in vacuo, and the residue was dissolved in $CDCl_3$. The percentages of **11a**, **12a**, **15**, and benzhydryl methyl ether by ^{1}H NMR spectroscopy (200 MHz, $CDCl_3$) were 26, 22, 52, and 52, respectively. The solvent was removed in vacuo, and the residue was separated by centrifugal chromatography (silica gel, 4:1 hexane/ethyl acetate) to give **11a** (19%), **12a** (17%), **15** (38%), and benzhydryl methyl ether (40%). The spectroscopic data for benzhydryl methyl ether were identical to those previously reported.[14]

Rearrangement of 10b in CD_3OD. The percentages of **11b**, **15** (the D analogue), and dimethoxymethane-d_3 were 25, 75, and 61, respectively, by ^{1}H NMR spectroscopy (200 MHz, methanol-d_4). Bulb to bulb distillation (0.01 mmHg) separated the volatiles from the pyrazoles. The presence of dimethoxymethane-d_3 in the volatiles was confirmed by gas chromatography and ^{1}H NMR spectroscopy spiking experiments with a sample of dimethoxymethane. The residue from bulb to bulb distillation was separated by centrifugal chromatography (silica gel, 1:1 hexane/

ethyl acetate) to give **11b** (18%) and **15** (D analogue) (58%).

Rearrangement of 10c in CD_3OD. The percentages of **11c**, **15** (a mixture of H and D analogues), isobutene, and *tert*-butyl methyl ether were 20, 80, 5, and 72, respectively, by ^1H NMR spectroscopy (90 MHz, methanol-d_4). Bulb to bulb distillation (0.01 mmHg) separated the volatiles from the pyrazoles. The presence of *tert*-butyl methyl ether-d_3 in the volatiles was confirmed by gas chromatography and ^1H NMR spiking experiments with a sample of *tert*-butyl methyl ether. The residue was separated by centrifugal chromatography (silica gel, 2:1 hexane/ethyl acetate) to give **11c** (14%) and **15** (56%).

Rearrangement of 10d in CH_3OH. The volatiles were removed in vacuo, and the residue was dissolved in $CDCl_3$. The percentages of **11d**, **12d**, **15**, and 1-adamantyl methyl ether determined by ^1H NMR spectroscopy (200 MHz, $CDCl_3$) were 54, 17, 29, and 23, respectively. The volatiles were removed in vacuo, and the residue was separated by centrifugal chromatography (silica gel, 4:1 hexane/ethyl acetate) to give **11d** (34%), **12d** (17%), **15** (27%), and 1-adamantyl methyl ether (16%). The spectral data for 1-adamantyl methyl ether were identical to those of a sample prepared by another route.[15a]

Rearrangement of 10e in CH_3OH. The volatiles were removed in vacuo, and the residue was dissolved in $CDCl_3$. The percentages of **11e**, **12e**, **15**, and *p*-methoxybenzyl methyl ether were determined to be 45, 4, 51, and 47, respectively, by ^1H NMR spectroscopy (200 MHz, $CDCl_3$). The solvent was removed in vacuo and the residue separated by centrifugal chromatography (silica gel, 3:2 hexane/ethyl acetate) to give **11e** (38%), **12e** (2%), **15** (51%), and *p*-methoxybenzyl methyl ether (45%). The spectral data for *p*-methoxybenzyl methyl ether were identical to those of a sample prepared by another route.[15b]

3*H*-Pyrazole **10e** was also generated in CH_3OH in the absence of 300-nm irradiation. Oxadiazoline **8e** (0.25 mmol) in CH_3OH (0.5 mL) was irradiated at −73 °C with 300-nm light for 7 h. The Rayonet bulbs were switched off, and DMAD (0.6 mmol) in 0.1 mL of CH_3OH was added to the photolysis mixture at −73 °C. The solution was then warmed quickly to ambient temperature, and the volatiles were removed in vacuo. The residue was dissolved in $CDCl_3$, and the percentages of **11e**, **12e**, **15**, and *p*-methoxybenzyl methyl ether, by ^1H NMR spectroscopy (200 MHz), were 56, 12, 32, and 28, respectively.

Thermal Rearrangements of 4*H*-Pyrazoles in Benzene-d_6. A. Rearrangement of 13b. Oxadiazoline **8b** (0.25 mmol) and DMAD (0.30 mmol) were dissolved in C_6D_6 (0.5 mL), degassed (three freeze–pump–thaw cycles), and sealed in an NMR tube. Irradiation at room temperature with 300-nm light (Rayonet apparatus) for 6 h gave rearrangement products **11b** (77%) and **13b** (23%). The tube was then heated at 90 °C, and progress of the rearrangement of **13b** was monitored by ^1H NMR spectroscopy at 200 MHz. Concentration vs time data (10 points) were obtained by normalizing the integrated intensity of the methyl singlet of methyl acetate (generated as a byproduct of the photolysis of **8b**) against the integrated intensity of the methyl singlet of **13b** for 2 half-lives. The resultant plot of ln [*I*] vs *t* yielded an observed rate constant (1.1×10^{-4} s^{-1}, correlation coefficient = 0.9904) for the decrease in concentration of **13b**. After the rearrangement of **13b** was complete, the solution consisted of **11b** (90%) and **12b** (10%). The volatiles were removed in vacuo, and the residue was purified by centrifugal chromatography (silica gel, 3:2 hexane/ethyl acetate) to give **11b** (75%) and **12b** (6%).

B. Rearrangement of 13e. Compound **13e** (0.072 g, 0.226 mmol) and methyl acetate (0.113 mmol, internal standard) were dissolved in C_6D_6 (0.5 mL), degassed (three freeze–pump–thaw cycles), and sealed in an NMR tube. The tube was then heated at 130 °C, and progress of the rearrangement of **13e** was monitored by ^1H NMR spectroscopy (200 MHz). Concentration vs time data were obtained by normalizing the integrated intensity of the methyl singlet of methyl acetate against the sum of the integrated intensities of the CH_2 singlets of the two 1*H*-pyrazole rearrangement products (**11e** and **12e**) for 2 half-lives. The resultant plot of ln [*I*] vs *t* yielded an observed rate constant (1.5×10^{-4} s^{-1}, correlation coefficient = 0.9939) for the increase in concentration of the two 1*H*-pyrazoles. After the thermal rearrangement of **13e** was complete, the mixture consisted of **11e** (58%) and **12e** (42%). The volatiles were removed in vacuo, and the residue was purified by centrifugal chromatography (silica gel, 1:1 hexane/ethyl acetate) to give **11e** (50%) and **12e** (35%).

Thermal Rearrangements of 4*H*-Pyrazoles in Methanol. A. Rearrangement of 13b. The volatiles from the photolysis mixture after generation of 3*H*-pyrazole **10b** in C_6D_6 (79% of **11b** and 21% of **13b**) were removed, and the residue was dissolved in CD_3OD. An NMR spectrum was taken immediately, and it revealed **11b** (79%), **15** (21%), and dimethoxymethane-d_3 (21%). Bulb to bulb distillation (0.01 mmHg) separated the volatiles from the pyrazoles. The presence of dimethoxymethane-d_3 in the volatiles was confirmed by gas chromatography and ^1H NMR spectroscopy spiking experiments with an authentic sample of dimethoxymethane. The residue from bulb to bulb distillation was separated by centrifugal chromatography (silica gel, 1:1 hexane/ethyl acetate) to give **11b** (65%) and **15** (D analogue) (16%).

B. Rearrangement of 13e. Compound **13e** (0.06 g, 0.189 mmol) was dissolved in methanol for 10 min. The methanol was then removed in vacuo, the residue was dissolved in $CDCl_3$, and a ^1H NMR spectrum was taken. ^1H NMR spectroscopy revealed a quantitative yield of **15** and *p*-methoxybenzyl methyl ether. The $CDCl_3$ was removed, and the residue was separated by centrifugal chromatography (silica gel, 3:2 hexane/ethyl acetate) to give **15** (76%) and *p*-methoxybenzyl methyl ether (80%).

Acknowledgment. We thank the McMaster University Regional Mass Spectrometry Facility for the mass spectral determinations and the Natural Sciences and Engineering Research Council of Canada for financial support.

Registry No. 7a, 141981-35-3; **7b**, 141981-36-4; **7c**, 119393-10-1; **7d**, 141981-37-5; **7e**, 141981-38-6; **8a** (isomer 1), 141981-39-7; **8a** (isomer 2), 141981-40-0; **8b** (isomer 1), 141981-41-1; **8b** (isomer 2), 141981-42-2; **8c**, 141981-43-3; **8d** (isomer 1), 141981-44-4; **8d** (isomer 2), 141981-45-5; **8e** (isomer 1), 141981-46-6; **8e** (isomer 2), 141981-47-7; **10a**, 141981-48-8; **10b**, 141981-49-9; **10c**, 125541-59-5; **10d**, 141981-50-2; **10e**, 141981-51-3; **11a**, 141981-48-8; **11b**, 125541-65-3; **11c**, 125541-64-2; **11d**, 141981-52-4; **11e**, 141981-53-5; **12a**, 141981-54-6; **12b**, 125541-66-4; **12c**, 141981-55-7; **12d**, 141981-56-8; **12e**, 141981-57-9; **13b**, 141981-58-0; **13e**, 141981-59-1; **15c**, 37387-73-8; $MeOCHPh_2$, 1016-09-7; $MeOCH_2OCD_3$, 141981-60-4; *t*-BuOMe, 1634-04-4; AdOMe, 6221-74-5; *p*-$MeOCH_2C_6H_4OMe$, 1515-81-7; $PhCH_2COMe$, 103-79-7; *t*-BuAc, 75-97-8; AdAc, 1660-04-4; isobutene, 115-11-7; acetylhydrazine, 1068-57-1; dimethyl acetylenedicarboxylate, 762-42-5.