University, Camrbidge, Mass., 1971; and our product was indistinguishable from a sample prepared by him.
(36) R. Criegee, *Org. Synth.*, **46**, 34 (1966).
(37) In previous work[2] we have observed that 1,2-dimethylenecyclobutane forms polymeric material, unless it is stored at low temperature under an inert atmosphere.
(38) R. Criegee, W. D. Wirth, W. Engel, and H.-A. Brune, *Chem. Ber.*, **96**, 2230 (1963).

Cycloaddition Reactions of 1,2,5,6-Tetramethyl-3,4,7,8-tetramethylenetricyclo[3.3.0.$0^{2,6}$]octane. Evidence for Chemical Consequences of Orbital Interactions in Molecules Containing Unsaturatively 1,3-Bridged Cyclobutane Rings

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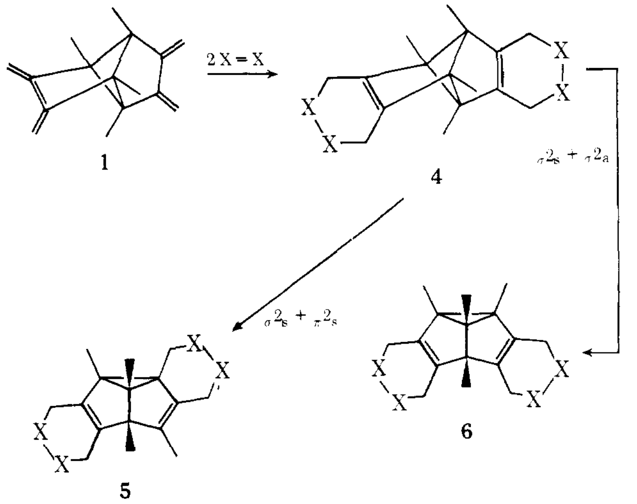
The title compound (1) reacts with tetracyanoethylene and *N*-phenyltriazolinedione to give rearranged adducts. Bond reorganization occurs after the first cycloaddition, and the structures of the products rule out a $_\sigma2_s + {}_\sigma2_a$ mechanism for rearrangement. With the latter dienophile an unrearranged monoadduct (**7b**) has been observed by NMR at low temperatures, and the activation parameters for its rearrangement to **8b** have been obtained. The energy of activation is consistent with that expected for a forbidden $_\sigma2_s + {}_\pi2_s$ process. The instability of molecules containing cyclobutane rings 1,3-bridged by ethylene, the contrasting thermal stability of **1**, and the reluctance of **1** to undergo Diels–Alder cycloaddition reactions are all rationalized by analysis of the interactions between the σ orbitals of the cyclobutane ring and the π orbitals of the unsaturated bridging groups. Calculations are reported that support this interpretation of the experimental results.

In the accompanying paper[2] we reported the transformation of 1,2,5,6-tetramethyl-3,4,7,8-tetramethylenetricycloocta-1,5-diene into 1,2,5,6-tetramethyl-3,4,7,8-tetramethylenetricyclo[3.3.0.$0^{2,6}$]octane (**1**), either by direct or sensitized photolysis or by pyrolysis. That **1** is formed in the thermal reaction is really most surprising, since tricyclo[3.3.0.$0^{2,6}$]octa-3,7-diene (**2**) is a very unstable compound, undergoing rapid rearrangement to semibullvalene (**3**) at room temperature.[3] Indeed, the thermal rearrangement of **2** to **3** is so facile for a reaction that either involves a diradical intermediate[3] or proceeds by a forbidden but concerted $_\sigma2_s + {}_\pi2_s$ mechanism[4] that a novel, symmetry allowed, $_\sigma2_s + {}_\sigma2_a$ pathway was proposed for this transformation.[5]



The availability of **1** appeared to afford an excellent opportunity to test whether a $_\sigma2_s + {}_\sigma2_a$ pathway was, in fact, involved in the rearrangement of **2** to **3**. Diels–Alder cycloadditions of 2 mol of a dienophile to **1** would provide **4**, a derivative of **2** in which the positions of the double bonds are labeled by the six-membered rings. Rearrangement of **4** by a forbidden $_\sigma2_s + {}_\pi2_s$ pathway, whether concerted or involving a diradical as a discrete intermediate, requires the formal shift of a double bond and leads to **5**. In contrast, since the π bonds are not involved in the $_\sigma2_s + {}_\sigma2_a$ mechanism, the labeling of the double bonds is different in the semibullvalene (**6**) that is the expected product if this pathway is utilized. Therefore, we undertook an investigation of the cycloaddition reactions of **1** in order to determine whether the semibullvalene formed had structure **5** or **6**.[6]

Results

To our surprise, compound **1** proved to be a most unreactive diene. Using such dienophiles as dimethyl acetylenedicarboxylate, dicyanoacetylene, and diethyl azodicarboxylate, we were unable to obtain an adduct of **1**. Although **1** did react with tetracyanoethylene (TCNE) to give a bis adduct, even with this potent dienophile reaction was surprisingly slow, requiring 2.5 h in refluxing tetrahydrofuran for completion. For comparison, the reaction of TCNE with 1,2-dimethylenecyclobutane in THF is instantaneous at room temperature.

The ^{1}H NMR spectrum of the TCNE bis adduct of **1** was entirely consistent with the formulation of its structure as **5** (X = $C(CN)_2$). Since **5** and **6** are both semibullvalenes, it was to be expected that both molecules would be rapidly fluxional at all but very low temperatures.[7] Whereas Cope rearrangement of **6** is not a degenerate process, the corresponding rearrangement of **5** is. Thus, on the NMR time scale **5**, because of its fluxionality, acquires an effective C_2 axis of symmetry, while **6** maintains only the plane of symmetry present in either of the nonequivalent divinylcyclopropane structures that can be written for it. Compounds **5** and **6** can, therefore, be most easily differentiated by the fact that the former should show only two types of methyl groups in its NMR spectrum, while the latter would be expected to exhibit three. At 100 MHz in acetone-d_6 the ^{1}H NMR spectrum of the TCNE bis adduct of **1** showed only two methyl resonances, thus leading to the assignment of its structure as **5**.[2b]

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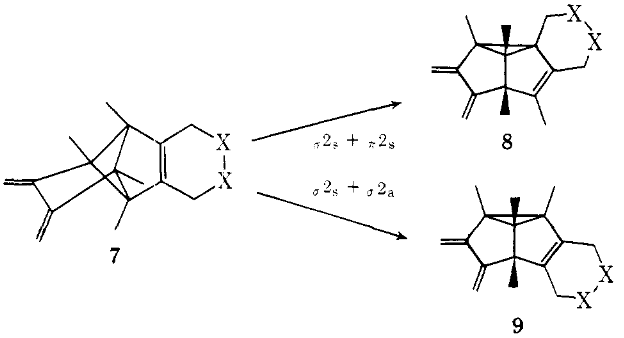
The observation of only two types of methyl resonances, although a necessary condition for assigning structure **5** to the bis adduct, is not sufficient to exclude conclusively structure **6**, for there exists the possibility that the two unique methyl groups in this latter structure might accidentally have the same chemical shift. If this were the case in one solvent, it might be that in another the accidental degeneracy would be lifted. It is also possible that the two methyl groups in one or more solvents might have slightly different chemical shifts but that higher magnetic fields are necessary to resolve them. Therefore, we obtained 220-MHz spectra of the TCNE bis adduct of **1** in both acetone-d_6 and pyridine-d_5,[8] but the two methyl resonances both remained sharp singlets. Although this finding increased our confidence that **5** did, in fact, represent the structure of the bis adduct, the possibility that we had obtained **6** instead could not be eliminated. Indeed, while additional NMR experiments could further increase the likelihood that **5** was the compound in hand, such studies could not unequivocally rule out **6**.

At this point we carried out an experiment which indicated that **4** was not involved at all in the transformation of **1** into the TCNE bis adduct that we had isolated. When the cycloaddition reaction between **1** and TCNE was conducted using only one equivalent of the dienophile, no monoadduct was isolated. Instead, a 1:1 mixture of the bis adduct and unreacted **1** was obtained. Clearly, the second Diels–Alder reaction must have been faster than the first. However, it was hard to see why cycloaddition at one diene unit of **1** to give **7a** should enhance the reactivity of the remaining diene moiety. On the other hand, the results of the experiment with one equivalent of TCNE could be rationalized if, under the reaction conditions, it was the monoadduct (**7a**) that rearranged. The chemistry of **1** indicated that the diene groups in it were unusually unreactive toward Diels–Alder cycloadditions, but there was no reason to believe that the diene units in either of the two possible rearrangement products, **8a** and **9a**, would exhibit anything but the high reactivity toward TCNE, usually observed in *cisoid* dienes. Thus, the initial slow cycloaddition to **1**, if followed by a rapid rearrangement of **7a** to **8a** or **9a**, would be expected to lead to reaction with a second molecule of TCNE at a rate much greater than the first.

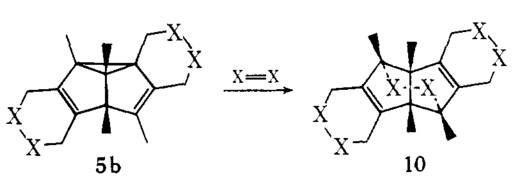


a, X = C(CN)$_2$; b, X—X = NCON(Ph)CON

The interpretation of the experiment with one equivalent of TCNE in terms of the monoadduct (**7a**) as the species that rearranged suggested an interesting possibility for unequivocally resolving the question of the mechanism of the rearrangement. Unlike the diadducts, **5** and **6**, the monoadducts, **8** and **9**, can be unambiguously differentiated by NMR spectroscopy, since prior to the second cycloaddition these molecules lack the other endocyclic double bond that is required for fluxionality. Therefore, in the product (**8**) expected from the $_\sigma2_s + {}_\pi2_s$, or the equivalent diradical pathway, the formal shift required of the double bond in **7** would be signalled by the appearance in the NMR spectrum of a methyl group attached to a doubly bonded carbon. In contrast, since in the $_\sigma2_s + {}_\sigma2_a$ mechanism the double bonds are not involved, all the methyl groups remain attached to saturated carbon atoms in the product (**9**) expected from this pathway. Thus, we sought a dienophile that would allow us to isolate the rearranged monoadduct of **1**.

Such a dienophile was found in *N*-phenyltriazolinedione (PTAD). At 0 °C in $CHCl_3$ equimolar amounts of **1** and PTAD reacted to give a rearranged monoadduct to which the structure **8b** could unequivocally be assigned. In particular, a methyl group appeared at δ 1.51 in the ^1H NMR spectrum of this compound. Not only was the chemical shift about that expected for allylic methyl protons, but the resonance appeared as a doublet with $J = 2$ Hz. The proton to which it was coupled was centered at δ 3.70 and represented the upfield half of an AB quartet, $J = 14$ Hz, each of the two upfield components of which were further split into quartets, $J = 2$ Hz. The 2-Hz splittings are due to coupling between the methyl group and the allylic proton that lies in the π cloud of the adjacent double bond and which is consequently shielded by it.[9] The formation of **8b** is wholly consistent with the $_\sigma2_s + {}_\pi2_s$, or equivalent diradical pathway, but conclusively excludes a $_\sigma2_s + {}_\sigma2_s$ mechanism.

Further confirmation of the structure of **8b** came from its reaction with another equivalent of PTAD to yield the bis adduct (**5b**). The ^1H NMR spectrum of **5b** showed, as expected, only two methyl resonances. Interestingly, when **1** was allowed to react with 2 mol of PTAD at room temperature, the major product was not **5b** but a triadduct to which the structure **10** was assigned on the basis of the NMR spectrum. The formation of **10** had a parallel in the reaction of octamethylsemibullvalene with azoesters and TCNE,[10] and we did, indeed, find that octamethylsemibullvalene also reacted with PTAD.[11] In this case, however, not only was the diazalumibullvalene derivative corresponding to **10** isolated,[12] but the diazatriquinacene derivative was obtained as well. Although the former adduct might be the result of an allowed $_\sigma2_s + {}_\pi2_s + {}_\pi2_s$ cycloaddition, the presence of the latter compound and the facile equilibration of the two adducts in solvents of high dielectric constant led us to postulate a common dipolar intermediate in the formation of both the "allowed" and "forbidden" PTAD adducts.[11] More recently, Askani has found that PTAD adds to less alkylated semibullvalenes to give only the "forbidden" diazatriquinancene type products, and scrambling of the alkyl groups in the products again indicates the intervention of a dipolar intermediate.[13] Thus, it is likely that in the formation of the triadduct (**10**) a similar intermediate is involved, despite the fact that **10** could, in principle, result from a concerted cycloaddition.



X—X = NCON(Ph)CON

The reason for the formation of the triadduct (**10**) when only 2 equiv of PTAD were used must be that either the cycloaddition to **1** or the rearrangement of **7b** is slow, compared to the cycloaddition to **8b** and the subsequent reaction of **5b** to give **10**. However, it was clear from the fact that the monoadduct (**8b**) could be isolated that the rearrangement must be the slow step. If the cycloaddition were the slow step, as it is in the reaction of TCNE with **1**, we would never have been able to obtain **8b**. It seemed possible, therefore, that we might be able to observe **7b** directly, before it rearranged to **8**. This did, in fact, turn out to be the case.

When 1 equiv of PTAD was added to a $CDCl_3$ solution of

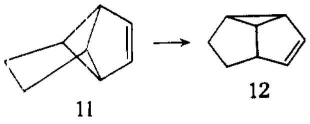
Table I. Rate Constants for the Rearrangement of 7b to 8b

T, °C	$k \times 10^3$, s^{-1}
16.2	0.259 ± 0.005
26.8	0.902 ± 0.030
34.4	2.36 ± 0.06
43.5	8.65 ± 0.40

1 in an NMR tube at −40 °C, no reaction occurred until the solution was warmed to −15 °C. At −5 °C the red color of the PTAD was completely discharged, and new singlets appeared in the ^{1}H NMR spectrum at δ 0.67 (6 H), 1.14 (6 H), 4.32 (4 H), 4.85 (2 H), and 5.48 (2 H).[14] The NMR spectrum of the unrearranged monoadduct (**7b**) remained unchanged for several hours at 0 °C; however, at higher temperatures transformation of **7b** to **8b** occurred. The rearrangement could be followed conveniently by NMR between 15 and 40 °C. The disappearance of **7b** could be monitored quantitatively by integration of the singlet at δ 0.67 and was found to follow good first-order kinetics. The rate constant for the rearrangement was obtained at four temperatures by least-squares fitting of the kinetic data. These rate constants and the probable errors in them are shown in Table I. As the temperature increased and the rearrangement became more rapid, the NMR method for following the reaction became less accurate, as indicated by the larger errors in the rate constants at the higher temperatures. A least-squares fit of the rate constants to the Arrhenius equation, $\log k = \log A - E_a/2.303RT$, gave $\log A = 13.9 \pm 1.1$ and $E_a = 23.2 \pm 1.2$ kcal/mol.

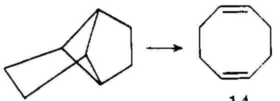
Discussion

Not only is the labeling study indicative of a ${}_{\sigma}2_{s} + {}_{\pi}2_{s}$ or equivalent diradical mechanism for the rearrangement of **7** to **8**, but the measured energy of activation is also in accord with such a pathway. Frey and Hopkins have found the activation energy for the rearrangement of tricyclo[3.3.0.0^{2,6}]octene (**11**) to tricyclo[3.3.0.0^{2,8}]octene (**12**) to be 35.3 kcal/mol.[15] Neglecting all the possible effects on the rate that the four methyl[16] and two methylene[17] groups present in **7** might have, as well as the additional alkyl substitution on the endocyclic double bond, and focussing only on the additional stabilization of a putative diradical intermediate by one of the exocyclic double bonds, the energy of activation for the rearrangement of **7** should be lower than that for **11** by the allylic resonance energy.[18] The actual difference in activation energies of 12 kcal/mol is (probably fortuitously) close to the value of 12–13 kcal/mol for the allylic resonance energy, obtained by Doering and Beasley.[19]



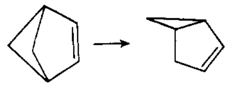
11 12

Because **7** is transformed rapidly to **8** at room temperature by a pathway that is forbidden in the Woodward–Hoffmann sense,[20] the rate of its rearrangement appears as a glaring anomaly. However, as pointed out above, the energy of activation for its rearrangement is lower than that for **11** by almost exactly the allylic resonance energy. Thus, the small magnitude of the activation energy for rearrangement of **11** is equally anomalous. Indeed, Frey has previously pointed out that the dramatic rate at which tricyclo[3.3.0.0^{2,6}]octadiene (**2**) rearranges to semibullvalene (**3**)[3] is consistent with an energy of activation for this process that is lower by only the allylic resonance energy than that for the transformation of **11** to **12**.[15] That the energy of activation for the rearrangement of **11** is, in fact, anomalously low can be judged by comparing it with that for the cleavage of tricyclo[3.3.0.0^{2,6}]octane (**13**) to 1,5-cyclooctadiene (**14**). If both reactions involve biradical intermediates, then, in the absence of other effects, the energy of activation for **11** → **12** should be approximately 12 kcal/mol lower than that for **13** → **14**. Since the energy of activation for the latter reaction is 56 kcal/mol,[21] the actual difference is 21 kcal/mol.



13 14

A similar disparity exists between the energy of activation for the rearrangement of bicyclo[2.1.1]hexene (**15**) to bicyclo[3.1.0]hexene and that for cleavage of bicyclo[2.1.1]hexane (**16**) to 1,5-hexadiene. Although the former process has been shown to proceed primarily by an allowed, concerted ${}_{\sigma}2_{a} + {}_{\pi}2_{s}$ pathway, the energetic advantage of the allowed over a forbidden or diradical pathway is known to be small.[15,22] Assuming, then, that the reactions again should vary in activation energy only by the allylic resonance energy, a difference of roughly 12 kcal/mol is expected. The observed energies of activation for the rearrangement of bicyclic compounds **15**[15] and **16**[23] are essentially the same as those for their tricyclic analogues, **11** and **13**. Thus, the activation energy for the rearrangement of the unsaturated compound is again on the order of 8–10 kcal/mol lower than expected.



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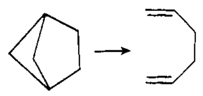

16

Since an activation energy represents an energy difference, the anomalously low activation energies for rearrangement of molecules containing a cyclobutane ring 1,3-bridged by ethylene (e.g., **2**, **7**, **11**, and **15**) can be explained either by effects that lower the energy of the transition states or raise the energy of the reactants. Our labeling study, which rules out a ${}_{\sigma}2_{s} + {}_{\sigma}2_{a}$ mechanism for the rearrangement of one of these molecules (**7**), is consistent with a biradical (or a forbidden but concerted ${}_{\sigma}2_{s} + {}_{\pi}2_{s}$)[4] pathway, and the activation energy for the rearrangement of **7**, when compared with that for **11**, is also indicative of such a pathway. Therefore, there is little reason to believe that the anomalously low activation energies are the result of transition state stabilization. Thus, one is left with reactant destabilization as the probable cause of the rapid rearrangements. Such destabilization of molecules like **11** and **15**, relative to their saturated analogues, **13** and **16**, should be manifested in anomalously high heats of hydrogenation. Regrettably, to the best of our knowledge, no such measurements have been made to either **11** or **15**. Consequently, we must rely on the data from the kinetic studies to obtain an estimate of 8–10 kcal/mol as the apparent destabilization caused by the introduction of a double bond into **13** or **16** to give **11** or **15**.

Such an estimate is prone to error, for underlying it is the assumption that both the satuarted and unsaturated systems rearrange by transition states that may be described as biradical in nature, so that in the absence of differential reactant destabilization the unsaturated systems should have energies of activation that are lower by exactly the allylic resonance energy of 12 kcal/mol[19] than their saturated analogues. Even if this assumption is more or less valid, it is not at all certain that the actual magnitude of differential reactant destabilization will be manifested in the comparison of activation

(6) Preliminary communication: A. Gold and W. T. Borden, *J. Am. Chem. Soc.*, **94,** 7179 (1972).

(7) H. E. Zimmerman and G. L. Grunwald, *J. Am. Chem. Soc.*, **88,** 183 (1966); F. A. L. Anet and G. E. Schenck, *Tetrahedron Lett.*, 4237 (1970); A. K. Cheng, F. A. L. Anet, J. Mioduski, and J. Meinwald, *J. Am. Chem. Soc.*, **96,** 2887 (1974).

(8) These spectra were obtained at the Central Research Laboratories of E. I. du Pont de Nemours & Co., through the kind cooperation of Dr. H. E. Simmons.

(9) See, for instance, R. R. Faser and B. F. Raby, *J. Am. Chem. Soc.*, **94,** 3458 (1972).

(10) R. Criegee and R. Askani, *Angew. Chem., Int. Ed. Engl.*, **7,** 537 (1968).

(11) Y. C. Toong, W. T. Borden, and A. Gold, *Tetrahedron Lett.*, 1549 (1975).

(12) One reason why we carried out the reaction of PTAD with octamethylsemibullvalene was that the PTAD triadduct (**10**) had a temperature-dependent NMR spectrum, and we wished to investigate the origin of this phenomenon in a simpler system. Although the temperature dependence could be due to slow flipping of the urazole rings in both molecules,[11] there is precedent for slow methyl group rotation in related systems [G. A. Olah, V. J. S. Staral, and L. Paquette, *J. Am. Chem. Soc.*, **98,** 1267 (1976)].

(13) R. Askani, R. Kirsten, and B. Dugall, *Tetrahedron Lett.*, 3891 (1976).

(14) From the NMR spectra of some related bicyclo[2.1.1]hexane derivatives studied by G. Capozzi and H. Hogeveen, *J. Am. Chem. Soc.*, **97,** 1479 (1975), it appears that butadiene has a larger shielding effect on a methyl group pendant over the π system than an ethylene bridge. On this basis it is possible to assign, at least tentatively, the two types of methyl resonances in **7b.**

(15) H. M. Frey and R. G. Hopkins, *J. Chem. Soc. B*, 1410 (1970).

(16) There is some evidence[2a] that suggests octamethyltricyclo[3.3.0.$0^{2,6}$]-octadiene rearranges more rapidly than the unsubstituted hydrocarbon.

(17) Some of the stabilizing π interaction between the two exocyclic double bonds present in **7** is presumably lost in the transition state for its rearrangement, where one double bond functions to stabilize an adjacent radical. In addition, the mixing between the orbitals of the butadiene bridge and those of the cyclobutane ring in **7** (vide infra) is altered in the transition state.

(18) It should be noted that such expectations are sometimes in stark disagreement with experimental reality. See, for instance, J. J. Gajewski, *J. Am. Chem. Soc.*, **97,** 3457 (1975). The explanation, proposed in this paper by Gajewski, of the nearly equal energies of activation for degenerate rearrangement of methylenecyclobutane and 1,2-dimethylenecyclobutane has been criticized; W. T. Borden and E. R. Davidson, *J. Am. Chem. Soc.*, **99,** 4587 (1977).

(19) W. von E. Doering and G. H. Beasley, *Tetrahedron*, **29,** 2231 (1973).

(20) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **11,** 781 (1969).

(21) R. Srinivasan and A. A. Levy, *J. Am. Chem. Soc.*, **85,** 3756 (1963).

(22) W. R. Roth and A. Friedrich, *Tetrahedron Lett.*, 2607 (1969). The effect of radical stabilizing substitutents on the rate of rearrangement also indicates that the allowed transition state has substantial biradical character; F. Scheidt and W. Kirmse, *Chem. Commun.*, 716 (1972).

(23) R. Srinivasan and A. Levy, *J. Am. Chem. Soc.*, **85,** 3363 (1963).

(24) One might expect that removal of two more hydrogen atoms from the remaining saturated bridge in **11**, to give **2**, should lower the activation energy by another 19 kcal/mol. Assuming that the preexponential factor is the same for both rearrangements, the anticipated activation energy of 16 kcal/mol for transformation of **2** to **3** is incompatible with the apparent stability of **2** at 0 °C.[3] The explanation of this discrepancy could be that less of the total reactant destabilization is released in the transition state for rearrangement of **2** than in that for **11.**

(25) J. Meinwald and F. Uno, *J. Am. Chem. Soc.*, **90,** 800 (1968).

(26) G. A. Abad, S. P. Jindal, and T. T. Tidwell, *J. Am. Chem. Soc.*, **95,** 6326 (1973).

(27) F. T. Bond, C.-Y. H[illegible] and O. McConnell, *J. Org. Chem.*, **41,** 1416 (1976).

(28) (a) D. L. Zebelman, S. H. Bauer, and J. F. Chiang, *Tetrahedron*, **28,** 2727 (1972); (b) *C. S. Wang and M. D. Harmony, J. Am. Chem. Soc.*, **98,** 1108 (1976).

(29) G. Capozzi and H. Hogeveen, *J. Am. Chem. Soc.*, **97,** 1479 (1975), have noted a similar lack of Diels–Alder reactivity in a derivative of 2,3-dimethylenebicyclo[2.1.1]hexane.

(30) W. L. Jorgensen and W. T. Borden, *J. Am. Chem. Soc.*, **95,** 6649 (1973).

(31) R. Hoffmann and R. B. Davidson, *J. Am. Chem. Soc.*, **93,** 5699 (1971).

(32) R. Glieter and T. Kobayashi, *Helv. Chim. Acta*, **54,** 1081 (1971).

(33) P. Bischof, R. Gleiter, M. J. Kukla, and L. A. Paquette, *J. Electron Spectrosc.*, **4,** 177 (1974).

(34) W. L. Jorgensen, *J. Am. Chem. Soc.*, **97,** 3082 (1975).

(35) The net destabilization, caused by the mixing between the MO's of the ring and bridge in **15**, is smaller than the destabilization, resulting from the interaction of the double bonds, in cyclobutadiene for two reasons. First the HOMO of the cyclobutane ring has appreciable coefficients on atoms that are not adjacent to the double bond. Second, the destabilizing effect of the HOMO–HOMO interaction in **15** is partially mitigated by a stabilizing mixing of the next highest occupied MO of the ring with the LUMO of the bridge.[30]

(36) A. T. Bloomquist and Y. Meinwald, *J. Am. Chem. Soc.*, **79,** 5316 (1957); R. Criegee, *Angew. Chem., Int. Ed. Engl.*, **1,** 519 (1962).

(37) Further evidence of the importance of orbital interactions in inhibiting Diels–Alder cycloadditions in such molecules comes from an apparent exception. H. Hogeveen and P. W. Kwant, *Tetradron Lett.*, 3747 (1973), have found that a molecule containing a bicyclobutane ring 2,4-bridged by butadiene readily undergoes Diels–Alder reactions. This apparent anomaly is readily understood when it is noted that there is a change in orbital ordering in going from a cyclobutane to a bicyclobutane ring. In bicyclobutane the highest occupied ring orbital that can interact with an unsaturated 2,4-bridging group has the correct symmetry for mixing with the HOMO of a butadiene and the LUMO of an ethylene bridge. The change in symmetry of the ring HOMO in replacing cyclobutane with bicyclobutane has been used to explain the difference in Diels–Alder reactivity between molecules containing butadiene groups bridging these rings [W. L. Jorgensen and W. T. Borden, *Tetrahedron Lett.*, 223 (1975)].

(38) The EH parameters used were taken from R. Hoffmann, S. Swaminathan, B. G. Odell, and R. Gleiter, *J. Am. Chem. Soc.*, **92,** 7091 (1970). It should be noted that no quantitative significance should be attached to energies calculated by the EH method.

(39) P. George, M. Trachtman, C. W. Bock and A. M. Brett, *Tetrahedron*, **32,** 317 (1976).

(40) The choice of geometries for these calculations presents a problem. Experimental geometries for many of the molecules are unavailable, and even when geometries have been published, some have subsequently been shown to be in error.[28b] In previous studies we selectively manipulated experimental geometries to obtain coordinates for molecules whose structures had not been determined or the accuracy of whose structure we doubted.[30,34] In the calculations reported here we used MINDO/3 method [R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97,** 1285 (1975)] to find minimum energy geometries. However, as noted previously, MINDO energies for some of these molecules are expected to be even less reliable than the energies from EH calculations, because of the well-known inability of calculations that neglect overlap to account for destabilization due to interaction of filled MO's.[30] Therefore, we were forced to rely on EH calculations for energies at MINDO/3 geometries—an incongruity whose potential for error we fully appreciate. However, since the EH method for the calculation of energies is at best semiquantitative anyway, this procedure for generating geometries recommended itself by virtue of its convenience and a certain measure of internal consistency. If quantitatively accurate values for the energies of the isodesmic reactions reported here were desired, complete geometry optimization[41] and energy calculation by a reliable ab initio method would be the procedure of choice. The cost/benefit ratio of such an undertaking has, however, dissuaded us from pursuing such a study.

(41) It should be noted that total overlap populations between atoms in strained polycyclic systems depend much more critically on the choice of geometry than do the π bond orders that we have used to analyze our computational results.[30,34] Therefore, interpretations, based on total overlap populations, of calculations that do not include geometry optimization [see, for instance, P. Th. van Duijnen, P. van der Ploeg, H. Hogeveen, and W. F. J. Hurdeman, *Tetrahedron Lett.*, 573 (1975)] should be viewed with some caution.

(42) For a recent discussion of the bonding in *cis*-2-butene see N. D. Epiotis, R. L. Yates, and F. Bernardi, *J. Am. Chem. Soc.*, **97,** 5961 (1975).

(43) As noted previously,[30] the magnitude of the destabilization is *underestimated* by analysis of just nearest neighbor π interactions between ring and bridge. The 1,3-π bond orders in **15** are also negative and much larger in magnitude, -0.208. The reason is that the mixing of the next to highest occupied MO of the cyclobutane ring with the LUMO of the bridge, which mitigates the destabilizing HOMO–HOMO interaction between nearest neighbors, actually enhances the magnitude of 1,3 π antibonding, since the mixing involves orbitals that are antisymmetric to the plane bisecting the double bond. Although 1,3-π overlap in **15** is only about a quarter of that between atoms 1 and 2, nevertheless the 1,3-π interaction is calculated (from comparison of the π overlap populations) to be more than five times as destabilizing as that between nearest neighbors. For similar reasons the 1,3-π bond orders in *cis*-2-butene are also expected to be negative, as, in fact, they are found to be by an EH calculation. Nevertheless, their magnitude is computed to be only a quarter the size of the 1,3-π bond orders in **15.**

(44) A previous EH calculation[30] at a different geometry[40] found these bond orders to be 0.078.

(45) Ab initio calculations [W. Hehre, *J. Am. Chem. Soc.*, **94,** 6592 (1972)] on vinylcyclopropane, vinylcyclobutane, and propene confirm that the stabilizing interaction between the four-membered ring and a double bond is greater than that of methyl but less than that of the three-membered ring.

(46) Actually, one would expect the reaction that replaces one ethylene bridge in **2** with butadiene to be more exothermic than the reaction that replaces the second since, in the molecule bridged by one butadiene and one ethylene the orbitals of the cyclobutane ring are not as contrained by symmetry as they are in the molecules that have two identical bridging groups. The energies of the two isodesmic reactions are calculated as -22.6 and -22.5 kcal/mol, respectively,[47] but the difference of only 0.1 kcal/mol cannot be regarded as at all significant. It should be noted, however, that, experimentally, **1** is a more reactive diene than **7b.** In fact, in the temperature range 0–15 °C rearrangement of **7b** competes effectively with the addition of a second mole of PTAD to it.

(47) The energy of the reaction in eq 1 is now calculated as +24 kcal/mol, whereas previously it was found to be +17 kcal/mol.[30] At the MINDO/3 geometries[40] **15** and **17** are found to be on the order of 60 kcal/mol higher in energy than previously. However, the increase in energy is greater for **15** by about 10 kcal/mol, but this is partially offset by a greater decrease in the energy of butadiene than in that of ethylene. It is amusing to note that if eq 3 is subtracted from eq 2, so that a reaction analogous to **1** is obtained but with ethylene and butadiene replaced by *cis*-2-butene and 2,3-dimethylbutadiene, the calculated energy is 18 kcal/mol—much closer to that computed previously for eq 1. The difference of 6 kcal/mol in the calculated energy of eq 1, depending on whether ethylene and butadiene or their dimethyl derivatives are used as reference, stems from the fact that the reaction, *cisoid*-butadiene + *cis*-2-butene → *cisoid*-2,3-dimethylbutadiene + ethylene, is computed (erroneously) to be exothermic by 6 kcal/mol.[40] The 6 kcal/mol difference in eq 1, due solely to which alkene and diene are chosen as reference, is indicative of the quantitative significance that should be attached to the energies reported here.

(48) J. C. Stickler and W. H. Pirkle, *J. Org. Chem.*, **31,** 3444 (1966).

bridging groups is additive. The reaction that replaces one ethylene in tricyclo[3.3.0.0^{2,6}]octadiene (**2**) by a butadiene bridge is found to be exothermic by virtually the same amount as the reaction that replaces the remaining ethylene by a second butadiene bridge, to give the hydrocarbon of which **1** is the tetramethyl derivative.[46] While this theoretical result confirms the expected additivity relationship,[24] the fact that these two numbers emerge from the EH calculations as almost *exactly* the same[46] and nearly identical with the energy now[40] calculated for the reverse of the reaction in eq 1 should probably be regarded as merely fortuitous.[47]

Conclusions

The labeling observed in and the activation parameters found for the thermal reorganization of **7** strongly indicate that this molecule and others (e.g., **2**, **11**, and **15**) that contain cyclobutane rings 1,3-bridged by ethylene do not profit from any special stabilization of the transition states for their rearrangements. Instead, an ethylene bridge seems to exert a destabilizing effect in these molecules, resulting in their unusually low activation energies for rearrangement. This effect does not appear to be due entirely to angle strain since **1**, a molecule possessing two unsaturated bridging groups, is formed at temperatures where the parent tricyclo[3.3.0.0^{2,6}]octane fragments to 1,5-cyclooctadiene. Thus, it appears that, in contrast to the destabilizing effect of ethylene, the butadiene bridges in **1** exert a stabilizing influence. The postulates of destabilization by ethylene and stabilization by butadiene bridging groups are consistent with the lack of Diels–Alder reactivity observed in molecules containing cyclobutane rings bridged 1,3 by butadiene. These two effects are also manifested in the energies of homodesmotic reactions, computed by the EH method. The experimental and theoretical results discussed in this paper provide evidence of the importance, in molecules containing unsaturatively 1,3-bridged cyclobutane rings, of interactions between the σ MO's of the ring and the π MO's of the bridging groups.

Experimental Section

Reaction of 1,2,5,6-Tetramethyl-3,4,7,8-tetramethylenetricyclo[3.3.0.0^{2,6}]octane (1) with TCNE to Give 5a. A solution of 30 mg of **1** and 35 mg of tetracyanoethylene (TCNE) in 1 mL of freshly distilled tetrahydrofuran was placed in a 10-mL round bottom flask. Since permethylated semibullvalene derivatives are known to be sensitive to oxygen,[10] the solution was degassed by bubbling nitrogen slowly through it for 1.5 h. An aliquot showed no reaction between **1** and TCNE had occurred during this time. The solution was then refluxed for 2.5 h. Removal of the solvent under vacuum left a brown solid, whose NMR spectrum showed the formation of a single cycloadduct. Three recrystallizations from chloroform yielded shiny white crystals, mp 283–286 °C dec. The NMR spectrum at 100 MHz (acetone-d_6) showed δ 1.20 (s, 6 H), 1.80 (s, 6 H), 2.76 (d, 2 H, J = 17 Hz), 3.28 (s, 4 H), 3.88 (d, 2 H, J = 17 Hz). At 220 MHz[8] the broad singlet at δ 3.28 was resolved into an AB quartet, J = 17 Hz. Exact mass[50] calcd for $C_{28}H_{20}N_8$: 468.1811. Found: 468.1807.

Reaction of 1 with PTAD to Give Rearranged Monoadduct (8b). A solution of 59 mg of **1** in 0.5 mL of chloroform was placed in a vial containing a micro magnetic stirring bar and under an atmosphere of argon. The solution was cooled to 0 °C in an ice bath, and 49 mg (1 equiv) of *N*-phenyltriazolinedione (PTAD), prepared by the method of Stickler and Pirkle,[48] was added dropwise by syringe in 2 mL of chloroform. The solvent was removed under vacuum and the NMR spectrum of the residue indicated the formation of only one major product, which was purified by preparative TLC on alumina, using methylene chloride as solvent. In addition to material at the baseline, bands were observed at R_f 0.91 and 0.75. The band at R_f 0.75 yielded pure **8b** as a glass: NMR (CDCl$_3$) δ 1.12 (s, 3 H), 1.26 (s, 3 H), 1.42 (s, 3 H), 1.51 (d, 3 H, J = 2 Hz), 3.36 (d, 1 H, J = 12 Hz), 3.70 (d of q, 1 H, J = 14 and 2 Hz), 3.96 (d, 1 H, J = 12 Hz), 4.51 (s, 1 H), 4.62 (d, 1 H, J = 14 Hz), 5.02 (s, 1 H), 5.03 (s, 1 H), 5.39 (s, 1 H), 7.3–7.6 (m, 5 H). Exact mass calcd for $C_{24}H_{25}N_3O_2$: 387.1947. Found: 387.1950.

Reaction of 8b with PTAD to Give Diadduct (5b). The reaction of 20 mg of **8b** with 9 mg of PTAD in 3 mL of chloroform was carried out as described above for the preparation of **8b.** The product was again purified by preparative TLC on alumina, and a glassy solid was again obtained from the second band.[49] The NMR spectrum (CDCl$_3$) showed δ 1.11 (s, 6 H), 1.68 (s, 6 H), 3.70 (d, 2 H, J = 16 Hz), 4.02 (broad s, 4 H), 4.50 (d, 2 H, J = 16 Hz), 7.47 (s, 10 H). Exact mass calcd for $C_{32}H_{30}N_6O_4$: 562.2329. Found: 562.2320.

***Reaction of 1 with 2 Equiv of PTAD at 25 °C to Give Triadduct* (10).** A solution of 12 mg of **1** in 3 mL of chloroform was added by syringe to a vial containing 20 mg of PTAD under a nitrogen atmosphere. After removal of the solvent under vacuum, the crude product was recrystallized from ethyl acetate to yield colorless crystals, mp 268–269 °C. The parent ion (M^+) at *m/e* 737 in the mass spectrum indicated a triadduct. The NMR spectrum (CDCl$_3$) showed δ 1.15 (s, 6 H), 1.94 (s, 6 H), 4.48 (broad s, 8 H), 7.40 (s, 5 H), 7.49 (s, 10 H). The three upfield signals appeared unusually broad. On cooling the NMR sample, further broadening was observed; on heating the sample, the lines sharpened.[12]

Reaction of 5b with PTAD to Give 10. A 5-mg sample of **5b** was dissolved in 0.5 mL of chloroform under argon and 17 mg of PTAD in 1 mL of chloroform was added at room temperature. After 1.5 h the solvent was removed under vacuum, and an NMR spectrum of the residue was obtained. It proved identical with that of **10**, obtained from the reaction of **1** with 2 equiv of PTAD.

Reaction of 1 with PTAD at −15 °C to Give Unrearranged Monoadduct (7b). A suspension of 10 mg (0.056 mmol) of PTAD in 0.5 mL of CDCl$_3$ was placed in an NMR tube and frozen at −78 °C. A solution of 15 mg (0.070 mmol) of **1** in 0.2 mL of CDCl$_3$ was added to the tube, which was placed in a variable temperature NMR probe at −40 °C. The probe was slowly warmed. At −15 °C a reaction was evident, which was completed by warming the tube to −5 °C. At this temperature the spectrum of **7b** was recorded: (CDCl$_3$) δ 0.67 (s, 6 H), 1.14 (s, 6 H), 4.32 (s, 4 H), 4.85 (s, 2 H), 5.48 (s, 2 H), 7.50 (s, 5 H).

Kinetics of the Rearrangement of 7b to 8b. A typical run was conducted by dissolving 10 mg of **1** in 0.2 mL of CDCl$_3$, adding the solution to an NMR tube, and cooling the tube to −78 °C. Then 9 mg of PTAD (slightly less than 1 equiv was always used) was added to the tube with a spatula and washed down the sides with 0.5 mL of CDCl$_3$. The NMR tube was then immersed in an ice bath at 0 °C and agitated frequently for 1.5–2 h to ensure mixing of the reactants. An NMR spectrum, taken at 0 °C, after this period showed the formation of **7b** but no detectable rearrangement to **8b**. The kinetics were run on a Varian HA-100 NMR spectrometer, equipped with a variable temperature probe. Before the tube containing **7b** was inserted, the probe temperature was determined, using a methanol standard and interpolating the temperature from the Varian calibration table. The instrument was tuned on a sample from a previous kinetic run, and the actual sample of **7b** was then inserted into the probe. Data collection was begun 90 s after sample insertion. The disappearance of **7b** was followed by rapid integration of the singlet at δ 0.67. The observed integrals were fitted by a standard least-squares program to the equation $\ln I = \ln I_0 - kt$, where I was the observed integral at time t, I_0 was the magnitude of the first integral, taken 90 s after sample insertion, and k was the derived rate constant, reported in Table I.

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Registry No.—**1**, 34106-16-6; **5a**, 33372-31-5; **5b**, 64235-49-0; **7b**, 64235-50-3; **8b**, 64235-51-4; **10**, 64235-52-5; TCNE, 670-54-2; PTAD, 4233-33-4.

References and Notes

(1) (a) Address correspondence to this author at the University ofWashington; (b) Purdue University.

(2) (a) W. T. Borden, A. Gold, and S. D. Young, *preceding paper in this issue*; (b) preliminary communication: W. T. Borden and A. Gold, *J. Am. Chem. Soc.*, **93,** 3830 (1971).

(3) J. Meinwald, D. Schmidt, and H. Tsuruta, *J. Am. Chem. Soc.,* **91,** 5877 (1969); H. E. Zimmerman, J. D. Robbins, and J. Schantl, *ibid.*, **91,** 5878 (1969).

(4) J. A. Berson and L. Salem, *J. Am. Chem. Soc.*, **94,** 8917 (1972).

(5) J. E. Baldwin and A. H. Andrist, *J. Am. Chem. Soc.*, **93,** 3289 (1971); M. J. Goldstein and R. Hoffmann, *ibid.*, **93,** 6193 (1971).

energies since whatever effect operates to destabilize the reactant may, to some extent, still be present in the transition state for its rearrangement. Consequently, the estimate of 8–10 kcal/mol as the destabilization resulting from the removal of two hydrogen atoms from the saturated bridges in **13** and **16** could prove to be a lower limit.[24]

While the estimate of 8–10 kcal/mol as the destabilization energy in trading a saturated for an unsaturated cyclobutane bridging group may have to be revised when thermodynamic measurements on **11** and **15** become available, there is qualitative evidence, independent of the data from the kinetic studies discussed above, that such destabilization exists. For instance, the introduction of a double bond into **16** proved particularly difficult.[25] Enolate formation in bicyclo[2.1.1]-hexan-2-one is a factor of 10^4 slower at room temperature than in bicyclo[2.2.2]octan-2-one,[26] and enol formation is so difficult in the former ketone that it can be heated at 100 °C in neat HBr–Br_2 without undergoing bromination.[27]

What, then, is the cause of the destabilization that results from replacing an ethano with an etheno bridge? The internal bond angles at the trigonal carbons in both **11** and **15** are about 103°.[28] Clearly, the replacement of the tetrahedral carbons in **13** and **16** with trigonal centers must introduce additional angle strain. However, if this were the whole story, one would be hard pressed to explain why the tetramethylenetricyclooctane (**1**), which possesses four trigonal carbons, is apparently so stable, being *formed* from the corresponding tetramethylenecyclooctadiene at temperatures well above that at which tricyclo[3.3.0.0^{2,6}]octane (**13**) undergoes *cleavage* to cyclooctadiene (**14**).[2] The formation of **1** under these conditions points to the conclusion that, while introduction of ethylene as a 1,3 cyclobutane bridging group is destabilizing, in contrast, when a saturated bridge is replaced by butadiene, the result is a net stabilization. This conclusion is consistent with and supported by the lack of Diels–Alder reactivity of **1**, **7**, and related molecules[29] since in a Diels–Alder cycloaddition a butadiene is exchanged for an ethylene bridging group.

We have previously rationalized the apparent preference for butadiene over ethylene as a cyclobutane 1,3-bridging group in terms of interactions between the σ orbitals of the ring and the π orbitals of the bridging groups.[30] The cyclobutane ring possesses a degenerate pair of highest occupied MO's.[31] One of these HOMO's has the correct symmetry to interact with the filled π MO of a 1,3-bridging ethylene group. This interaction results in the existence of a very high-lying filled MO in molecules containing cyclobutane rings 1,3-bridged by ethylene, the presence of which is indicated by the long wavelength UV absorption of such molecules[30–32] and by their photoelectron spectra.[33] Chemically, the interaction between filled MO's has a net destabilizing effect, as revealed by calculations that include overlap.[30] Indeed, the orbital interaction between the HOMO's of the ring and bridge in a molecule like bicyclo[2.1.1]hexene (**15**) is reminiscent of that between the two ethylene units in cyclobutadiene, of which **15** may be considered a bis-homo derivative, and to which **15** has been compared.[34,35] In contrast to the case of ethylene, a butadiene bridging group has a lowest unoccupied MO (LUMO) that can mix with one of the HOMO's of the ring. This interaction is stabilizing,[30] and it is qualitatively similar to that between ethylene and butadiene in dimethylenecyclobutene, with which 2,3-dimethylenebicyclo[2.1.1]hexane (**17**) has been compared.[34] To continue the analogy, just as dimethylenecyclobutene does not undergo Diels–Alder reactions,[36] which would result in the replacement of butadiene by ethylene, so Diels–Alder reactions in molecules containing cyclobutane rings 1,3-bridged by butadiene (e.g., **1** and **7**)[29] are expected to be difficult.[37]

In previous studies[30,34] we have semiquantitatively estimated the destabilization that results from replacing a butadiene bridge with ethylene by calculating, using the extended Hückel (EH) method,[38] the heats of isodesmic reactions of the type shown in eq 1.

$$\mathbf{17} + \text{ethylene} \rightarrow \mathbf{15} + \textit{cisoid}\text{-butadiene} \qquad (1)$$

The same technique can be used to investigate theoretically the consequences of replacing the saturated bridge in bicyclo[2.1.1]hexane (**16**) with the unsaturated one in bicyclo[2.1.1]hexene (**15**). We find the homodesmotic reaction[39] (eq 2)

$$\mathbf{16} + \textit{cis}\text{-2-butene} \rightarrow \mathbf{15} + \textit{cisoid}\text{-butane} \qquad (2)$$

to be endothermic by 20 kcal/mol,[38,40] in agreement with the destabilization of **15**, relative to **16**, indicated by comparison of their energies of activation for rearrangement.

It is interesting to analyze why this reaction is unfavorable. As discussed above, angle strain must certainly contribute to destabilizing **15** relative to **16**, but there is also a contribution from orbital interactions. This is revealed by the π bond orders,[30] obtained from the EH calculations. As expected, the π bond orders, computed between the p orbitals perpendicular to the plane containing the four carbon atoms in *cisoid*-butane, are found to be nearly zero. In fact, they are found to be slightly negative, the calculated value being −0.012. The π bond orders between the ring and the saturated bridge in **16** are also found to be small and slightly negative, −0.007. Despite the use of a different geometry for **15**[40] than the one employed previously,[30] the π bond orders between ring and bridge are found to be almost the same, −0.009. Where does the destabilization in **15** come from then? Its source is revealed by comparison of the π bond orders in **15** with those in *cis*-2-butene. In the latter olefin the π bond orders between saturated and unsaturated carbons are positive and nearly 0.05 in magnitude. They reflect a stabilizing interaction between the π orbitals of the double bond and the pseudo π orbitals of the methyl groups.[42] In contrast, the π interaction between the ring and bridge in **15** is actually somewhat destabilizing.[43] Consequently, the double bond in **15** is abnormal in the sense that the π interaction between it and the two carbons attached to it causes a net destabilization of the molecule[43]—a marked difference between this double bond and the more typical one in 2-butene.

The energy calculated for the reaction in eq 3 should reflect the relative favorability of replacing the saturated bridge in **16** by butadiene, rather than by ethylene. Indeed, the computed endothermicity is reduced to only 2 kcal/mol.[38] The origin of the relative favorability of the reaction in eq 3, compared to that in eq 2, is again revealed by the EH π bond orders. While the calculated bond orders between the saturated and unsaturated carbons in 2,3-dimethylbutadiene are almost exactly the same as those in 2-butene, the π bond orders in **17** are, unlike those in **15**, positive. In fact, they are calculated to be 0.065,[44] which is larger in magnitude than those in 2,3-dimethylbutadiene. This result is in accord with the expectation that, with the proper unsaturated bridging group, a cyclobutane ring should be capable of a greater stabilizing conjugative interaction than methyl.[45] This fact explains why the reaction in eq 3 is calculated to be nearly thermoneutral[38] despite the increase in angle strain in going from **16** to **17**.

$$\mathbf{16} + \textit{cisoid}\text{-2,3-dimethylbutadiene} \rightarrow \mathbf{17} + \textit{cisoid}\text{-butane} \qquad (3)$$

We have also used the calculated energies of homodesmotic reactions, similar to that in eq 1, to verify that in tricyclic systems like **1**, **2**, and **11**, where the cyclobutane ring is spanned by two unsaturated bridges, the net effect of the

(49) The band nearest the baseline was found to contain triadduct (**10**). An NMR spectrum of the crude product mixture showed **5b** and **10** to be the only products formed.

(50) Repeated attempts to obtain a correct elemental analysis on **5a** always gave results that were too low in C, H, and N. Given the extreme reactivity of octamethylsemibullvalene toward oxygen,[10] a reasonable hypothesis is that **5a**, itself a peralkylated semibullvalene, underwent some oxidation prior to being analyzed.

Alkyl Nitrate Nitration of Active Methylene Compounds. Nitration of Aldimines[1]

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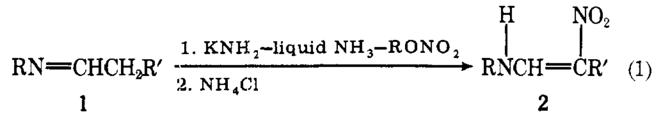
The alkyl nitrate nitration of aldimines **1** derived from aldehydes and aliphatic or alicyclic amines affords the corresponding 1-alkylamino-2-nitro-1-alkenes **2**. The spectral data of **2** show the presence of both the *Z* and *E* isomers, the former predominating in both the solid state and in nonpolar solvents.

In continuation[2] of our studies of the alkyl nitration, we are now reporting on its application to the synthesis of 1-alkylamino-2-nitro-1-alkenes **2** (eq 1).



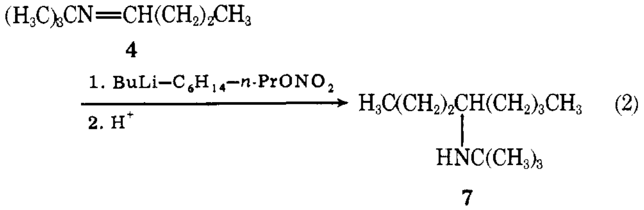
$$\underset{\mathbf{1}}{\mathrm{RN{=}CHCH_2R'}} \xrightarrow[\text{2. NH}_4\text{Cl}]{\text{1. KNH}_2\text{–liquid NH}_3\text{–RONO}_2} \underset{\mathbf{2}}{\mathrm{R\overset{H}{N}CH{=}\overset{NO_2}{C}R'}} \quad (1)$$

Methods that have been used to prepare **2** include the condensation of sodium nitromalonaldehyde with hydrochlorides of primary and secondary amines;[3] the condensation of α-nitro ketones with primary aromatic amines;[4] the reaction of morpholine and piperidine with alkoxyalkylidenemalonic esters and nitromethane;[5] the reaction between sodium methazonate and salts of primary[6a] and secondary amines;[6b] the reaction of vicinal dinitroalkenes[7a] or chloronitroalkenes[7b] with amines; and the condensation of nitroalkanes with N,N-disubstituted amide acetals[8] or with amide–dimethyl sulfate complexes.[9]

A consideration of the available methods has shown that they are limited in scope. Moreover, they suffer from the lack of readily available starting materials and frequently from low yields.

The nitration reaction in eq 1 was studied in several base–solvent systems with *N*-propylidene-*tert*-butylamine [**3**, R = $C(CH_3)_3$; R′ = CH_3] and *N*-butylidene-*tert*-butylamine [**4**, R = $C(CH_3)_3$; R′ = C_2H_5] as model compounds. As shown in Table I, the highest yields of 1-(*tert*-butylamino)-2-nitro-1-propene (**5**) and of 1-(*tert*-butylamino)-2-nitro-1-butene (**6**) (53 and 51%, respectively) were obtained in the potassium amide–liquid ammonia system when the molar ratio of **1** to base to nitrating agent was 1:2:1.5 and when 30 min was allowed for both anion formation and nitration. It is of interest that in a control test only 18% of **3** was recovered when it was subjected to potassium amide in liquid ammonia. A considerable amount of polymeric material was formed which was not identified. Only tar-like material was obtained when **3** was nitrated in lithium amide–liquid ammonia.

Nitration of **4** in *n*-butyllithium–hexane did not give **6** but, instead, afforded (*N*-*tert*-butyl)-4-aminooctane (**7**) which arose from a nucleophilic attack of butyllithium on the azomethine carbon[10] (eq 2). Nitrations of **4** with *n*-propyl nitrate were successful in lithium diisopropylamide employing hexane or THF as solvents, but the yield of **6** did not exceed 30%.

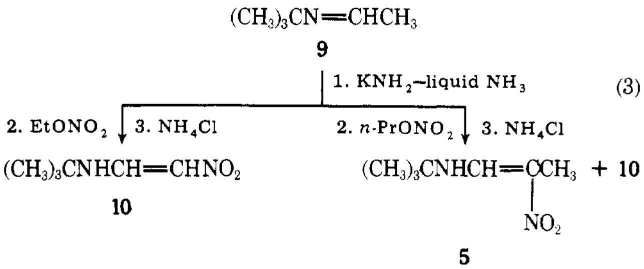


$$\underset{\mathbf{4}}{\mathrm{(H_3C)_3CN{=}CH(CH_2)_2CH_3}} \xrightarrow[\text{2. H}^+]{\text{1. BuLi–C}_6\text{H}_{14}\text{–}n\text{-PrONO}_2} \underset{\mathbf{7}}{\mathrm{H_3C(CH_2)_2\underset{HNC(CH_3)_3}{CH}(CH_2)_3CH_3}} \quad (2)$$

In order to determine the scope of the reaction, aldimines of varied structures were nitrated. Variations in the alkylamino moiety had some effect on the yield of the aminonitroalkenes **2** as indicated in Table II. The low yield of 1-(isopropylamino)-2-nitro-1-propene (**8**) is probably due to its instability. It decomposed on recrystallization from hot hexane with the evolution of oxides of nitrogen and also on standing at ambient temperatures.

As shown in Table II, aldimines derived from primary aliphatic aldehydes underwent nitration in the potassium amide–liquid ammonia system to afford the expected aminonitroalkenes.

An interesting side reaction was observed in the nitration of *N*-ethylidene-*tert*-butylamine [**9**, R = $C(CH_3)_3$; R′ = H] with *N*-propyl nitrate. In addition to 1-(*tert*-butylamino)-2-nitroethene (**10**) there was also formed compound **5** in 10% yield (eq 3). Only **10** was obtained when **9** was nitrated with ethyl nitrate. Traces of **5** were also found in nitrations of **4** and *N*-heptylidene-*tert*-butylamine with *n*-propyl nitrate.



$(CH_3)_3CN{=}CHCH_3$ **9**

1. KNH_2–liquid NH_3 (3)

2. $EtONO_2$ 3. NH_4Cl → $(CH_3)_3CNHCH{=}CHNO_2$ **10**

2. n-$PrONO_2$ 3. NH_4Cl → $(CH_3)_3CNHCH{=}C(NO_2)CH_3$ **5** + **10**

The formation of **5** in these reactions is very likely due to aldehyde interchange between the aldimines and propanal. In a control test it was established that **3** was formed in addition to considerable amounts of aldol condensation products when **4** was treated with propanal in potassium amide–liquid ammonia (eq 4).

$$\mathbf{4} + \mathrm{H_3CCH_2CHO} \xrightarrow[\text{2. NH}_4\text{Cl}]{\text{1. KNH}_2\text{–liquid NH}_3} \underset{\mathbf{3}}{\mathrm{(H_3C)_3CN{=}CHCH_2CH_3}} + \mathbf{4} \quad (4)$$

The formation of propanal in the nitrations with *n*-propyl