Synthesis and Dimerization of Tricyclo[3.3.3.0²,⁶]undec-2(6)-ene. X-Ray Structure of the Dimer as Evidence for a Concerted Ene Reaction in Dimer Formation

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Abstract: The title compound (**8**) has been prepared by a route involving ring expansion of bicyclo[3.2.2]nonane-6,8-dione (**1**) to bicyclo[3.3.3]undecane-2,6-dione (**4**), transannular reductive ring closure of **4** to tricyclo[3.3.3.0²,⁶]undecane-2,6-diol (**6**), and formation of the olefin (**8**) from the thionocarbonate (**9**) derived from **6**. The olefin (**8**) has been trapped with diphenylisobenzofuran to give a Diels–Alder adduct (**10**). In the absence of trapping agent, a dimer (**11**) was obtained, which is the formal product of an ene type reaction. On prolonged heating, **11** rearranged to **13** by a 1,3 hydrogen shift, which relieves some of the strain present in **11**. On hydrogenation, both **11** and **13** gave **14**. An x-ray crystal structure of **14** demonstrated that the transition state for dimer formation contains two molecules of the same, rather than of opposite, chirality, proving that **11**, not **12**, correctly represents the structure of the dimer. The formation of **11**, taken together with the apparent absence of dimers of the [$_\pi2_s + _\pi2_s$] type, is interpreted as evidence for a concerted ene reaction in the dimerzation of **8**. The implications of this conclusion are discussed.

As part of a study of olefins of the class to which **7** belongs, where the carbon atoms forming the double bond are pyramidalized,[2] we investigated a route to bicyclo[3.3.3]undecane-3,7-dione (**3**), involving ring expansion of bicyclo[3.2.2]nonane-6,8-dione (**1**)[3] via the bis amino alcohol (**2**). Depending on which bond in **2** migrates preferentially in the Tiffeneau–Demjanov reaction,[4] the product obtained can be either **3** or **4**. Submission of **4** to the sequence of reactions—transannular reductive ring closure[5] and olefin formation from the resulting

diol—intended for use in the preparation of **7** from **3** should lead to another interesting bridgehead olefin (**8**).[6] In this molecule, tricyclo[3.3.3.0²,⁶]undec-2(6)-ene, although the carbon atoms forming the double bond may be somewhat pyramidalized,[7] overlap between the atomic orbitals forming the π bond is diminished chiefly by torsion. In fact, **8** may be regarded in the Wiseman analysis of bridgehead olefins[8] as a derivative of *trans*-cycloheptene, in which the two ethano bridges serve to prevent the trans → cis isomerization that occurs in the parent olefin.[9] Wiseman and Chong prepared a mixture of two *trans*-cycloheptene derivatives in which a single ethano bridge prevents isomerization about the double bond, and they found that these molecules were stable at −70 °C but dimerized on warming to room temperature.[10] We naively thought that the second ethano bridge in **8** might tend to inhibit dimerization sterically, since the double bond in **8** is tetrasubstituted. In addition, the second ethano bridge in **8** renders impossible the [$_\pi2_s + _\pi2_a$] pathway that has been proposed for the dimerization of some trans cycloalkenes.[11,12] Therefore, we undertook the ring expansion of **1** with the expectation that, whether **3** or **4** was the product obtained, either could be transformed into an olefin of some interest.

Results

Bicyclo[3.2.2]nonane-6,8-dione (**1**) was prepared as described by Wood and Woo,[3] except for the isolation of the diketone following decarboxylation of the keto acid precursor in triglyme. We found a more satisfactory procedure to be treatment of the triglyme solution of the diketone with Girard's reagent T, which converted the diketone into a water-soluble derivative. The triglyme could then be removed efficiently by extraction of the aqueous solution with methylene chloride; acid hydrolysis regenerated **1**, uncontaminated by triglyme.

A number of methods were investigated for the ring expansion of **1**. Diazomethane failed to react with the diketone. Similarly, attempts to form a biscyanohydrin and a diadduct with nitromethane led principally to recovered starting material. A diepoxide was formed when the diketone was treated with dimethylsulfonium or dimethylsulfoxonium methylide,[13] and the diepoxide could be converted to the bisamino alcohol **2** by heating at 100 °C in methanol saturated with ammonia.
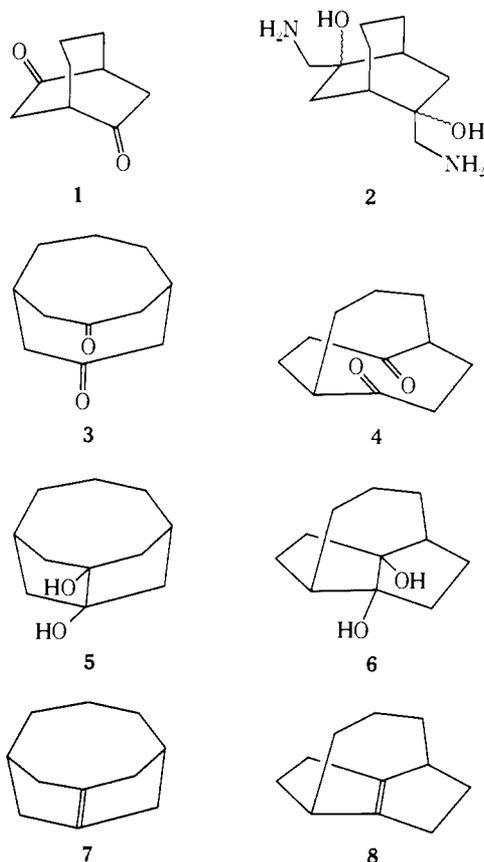
However, a cleaner product was more conveniently and reproducibly obtained by reaction of **1** with excess isocyanomethyllithium,[14] followed by hydrolysis of the bis adduct to **2**. Some mono adduct was always obtained from the first reaction, no matter how large an excess of isocyanomethyllithium was used, suggesting that enolate formation competes with addition. Nevertheless, the bis adduct could be isolated in 65% yield by crystallization. The mother liquors were found to contain a mixture of mono and bis adducts, which could be separated by preparative thin layer chromatography; or the mixture could just be recycled through a subsequent isocyanomethyllithium addition reaction.

Transformation of **2** into a ring-expanded diketone was effected by addition of sodium nitrite to the crude hydrochloride salt in a two-phase mixture of benzene and buffered acetic acid. The product consisted of two compounds, barely separable by analytical TLC. That the major product was **4** rather than **3** was indicated by the [^1]H NMR of the crude material, which showed two methine and four methylene protons deshielded by their adjacency to carbonyls. Confirmation of the structural assignment came from reduction of the crude product with a zinc amalgam in aqueous HCl[5] to a crystalline diol, whose proton decoupled [^13]C NMR consisted of six resonances. This corresponds to the number of unique carbon atoms in **6**. If the isomeric diketone (**3**) had been obtained, the diol would have been expected to show five resonances.[15] The formation of **4** as the principal product of ring expansion indicates that the least substituted carbon migrates preferentially upon diazotization of **2**, a not at all unprecedented result.[16]

Since the Corey–Winter reaction[17] has been used to transform *trans*-1,2-cycloheptanediol to *trans*-cycloheptene,[9] it was the first method that we tried in order to effect the analogous conversion of **6** to **8**. Ultimately, it proved to be the method that we found most effective. Like our model compound, bicyclo[3.3.0]octane-1,5-diol,[5] **6** did not react with thiocarbonyldiimidazole. However, the thionocarbonate could be formed, using the procedure worked out on the model diol. When **6** was first converted to the lithium salt and then heated with thiocarbonyldiimidazole in refluxing tetrahydrofuran, the crystalline thionocarbonate (**9**) was obtained in 82% yield. Its proton decoupled [^13]C NMR spectrum showed, in addition to the downfield resonance for the thiocarbonyl carbon, six singlets at higher field, thus providing further evidence for the structures assigned to the diketone **4** and diol **6**. When the thionocarbonate was heated under nitrogen in degassed triethyl phosphite, containing 1.1 equiv of diphenylisobenzofuran as trapping agent, a crystalline Diels–Alder adduct (**10**) could be isolated in 85% yield. The adduct possesses no element of symmetry, and resonances from all 13 saturated carbon atoms were resolved in the [^13]C NMR spectrum of **10**.

9 DPIBF (EtO)₃P → **10**
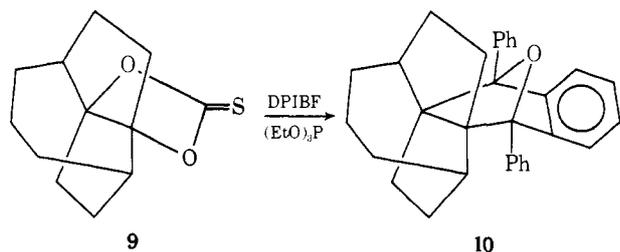
In the absence of trapping agent a semicrystalline hydrocarbon product was obtained in essentially quantitative yield. The mass spectrum indicated it to be a dimer of **8**; the presence of absorptions in the olefinic region of both the [^13]C and [^1]H NMR spectra showed that, unlike the dimers formed from other bridgehead olefins,[8] ours was not of the formal $[_\pi2_s + _\pi2_s]$ type. However, the appearance of the NMR spectra varied with reaction time.

After 6 h, and following a chromatographic separation of the hydrocarbon from unreacted **9**, the [^1]H NMR showed a broad doublet at δ 5.50, $J = 5$ Hz, which integrated to roughly one proton. Decoupling experiments established that this proton was coupled to three others at δ 3.65 ($J = 1.5$ Hz), 2.92 ($J < 1$ Hz), and 1.88 ($J = 5$ Hz). Further, the protons at δ 3.65 and 1.88 were coupled to each other with $|J| = 16$ Hz. The magnitude of this coupling constant indicated that these protons were geminal, and the [^1]H NMR was thus consistent with the presence of the structural unit $-CH_2CH=C-CH-$ in the dimer. As expected, the [^13]C NMR spectrum showed two peaks in the olefinic region, a singlet at δ 162.02 and a doublet at δ 127.19. There was, however, an anomalous feature of the [^1]H NMR spectrum in that the geminal allylic proton at higher field was coupled more strongly to the olefinic proton than was the one at lower field. The larger coupling to the higher field proton indicated that it was closer to the plane containing the olefinic proton and carbons. However, it is almost always the case that the geminal allylic proton that lies closer to this plane appears at lower field than the one that is closer to the π cloud of a double bond.[18] Indeed, not only was the resonance for the allylic proton at δ 3.55 unexpectedly downfield from that for the proton closer to the nodal plane of the double bond, but also, in an absolute sense, it seemed much too far downfield for a proton attached to a secondary allylic carbon. Nevertheless, the rest of the spectral data, including the mass spectrum, which showed major fragments at one mass unit above and one below the mass of the olefin (**8**), were consistent with the formulation of the structure of the dimer as that expected from an ene reaction.[19]

Since the olefin (**8**) is chiral, there are, in fact, two possible dimers (**11** and **12**) with this structure. The former results from reaction between two molecules of **8** with the same chirality, while the latter arises from combination of two molecules of **8** with opposite chirality. That only one of the two possible dimers was actually formed was indicated by the proton decoupled [^13]C NMR spectrum of the product, which showed 22 lines, corresponding to the number of carbon atoms in just one of the dimers. Construction of models led to the conclusion that, if the ene reaction were concerted, with hydrogen transfer occurring in the rate-determining step, the formation of **11** should be favored. The basis for this conclusion is indicated in Figure 1. In a transition state involving two molecules of the same chirality, the torsion about the double bonds is such that the p orbitals not involved in C–C σ bonding point away from each other and toward the allylic hydrogen that must be abstracted in order to complete the ene reaction. The reverse is true in the transition state leading to **12**. In this latter transition state the orbital alignment for hydrogen abstraction can be improved by rotation about the incipient C–C bond between monomer fragments, but only at the expense of introducing severe nonbonded interactions between the fragments. Consequently, on the basis of model building, we suggested in our preliminary communication[6] that **11** corresponds to the structure of the dimer formed.

Model building also suggested a possible explanation for the appearance at anomalously low field in the [^1]H NMR spectrum of the allylic proton that lies closest to the π cloud of the double bond in the dimer. Models of **11** and **12** showed that the bond to this proton points toward the saturated half of both molecules. Moreover, in all conformations of both **11** and **12** in which the bonds to the bridgehead carbons that join the halves are staggered, this proton experiences a strong nonbonded interaction with a proton in the saturated half of the molecule. Since steric compression is known to result in deshielding of protons,[20] the resonance of this allylic proton at anomalously low field can be rationalized.

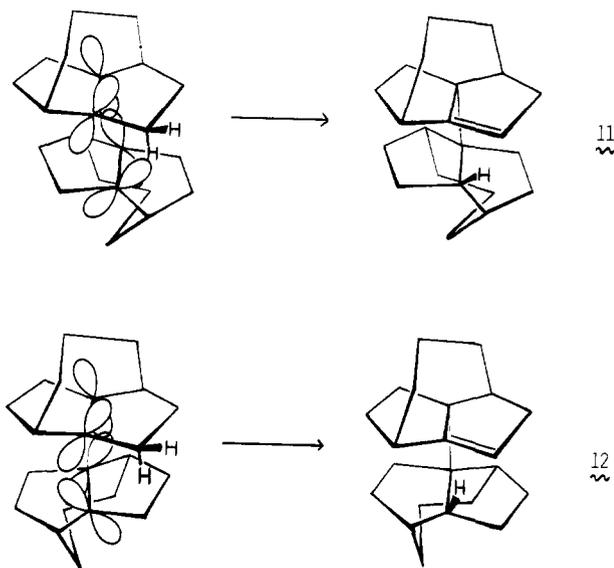As noted above, the appearance of the NMR spectra of the dimer depended on reaction time. After 74 h the [^1]H NMR

Figure 1. Dimerization of two molecules of 8 with the same and with opposite chirality to give respectively 11 and 12.

Figure 2. A computer-generated drawing of the hydrogenated dimer (14). Hydrogens have been omitted for clarity.

spectrum showed no trace of the dimer tentatively assigned structure 11. The broad doublet at δ 5.50 was replaced by a triplet at δ 5.68, integrating for two protons and coupled with J = 1.8 Hz to a proton at δ 2.74 and another at δ 2.65. The ^{13}C NMR spectrum also indicated the presence of two olefinic protons, since the resonances at δ 137.26 and 132.38 both appeared as doublets in the undecoupled spectrum. On the basis of the spectroscopic evidence, including the mass spectrum which again showed major peaks at the mass of the olefin (8) ±1 mass unit, the dimer obtained at long reaction times was assigned structure 13.

11   13
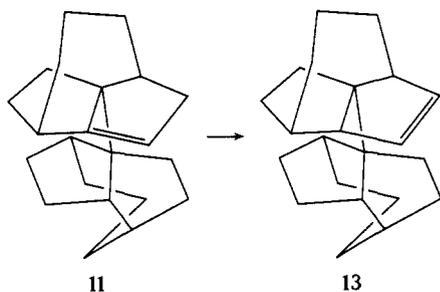
In a formal sense 13 is the product of a forbidden 1,3 sigmatropic shift[11] in 11. This transformation results in the release of substantial strain, since in the Wiseman analysis[8] the double bond in 11 is trans in two eight-membered rings.[21] At reaction times intermediate between 6 and 74 h the NMR spectra showed a mixture of 11 and 13 to be present. For instance, after 20 h the product was a 7:3 mixture of 11 and 13, as estimated by careful integration of the olefinic portion of the ^{1}H NMR spectrum. Resubmission of this sample to heating in refluxing triethyl phosphite for an additional 18 h resulted in a 6:4 mixture. It is noteworthy that when the reaction of the thionocarbonate was carried out uninterruptedly for 36 h, the ratio of 11 to 13 was not 6:4 but 2:8. This observation suggests that the rearrangement of 11 to 13 is catalyzed and, hence, as expected,[11] is probably not a concerted process.

Proof that 11 and 13 differ only in the position of the double bond was obtained by the hydrogenation of both olefins to the same saturated compound (14). The ^{13}C NMR spectrum of 14 provided evidence that the gross structures assigned the two dimers were correct, since only 11 singlets appeared in the proton decoupled spectrum. However, since 14 would contain
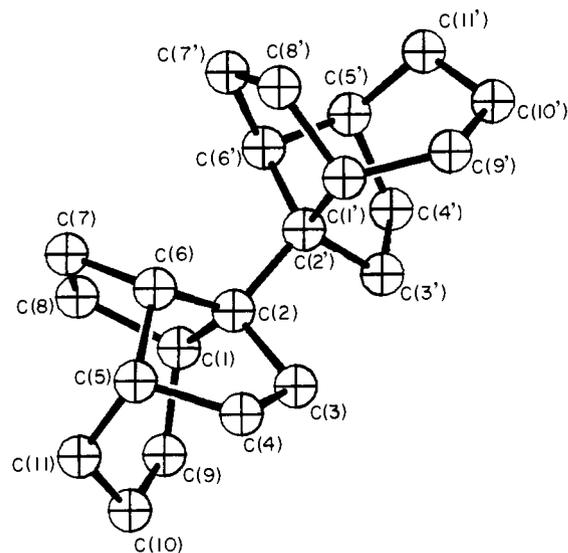
11 unique carbons, whether its halves were related by a plane or an axis of symmetry, the ^{13}C NMR spectrum did not exclude 12 as the initially formed dimer (or the molecule resulting from a 1,3-sigmatropic shift in 12 as the rearrangement product).

Which dimer, 11 or 12, was actually formed could, in principle, be ascertained by resolving the diol 6 into its optical antipodes and hydrogenating the dimer obtained. If the dimer had the structure 11, the hydrogenation product (14) would be chiral and should exhibit optical activity. If, however, 12 correctly represented the structure of the dimer, 14 would contain a plane of symmetry and so should show no rotation of the plane of polarized light. In practice, the necessity for resolving 6 was obviated by the discovery that 14 formed crystals suitable for an x-ray crystallographic study.

Preliminary x-ray photographs of crystals of the hydrogenated dimer, grown from a supersaturated ethanol solution, revealed monoclinic symmetry. A least-squares fitting of 15 high-angle reflections ($35° \leq 2\theta \leq 45°$) gave a = 12.350 (3), b = 7.109 (3), c = 19.668 (4) Å, and β = 100.20 (6)°. Systematic extinctions conformed to the monoclinic space group $P2_1/n$, and a measured and calculated (Z = 4) density of 1.17 g/cm^3 indicated that the asymmetric unit had composition $C_{22}H_{34}$. All unique reflections with $2\theta \leq 114.1°$ were measured on a computer-controlled four-circle diffractometer using graphite monochromated Cu Kα (1.54178 Å) x rays. Of the 2297 independent diffraction maxima investigated, 1572 were judged observed after correction for Lorentz, polarization, and background effects ($F_o \geq 3\sigma(F_o)$). The angular dependence of the reflections was removed as they were converted to normalized structure factors. The structure was solved by a multisolution, weighted sign determining procedure.[22] Full-matrix, least-squares refinements with anisotropic temperature factors for all nonhydrogen atoms and isotropic temperature factors for all hydrogens converged to a standard crystallographic residual of 0.060 for the observed reflections.[23] There were no significant residual peaks in a final difference electron density synthesis or abnormally short intermolecular contacts.

Fractional coordinates and temperature factors, bond distances, and bond angles are given in Tables I-III. A computer-generated perspective drawing of the final x-ray model, less hydrogens, is given in Figure 2. The conformation about the bond [C(2)-C(2')] joining the two halves of the molecule is a staggered one; nevertheless, this bond is rather long, 1.589

Table I. Fractional Coordinates and Temperature Factors for **14**[a]

Atom	x	y	z	B_{11} or B	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	0.0291 (3)	0.1863 (5)	0.3254 (2)	0.0101 (3)	0.0175 (7)	0.0029 (1)	−0.0014 (4)	−0.0011 (1)	0.0006 (2)
C(2)	0.0855 (3)	0.3617 (4)	0.3641 (1)	0.0083 (3)	0.0151 (6)	0.0025 (1)	0.0002 (3)	−0.0001 (1)	0.0002 (2)
C(3)	0.0065 (3)	0.4911 (5)	0.3971 (2)	0.0099 (3)	0.0196 (8)	0.0030 (1)	0.0028 (5)	−0.0004 (1)	−0.0003 (3)
C(4)	−0.0183 (4)	0.6613 (6)	0.3493 (2)	0.0128 (4)	0.0204 (9)	0.0036 (1)	0.0036 (5)	−0.0009 (2)	0.0001 (3)
C(5)	0.0080 (3)	0.5976 (5)	0.2809 (2)	0.0127 (4)	0.0179 (7)	0.0029 (1)	0.0003 (4)	−0.0003 (2)	0.0016 (2)
C(6)	0.1123 (3)	0.4785 (5)	0.3036 (2)	0.0098 (3)	0.0198 (8)	0.0026 (1)	−0.0022 (4)	−0.0005 (1)	0.0007 (2)
C(7)	0.1396 (4)	0.3438 (6)	0.2491 (2)	0.0120 (4)	0.0318 (11)	0.0025 (1)	0.0006 (6)	0.0003 (2)	−0.0001 (3)
C(8)	0.0811 (4)	0.1617 (6)	0.2609 (2)	0.0119 (4)	0.0252 (10)	0.0032 (1)	0.0017 (6)	−0.0014 (2)	−0.0020 (3)
C(9)	−0.0972 (3)	0.1885 (6)	0.3073 (3)	0.0101 (4)	0.0259 (10)	0.0045 (1)	−0.0037 (5)	−0.0012 (2)	0.0004 (3)
C(10)	−0.1548 (4)	0.3622 (7)	0.2716 (2)	0.0091 (3)	0.0332 (11)	0.0042 (1)	−0.0003 (6)	−0.0016 (2)	0.0008 (4)
C(11)	−0.0882 (3)	0.4969 (6)	0.2353 (2)	0.0109 (3)	0.0266 (9)	0.0032 (1)	0.0032 (5)	−0.0012 (2)	0.0010 (3)
C(1′)	0.2548 (3)	0.4752 (5)	0.4520 (2)	0.0091 (3)	0.0208 (8)	0.0030 (1)	0.0010 (4)	−0.0003 (1)	−0.0003 (2)
C(2′)	0.1826 (3)	0.3021 (4)	0.4246 (1)	0.0088 (3)	0.0154 (6)	0.0024 (1)	0.0010 (4)	−0.0004 (1)	0.0007 (2)
C(3′)	0.1295 (3)	0.1968 (5)	0.4799 (2)	0.0102 (4)	0.0224 (8)	0.0028 (1)	0.0014 (4)	−0.0001 (2)	0.0011 (3)
C(4′)	0.1960 (4)	0.0184 (6)	0.4997 (2)	0.0130 (4)	0.0221 (9)	0.0038 (1)	0.0009 (5)	−0.0001 (2)	0.0019 (3)
C(5′)	0.3068 (3)	0.0567 (6)	0.4766 (2)	0.0109 (4)	0.0228 (9)	0.0039 (1)	0.0038 (5)	−0.0005 (2)	0.0003 (3)
C(6′)	0.2693 (3)	0.1603 (5)	0.4083 (2)	0.0095 (3)	0.0191 (8)	0.0034 (1)	0.0018 (4)	−0.0008 (2)	−0.0005 (3)
C(7′)	0.3591 (4)	0.2748 (6)	0.3832 (2)	0.0106 (4)	0.0332 (12)	0.0035 (1)	0.0019 (6)	0.0001 (2)	−0.0001 (3)
C(8′)	0.3562 (4)	0.4682 (6)	0.4146 (2)	0.0107 (4)	0.0312 (11)	0.0036 (1)	−0.0026 (5)	−0.0002 (2)	0.0009 (3)
C(9′)	0.2917 (4)	0.4931 (6)	0.5300 (2)	0.0113 (4)	0.0261 (10)	0.0032 (1)	0.0007 (6)	−0.0009 (2)	−0.0015 (3)
C(10′)	0.3422 (4)	0.3193 (7)	0.5704 (2)	0.0119 (4)	0.0352 (12)	0.0029 (1)	0.0013 (6)	−0.0013 (2)	−0.0005 (3)
C(11′)	0.3888 (4)	0.1620 (7)	0.5316 (2)	0.0117 (4)	0.0322 (11)	0.0034 (1)	0.0044 (6)	−0.0012 (2)	0.0015 (3)

Atom	x	y	z	B_{11} or B
H1	0.048 (2)	0.080 (5)	0.355 (2)	3.5 (6)
H3A	0.041 (2)	0.529 (4)	0.445 (2)	3.8 (6)
H3B	−0.060 (3)	0.413 (5)	0.397 (2)	5.1 (8)
H4A	0.034 (3)	0.763 (6)	0.366 (2)	5.7 (9)
H4B	−0.096 (3)	0.700 (6)	0.340 (2)	5.1 (9)
H5	0.023 (3)	0.700 (6)	0.252 (2)	6.1 (8)
H6	0.168 (3)	0.566 (4)	0.317 (1)	3.3 (6)
H7A	0.224 (4)	0.326 (6)	0.259 (2)	7.3 (10)
H7B	0.118 (3)	0.394 (5)	0.203 (2)	5.6 (8)
H8A	0.030 (3)	0.125 (5)	0.224 (2)	5.8 (8)
H8B	0.137 (3)	0.065 (6)	0.270 (2)	5.2 (8)
H9A	−0.125 (3)	0.166 (6)	0.354 (2)	5.4 (10)
H9B	−0.118 (4)	0.077 (7)	0.279 (2)	7.2 (10)
H10A	−0.185 (3)	0.450 (7)	0.308 (2)	8.0 (10)
H10B	−0.211 (4)	0.314 (6)	0.238 (2)	6.6 (10)
H11A	−0.062 (3)	0.430 (5)	0.194 (2)	5.0 (8)
H11B2	−0.136 (3)	0.597 (6)	0.215 (2)	4.7 (8)
H1′	0.215 (2)	0.592 (4)	0.437 (1)	2.9 (5)
H3′A	0.053 (3)	0.160 (5)	0.462 (2)	5.1 (8)
H3′B	0.130 (3)	0.268 (5)	0.520 (2)	4.8 (8)
H4′A	0.158 (3)	−0.092 (6)	0.474 (2)	6.2 (9)
H4′B	0.208 (2)	−0.007 (5)	0.551 (2)	4.5 (7)
H5′	0.343 (3)	−0.063 (5)	0.467 (2)	4.3 (7)
H6′	0.234 (3)	0.068 (5)	0.376 (2)	4 3 (7)
H7′A	0.348 (2)	0.273 (4)	0.332 (2)	4.2 (7)
H7′B	0.427 (4)	0.207 (6)	0.400 (2)	7.4 (11)
H8′A	0.345 (3)	0.564 (6)	0.379 (2)	5.9 (9)
H8′B	0.426 (3)	0.500 (5)	0.450 (2)	6.3 (8)
H9′A	0.235 (4)	0.542 (7)	0.551 (2)	7.7 (13)
H9′B	0.345 (3)	0.601 (5)	0.540 (2)	4.6 (7)
H10′A	0.288 (4)	0.252 (7)	0.598 (2)	7.8 (11)
H10′B	0.398 (4)	0.367 (6)	0.604 (2)	7.2 (10)
H11′A	0.445 (4)	0.218 (8)	0.511 (3)	8.7 (14)
H11′B	0.416 (3)	0.066 (6)	0.569 (2)	6.2 (9)

[a] Standard deviations of the least significant figures are given in parentheses. Hydrogens are assigned the same numbers as the heavy atoms to which they are bonded.

Table II. Bond Distances of **14**[a]

C(1)–C(2)	1.559 (4)	C(1′)–C(2′)	1.559 (5)
C(1)–C(8)	1.529 (6)	C(1′)–C(8′)	1.561 (6)
C(1)–C(9)	1.538 (5)	C(1′)–C(9′)	1.525 (5)
C(2)–C(3)	1.563 (5)	C(2′)–C(3′)	1.557 (5)
C(2)–C(6)	1.535 (5)	C(2′)–C(6′)	1.545 (5)
C(2)–C(2′)	1.589 (4)	C(3′)–C(4′)	1.524 (6)
C(3)–C(4)	1.530 (5)	C(4′)–C(5′)	1.540 (7)
C(4)–C(5)	1.507 (6)	C(5′)–C(6′)	1.530 (5)
C(5)–C(6)	1.540 (5)	C(5′)–C(11′)	1.538 (6)
C(5)–C(11)	1.533 (5)	C(6′)–C(7′)	1.526 (6)
C(6)–C(7)	1.520 (5)	C(7′)–C(8′)	1.511 (6)
C(7)–C(8)	1.520 (6)	C(9′)–C(10′)	1.540 (6)
C(9)–C(10)	1.532 (6)	C(10′)–C(11′)	1.523 (7)
C(10)–C(11)	1.519 (7)		

[a] The standard deviation of the least significant figure of each distance is given in parentheses.

(4) Å. It should be noted, however, that a bond of similar length is found between the tetrasubstituted bridgehead carbons in 1-biadamantane.[24]

The most important aspect of the structure of **14** is the fact that it represents one member of a *dl* pair, the enantiomer of which is generated by the crystal symmetry. Since **14** is chiral, the two halves of the molecule must be of the same, rather than

of opposite, chirality. Therefore, the transition state for dimer formation must be comprised of two molecules of the same chirality, thus proving that **11** does, in fact, correctly represent the structure of the initially formed dimer.

Discussion

The formation of **11** as the sole primary product isolable from the dimerization of **8** is, as discussed above, wholly consistent with hydrogen transfer being involved in the transition state for dimer formation.[25] Taken together with the apparent absence of dimers of the $[_\pi 2_s + _\pi 2_s]$ type, whose presence would be expected if diradicals were produced by creation of the C–C σ bond in a step prior to hydrogen transfer, the formation of only **11** strongly suggests a concerted $[_\pi 2_s + _\pi 2_s + _\sigma 2_s]$ ene mechanism[19] for dimerization.

If, as appears to be the case, **8** dimerizes by a concerted ene mechanism, the question arises as to why this reaction mode is not utilized by other bridgehead olefins.[8] While it is entirely possible that the tetrasubstitution of the double bond in **8** functions, as we hoped it would, to inhibit formation of $[_\pi 2_s + _\pi 2_s]$ products, we believe that this is not the primary reason an ene-type dimer is formed. Instead, it seems likely that, in contrast to the case with other bridgehead olefins, the geometry of **8** makes a concerted ene reaction feasible. Indeed, as illus-

Table III. Bond Angles of 14[a]

C(2)-C(1)-C(8)	106.2 (3)
C(2)-C(1)-C(9)	116.8 (3)
C(8)-C(1)-C(9)	111.6 (3)
C(1)-C(2)-C(3)	114.6 (3)
C(1)-C(2)-C(6)	101.1 (2)
C(1)-C(2)-C(2')	111.4 (2)
C(3)-C(2)-C(6)	103.9 (3)
C(3)-C(2)-C(2')	106.8 (2)
C(6)-C(2)-C(2')	119.2 (3)
C(2)-C(3)-C(4)	106.4 (3)
C(3)-C(4)-C(5)	105.0 (3)
C(4)-C(5)-C(6)	102.1 (3)
C(4)-C(5)-C(11)	113.3 (4)
C(6)-C(5)-C(11)	115.7 (3)
C(2)-C(6)-C(5)	103.7 (3)
C(2)-C(6)-C(7)	108.1 (3)
C(5)-C(6)-C(7)	114.9 (3)
C(6)-C(7)-C(8)	104.9 (3)
C(1)-C(8)-C(7)	108.1 (3)
C(1)-C(9)-C(10)	118.9 (4)
C(9)-C(10)-C(11)	118.5 (4)
C(5)-C(11)-C(10)	116.6 (3)
C(2')-C(1')-C(8')	105.7 (3)
C(2')-C(1')-C(9')	117.6 (3)
C(8')-C(1')-C(9')	110.8 (3)
C(2)-C(2')-C(1')	111.0 (2)
C(2)-C(2')-C(3')	107.2 (3)
C(2)-C(2')-C(6')	118.5 (2)
C(1')-C(2')-C(3')	115.1 (3)
C(1')-C(2')-C(6')	102.2 (3)
C(3')-C(2')-C(6')	102.9 (3)
C(2')-C(3')-C(4')	107.7 (3)
C(3')-C(4')-C(5')	104.2 (3)
C(4')-C(5')-C(6')	101.3 (3)
C(4')-C(5')-C(11')	112.8 (4)
C(6')-C(5')-C(11')	116.3 (3)
C(2')-C(6')-C(5')	104.2 (3)
C(2')-C(6')-C(7')	106.8 (3)
C(5')-C(6')-C(7')	114.6 (3)
C(6')-C(7')-C(8')	106.4 (4)
C(1')-C(8')-C(7')	107.5 (4)
C(1')-C(9')-C(10')	118.2 (3)
C(9')-C(10')-C(11')	119.0 (4)
C(5')-C(11')-C(10')	116.7 (4)

[a] The standard deviation of the least significant figure of each angle is given in parentheses.

trated in Figure 1, the geometry of **8** is extremely well suited to a concerted ene reaction leading to **11**.

Provided that the ene reaction is not interdicted by stereochemistry (as it most often is) in the dimerization of torsionally strained olefins, it may, quite generally, prove to be the preferred pathway. Support for this view comes from comparison of the dimer formed from the photoadduct of benzene and butadiene[26] with that formed from the photoadduct of benzene and isoprene.[27] The photoadducts may be viewed as derivatives of cis,trans-1,5-cyclooctadiene; and like this diene[12a] (and its 1,4 isomer),[12b] the former photoadduct gives a dimer containing a four-membered ring. The stereochemistry of the dimer isolated is consistent with a $[_\pi 2_s + _\pi 2_a]$ reaction pathway,[11] although in the dimerization of the cis,trans-cyclooctadienes mixtures of stereoisomers are formed.[12] In the butadiene photoadduct, as in the cis,trans-cyclooctadienes, models show that the C-H bonds allylic to the trans olefinic linkage are nearly orthogonal to the p orbitals of the π bond. Consequently, an ene pathway for dimerization is stereochemically inaccessible. In contrast, the photoadduct of benzene with isoprene does give an ene-type dimer. It is possible that the additional methyl group, by making the double bond in this photoadduct trisubstituted, inhibits formation of the type of

dimer obtained from the butadiene photoadduct. However, we believe that the chief factor responsible for the change in the type of dimer formed is that the additional methyl group in the isoprene photoadduct provides a C-H bond that can lie in the same plane as the adjacent p orbital of the strained double bond. Thus, a concerted ene reaction becomes stereochemically feasible and appears to be the pathway utilized.

Experimental Section

Bicyclo[3.2.2]nonane-6,8-dione (1).[3] In a 1-L flask were placed 25.6 g (0.107 mol) of bicyclo[3.2.2]nonane-6,8-dione-1,5-dicarboxylic acid[3] and 340 mL of triglyme. The solution was heated at reflux for 3 h, by which time CO_2 evolution had ceased. The reaction mixture was allowed to cool to 40 °C. The diketone was isolated via its Girard salt as follows. Girard's "T" reagent (43 g, 0.256 mol), 80 mL of H_2O, 85 mL of glacial acetic acid, and enough 95% ethanol to make a homogeneous mixture (~360 mL) were added to the reaction medium and heated at reflux for 1 h, then cooled. Most of the ethanol and acetic acid were removed by rotary evaporation, and the resulting material was dissolved in 800 mL of H_2O. This aqueous solution was thoroughly extracted with CH_2Cl_2 (6 × 250 mL) to remove the triglyme, then heated at 90–100 °C to drive off residual CH_2Cl_2. HOAc, and EtOH. Next, 128 mL of concentrated HCl was added, and the mixture was heated at reflux for 1 h. The cooled solution was saturated with NaCl and extracted with 1200 mL of CH_2Cl_2, in four portions. The combined CH_2Cl_2 layers were washed with 2 × 200 mL of 10% $NaHCO_3$ solution and 250 mL of saturated sodium chloride solution, dried over $HgSO_4$, and concentrated by rotary evaporation to leave 11.7 g (73%) of diketone **1**. Recrystallization from 1:1 benzene–hexane gave 9.0 g of material, mp 204–210 °C (lit.[3] 218–223 °C).

6,8-Bis(isocyanomethyl)bicyclo[3.2.2]nonane-6,8-diol. Butyllithium (33.7 mL, 2.17 M in hexane, 73 mmol) was added dropwise over a period of 10 min to a mechanically stirred solution of methyl isocyanide (2.99 g, 73 mmol) in tetrahydrofuran (356 mL, freshly distilled from lithium aluminum hydride) at −60 °C under a nitrogen atmosphere. Stirring was continued 10 min beyond completion of the addition. A solution of bicyclo[3.2.2]nonane-6,8-dione (3.68 g, 24.2 mmol) in THF (60 mL) was then added dropwise at such a rate as to maintain an internal temperature of −60 ± 3 °C. Addition time was about 20 min. The mixture was stirred vigorously at −60 to −65 °C for 1 h more at which time acetic acid (4.16 mL) dissolved in THF (60 mL) was added rapidly with stirring. The mixture was then poured onto ice (ca. 750 mL), and extracted first with ether (3 × 800 mL) and then with methylene chloride (400 mL). The combined organic extracts were dried over sodium sulfate and evaporated to dryness to give 6.60 g of a dark oil. Crystallization from methylene chloride (−20 °C) gave 3.79 g of the colorless diadduct in two crops as a mixture of two major isomers, separable by analytical TLC. The mother liquor, from which no more bis adduct could be crystallized, contained a mixture of mono and bis adducts, which were either separated by preparative TLC or recycled to give more bis adduct. The spectral data for the bis adduct follow: IR (KBr) 3330, 2920, 2890, 2830, 2140 (sh), 2120 (sh), 1385, 1375, 1125, 1105, 970, 945, cm^{-1}; NMR (CD_3COCD_3) δ 4.20 (s, 2 H), 3.60 (s, 4 H), 2.2 and 1.8 (m, 12 H); MS m/e 234 (M$^+$), 194 (M − CH_2NC), 149, 121, 107, 93, 91, 79, 67, 55, 43, 41.

Exact mass. Calcd for $C_{13}H_{18}N_2O_2$: 234.1368. Found: 234.1372.

Bicyclo[3.3.3]undecane-2,6-dione (4). 6,8-Bis(isocyanomethyl)-bicyclo[3.2.2]nonane-6,8-diol (7.14 g) was dissolved in 120 mL of methanol and the solution was cooled in an ice bath. Concentrated hydrochloric acid (60 mL) was slowly added with stirring. When the initially vigorous reaction had subsided, the mixture was refluxed for 90 min and then evaporated to dryness under reduced pressure. The resulting hydrochloride salt was pumped under vacuum for 12 h to remove any excess HCl. The crude product was then dissolved in water (64 mL) and acetic acid (7.54 mL), sodium acetate (6.29 g), and benzene (120 mL) were added. The two-phase mixture was cooled in an ice bath, and a solution of sodium nitrite (8.68 g) in water (32 mL) was added with vigorous stirring in portions over a 30-min period. The solution was stirred for an additional 18 h after which time the two phases were separated. The aqueous layer was extracted with benzene (120 mL) and the combined organic phases were dried over sodium sulfate. Evaporation to dryness gave 4.70 g of a semicrystalline product (87%). TLC analysis (silica gel/ether) showed two com-

pounds, barely separable. The IR spectrum (KBr) of the mixture showed strong carbonyl absorption at 1692 cm^{-1}, and the ^{1}H NMR (CDCl$_3$) consisted of a complex series of multiplets δ 1.3-3.2. In benzene these were resolved into groups centered at δ 1.23 (6 H), 1.70 (4 H), 2.22 (4 H), and 2.60 (2 H).

Tricyclo[3.3.0^{2,6}]undecane-2,6-diol (6). The crude mixture of bicycloundecanediones (2.55 g) was suspended in water (175 mL) and zinc amalgam (prepared by vigorously stirring 1.96 g of mercuric chloride and 19.60 g of zinc dust in 100 mL of 0.5 N HCl for 10 min) was added. The mixture was cooled in an ice bath and with vigorous stirring concentrated HCl (175 mL) was slowly added. The temperature was maintained and the mixture was stirred for a total of 4 h. The water was decanted and then extracted with one portion of pentane (200 mL) to remove any hydrocarbon products. The pentane was washed once with water (150 mL) and the combined aqueous layers were saturated with NaCl. Extraction with chloroform (5 × 300 mL), drying over sodium sulfate, and evaporation to dryness gave crystalline diol (1.73 g, 67%), a single compound as judged by GLC and TLC. Recrystallization of the diol from methylene chloride-heptane or benzene-heptane gave analytically pure material with mp 241-244 °C dec. The spectral data for the diol follow: IR (CH$_2$Cl$_2$) 3590, 3540, 2930, 2865, 1465, 1360, 1100, 960 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.45 (br s, 2 H), 1.2-2.7 (16 H, multiplets centered at 2.15 and 1.58); ^{13}C NMR (CDCl$_3$) δ 91.11, 44.67, 31.38, 29.29, 27.24, 18.14; MS m/e 182 (M$^+$), 164 (M $-$ H$_2$O), 154, 136, 126, 98, 97, 94, 93, 91.

Anal. Calcd for C$_{11}$H$_{18}$O$_2$: C, 72.49; H, 9.95. Found: C, 72.40; H, 9.98.

Exact mass. Calcd for C$_{11}$H$_{18}$O$_2$: 182.1306. Found: 182.1335.

Tricyclo[3.3.0^{2,6}]undecane-2,6-diol Thionocarbonate (9). The diol 6 (455 mg) was dissolved in THF (20 mL, distilled from LiAlH$_4$) and the solution cooled to 0 °C under argon. Butyllithium (2.07 mL, 2.17 M in hexane) was added slowly via syringe with stirring. After 5 min thiocarbonyldiimidazole (775 mg) was added in portions with stirring. The reaction mixture was then refluxed for 5 h, cooled, and poured into water. The water was extracted with methylene chloride (100 mL) and the organic phase was washed twice with water, dried, and evaporated to give a dark semisolid. This material was dissolved in benzene and filtered through a short Florisil column to give 461 mg of beautifully crystalline thionocarbonate (82%). Recrystallization from methylene chloride-heptane gave an analytical sample with mp 186.5-187 °C. The spectral data for 9 follow: IR (CH$_2$Cl$_2$) 2930, 2880, 1475, 1340 (sh), 1305, 1290, 1208, 1197, 1181 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.6-2.8, complex pattern of multiplets; ^{13}C NMR (CDCl$_3$) δ 192.66, 109.76, 39.12, 35.00, 29.53, 28.45, 20.67, MS m/e 224 (M$^+$), 164 (M $-$ COS), 94, 93, 91, 79.

Anal. Calcd for C$_{12}$H$_{16}$O$_2$S: C, 64.25; H, 7.19; S, 14.29. Found: C, 64.36; H, 6.92; S, 14.45.

Exact mass. Calcd for C$_{11}$H$_{16}$O$_2$S: 224.0871. Found: 224.0854.

Generation and Trapping of Tricyclo[3.3.0^{2,6}]undec-2(6)-ene (8) with Diphenylisobenzofuran to Give 10. The thionocarbonate 9 (209 mg, 0.93 mmol) and diphenylisobenzofuran (276 mg, 1.02 mmol) were dissolved in triethyl phosphite (4 mL). The solution was deoxygenated under water aspirator pressure and placed under a nitrogen atmosphere. The reaction mixture was refluxed for 36 h, evaporated to dryness under reduced pressure, and dissolved in CH$_2$Cl$_2$. A CH$_2$Cl$_2$ solution of maleic anhydride was added until the fluorescent yellow color of the excess trapping agent was discharged. The mixture was evaporated to dryness, dissolved in benzene, and then filtered through a short column of Florisil. The eluted material was recrystallized from CH$_2$Cl$_2$-methanol to give 310 mg (85%) of colorless, crystalline adduct, mp 245-246 °C dec. The spectral data for the adduct follow: IR (CH$_2$Cl$_2$) 2940, 2915, 2875, 1603, 1494, 1460, 1343, 1300, 1012, 993 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.3-7.9 (m, 10 H), 7.10 (m, 4 H), 2.55 (m, 1 H), 1.2-2.3 (m, 15 H); ^{13}C NMR (CDCl$_3$) δ 150.37 (s), 148.57 (s), 140.86 (s), 137.73 (s), 128.11 (d), 127.04 (d), 126.94 (d), 125.78 (d), 121.14 (d), 120.16 (d), 94.51 (s), 94.08 (s), 74.55 (s), 73.92 (s), 42.64 (d), 38.81 (t), 38.37 (t), 38.12 (d), 32.55 (t), 32.55 (t), 32.32 (t), 31.34 (t), 22.03 (t); MS m/e 418 (M$^+$), 271, 270, 241, 165, 105, 77.

Anal. Calcd for C$_{31}$H$_{30}$O: C, 88.95; H, 7.22. Found: C, 89.01; H, 7.20.

Exact mass. Calcd for C$_{31}$H$_{30}$O: 418.2297. Found: 418.2280.

Generation and Dimerization of Tricyclo[3.3.0^{2,6}]undec-2(6)-ene (8). Isolation of the Initial Dimer (11) and Its Isomer (13). Tricycloundecanediol thionocarbonate (170 mg, 0.76 mmol) was dissolved in triethyl phosphite (4.0 mL, freshly distilled from sodium chips under

reduced pressure). The system was rigorously degassed by several successive freeze-thaw cycles under vacuum and placed under an argon atmosphere. The solution was refluxed for 20 h, cooled, and evaporated to dryness at room temperature under vacuum. The residue was dissolved in hexane and passed through a short Florisil column, eluting with hexane to give 112 mg of dimeric hydrocarbon (100%). Careful integration of the olefinic region of the ^{1}H NMR spectrum showed this to be a 7:3 mixture of the originally formed dimer (11) and its double bond isomer (13). The hydrocarbon mixture was redissolved in triethyl phosphite, degassed, and refluxed under argon for 18 h more. Integration of the ^{1}H NMR spectrum of the hydrocarbon mixture showed it to be a 6:4 mixture. Reaction of the thionocarbonate without interruption for 36 h gave instead an estimated 2:8 mixture.

A pure sample of 11 was obtained by stopping the reaction at 6 h. Isolation of the hydrocarbon as above, followed by purification by preparative TLC (silica gel/hexane), gave dimer with the following properties: IR (CCl$_4$) 2935, 2860, 1720 (w), 1695 (w), 1460, 902 cm^{-1}; (film) 2910, 1710, 1460, 902, 810 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.50 (br d, J = 5 Hz, 1 H), 3.55 (br d, J = 16 Hz, 1 H), 2.92 (m, one J = 6.5 Hz, 1 H), 0.8-2.6 (complex multiplet with maxima at 2.4, 2.1, and 1.6, 29 H). Irradiation at δ 1.88 caused the δ 5.50 resonance to become a singlet and the δ 3.55 resonance to become a broad singlet. Irradiation at δ 2.22 eliminated the 6.5 Hz coupling of the δ 2.92 resonance. Irradiation at δ 2.92 caused the δ 5.50 resonance to become a doublet of doublets, J = 5 and 1.5 Hz, and the δ 3.55 doublet to sharpen slightly. Irradiation at δ 3.55 caused the δ 5.50 doublet to sharpen considerably. Irradiation of the δ 5.50 resonance caused sharpening of the resonances at δ 3.55 and δ 2.92. ^{13}C NMR (CDCl$_3$) δ 162.02 (s), 127.19 (d), 69.61, 67.37, 53.46, 47.75, 44.09, 43.26, 42.82, 42.23, 39.99, 37.40, 35.49, 34.28, 31.24, 31.10, 30.89, 28.27, 27.32, 25.34, 24.81, 20.55; MS m/e (rel intensity) 296 (M$^+$, 41), 149 (73), 148 (35), 147 (54), 146 (63), 120 (43), 119 (34), 105 (51), 91 (100), 81 (47), 79 (62), 67 (79).

Exact mass. Calcd for C$_{22}$H$_{32}$: 296.2504. Found: 296.2452.

A pure sample of the rearranged dimer (13) was obtained by stopping the reaction at 74 h. Isolation of the hydrocarbon as above, followed by purification on a short silica gel column (heptane), gave 13 with the following properties: IR (CH$_2$Cl$_2$) 2940, 2880, 1730 (w), 1490 (w), 1465 cm^{-1} (w); ^{1}H NMR (CDCl$_3$) δ 5.68 (triplet, J = 1.8 Hz, 2 H), 2.74 (d, J = 1.8 Hz), and 2.65 (d, J = 1.8 Hz) within a complex multiplet δ 1.0-2.9, 30 H. Irradiation at δ 5.68 caused the two resonances at δ 2.74 and 2.65 to become singlets. Irradiation at δ 2.70 caused the δ 5.68 resonance to become a singlet. ^{13}C NMR (CDCl$_3$) δ 137.26 (d), 132.38 (d), 65.03, 64.21, 56.15, 51.03, 49.32, 43.11, 42.82, 42.08, 36.91, 33.50, 32.77, 32.42, 31.33, 30.93, 27.73, 27.44, 26.96, 24.90, 22.29, 20.51; MS m/e (rel intensity) 296 (M$^+$, 72), 149 (100), 148 (32), 147 (51), 146 (97), 120 (60), 119 (38), 105 (39), 93 (38), 91 (64), 81 (48), 79 (57), 67 (96).

Exact mass. Calcd for C$_{22}$H$_{32}$: 296.2504. Found: 296.2458.

Hydrogenation of the Dimers to Give 14. The rearranged dimer 13 (40 mg) was dissolved in ethanol (10 mL) and hydrogenated with palladium on charcoal (20 mg) in a microhydrogenation apparatus. The system was degassed and then filled with hydrogen generated from the reaction of ethanolic sodium borohydride and acetic acid in a separate flask, using a balloon reservoir. When hydrogen uptake was complete, the solution was filtered through Celite to remove the catalyst. Upon evaporation of the solvent, the crude hydrocarbon was dissolved in pentane and filtered through a short silica gel column. The solvent was evaporated to dryness and the product sublimed to give 39 mg of crystalline product. This was recrystallized from ethanol to give needles for x-ray analysis, mp 131-132.5 °C. The spectroscopic data collected for 14 follow: IR (CHCl$_3$) 2935, 2880, 1482, 1458 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.0-2.5 (complex series of multiplets with maxima at 2.20 and 1.63); ^{13}C NMR (CDCl$_3$) δ 65.89 (s), 51.71 (d), 43.44 (d), 42.88 (d), 36.65 (t), 34.64 (t), 31.88 (t), 30.98 (t), 26.73 (t), 25.11 (t), 20.47 (t); MS m/e 298 (M$^+$), 150, 149, 148, 107, 106, 93, 67, 55, 41.

Exact mass. Calcd for C$_{22}$H$_{34}$: 298.2661. Found: 298.2658.

In similar experiments, both the initially formed dimer (11) and a mixture of 11 and 13 were hydrogenated. The products form both experiments were compared with the sample from the one described above, and they were found to be identical in all respects, including ^{13}C NMR.

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Supplementary Material Available: The observed and calculated structure factors for **14** (7 pages). Ordering information is given on any current masthead page.

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Infrared Laser Induced Organic Reactions. 1. Irradiation of Ethyl Acetate with a Pulsed CO$_2$ Laser. Selective Inducement vs. Thermal Reaction[1]

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Abstract: Gas phase samples of ethyl acetate (**1**) were irradiated with a pulsed CO$_2$ laser to produce acetic acid and ethylene. The elimination of HBr from isopropyl bromide (**2**) was used as an internal standard to monitor thermal effects. Under nonfocused conditions (E_{irr} = 0.7–0.8 J/cm^2), ethylene was produced at 12–16% conversion per flash (CPF), nearly all of which was due to thermal processes. Under partially focused beam conditions (E_{irr} = 0.8–8.0 J/cm^2), it was possible to demonstrate laser-induced, nonequilibrium chemistry by showing that ethylene was produced in an amount that was greater than expected via the thermal route. These studies indicated that both low pressure and high energy of irradiations were necessary for the non-equilibrium pathway. Because of the similarities in Arrhenius parameters for the decomposition of **1** and **2**, it was possible to identify the amount of ethylene produced by both the thermal pathway and that produced via the nonequilibrium pathway.

Much interest has developed recently in the use of intense infrared radiation to augment chemical reactions. Considerable effort has been directed toward isotope separation[2] and understanding the multiple photon absorption process[3] using small molecules, while little has been done with relatively large organic molecules.[4] We wish to report the CO$_2$ laser augmented decomposition of ethyl acetate; a simple technique was employed by which the amount of laser-induced, nonequilibrium chemistry vs. simply heating was evaluated.[1]

The thermal decomposition of ethyl acetate proceeds through a cyclic transition state to yield ethylene and acetic acid with a rate constant of $k = 10^{12.59} \exp(-48\,000/RT)$.[5a] This reaction can be induced with a pulsed CO$_2$ laser under both nonfocused and partially focused beam conditions; ethylene and acetic acid are the sole products as determined by gas chromatography and infrared spectroscopy of the reaction

$$CH_3\overset{O}{\overset{\|}{C}}OCH_2CH_3 \longrightarrow \left[CH_3C \overset{O}{\underset{O—CH_2}{\diagdown}} \overset{H}{\underset{CH_2}{\diagup}} \right]^{\ddagger}$$

$$\longrightarrow CH_3CO_2H + CH_2{=}CH_2$$