George Gessert in providing illustrations of polyoxoanions appearing here and in our previous publications.[3]

Supplementary Material Available: Detailed synthetic procedures for the synthesis of $(Bu_4N)_6H_2Si_2W_{18}Nb_6O_{77}$ and $(Bu_4N)_7HSi_2W_{18}Nb_6O_{77}$; IR data and the ultracentrifugation solution molecular weight measurements on $Si_2W_{18}Nb_6O_{77}^{8-}$ and $SiW_9Nb_3O_{40}^{7-}$ (7 pages). Ordering information is given on any current masthead page.

Alternative Precursors to 1,4-Acyl Alkyl Biradicals: Cyclic *N*-Acyl-1,1-diazenes

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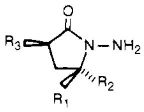
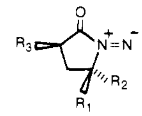
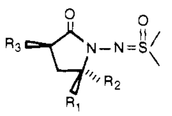
The photochemistry of cyclobutanone derivatives is unique relative to other cycloalkanones both with regard to the nature and stereoselectivity of the photoprocesses.[1] The regioselectivity has been rationalized in terms of initial α cleavage to form the most stable acyl alkyl biradical. In order to reconcile the high stereoselectivities for product formation and the lack of isomerization in the starting materials, it is necessary to postulate that the subsequent reactions of the proposed biradical are rapid with respect to bond rotation. In addition, theoretical studies have suggested that the acyl alkyl biradical is not necessarily even an intermediate[2] in the unusual photochemistry ring expansion to form oxacarbenes in protic solvents.

While there has been considerable experimental and theoretical efforts directed toward understanding the photochemistry of cyclobutanone derivatives, many questions still remain regarding the proposed intermediates.[1] What is clearly needed is an alternative source of 1,4-acyl alkyl biradicals in order to compare the chemistry with that observed from photolysis. Accordingly, we describe here the in situ generation and decomposition of the cyclic N-acyl-1,1-diazenes[3] **2a–d** as alternative sources of 1,4-acyl alkyl biradicals and discuss the similarity and differences relative to the photochemistry of the corresponding substituted cyclobutanones **4a–d**.

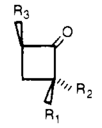




2a-d



3a-d

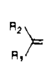
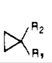
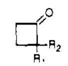
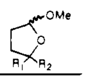
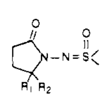
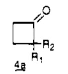
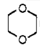
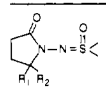
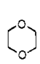
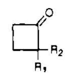


4a-d

1a $R_1 = R_2 = Ph$, $R_3 = H$
1b $R_1 = Me$, $R_2 = Ph$, $R_3 = H$
1c $R_1 = Me$, $R_2 = Ph$, $R_3 = Me$
1d $R_1 = Ph$, $R_2 = Me$, $R_3 = Me$

Since 1,1-diazene–dimethyl sulfoxide adducts have been described as useful in situ thermal and photochemical sources of the corresponding 1,1-diazenes,[4] we prepared the sulfoximines **3a,b** by the oxidation of **1a** and **1b**[5] with lead tetraacetate in the presence of Me_2SO. The thermal decomposition of **3a,b** followed first-order kinetics over the measurement interval (70–110 °C). The mass balance of volatile products was >95% and the results are shown in Table I[6] in comparison with those from the photochemical decomposition of the corresponding cyclobutanones **4a,b**.[7] It is obvious that although the cyclobutanones **4a** and **4b** are the major products from the decomposition of **3a** and **3b**, the relative proportion of olefin from β-elimination and the cyclopropane from decarbonylation both increase with temperature. No significant external heavy atom effect was observed when **3a** was decomposed in dibromomethane (entry 3). In methanol the cyclic acetals (see Table I) were major products. The use of methanol-d_1 in the decomposition of **3a** resulted in the formation of cyclic acetal which was >90% (^{1}H NMR and mass spectroscopic analysis) deuterated at the methine site of the acetal carbon atom. This result strongly suggests that the corresponding cyclic oxacarbene is an intermediate in the thermal process and demonstrates unambiguously that these intermediates can result from the cyclization of 1,4-acyl alkyl biradicals. Another remarkable feature is the observed *increase* in the relative yield of the cyclic acetals (Table I, entries 5 and 11) at the lower temperatures. In this regard, Agosta and co-workers[8] have previously reported cyclobutanones as major products from cyclic oxacarbenes generated pyrolytically, thus establishing a possible alternative thermal reaction pathway for

Table I[a]

Cmpd	Entry	Reaction Conditions					
 3a $R_1 = R_2 = Ph$	1		100°	11.6 (58.5)[a]	8.2 (41.4)[a]	80.2 —	— —
	2		25°[b]	8.8 (54.1)	5.1 (42.8)	88.0 —	— —
	3	CH_2Br_2	100°	13.2	10.2	76.4	—
	4	MeOH	100°	8.3 (38.2)	6.9 (31.7)	78.3 —	6.5 (30.0)
	5		25°[b]	2.5 (16.7)	1.6 (10.7)	— —	10.9 (72.6)
 4a	6	hν,  (0.12)[c,d]	25°	81	19	—	—
	7	hν, MeOH (0.13)[c,d]	25°	58	14	—	28
 3b $R_1 = Ph$, $R_2 = Me$	8		100°	7.4 (39.5)	11.3 (60.4)	78.5 —	—
	9		25°[b]	5.0 (37.8)	8.2 (62.1)	86.7 —	—
	10	MeOH	100°	3.6 (11.7)	6.9 (22.3)	69.0 —	20.4 (66.0)
	11		25°[b]	1.3 (3.8)	3.8 (11.3)	66.5 —	28.3 (84.2)
 4b	12	hν,  (0.12)[c,d]	25°	76	24	—	—
	13	hν, MeOH (0.11)[c,d]	25°	37	12	—	51

[a] Thermolysis products from **3a** and **3b**. Tubes were freeze–thaw degassed and sealed. The mass balance of volatile products was >95%. (a) Relative product yields excluding ring closure; (b) product yields extrapolated to 25 °C from measurements made between 70 and 110 °C; (c) solutions for irradiation (0.05 M) were degassed and sealed in Pyrex tubes: (d) quantum yields were determined at 313 nm by using a calibrated thermopile from Eppley Laboratory, Inc., to determine the light intensity; yields were determined by GLPC analysis at low conversions (<20%).

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(1) For an excellent review of the photochemistry of cyclobutanone derivatives, see: Morton, D. R.; Turro, N. J. *Adv. Photochem.* **1974**, *9*, 197 and references cited therein.

(2) (a) Quinkert, G.; Jacobs, P.; Stohrer, W.-D. *Agnew. Chem., Int. Ed. Engl.* **1974**, *13*, 197. (b) Quinkert, G.; Kaiser, K. H.; Stohrer, W.-D. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 98. (c) Stohrer, W.-D.; Weich, G.; Quinkert, G. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 199. (d) Stohrer, W.-D.; Weich, G.; Quinkert, G. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 200.

(3) Recently, Dervan and co-workers have described the spectral characterization of some persistent cycloalkyl 1,1-diazenes and studied their use as radical precursors: (a) Hinsberg, W.-D. III; Schultz, P. G.; Dervan, P. B. *J. Am. Chem. Soc.* **1982**, *104*, 766. (b) Schultz, P. G.; Dervan, P. B. *J. Am. Chem. Soc.* **1982**, *104*, 6660. (c) McIntyre, D. K.; Dervan, P. B. *J. Am. Chem. Soc.* **1982**, *104*, 6466. (d) Dervan, P. B.; Squillacote, M. E.; Lahti, P. M.; Sylvester, A. P.; Roberts, J. D. *J. Am. Chem. Soc.* **1981**, *103*, 1120.

(4) (a) Andersen, D. J.; Gilchrist, T. L.; Horwell, D. C.; Rees, C. W. *J. Chem. Soc., Chem. Commun.* **1969**, 146. (b) Gilchrist, T. L.; Rees, C. W.; Stanton, E. *J. Chem. Soc. C* **1971**, 988. Andersen, D. J.; Horwell, D. C.; Stanton, E. *J. Chem. Soc., Perkin Trans. 1* **1972**, 1317. (d) Kim, M.; White, J. D. *J. Am. Chem. Soc.* **1974**, *98*, 451.

(5) Miller, R. V.; Gölitz, P.; Janssen, J.; Lemmens, J. *J. Am. Chem. Soc.* **1984**, *106*, 1508.

(6) The structure of all new compounds is supported by analytical and spectral data.

(7) Trost, B. M.; Bogdanowicz, M. J. *J. Am. Chem. Soc.* **1973**, *95*, 5321.

(8) (a) Agosta, W. C.; Foster, A. M. *J. Chem. Soc., Chem. Commun.* **1971**, 433. (b) Foster, A. M.; Agosta, W. C. *J. Am. Chem. Soc.* **1972**, *94*, 5777. (c) Foster, A. M.; Agosta, W. C. *J. Am. Chem. Soc.* **1973**, *95*, 608.

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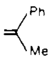
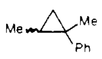
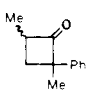
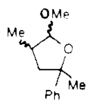
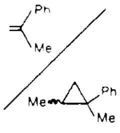
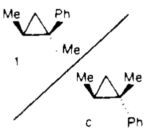
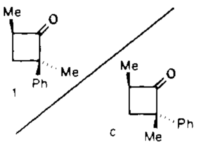
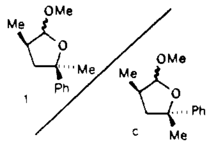
Table II[a]

Entry	Starting Material	Solvent								
1	**3d**, Δ	THF (25°)[a]	0.2 (9.1)[b]	2.0 (90.9)[b]	97.8 —	— —	0.1 —	0.9 —	15.7[c] —	—
2	**2d**, hν	Et$_2$O (25°)	1.2 (9.8)	11.0 (90.2)	87.8 —	— —	0.1 —	0.9 —	11.5 —	—
3	**4d**, hν	THF (25°)	56.8	43.3	—	—	1.3	1.3	>19	—
4	**3c**, Δ	THF (25°)[a]	0.1 (14.3)	0.6 (85.7)	99.3 —	— —	0.2 —	~1.0 —	< 0.5 —	— —
5	**2c**, hν	Et$_2$O (25°)	1.5 (11.0)	7.6 (83.5)	90.9 —	—	0.2	1.7	< 0.5	—
6	**4c**, hν	THF (25°)	51.6	48.4	—	—	1.1	2.6	< 0.5	—
7	**3d**, Δ	MeOH (25°)[a]	0.3 (3.1)	1.4 (15.5)	90.3 —	7.9 (81.4)	0.2 —	0.8 —	?[d] —	10[c]
8	**4d**, hν	MeOH (25°)	16.0	11.8	—	72.2	1.4	1.3	>19	>19
9	**3c**, Δ	MeOH (25°)[a]	0.1 (0.8)	0.5 (3.8)	86.7 —	12.7 (95.4)	0.2 —	0.1 —	?[d] —	< 0.5
10	**4c**, hν	MeOH (25°)	19.9	17.1	—	63.0	1.2	2.6	< 0.5	< 0.5

[a] Thermal and photochemical decomposition of the stereotagged diazenes and cyclobutanones. (a) Yields from the thermal processes are extrapolated to 25 °C; (b) relative yields not including cyclobutanone product for comparison with the cyclobutanone photolyses; (c) isomers were analyzed by GLPC (6 ft × $^1/_4$ in. glass column packed with 10% SILAR-10C on Chromosorb W); (d) the isomers were interconverted under the reaction conditions.

these intermediates at elevated temperatures.

The stereotagged biradicals were generated either by pyrolysis of the sulfoximines **3c** and **3d**[9] (70–110 °C) or by the direct photolysis of the corresponding *N*-acyl-1,1-diazenes **2c** or **2d**. Regarding the photolysis, it should be noted that the diazenes were used as generated without purification[10] and that they were thermally stable over the irradiation period. These results are shown in Table II together with those from the photolyses of the cyclobutanones **4c,d**. The photochemical decomposition of the diazenes could not be carried out in methanol since they were unstable in this nucleophilic medium.[5] Similarly, the stereoselectivity of cyclobutanone formation from the sulfoximines **3c** and **3d** could not be determined in methanol due to the rapid epimerization of **4c** and **4d** under the reaction conditions.

Examination of the results shown in Table II reveals a number of interesting features. For the most part, there is little difference in either the product ratios or the stereoselectivites observed in the photochemical decomposition of the diazenes and the thermal decomposition of the corresponding sulfoximines, except that photolysis resulted in slightly more β-elimination and decarbonylation relative to ring closure. The decomposition of the stereoisomeric diazenes (either thermal or photochemical) results predominantly in ring closure, although, as described earlier, the relative amounts of β-elimination and decarbonylation increase with temperature. Consistently, in methanol, cyclic acetal formation becomes a major reactive outlet for the biradical generated thermally from either **3c** or **3d** (entries 7 and 9).

The stereochemical results from the thermolysis of **3c,d** and from the photolysis of **2c,d** and the cyclobutanones **4c,d** are particularly interesting. In each case, the corresponding cyclobutanones (entries 1, 2, 4, and 5) were generated in a highly stereoselective fashion with predominantly retention of configuration. A similar stereoselectivity was observed in the formation of the cyclic acetals (entries 7 and 9) when the pyrolysis was conducted in methanol. This result demonstrates for the first time that 1,4-acyl alkyl biradicals generated in an unambiguous fashion are capable of both reclosure to cyclobutanones and ring expansion to oxacarbenes without significant isomerization caused by single-bond rotation. The result should be compared with the absence of isomerization in the starting materials as well as with the stereospecific formation of the cyclic acetals upon irradiation of **4c** and **4d** (entries 3, 6, 8, and 10).

Further comparison of the results obtained from the acyl-1,1-diazenes with those obtained in the photolysis of the corresponding cyclobutanones (Tables I and II) shows that even though the products in each case are identical in structure and stereochemistry, the product ratios are very different. For example, the cyclobutanones upon photolysis always show much more β-elimination than the corresponding 1,1-diazenes. Similar results were observed in methanol although cyclic acetal formation becomes a major pathway for both the diazenes and the cyclobutanones.

One particularly appealing rationalization of these results is suggested by a recent theoretical treatment of cyclobutanone photochemistry by Turro and co-workers.[1,11] These authors suggest that the strain relief attending α-cleavage of cyclobutanone makes energetically accessible a linear acyl alkyl biradical state which is also a symmetry-allowed transformation of the nπ* excited state. The subsequent reactions have been described as a composite of those ensuing from the linear, biradical state directly and those resulting from the lower energy bent biradical decay state. On the other hand, the pyrolysis of the sulfoximine derivatives or the photolysis of the 1,1-diazenes themselves would be expected to produce only a lower energy bent biradical state and thus product ratios should reflect the chemical reactivity of this state alone. This proposal nicely rationalizes the identical products produced both from both processes while suggesting a possible explanation for the varying product ratios.

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(9) Details on the synthesis and characterization of the stereotagged derivatives are available as supplementary material.

(10) The diazenes were generated as described[5] by the oxidation of **1c** and **1d** with *tert*-butyl hypochlorite in ether in the presence of 2,6-lutidine. The spectral properties of **2c,d** were very similar to those previously reported for **2a,b**.[5] These samples were irradiated until the purple color disappeared by use of a 450-W Hanovia immersion lamp and a piece of Corning 332 (λ > 330 nm) tubing as a filter. The cyclobutanones were irradiated in a Rayonet Reactor RPR-100 (Southern New England Ultraviolet) using 3000-Å lamps. The GLPC analyses were performed by use of 6 ft × $^1/_4$ in. glass columns packed with 10% SILAR-10C on 60/80 Chromosorb W.

(11) Turro, N. J.; Farneth, W. E.; Devaquet, A. *J. Am. Chem. Soc.* **1976**, *98*, 7425.

Registry No. 1a, 88730-05-6; **1b**, 88730-06-7; **1c**, 92472-05-4; **1d**, 92472-06-5; **2a**, 92472-07-6; **2b**, 92472-08-7; **2c**, 92472-09-8; **2d**, 92472-10-1; **3a**, 92472-11-2; **3b**, 92472-12-3; **3c**, 92472-13-4; **3d**, 92472-14-5; **4a**, 24104-20-9; **4b**, 75750-06-0; **4c**, 92472-15-6; **4c** (dinitrophenylhydrazone), 92472-19-0; **4d**, 92472-16-7; DMSO, 67-68-5; $Ph_2C{=}CH_2$, 612-00-0; $PhC(Me){=}CH_2$, 98-83-9; 1,1-diphenylcyclopropane, 3282-18-6; 1-methyl-1-phenylcyclopropane, 2214-14-4; *cis*-1,2-dimethyl-1-phenylcyclopropane, 77422-55-0; *trans*-1,2-dimethyl-1-phenylcyclopropane, 35496-06-1; 2,2-diphenyl-5-methoxytetrahydrofuran, 92472-17-8; 2,4-dimethyl-5-methoxy-2-phenyltetrahydrofuran, 92472-18-9; 5-methoxy-2-methyl-2-phenyltetrahydrofuran, 82194-21-6.

Supplementary Material Available: Table and figures on the synthesis and characterization of stereotagged derivatives (4 pages). Ordering information is given on any current masthead page.

Dilithium Tribenzylidenemethane-2TMEDA: The First X-ray Structure of a Y-Conjugated Trimethylenemethane Dianion Derivative

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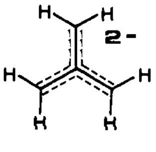
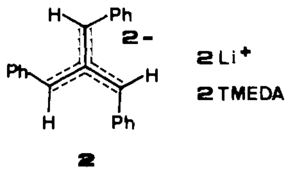
Received June 19, 1984

Klein's[1] recognition of the "Y-conjugated"[2] nature of the trimethylenemethane dianion (**1**) has led to widespread appreciation of the general importance of these species.[1-5] Such "dianions" owe their remarkable stabilities, relative to alternative linear and even cyclic 6π-electron topographies, to the favorable charge distributions which reduce electrostatic repulsions.[4] However, so-called "dianions" are better regarded as dimetallo compounds; their structures and stabilities may depend largely on the counterion interactions.[5-7] We now report the first[8] X-ray structure of a trimethylenemethane dianion dilithium salt, the symmetrically substituted dilithium tribenzylidenemethane-2TMEDA (TMEDA = tetramethylethylenediamine) (**2**).[3b]



1

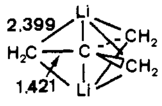


2

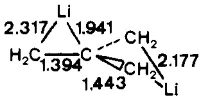
The X-ray structure of **2**[9] (Figures 1 and 2) does not, however, show the 3-fold symmetry indicated by MNDO calculations on the tribenzylidenemethane dianion itself;[3b] one of the three bonds to the central carbon atom is considerably shorter (1.388 (4) Å) than the other two (1.433 (3) and 1.460 (3) Å). This asymmetry is larger than would be expected from the perturbation of the two TMEDA ligands and must be caused by interactions with the two lithiums. One cation, Li(4), favors an allyl lithium-like[10] bridging position between C(17) and C(27). The asymmetry of this bridge (Li(4)-C(17) = 2.304 (5), Li(4)-C(27) = 2.234 (5) Å) can be attributed to the conformations of the phenyl groups on C(17) and C(27). The other lithium, Li(3), bridges the short C(7)-C(8) bond, and longer C-Li contacts to C(17) and the *ortho* carbon of one ring C(12) also are present. Why is this structure preferred? Consideration of the parent system provides some insights.

Calculations confirm the qualitative theoretical expectations:[1,4] the trimethylenemethane dianion (**1**) prefers D_{3h} symmetry. However, as an isolated entity, this species is unrealistic, since the second "anionic" electron will not be bound. The counterions are *required* for stability, and their presence controls the geometric preference.[5-8]

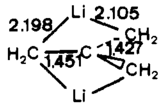
Ab initio calculations (3-21G basis set)[11] on various $C(CH_2)_3Li_2$ geometries reveal **3-5** to be the most favorable alternatives. The most symmetrical D_{3h} form (**3**), with the lithiums imposed to lie along the 3-fold axis, is *not* lowest in energy. On average, the lithium atoms are farther from the anion-bearing CH_2 carbons, and electrostatic interactions with the small lithium cations are not optimal. If the symmetry is reduced to C_s, a structure (**4**) is obtained which is only 0.1 kcal/mol more stable than **3**, and a doubly 1,3-lithium-bridged form (**5**, C_2) is 4.2 kcal/mol lower in energy. However, **5** has nearly equal C-C bond lengths and does not conform to the experimentally observed structure of the triphenyl derivative, **2**. The X-ray structure of **2** (Figures 1 and 2) corresponds more closely to that of **4**, which has two longer (1.443 Å) and one short (1.394 Å) C-C bonds. The potential energy surface is rather flat, and the further interactions of the lithium atoms with the phenyl groups are responsible for the structural preference observed in **2**.



3 D_{3h}



4 C_s



5 C_2

The C(7)-C(8) distance in **2** (Figures 1 and 2) is similar to that found for one of the disordered forms of the dilithiated stilbene

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(9) Triclinic (from hexane), space group $P\bar{1}$, $Z = 2$, $a = 8.627$ (6) Å, $b = 11.867$ (4) Å, $c = 17.026$ (9) Å, $\alpha = 72.51$ (4)°; $\beta = 83.88$ (6)°, $\gamma = 76.84$ (5)°, $V = 1617$ Å^3; $d_c = 1.085$ g/cm^3, $\lambda = 0.71069$ Å, $2° < \theta < 27°$; 63 292 reflection profiles were averaged to a set of 7039 structure factors (F^2), 3900 of which were stronger than 2σ. The structure was solved with MULTAN 76 and refined by X-RAY 76. The final R values based on the 3900 $F_0{}^2 2\sigma$ are $R(F^2) = 0.152$ and $R_w(F^2) = 0.147$. These relatively poor values are partly due to disorder in the TMEDA moieties (a number of similar cases are known[6a]). The structure of the rest of the system is considered to be significantly better. Further details of the crystal structure investigation are available on request from the Cambridge Crystallographic Data Center, University Chemical Laboratory, Cambridge CB2 1EW, England.

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(11) The GAUSSIAN 82 program, release A (Binkley, J. S.; Frisch, M. J.; Raghavachari, K.; De Frees, D. J.; Schlegel, H. B.; Whiteside, R. A.; Fluder, E.; Seeger, R.; Pople, J. A. Carnegie-Mellon University, Pittsburgh, PA, 1983), adapted to CDC computers by A. Sawaryn, was employed. The 3-21G//3-21G energies of **3**, **4**, and **5** (in au) are, respectively, -168.851 18, -168.851 35, and -168.857 88.

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