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DIENOPHILIC AND DIPOLAR ADDITIONS TO BICYCLO[2.1.0]PENT-2-ENE

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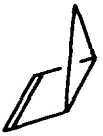
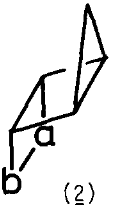
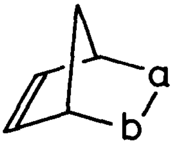
SUMMARY: The dienophiles triazolinedione , singlet oxygen and in part tetracyanoethylene cycloadd to bicyclo[2.1.0]pent-2-ene (1) across the central σ-bond to give bicyclo[2.2.1] heptene-type adducts, while the dipoles phenyl azide, benzonitrile oxide and diphenyldiazomethane cycloadd at the π-bond with expected exo stereochemistry.

Bicyclo[2.1.0]pent-2-ene (1) represents an interesting substrate for cycloaddition in view of its various possible reaction modes. In principle, (2+2)-addition at the double bond could afford the exo-adduct 2, at the strained σ-bond would result in bicyclo[2.2.1]-adduct 3, homocycloaddition would give the bicyclo[3.2.0]-adduct 4, and cycloaddition with skeletal rearrangement would lead to adduct 5. In view of our interest in the latter cycloaddition mode, we examined the reaction of bicyclo[2.1.0]pent-2-ene (1) with triazolinediones.[1] Herein we report that the reaction of 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) with bicyclopentene 1 in a 1:1 mixture of THF-CH_2Cl_2 at -78°C gave the urazole 6a as sole product in 78% yield.[2] Similarly, with 4-methyl-1,2,4-triazoline-3,5-dione (MTAD) the urazole 6b was obtained in 82% yield. These adducts were not derived from adventitious cyclopentadiene because the freshly prepared bicyclopentene was treated with dimsyl anion prior to use to remove cyclopentadiene impurities.[3] Low temperature ^1H-NMR of the resulting solution of bicyclopentene showed not even traces of cyclopentadiene nor of its addition product with bicyclopentene.[4]


(1)



(2)



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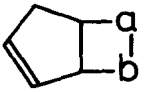

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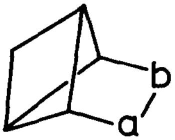

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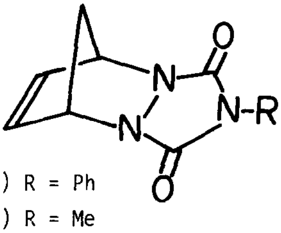
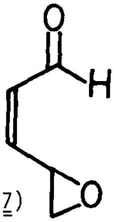


(6a) R = Ph
(6b) R = Me



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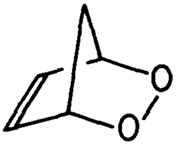
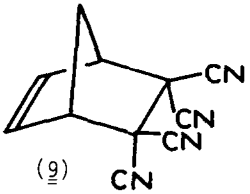


(8)

Appropriate control experiments demonstrated that bicyclopentene did not isomerize to cyclopentadiene under the cycloaddition conditions of PTAD. Thus, while ethyl azodicarboxylate did not react with bicyclopentene, it reacted efficiently with cyclopentadiene under the PTAD cycloaddition conditions. Even when using ethyl azodicarboxylate as solvent, bicyclopentene reacted with PTAD to give exclusively cycloadduct 6a. Not even traces of the expected product between cyclopentadiene and ethyl azodicarboxylate were observed. Had PTAD caused *in situ* isomerization of bicyclopentene into cyclopentadiene, its cycloadduct with ethyl azodicarboxylate should have been formed in detectable amounts (at least 0.1%), especially since the latter was used as solvent.

Other reactive dienophiles were then tried out to assess the generality of this cycloadditon mode. Thus, photo-sensitized oxygenation of bicyclopentene in CH_2Cl_2 at -78°C, using tetraphenylporphyrin as sensitizer, gave the epoxy-aldehyde 7 in 10% yield, a product known to be derived from rearrangement of the endoperoxide 8.[5] Presumably analogous to the TAD's, the singlet oxygen dienophile added across the strained σ-bond of bicyclopentene.

Reaction with tetracyanoethylene (TCNE) in THF at 0°C gave a mixture of the cycloadducts 9 and 10 in 20% and 80% yields (by ^{1}H-NMR), respectively. In contrast to previous claims[2], the bicyclo[2.2.1]-adduct 9 was not produced from cycloaddition of TCNE to adventitious cyclopentadiene derived from the bicyclopentene, as confirmed by control experiments analogous to those run for PTAD. Furthermore, the TCNE-adduct 10, possibly the product of homo-cycloaddition, did not isomerize into 9 under the reaction or isolation conditions.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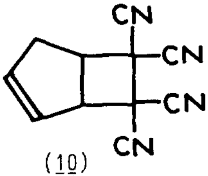
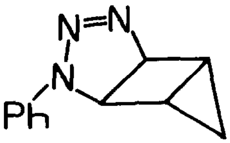
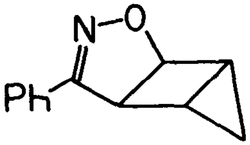

(10)

In contrast to these reactive dienophiles, 1,3-dipolar cycloaddition took place exclusively at the double bond. For example, phenyl azide in 1:1 THF-CH_2Cl_2, benzonitrile oxide in 1:1 THF-C_6H_6, and diphenyldiazomethane in 1:1 THF-CH_2Cl_2, all at ca. 0°C, afforded the cycloadducts 11 - 13, respectively.[6] Decoupling experiments of the 400 MHz ^{1}H-NMR spectra established that 1,3-dipolar cycloaddition took place *exo* to the cyclopropane ring, as expected on the basis of the concept of *endo*-bending of the olefinic hydrogens.[7]


(11)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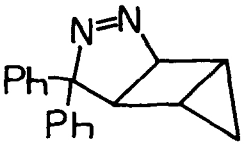
(13)

On the basis of the examples investigated here, an interesting dichotomy emerges concerning the cycloaddition behavior of bicyclopentene. As expected, 1,3-dipoles cycloadd at the π-bond, but surprisingly dienophiles appear to prefer the strained σ-bond. Whether the dienophile reacted directly with the strained σ-bond[2] or via electron transfer[8] cannot be answered at this point.

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≠ Undergraduate research participant (summer 1981).

\# Alexander von Humboldt fellow (1982 - 83).

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2. Baldwin, J. E.; Pinschmidt, Jr., R. K. *Tetrahedron Lett.* **1971**, 935 describe in a footnote that in preliminary experiments very complex reaction mixtures are produced from bicyclopentene and triazolinediones.
3. Andrist, A. H.; Baldwin, J. E.; Pinschmidt, R. K. *Org. Syn.* **1977**, **55**, 15.
4. Baldwin, J. E.; Pinschmidt, Jr., R. K. *J. Am. Chem. Soc.* **1970**, **92**, 5247.
5. Schulte-Elte, K. K.; Willhalm, B.; Ohloff, G. *Angew. Chem.* **1969**, **81**, 1045.
6. Adduct **11** was obtained in 40% yield, mp 83.5 - 84.5°C (plates from t-butyl methyl ether at -78°C).-

   IR (CCl_4): 3035, 2995, 2970, 1600, 1500, 1490, 1455, 1365, 1110, 1100, 1070, 1060, 1035, 1025, 990, 970, 920, 900, 880, 685 cm^{-1}.-

   UV (95% EtOH): λ_{max} (log ε) = 350 (2.9), 274 (3.2), 242 (3.6), 223 sh (3.8) nm.-

   ^1H-NMR ($CDCl_3$, 400 MHz): δ = 0.85 (pseudo td, 1H, J = 7.3, 7.3, 5.5 Hz), 0.86 (pseudo dt, 1H, J = 5.5, 2.0, 2.0 Hz), 2.08 (dddd, 1H, J = 7.3, 5.5, 2.5, 2.0 Hz), 2.12 (pseudo ddt, 1H, J = 7.3, 5.5, 2.0, 2.0 Hz), 3.98 (dd, 1H, J = 5.4, 2.0 Hz), 4.80 (dd, 1H, J = 5.4, 2.5 Hz), 7.02 - 7.06 (m, 1H), 7.25 - 7.28 (m, 2H), 7.33 - 7.38 (m, 2H).-

   ^{13}C-NMR ($CDCl_3$, 100.61 MHz): δ = 10.75 (dd, J = 165 Hz), 19.30 (d, J = 187 Hz), 20.69 (d, J = 185 Hz), 56.60 (d, J = 157 Hz), 82.73 (d, J = 160 Hz), 114.08 (d, J = 165 Hz), 122.45 (d, J = 160 Hz), 129.31 (d, J = 160 Hz), 140.05 (s).-

   MS (70 eV): m/e = 185 (0.8%, M^+), 157 (28%), 156 (100%), 104 (20%), 77 (64%), 51 (38%), 28 (45%).-

   Adduct **12** was obtained in 65% yield, mp 77 - 78°C (needles from t-butyl methyl ether at 0°C).

   IR (KBr): 3030, 3020, 2960, 2900, 1580, 1550, 1480, 1430, 1340, 1250, 1180, 1060, 1050, 1030, 1020, 990, 920, 860, 850, 790, 750, 740, 680 cm^{-1}.-

   UV (95% EtOH): λ_{max} (log ε) = 265 (4.1), 212 nm (end absorption).-

   ^1H-NMR ($CDCl_3$), 400 MHz): δ = 0.83 (pseudo dt, 1H, J = 5.5, 1.3, 1.3 Hz), 0.84 (pseudo dt, 1H, J = 6.0, 5.5, 5.5 Hz), 2.03 (dddd, 1H, J = 6.0, 4.0, 1.5, 1.3 Hz), 2.11 (dddd, 1H, J = 5.5, 4.0, 2.8, 1.3 Hz), 3.76 (dd, 1H, J = 4.0, 1.5 Hz), 4.76 (dd, 1H, J = 4.0, 2.8 Hz), 7.30 - 7.46 (m, 3H), 7.62 - 7.80 (m, 2H).-

   ^{13}C-NMR ($CDCl_3$, 100.61 MHz): δ = 13.40 (dd, J = 165, 158 Hz), 19.96 (d, J = 181 Hz), 27.12 (d, J = 185 Hz), 24.60 (d, J = 147 Hz), 84.16 (d, J = 165 Hz), 125.96 (d, J = 158 Hz), 127.68 (d, J = 159 Hz), 129.96 (d, J = 158 Hz), 138.00 (s), 157.80 (s).-

   MS (70 eV): m/e = 185 (59%, M^+), 156 (58%), 155 (43%), 129 (23%), 128 (23%), 82 (28%), 77 (90%), 66 (100%), 53 (41%), 51 (55%).-

Adduct 13 was obtained in 96% yield, mp 95 - 96°C (needles from t-butyl methyl ether at 0°C).-
IR (KBr): 3280, 3240, 3000, 2960, 2940, 1580, 1560, 1490, 1450, 1300, 1250, 1220, 1210, 1090, 1070, 1020, 980, 970, 910, 890, 830, 770, 760, 700, 690, 650, 630 cm^{-1}.-
UV (95% EtOH): λ_{max} (log ε) = 330 (2.5), 257 sh (4.1), 220 nm (end absorption).
^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 0.89 (pseudo dt, 1H, J = 6.5, 5.5, 5.5 Hz), 0.96 (pseudo dt, 1H, J = 5.5, 1.5, 1.5 Hz), 1.00 (dddd, 1H, J = 6.5, 5.5, 3.0, 1.5 Hz), 1.99 (pseudo tt, 1H, J = 5.5, 5.5, 1.5, 1.5 Hz), 2.80 (dd, 1H, J = 3.0, 1.5 Hz), 5.20 (pseudo t, 1H, J = 3.0, 3.0 Hz), 7.02 - 7.48 (m, 10 H).-
^{13}C-NMR ($CDCl_3$, 100.61 MHz): δ = 15.48 (t), 16.69 (d), 19.55 (d), 45.93 (d), 94.70 (d), 100.37 (s), 127.21 (d), 127.66 (d), 127.98 (d), 128.25 (d), 128.47 (d), 128.57 (d), 141.85 (s), 142.66 (s).-
MS (70 eV): m/e = 260 (0.1%, M^+), 232 (37%), 231 (31%), 217 (55%), 216 (37%), 215 (44%), 205 (28%), 204 (36%), 203 (38%), 202 (45%), 191 (83%), 189 (26%), 167 (73%), 165 (75%), 155 (43%), 154 (38%), 153 (44%), 152 (37%), 141 (59%), 128 (53%), 115 (39%), 101 (24%), 91 (100%), 77 (37%), 51 (27%), 28 (26%).-

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8. For example, even meticulously purified PTAD is known to contain radical impurities (cf. Hall, J. H.; Bigard, W. E.; Fargher, J. M.; Jones, M. L. J. Org. Chem. 1982, 47, 1982), which might catalize electron transfer reactions.

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