erable role in the activation energy of the back reaction (E_{-1}).

The correlation equations of activation energy with E_{strain} or ∠OCCO of the dioxetane, as obtained from MM2, mean that increased strain in the dioxetane corresponds to higher activation energies. This suggests a reactant-like transition structure and the correlation of E_{strain} of the biradical further imposes biradical character in the transition structure. A transition-state structure that is intermediate in character between the dioxetane reactant and the biradical intermediate is also suggested by the slope of 0.60 in the correlation between $\Delta G^{\ddagger}$ and the difference in the gauche biradical and the dioxetane strain energies.

Acknowledgment. I thank Professor Mark Midland for copy of PCMODEL before commercial release and Professor Dewitt Coffey for help with the Cyber/QCPE version of MM2. Thanks also go to the California State University system and Professor Richard Deming (CSU Fullerton) for implementation of the Molecular Design Ltd. software and to Professor H. E. O'Neal for insightful discussions. I would also like to thank Dr. Richard Hilderbrandt and Jack Rogers of the San Diego Supercomputer Center (SDSC) for valuable consultation and the SDSC where the GAUSSIAN 82 calculations on dioxetane and methyldioxetane were made. Acknowledgement is gratefully made to Professor Warren Hehre for help with the GAUSSIAN 82 calculation on methyldioxetane. Finally, support of this work was provided by NSF, grant CHE-8413738.

Notes

[3,3]- and [1,3]-Sigmatropic Amino-Claisen Rearrangements of Electron-Rich Alkenes [1,3,1′,3′-Tetraallyl-2,2′-biimidazolidinylidenes]

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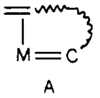
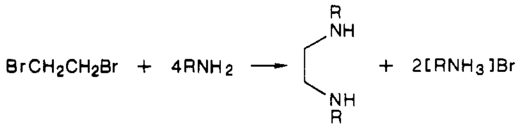
We have for some years used 1,3,1′,3′-tetrasubstituted 2,2′-biimidazolidinylidenes such as 1 as (i) sources of carbenemetal complexes $M{=}\overline{CN(R)(CH_2)_2N}R$[1] or (ii) powerful reducing agents: 1 being oxidized successively to $1^{\bullet+}$ and 1^{2+}.[2] The present study arose from a search for *R*-functionalized carbenemetal complexes. Allyls or but-3-enyls were considered to be particularly interesting, because such 1,3,1′,3′-tetrasubstituted 2,2′-biimidazolidinylidenes were anticipated to be capable of generating carbene(alkene)metal complexes A (the latter are implicated in alkene metathesis); we shall report on such chemistry elsewhere. Compounds 1 are generally prepared from an *N,N*′-disubstituted 1,2-diaminoethane and the dimethyl acetal of dimethylformamide. We now show that using standard conditions [(a) in Scheme I] compounds 1 are accessible for R = crotyl (**1b**) or but-3-enyl (**1c**), whereas for R = allyl the rearranged product **2a** was obtained. Moreover, the similar [3,3]-sigmatropic amino-Claisen rearrangement product **2b** was isolated by heating **1b** [(b) in Scheme I], while photolysis [(c) in Scheme I] of **1b** gave not only **2b** but also the [1,3] rearrangement isomer **2b′**.



A

Two of the starting diamines are new and were prepared as shown in eq 1 [R = $CH_2CH{=}CHMe$ or $(CH_2)_2CH{=}CH_2$].



$$BrCH_2CH_2Br + 4RNH_2 \longrightarrow RNHCH_2CH_2NHR + 2[RNH_3]Br \qquad (1)$$

Because of their large size it was impractical to carry out molecular orbital calculation on allylic molecules of types 1 and 2. The methyl analogues **1d** and **2d** were selected as appropriate models and MNDO was the MO method of choice.[3] This gave the following heats of formation: **1d** 204.6 kJ mol^{-1} and **2d** 168.1 kJ mol^{-1}, whence ΔH for the isomerization of gaseous 1,2,1′,2′-tetramethyl-2,2′-biimidazolidinylidene **1d** into the gaseous isomer **2d** is predicted to be −36.5 kJ mol^{-1}. (The heats of sublimation of **1d** and **2d** are expected to be similar.) To test further the validity of the MNDO method, we have demonstrated (Table I) that there is a good correlation between MNDO calculated and experimental geometrical parameters for **1d** (1, R = Me) (electron diffraction)[4] and **2e** (2, R = CH_2Ph) (X-ray);[5] experimental data for **2d** (2, R = Me) are not at hand.

The following conclusions emerge. (i) The tetraallylbiimidazolidinylidene **1a** (1, R = $CH_2CH{=}CH_2$) is not accessible under our reaction conditions [(a) in Scheme I] and if formed it spontaneously rearranges to the isomer **2a**. (ii) The thermal allylic isomerization 1 → 2 are believed to be intramolecular [3,3]-sigmatropic rearrangements, cf., the transition state B; because from **1b** (R = $CH_2CH{=}CHMe$) only one product **2b** [R = $CH_2CH{=}CHMe$, R′ = $CH(Me)CH{=}CH_2$] was obtained. (iii) The corresponding photochemical transformations are thought

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(1) Lappert, M. F. *J. Organomet. Chem.* **1988**, *358*, 185 and references therein.

(2) Goldwhite, H.; Kaminski, J.; Millhauser, G.; Ortiz, J.; Vargas, M.; Vertal, L.; Lappert, M. F.; Smith S. J. *J. Organomet. Chem.* **1986**, *310*, 21 and references therein.

(3) Dewar, M. J. S.; Storch, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 3898 and references therein. Calculations were carried out with full optimization of geometry.

(4) Lappert, M. F.; Spyropoulos, K.; Traetteberg, M. Unpublished results. Spyropoulos, K. D.Phil.Thesis, University of Sussex, 1985; the molecule has D_2 symmetry with a pyramidal configuration about nitrogen.

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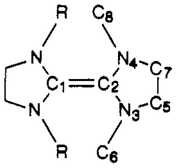
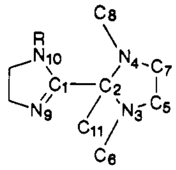
Table I. Some Experimental (esd's in parentheses) and MNDO-Calculated Structural Parameters for 1d, 2d, and 2e

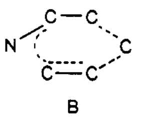

1d: R = Me

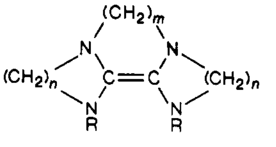

2d: R = Me
e: R = CH_2Ph

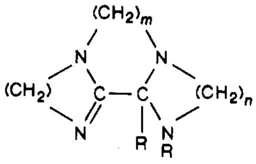
	electron diffrctn: **1d**[4]	MNDO: **1d**[a]	X-ray: **2e**[5]	MNDO: **2d**[a]
	Bond Lengths (Å)			
C_1–C_2	1.387 (11)	1.376	1.536 (4)	1.554
C_2–N_3	1.401 (4)	1.440	1.466 (4)/1.475 (4)	1.478[b]
N_3–C_5	1.491 (6)	1.484	1.453 (4)/1.456 (4)	1.468
N_3–C_6	1.465 (6)	1.484		
C_5–C_7	1.529 (9)	1.542		
C_1–N_9			1.392 (2)	1.418
C_1–N_{10}			1.276 (3)	1.312
	Bond Angles (deg)			
$C_1C_2N_3$	123.7 (0.3)	125.0	115.3 (2)/107.8 (2)	111.6
$C_2N_3C_6$	117.7 (0.5)	118.2		
$C_1C_2C_{11}$			107.9 (2)	110.9
$C_2C_1N_{10}$			120.6 (2)	119.8
$C_2C_1N_9$			124.2 (2)	128.5
	Dihedral Angles (deg)			
$C_1C_2N_3C_6$	53.5 (8)	48.4		
plane A $N_{10}C_1N_9$			89.2	82.5
plane B $N_3C_2N_4$				

[a] Average error, 0.016 Å or 2.7°.[7] [b] Although C_2N_3 and C_2N_4 are different in the crystal structure of **2e**, in **2d** they were assumed to be equal.

to be either wholly or in part intermolecular, [1,3], because irradiation of **1b** afforded not only **2b** but also the isomer **2b′** (R = $CH_2CH{=}CHMe$ = R′); these rearrangements may involve free radical intermediates (cf. ref 6). (iv) The rearrangements **1** $\xrightarrow{\Delta}$ **2** are thermodynamically favored and will be kinetically accessible if R is allylic or $\dot{R}$ or $\bar{R}$ is otherwise resonance stabilized, e. g., R = CH_2Ph, and not sterically hindered as in **1c** [i.e., R = $(CH_2)_2CH{=}CH_2$]. (v) The molecular structure of even the simplest *N,N′,N″,N‴*-tetraalkyl electron-rich alkene, namely, **1d** (**1**, R = Me), reveals that there is some slight delocalization (cf., the C_1–C_2 bond length, Table I) between the formal olefinic C_2 fragment and the 4 N's, even though the local geometry around each N is pyramidal rather than planar. Propositions ii and iii are related to those previously reported on $=\!\![\overline{CSC_6H_4N}R\text{-}o]_2 \xrightarrow{\Delta} o\text{-}\overline{SC_6H_4N{=}C}\overline{C(R')N(R)C_6H_4S}\text{-}o$,[6] C (R = CH_2Ph, *n* = 2 or 3, *m* = 2 or 3) $\xrightarrow{\Delta}$ D,[4] and **1e** $\xrightarrow{\Delta}$ **2e**.[5]


B


C


D

Experimental Section

All experiments were performed under argon, using standard vacuum-line and Schlenk techniques. Solvents were freshly distilled, dried, and degassed. NMR spectra were recorded either on a Bruker WP 80 or a WM 360 spectrometer. Electron-impact mass spectra were obtained on a Kratos 80 instrument at 70 eV. IR spectra were recorded on a Perkin-Elmer 597 spectrometer. Melting points are uncorrected. Photochemical experiments were carried out on a Rayonet R.S. reactor.

1,2-Bis(allylamino)ethane,[8] 1-aminobut-2-ene,[9] and 4-aminobut-1-ene[10] were prepared by literature procedures. *N,N′*-Dimethylformamide dimethyl acetal (Aldrich) and 1,2-dibromoethane (Fisons) were commercially available samples.

1,2-Bis(crotylamino)ethane. 1,2-Dibromoethane (2.11 g, 11 mmol) was slowly added to a stirred ice-cooled aqueous solution of 1-aminobut-2-ene (4.9 g, 56 mmol). The mixture was allowed to warm to room temperature and was refluxed for 20 h and then cooled to room temperature; sodium hydroxide (1.7 g, 43 mmol), dissolved in the minimum amount of water, was added. The excess of 1-aminobut-2-ene was removed by distillation. Two layers remained; the upper red-brown layer was separated and 1,2-bis(crotylamino)ethane (0.8 g, 43%) was collected by fractional distillation, bp 87 °C (4 Torr). Anal. Calcd for $C_{10}H_{22}Cl_2N_2$: C, 49.8; H, 9.1; N, 11.6. Found: C, 49.5; H, 8.8; N, 11.4. IR (film, cm^{-1}): 3300 (NH), 1670 (C=C). ^1H NMR (360 MHz, $CDCl_3$): δ 1.4 (s, 2 H), 1.5 (dd, 6 H), 2.6 (s, 4 H), 3.0 (m, 4 H), 5.4–5.5 (m, 4 H). $^{13}C\{^1H\}$ NMR (90.5 MHz, C_6D_6): δ, 17.7 (s, $\mathit{C}H_3$), 49.4 (s, $N\mathit{C}H_2\mathit{C}H_2N$), 52.1 (s, $MeCHCH\mathit{C}H_2$), 126.0 (s, $Me\mathit{C}H$), 131.1 (s, $MeCH\mathit{C}HCH_2$).

1,2-Bis(but-1′-enylamino)ethane. This compound was obtained by a similar procedure to that described above for 1,2-bis(crotylamino)ethane. It had bp 94 °C (5 Torr). Anal. Calcd

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(6) Baldwin, J. E.; Branz, S. E.; Walker, J. A. *J. Org. Chem.* **1977**, *42*, 4142. Baldwin, J. E.; Walker, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 596.

(7) Jug, K.; Nanda, D. N. *Theoret. Chim. Acta (Berlin)* **1980**, *57*, 107.

(8) Boon, W. R. *J. Chem. Soc.* **1947**, *30*, 07.

(9) Roberts, J. D.; Mazur, R. H. *J. Am. Chem. Soc.* **1951**, *73*, 2509.

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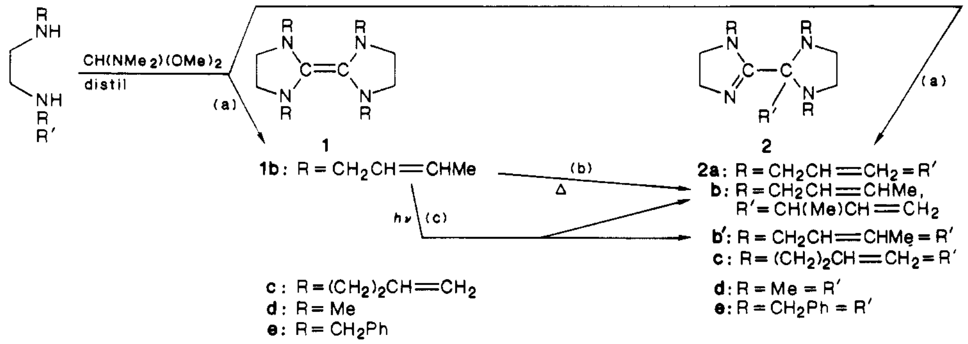
Scheme I[a]



[a] Reagents: (a) $C_6H_{11}Me$, reflux, 3 h, then elimination of MeOH and Me_2NH by distillation; (b) PhMe, reflux, 3 h; (c) irradiation in C_6D_6 at 350 nm, 2.5 h.

for $C_{10}H_{22}Cl_2N_2$: C, 49.8; H, 9.1; N, 11.6. Found: C, 49.6; H, 9.7; N, 11.3. IR (film, cm^{-1}): 3300 (NH), 1640 (C═C). ^1H NMR (360 MHz, $CDCl_3$): δ 1.2 (s, 2 H), 2–2.6 (m, 6 H), 4.8–5 (m, 4 H), 5.4–5.9 (m, 2 H). $^{13}C\{^1H\}$ NMR (90.5 MHz, C_6D_6): δ 48.9 (s, NCH_2CH_2N), 49.3 (s, $NCH_2CH_2CH{=}CH_2$), 115.2 (s, $CH{=}CH_2$) 136.7 (s, $NCH_2CH{=}$).

1,3,1′,3′-Tetracrotyl- (1b) and Tetrabut-1′-enylbiimidazolidinylidene (1c). The appropriate diamine (30 mmol) and an excess of *N*,*N*-dimethylformamide dimethyl acetal (40 mmol) were heated under reflux for ca. 3 h in methylcyclohexane (100 mL). The reaction mixture was then heated to 130 °C under distillation conditions and the produced methanol and dimethylamine were removed by distillation [together with excess of $CH(NMe_2)(OMe)_2$]. The residual oil was dissolved in benzene and filtered through Celite, and the solvent was removed from the filtrate in vacuo affording the appropriate title compound **1b** or **1c** as a very viscous oil. $^{13}C\{^1H\}$ NMR (90.5 MHz, C_6D_6) **1b** 130.3 ($CH{=}CHMe$), 126.7 ($CH{=}CHMe$), 125.6 (C_{sp^2}), 53.9 ($CH_2CH{=}$), 49.1 (NCH_2CH_2N); **1c** 137.3 ($CH{=}CH_2$), 115.7 ($CH{=}CH_2$), 49.9 [$(CH_2)_2CH$], 49.5 (NCH_2CH_2N). Their spectra showed them to be reasonably pure compounds.

[1,3]-Sigmatropic Amino-Claisen Rearrangement Product (2a) of 1,3,1′,3′-Tetraallylbiimidazolidinylidene (1a). A stirred solution of *N*,*N*-dimethylformamide dimethyl acetal (4.9 g, 40 mmol) and 1,2-bis(allylamino)ethane (4.37 g, 30 mmol) was heated under reflux for 3 h at 90 °C. The reaction mixture was then heated at 120 °C under distillation conditions and the produced methanol and dimethylamine as well as other volatiles were distilled off. The residue was freed from further volatile materials at 30 °C (10^{-2} Torr) to yield a yellow oil. This was extracted with pentane and the extract was filtered through Celite. After elimination from the filtrate of pentane in vacuo **2a** (2.55 g, 58%) was obtained. Anal. Calcd for $C_{18}H_{28}N_4$: C, 72.2, H, 9.3; N, 18.7. Found: C, 72.2; H, 9.4; N, 18.6. ^1H NMR (360 MHz, C_6D_6): δ 2.5 (m, 2 H), 2.7 (m, 6 H), 3.0 (m, 2 H), 3.2 (m, 2 H), 3.3 (m, 2 H), 3.8 (d, 2 H), 4.8 (m, 8 H), 5.6 (m, 3 H), 5.9 (m, 1 H) (the spectrum was assigned with the aid of computer simulation). $^{13}C\{^1H\}$ NMR (90.5 MHz, C_6D_6): δ 165.7, 81.9, 52.5, 52.4, 52.1, 52.0, 48.9, 39.4 (each signal was assigned by spin–echo experiments, consistent with the proposed structure).

Thermal Isomerization of 1,3,1′,3′-Tetracrotylbiimidazolidinylidene (1b). Compound **1b** (0.1 g, 0.28 mmol) was heated under reflux in toluene (10 mL) for ca. 3 h. The mixture was filtered through Celite. Solvent was eliminated from the filtrate in vacuo to afford a residue (0.08 g), comprised mainly of the rearrangement product **2b** with as principal contaminant unreacted **1b**. ^{13}C NMR (90.5 MHz, spin–echo mode, C_6D_6): δ 47.4 ($CCHMe$), 113.7 ($CH{=}CH_2$), 144.5 ($CH{=}CH_2$), 165.4 ($C{=}NCH_2$).

Photochemical Isomerization of 1,3,1′,3′-Tetracrotylbiimidazolidinylidene (1b). Compound **1b** (0.1 g, 0.28 mmol) was dissolved in benzene-d_6 and its ^1H NMR and ^{13}C NMR spectra were recorded. After irradiation at 350 nm for 2.5 h, the ^1H NMR spectrum showed the presence of some rearranged product. The irradiation was continued for a further 2.5 h, when no starting material was detectable. The identity of the rearranged products **2b** and **2b′** was established by $^{13}C\{^1H\}$ NMR (90.5 MHz, spin–echo mode, C_6D_6): δ **2b** 165.4 ($C{=}NCH_2$), 144.5 ($CH{=}CH_2$), 113.7 ($CH{=}CH_2$), 47.4 ($CCHMe$); **2b′** 52.1 ($NCHCH{=}$), 38.08 ($CCH_2CH{=}$), 18.3 ($={CHCH_3}$), 17.7 ($={CHCH_3}$).

Acknowledgment. We thank Professor J. N. Murrell for helpful discussions, Professor M. Traetteberg for the electron diffraction data on **1d** in Table I,[4] Drs. P. B. Hitchcock and H. A. Jasim for the X-ray data on **2e** in Table I,[5] and Universidad Nacional Autonoma de Mexico for a grant (to J.A.C.).

Registry No. **1b**, 122145-25-9; **1c**, 122145-26-0; **1d**, 1911-01-9; **2a**, 122171-14-6; **2b**, 122171-15-7; **2b′**, 122145-27-1; **2d**, 122145-28-2; $Br(CH_2)_2Br$, 106-93-4; $CH_3CH{=}CHCH_2NH_2$, 21035-54-1; $CH_2{=}CH(CH_2)_2NH_2$, 2524-49-4; $CH(NMe_2)(OMe)_2$, 4637-24-5; $CH_3CH{=}CHCH_2NH(CH_2)_2NHCH_2CH{=}CHCH_3$, 65838-12-2; $CH_2{=}CH(CH_2)_2[NH(CH_2)_2]_2CH{=}CH_2$, 122145-24-8; $CH_2{=}CHCH_2NH(CH_2)_2NHCH_2CH{=}CH_2$, 61798-21-8.

Microbial Transformations. 12. Regiospecific and Asymmetric Oxidation of the Remote Double Bond of Geraniol

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Received January 17, 1989

In spite of numerous efforts, the stereospecific oxidation of double bonds is still an important challenge to the organic chemist.[1] In the course of our work related to the microbiological oxidation of various substrates,[2] we have been interested in the possibility of regio- and stereospecifically[3] oxidizing the "remote" double bond of phenylcarbamate derivatives of geraniol and nerol **1** and **2**. This choice of substrate was dictated by three considerations. First, we have previously shown that the bio-

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(1) (a) Pfenninger, A. *Synthesis* **1986**, 89. (b) Gao, Y. G.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765.

(2) See, for instance: Archelas, A.; Fourneron, J. D.; Furstoss, R. *J. Org. Chem.* **1988**, *53*, 1797.

(3) Owing to the confusing use of the term *enantioselective* made in the current literature, which describes as well synthesis starting from optically active precursors, kinetic differentiation between enantiomers, or stereospecific selection of enantiotopic faces of a prochiral substrate, we consider that this type of reaction—i.e., the stereospecific transformation of a prochiral substrate into one single product enantiomer—should be called an *enantiogenic* reaction (since only one *enantio*mer is *gen*erated), rather than an *enantioselective* reaction (since no *selection* between two enantiomers is made on the starting compound).

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