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THE DOMINANT ROLE OF HYPERCONJUGATION IN THE 9-OXABICYCLO[4.2.1] NONA-2,4,7-TRIENE SERIES[1]

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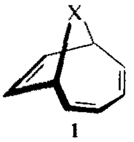
Abstract—The synthesis and photodimerization of 9-oxabicyclo[4.2.1]nona-2,4,7-triene are described. The electronic structure of 9-oxabicyclo[4.2.1]nona-2,4,7-triene and variously saturated derivatives thereof was examined by means of UV photoelectron spectroscopy and calculation. The combined results give no indication of specific through-space lone-pair/π or π/π interaction between the various appendages but offer clear sign of hyperconjugative coupling.

We have, in recent years, expressed active interest in the heteroatomic lone pair and its ability to partake in non-bonded p–π interaction. Our studies in this area have dealt chiefly with the general 9-heterobicyclo[4.2.1]nona-2,4,7-triene system shown in **1** whose rigid frame provides one with the necessary molecular environment for examining the stereoelectronic factors which control the development of nonbonded p–π interaction between a lone pair and one or more neighboring π systems. Employing photoelectron spectroscopy (pes) as a method for locating the energies of various key filled MO levels we have recently succeeded in demonstrating (i)[2] that 9-azabicyclo[4.2.1]nona-2,4,7-triene (**1a**), is best viewed as a heterobicycloconjugated molecule, i.e. one in which all three formally isolated bridges (nitrogen, ethylene and butadiene) interact with one another and (ii)[3] that the thia analog **1b** must be regarded merely as a heterohomoconjugated substance in the sense that here only the ethylene bridge interacts to any significant degree with the heteroatomic lone pair. For obvious reasons, the realization that the lone pair associated with the bridging heteroatom in **1** generates distinctly different types of nonboned p–π interaction in **1a** and **1b** prompted a photoelectron-spectroscopic (pes) examination of what might be regarded as the third common member of the family, namely the oxa analog **1c**. Of particular significance in the case of **1c** was, of course, the expectation that the lone pair associated with the highly electronegative oxygen bridge should possess a substantially lower energy than its counterparts in **1a** and **1b** and thus provide for better energy matching with the filled π levels of the surrounding ethylene and butadiene segments of the molecule.[4]

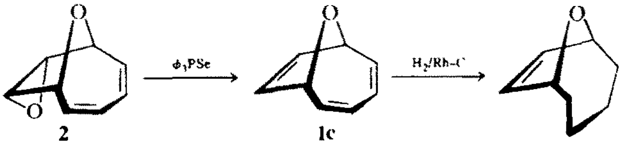
Synthesis and photoinduced response of **1c**. Since the desired oxabicyclic model (**1c**) was unknown at the outset of this investigation attention in this project was first concentrated on its preparation from readily accessible progenitors. To this end, we elected to examine the dioxatricycle shown in **2**, a molecule recently prepared in our laboratories[5] by a simple 3-step sequence from cyclooctatetraene. The desired de-epoxidation of **2** was effected on exposure to triphenyl phosphine selenide in boiling benzene, yielding oxatriene **1c** as a colorless oil with fully consistent spectroscopic (NMR, IR, UV, MS) characteristics.[6,7]

The variously saturated analogs of **1c** shown in **3**,[8] **4**[9]

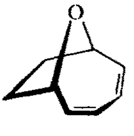


1

a: X = NH
b: X = S
c: X = O
d: X = NCN



2 **1c** **3**



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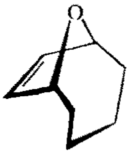
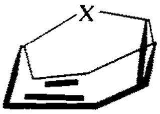


5

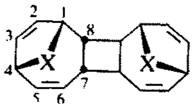
and **5**[9] which were of course also needed in the present study, were prepared by well established methods previously developed elsewhere.[8,9]

Following the synthesis of oxatriene **1c** attention was briefly concentrated in a study of photoinduced response, in the hope of gaining preliminary insight into the electronic makeup of the molecule. Specifically, it was felt that since the photoinduced response of cyanamide **1** (X = NCN)[10] and sulfide **1b**[11] had already been examined in some detail,[12–15] direct comparison of the photobehavior of **1c** with these earlier findings might expose behavioral differences that chiefly reflect the nature of the heteroatomic unit and, in particular, the ability of its lone pair to interact with the rest of the molecule.

In practice, **1c** was found to undergo ready, specific, dimerization when exposed to sensitized (Michler's Ketone) irradiation in deaerated acetone at 0°. The product, isolated as a white crystalline solid (m.p. 116–116.5°) was formulated as shown in **7a** on the basis of its NMR spectrum which is virtually superimposable, peak for peak, to that of the well characterized diamine **7b**.[13,16] Perhaps the most notable characteristic of the photodimerization of **1c** is that it occurs predominantly and possibly exclusively over a wide range of concentration (solutions as dilute as 0.05% w(g)/v(ml) were employed) without any indication of prior skeletal rearrangement. The photobehavior of **1c** is thus seen to sharply contrast that of the sulfur counterpart (examined under analogous conditions and a concentration as high as 1% w(g)/v(ml)) which is known not to dimerize but to photorearrange to **6a** instead.[15] In turn, the response of cyanamide **1d** to photosensitized irradiation is intermediate between those of **1b** and **1c**, the molecule (**1d**) undergoing efficient dimerization to **7c** at high concentration (3% w(g)/v(ml))[13] and virtually exclusive rearrangement to **6b** at low concentration (0.05% w(g)/v(ml)).[14] Obviously, the structurally related heterobicycles **1d**, **1b** and **1c** do differ in their response to sensitized irradiation. Moreover, the photobehavior of these substances is seen to follow an interesting trend whereby a molecule's tendency to dimerize (**1c** > **1d** > **1b**) appears to parallel the strength of its bridging C–X link. Translated into mechanism, this trend strongly points to the possibility that C–X bond rupture is a necessary requirement for rearrangement of **1** to **6**.



6a: X = S
b: X = NCN



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7a: X = O
b: X = NH
c: X = NCN

Spectroscopic assignments. In Figs. 1–4 are depicted the pe spectra of compounds **3**, **4**, **5** and **1c** respectively. Brief inspection reveals each spectrum to consist of the expected number of low-energy bands denoting ionization from π-bonding and/or nonbonding levels. Peak assignments are, for the most part, straightforward. Thus, starting with the fully saturated model, **3**, we may securely assign the single sharp, low-energy, band present in the spectrum (band 1 in Fig. 1) to ionization of an oxygen lone pair (n_s);[17] interestingly lone pair ionization here (9.12 eV) occurs with far greater ease (*ca.* 0.5 eV) than in such model compounds as tetrahydrafuran (9.65 eV),[18] diethyl ether (9.63 eV),[18] diisopropyl ether (9.56 eV)[19] and 7-oxabicyclo[2.2.1]heptane (9.57).[20] Oxadiene **4** exhibits (Fig. 2) "normal" lone pair ionization (n_s = 9.51 eV) as well as two butadiene bands, $\pi^{17}_{4,a}$ = 8.55 eV and $\pi^{17}_{4,s}$ = 10.75 eV, whose separation (2.20 eV) closely corresponds to those observed in such models as bicyclo[4.2.1]nona-2,4-diene (2.23 eV),[2] 9-methylene-bicyclo[4.2.1]nona-2,4-diene (2.49 eV),[21] 9-azabicyclo[4.2.1]nona-2,4-diene (2.37 eV)[2] and 9-thiabicyclo[4.2.1]nona-2,4-diene

Fig. 1. Low-energy segment of the photoelectron spectrum of 9-oxabicyclo[4.2.1]nonane (**3**) with assignment. The value attached to the band denotes the vertical ionization potential in eV.

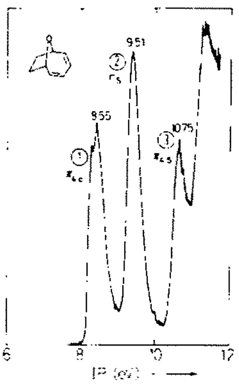


Fig. 2. Low-energy segment of the photoelectron spectrum of 9-oxabicyclo[4.2.1]nona-2,4-diene (**4**) with assignments. The values attached to each band denote vertical ionization potentials in eV.

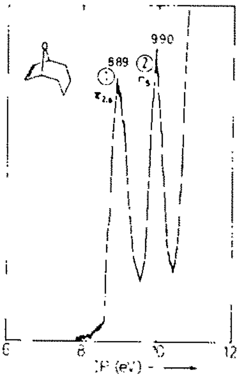


Fig. 3. Low-energy segment of the photoelectron spectrum of 9-oxabicyclo[4.2.1]nona-7-ene (**5**) with assignments. The values attached to each band denote vertical ionization potentials in eV.

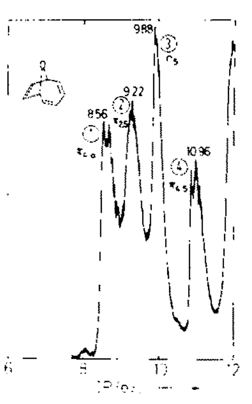


Fig. 4. Low-energy segment of the photoelectron spectrum of 9-oxabicyclo[4.2.1]nona-2,4,7-triene (**1c**) with assignments. The values attached to each band denote vertical ionization potentials in eV.

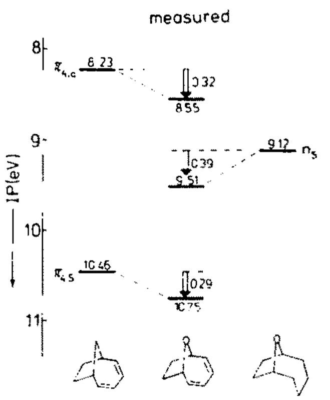
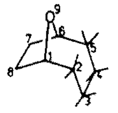


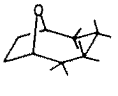
Fig. 5. Correlation diagram relating to the measured low-energy ion states of bicyclo[4.2.1]nona-2,4-diene, 9-oxabicyclo-[4.2.1]nona-2,4-diene (**4**), and 9-oxabicyclo[4.2.1]nonane (**3**). The arrows denote ion-state energy shifts in **4** relative to the model compounds.

(1.92 eV).[3] Further, one finds the vibrational structure of band 1[22] to closely resemble that of its counterparts in the spectra of bicyclo[4.2.1]nona-2,4-diene[21,22] and 9-methylenebicyclo[4.2.1]nona-2,4-diene.[21,22] Band assignments 1 (8.89 eV) = $\pi_{2,s}^{17}$ and 2 (9.90 eV) = n_s in the spectrum of "ene" **5** (Fig. 3) were made on the basis of well documented analogy, their counterparts respectively appearing at 8.97 eV in the spectrum of bicyclo[2.2.1]hept-2-ene[23] and 9.83 eV in the spectrum of 7-oxabicyclo[2.2.1]hept-2-ene.[20] Finally, the band assignments given in the spectrum of **1c** (Fig. 4) consistently follow from those discussed above for **3** and **4**.

Interpretive discussion. We shall now make use of the pes data described in the previous section and, when necessary, proper calculation (especially concentrating on the effect of interrupted conjugation)[24] in an effort to gain insight into the major type(s) of nonbonded interaction generated by the lone pair of the bridging heteroatom in [4.2.1] 9-oxabicycles **1c**, **3**, **4** and **5**. In order to accomplish this it was, of course, necessary to first expose the factor(s) responsible for the abnormally low energy needed to ionize the lone pair (position of n_s band) of the fully saturated model **3**. One gains useful insight into this apparent discrepancy in n_s ionization energy between **3** and the various chosen model compounds (*vide supra*) by examining the results of MINDO/2[25] and CNDO/2[26] calculations which reveal that (i) "folded" conformation F ought to be more stable than its "extended" relative E and



F



E

(ii) nonbonded interaction between the lone pair in F and its proximal, "syn"-directed, protons bound to C(2) and C(5) should have a destabilizing influence on the lone pair. The observed decrease (*ca.* 0.5 eV) in lone pair ionization energy of **3** relative to that measured in appropriate models (*vide supra*) is thus best accounted for by nonbonded destabilization of the lone pair as described in (ii).

Figure 5 depicts a level diagram correlating the measured n_s and π_4 energies of oxadiene **4** with those of model compounds bicyclo[4.2.1]nona-2,4-diene and **3**. It is immediately seen that combining lone pair and butadiene as in **4** leads to substantial stabilization of *all* pertinent levels relative to their isolated counterparts. Closer scrutiny of the situation reveals, however, that the observed energy lowerings do not, in all likelihood, result from direct nonbonded interaction of the two p(π) bridges. Specifically, one notes that lone pair ionization (n_s band) in **4** (9.51 eV) is essentially isoenergetic with that measured in four suitable *fully saturated* models (*vide supra*) whose n_s band averages at 9.6 ± 0.05 eV, thus suggesting that the observed 0.39 eV lowering in n_s on passing from **3** to **4** is best attributable not to any interaction between lone pair and butadiene in **4** but rather to the fact that the lone pair of the chosen "model", **3**, is, for reasons discussed above, associated with an anomalously high energy. As a result, of course, the energy lowerings in π_4 (a or s) observed on passing from the hydrocarbon model to **4** cannot be due to direct nonbonded interaction between lone pair and butadiene in this molecule. Instead, the overall stabilization of the π appendage witnessed on changing the bridging unit from CH_2 to oxygen may rationally be accounted for in terms of a reduction in hyperconjugative destabilization (net energy lowering) imparted to the butadiene moiety by the remainder of the molecule on passing from bicyclo[4.2.1]nona-2,4-diene to **4**. In other words, what we propose here as the best possible explanation for the energy lowering observed in the butadiene segment of **4** is simply that hyperconjugative interaction of this unit with the appendage (present in **4**) is less destabilizing than with the related segment (present in the hydrocarbon model). Significantly, our interpretation of the situation with regards to the virtual absence of direct nonbonded η_s-$\pi_{4,s}$ interaction in **4** receives strong support from the results of a CNDO/S calculation specifically designed to take into account the effect of conjugative coupling[27,28] by locating the energies of n_s, $\pi_{4,s}$ and $\pi_{4,a}$ in **4** and comparing them to those of a hypothetical specimen where the butadiene appendage is assumed to be π conjugatively decoupled from the remainder of the system. Simple inspection of the diagramatic representation of these results given in Fig. 6 clearly reveals that conjugative decoupling of the butadiene appendage from the remainder of the molecule substantially stabilizes the $\pi_{4,s}$ and $\pi_{4,a}$ levels of the olefin but exerts virtually no influence on the position of the n_s level. The obvious conclusion to be drawn then in terms of interacting segments is the same as that derived from experiment (Fig. 5) namely

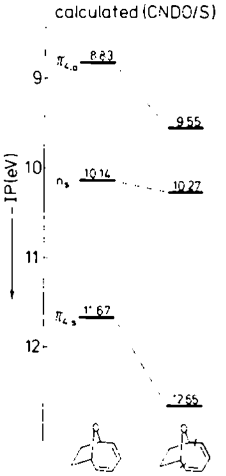
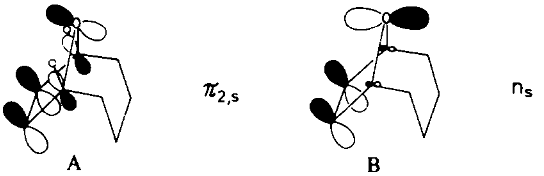


Fig. 6. Correlation diagram relating to the relevant calculated Koopmans' ion states of 9-oxabicyclo[4.2.1]nona-2,4-diene (4) and the same molecule with the butadiene π system conjugatively decoupled.

that *there is no significant through-space interaction between lone pair and butadiene in* **4**.



Turning now to the pe spectrum of "ene" **5** shown in Fig. 3, we note that lone pair ionization here ($n_s = 9.90$ eV) requires the input of significantly higher energy than is needed to activate the same process in oxadiene **4** ($n_s = 9.51$ eV). Now, since the position of the n_s band in the pes of **4** is, for reasons advanced earlier in this report, deemed to be "normal" for a noninteracting lone pair of the general 9-oxa[4.2.1]bicyclic frame, the extra stabilization of the n_s level in **5** must, for obvious reasons, be the result of n_s–$\pi_{2,s}$ interaction. Simple inspection of the key $\pi_{2,s}$ and n_s levels of **5** (depicted in A and B respectively) clearly reveals that this interaction must be hyperconjugative in nature. Significantly, this prediction receives strong support from the results of a calculation carried out with conjugative decoupling of the π bridge from the rest of the molecule (in manner akin to that described for **4**) which indicates that coupling with the ethylenic bridge ought to lead to a hyperconjugative energy lowering of the n_s level by 0.47 eV which closely matches the observed (pes) energy difference between the n_s levels of **5** and **4**. An equally gratifying theoretical interpretation of pes observables was secured through a quantitative assessment of the perturbing influence exerted on the lone pair of **5** by the saturated four-carbon bridge. The two-step MINDO/2 synthesis of **5** devised for this purpose is given in Scheme 1(a) and is seen to involve puckering of 2,5-dihydrofuran followed by symmetrical C_4 cycloalkylation. Brief inspection of the numerical results obtained by this treatment, given in the upper half of Fig. 7, reveals (i) that both, the n_s and the $\pi_{2,s}$ levels of 2,5-dihydrofuran are destabilized by the attachment of the saturated C_4 bridge and, most important, (ii) that the degree of destabilization calculated in each case is in excellent agreement with the experimental value (shown in the lower half of Fig. 7) obtained by evaluating Scheme 1(a) purely on the basis of pes information.[29]

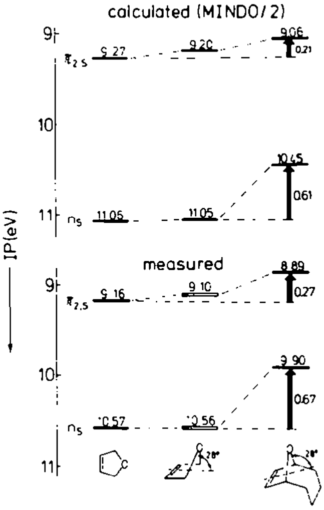
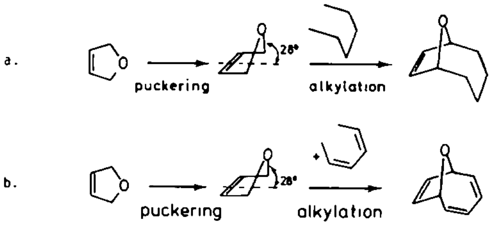


Fig. 7.[29] Correlation diagram relating to the relevant calculated Koopmans' ion states (upper part of Fig.) and measured ion states (lower part of Fig.) for planar and puckered 2,5-dihydrofuran and 9-oxabicyclo[4.2.1]nona-7-ene (5).

It is perhaps worth noting in this connection that the hyperconjugative destabilization introduced by the symmetrical attachment of a C_4 saturated bridge onto 2,5-dihydrofuran is more heavily experienced by the lone pair than by the ethylene.



Scheme 1.

The diagram in Fig. 8 depicts the energy relationship between the photoelectron spectroscopic ionic states of models **4**, **5** and their counterparts in the trienic analog **1c**. Brief examination of this level diagram reveals that among isosymmetric levels (i) both the n_s and $\pi_{4,s}$ ionic states are noticeably stabilized (by 0.37 eV and 0.21 eV respectively) on changing their environment from **4** to **1c** and (ii) only the $\pi_{2,s}$ level is stabilized (by 0.33 eV) on passing from **5** to **1c**, the position of the crucial n_s level remaining essentially invariant during this transformation. The energy changes one witnesses upon modifying the molecular environment from **4** and **5** to **1c** are best understood by examining the level diagram depicted in Figs. 9 and 10 which respectively describe the spectroscopic and theoretical "synthesis" of **1c** from 2,5-dihydrofuran and butadiene.[30] Most important in this connection is perhaps the observation that in the pes "synthesis" of the 9-oxa[4.2.1]bicyclic frames **1c** and **5** the lone pair (n_s) of the common precursor, i.e. 2,5-dihydrofuran, undergoes the same degree of destabilization (0.68 ± 0.01 eV) (compare Fig. 9 with lower half of Fig. 7)

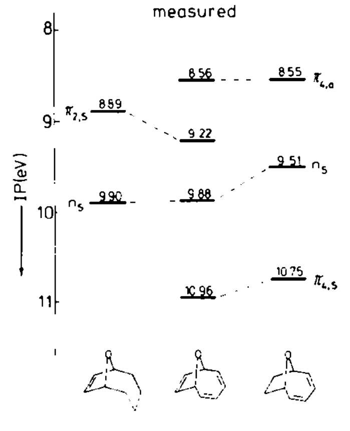


Fig. 8. Correlation diagram relating to the relevant measured ion states of 9-oxabicyclo[4.2.1]nona-7-ene (**5**), 9-oxabicyclo-[4.2.1]nona-2,4,7-triene (**1c**) and 9-oxabicyclo[4.2.1]-nona-2,4-diene (**4**).

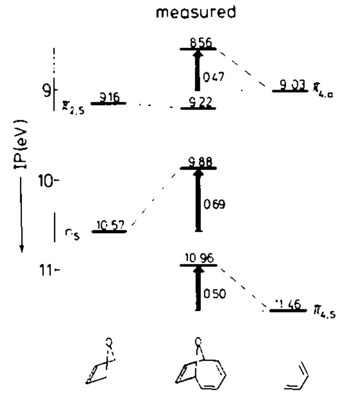


Fig. 9. Correlation diagram relating to the relevant measured ion states of 2.5-dihydrofuran, 9-oxabicyclo[4.2.1]nona-2,4,7-triene (**1c**), and butadiene. The arrows indicate the state shifts caused by the coupling of both subunit moieties.

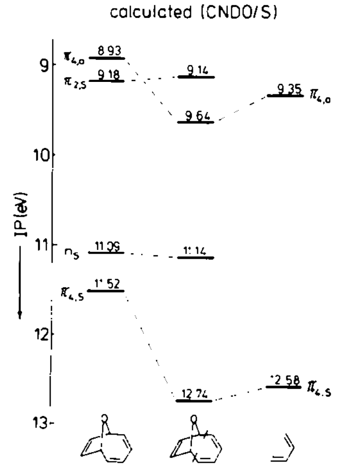


Fig. 10. Correlation diagram relating to the relevant Koopmans' ion states of 9-oxabicyclo[4.2.1]nona-2,4-triene (**1c**), the same molecule with its butadiene π segment conjugatively decoupled, and cis-butadiene.

regardless of whether annelation to the bicyclic frame requires the attachment of a butane or a butadiene unit. In other words, the energy of the lone pair appears to be insensitive to the presence of a π system in the C_4 moiety of **1c** and thus *not* to partake in nonbonded (through-space) η–π interaction with the butadiene appendage. Moreover, the obvious possibility that the observed near-identity in the position of the n_s levels of **1c** and **5** might be due chiefly to a cancellation of factors in spite of significant through-space η–π interaction between oxygen lone pair (n_s) and butadiene ($\pi_{4,s}$) is rendered unlikely in light of the computational results, described in Fig. 10, which clearly reveal that conjugative decoupling of the butadiene unit of **1c** from the rest of the molecule has no effect on the position of the n_s level. A similar analysis of the results depicted in Figs. 7, 9 and 10 in terms of $\pi_{2,s}$ energetics allows one to draw an analogous conclusion about the ethylene unit of **1c**, namely that it is not subject to any significant through-space interaction with the neighboring heteroatomic and butadiene segments.

In brief conclusion then we might stress that the pes findings and theoretical computations described in this report give no indication that oxatriene **1c** sustains bicycloconjugation, i.e. closed loop through-space coupling between the n_s, $\pi_{2,s}$ and $\pi_{4,s}$ levels. On the other hand, the combined information does reveal the three appendages of oxabicycles **1c**, **4** and **5** to be extensively involved in hyperconjugative interactions.

A theoretical analysis emphasizing the recognition of factors which are possibly responsible for the observed differences in nonbonded interaction between heterobicyclic relatives **1a**, **1b** and **1c** will be given in a later report.

EXPERIMENTAL

All b.ps and m.ps are uncorrected. NMR spectra were recorded at 60 MHz (Bruker HX-60) or 100 MHz (Varian XL-100). UV spectra were recorded on a "Cary" 118 spectrophotometer. IR spectra were recorded on a Perkin–Elmer 137 spectrophotometer. PE spectra were recorded on a Perkin–Elmer PS-18 spectrophotometer operating at the He–I (584 Å) line. Mass spectra were recorded at 70 eV. Microanalyses were performed at Galbraith Laboratories, Knoxville, Tennessee.

Synthesis of 9-oxabicyclo[4.2.1]*nona*-2,4,7-*triene* (**1c**). To a stirring soln of **2** (0.272 g, 2.0 mmol) and commercial triphenylphosphine selenide (0.8 g) in dry, deaerated, benzene (60 ml) was added a soln of trifluoroacetic acid (0.228 g, 2.0 mmol) in benzene (10 ml) over a period of *ca.* 2 min and the resulting mixture allowed to stir for 3 hr at ambient temp. then 19 hr at the reflux temp. The dark soln was first allowed to cool to room temp. then treated with solid $NaHCO_3$ (*ca.* 50 mg) and the resulting suspension allowed to stir for 15 min. Filtration produced a dark soln which was concentrated at the water aspirator to yield a dark brown residue (1 g). This, in turn, was treated with ether (5 ml), the resulting mixture was filtered and the filtrate subjected to preparative VPC (6 × 0.25 in. aluminum column packed with 10% SE-30 on Chromosorb W) at 130° to afford **1c** (27 mg) as a colorless oil. Further purification by distillation (35–40°/0.8 mm) produced pure **1c** (19 mg, 8% yield): IR (neat), prominent maxima at 1080, 985, 907, 875 and 812 cm^{-1}, UV (C_6H_{14}) λ_{max} 253 nm (ϵ 4200), 263 (3800) and 273 (2400); NMR (60 MHz, $CDCl_3$) τ3.8–4.1 (4H, m), 4.5 (2H, s) and 4.8 (2H, d, J = 3.5 Hz); MS (70 eV), parent ion at *m/e* 120 (0.5%), base peak at *m/e* 91.

Catalytic hydrogenation of **1c**. To a prehydrogenated suspension of 5% rhodium-on-charcoal (30 mg) in EtOH (10 ml) was added a soln of **1c** (30 mg, 0.25 mmol) in EtOH (5 ml) and the resulting suspension was allowed to shake for 1 hr under 15 psi of H_2. The catalyst was then removed by filtration, the resulting filtrate concentrated at the water aspirator to produce a colorless oil (27 mg, 90% yield) which was, in turn, subjected to preparative

VPC (6 ft × 0.25 in. aluminum column packed with 10% SE-30 on Chromosorb W) at 130° to yield pure **2** identical in all respects (m.p. IR, VPC) with an authentic sample.[8]

Sensitized irradiation of **1c**

Preparation of **7a**. A soln of **1c** (160 mg, 1.33 mmol) and "Michler's ketone" (160 mg) in deaerated acetone (250 ml) was irradiated at 0° and for 45 min, with a "Hanovia" 450-W mercury arc contained in an immersion well fitted with a pyrex filter. The photolysate was then concentrated at the water aspirator at *ca.* 0° to yield a solid residue which, in turn was dissolved in the minimum amount of dichloromethane and the resulting soln applied onto a column (300 × 12 mm) wet-packed (petroleum ether) with activity II "Woelm" neutral alumina and maintained at *ca.* −15°. The column was eluted, first with 1:9 (v/v) ethyl ether-petroleum ether (350 ml) to yield **1c** (30 mg) then with 2:8 (v/v) ethyl ether-petroleum ether to produce photodimer **7a** (80 mg, 50% yield). Recrystallization of **7a** from petroleum ether produced an analytically pure sample (65 mg, 41% yield) as a white solid, m.p. 116–116.5°: IR (KBr), prominent maxima at 2850, 1320, 1080, 990, 925, 890 and 820 cm^{-1}, UV (C_6H_{14}), λ_{max} 210 nm (ϵ5,000); NMR (100 MHz, $CDCl_3$) τ3.96 (2H, dt, $H_2(H'_2)$ or $H_3(H'_3)$, J = 6.5, 1.5 Hz), 4.06 (2H, dt, $H_3(H'_3)$ or $H_2(H'_2)$, J = 6.5, 1.5 (Hz), τ4.24 (2H, ddd, $H_5(H'_5)$, J = 11.5, 5.0, 1.5 Hz), 4.42 (2H, dd, $H_6(H'_6)$, J = 11.5, 3.0 Hz), 4.88 (2H, d, $H_4(H'_4)$, J = 5.0 Hz), 5.14 (2H, s, H_1), 6.84 (2Hd, $H_7(H'_7)$ or $H_8(H'_8)$, J = 8.0 Hz) and 7.20 (2H, bd, $H_8(H'_8)$ or $H_7(H'_7)$, J ~ 8 Hz); MS (70 eV), parent ion at *m/e* 240 (~0.1%), base peak at *m/e* 91. *Anal.* Calc.: C 79.98, H 6.71; found C 80.15, H 6.59. *Mol. Wt.* Calc.: 240; found (benzene) 250.

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