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# PHOTOCYCLOADDITION OF THE *cis*- AND *trans*-2-BUTENES TO DIMETHYL ACETYLENEDICARBOXYLATE[1]

S. Majeti, V. A. Majeti, and C. S. Foote
Contribution No. 3329 from the
Department of Chemistry, University of California,
Los Angeles, California 90024, U.S.A.

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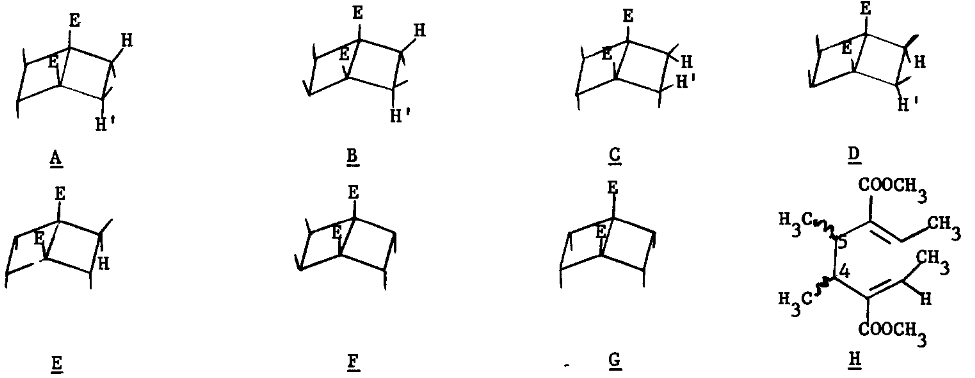
The photocycloaddition of dimethyl acetylenedicarboxylate (DMAD) to carbon-carbon multiple bonds to give cyclobutene derivatives has been of considerable interest, and its reactions with aromatic molecules have been successfully used for the synthesis of cyclooctatetraene derivatives[2]. However, in many of the known cases the ester assumes its role as the ground state partner. In an attempt to understand the behavior of acetylenic esters as excited species, we studied the reactions of DMAD in *cis*- and *trans*-2-butenes, and now report the formation and stereochemistry of bicyclo[2.2.0]hexanes in this reaction.

Dilute solutions of DMAD in *cis*- and *trans*-2-butenes were irradiated for 24 hours at -78°C using a 100 W medium pressure Hg lamp through quartz. The residue after evaporation contained unreacted DMAD and five major products which were separated by gas chromatography and characterized by their spectroscopic and analytical data.

Chart I shows the seven possible *cis*-fused 1,2-cyclodiadducts of the 2-butenes to DMAD. Of these seven isomers, only four (A-D) could be isolated from either olefin in significant quantities. In addition to the four cyclic products, an acyclic 2,6-octadiene (H) was isolated. The five products accounted for about 50% of the total residue, several minor components were present which could not be isolated in sufficient quantities for characterization.

Mass spectral and elemental analyses revealed all the products to be composed of one molecule of the ester and two molecules of the olefin, corresponding to the molecular formula $C_{14}H_{22}O_4$. All four of the bicyclic products showed a strong band at 1725cm$^{-1}$ in their ir spectra indicating the presence of an ester carbonyl. Their nmr spectra contained no absorptions due to olefinic protons. Compound H had conjugated ester bands at 1720 and 1630cm$^{-1}$ in its ir spectrum. Stereochemical assignment of the five products was based primarily on their symmetry properties, as deduced from their 220 MHz nmr[3] spectral data (Table 1)

Chart I



E = COOCH$_3$

It is inferred from the nmr data that product A is the all-trans isomer as the signals due to four methyl groups appear as two sets of doublets and the ester methyl signal appears as a singlet. The methine proton region is composed of two multiplets and the trans $J_{H-H'}$ coupling constant is calculated to be 9.6 Hz. Product B is designated as the cis,cis,trans isomer, as the four methyl groups appear as four distinct doublets and the ester methyls as two singlets. The multiplet at 2.97 δ is resolved as a quintet under high resolution with $J_{H-H'}$ = 7.5 Hz whereas the other two multiplets are too complex to resolve. Both structures B and E can accomodate the observed data, however, structure B is preferred since steric crowding in E which possesses three endo methyl groups makes it a less likely candidate. Furthermore, the appearance of a single methine proton at such lowfield (2.97 δ) can be better explained with structure B, the downfield shift may be due to long-range deshielding by the carbonyl of the ester. Similar downfield shifts are well known in other cases.[4] Product C is characterized as the trans,cis,trans isomer since the four methyl groups form two sets of doublets, and since the two ester methyls are nonequivalent. Only isomer C can explain the above spectral data. The last bicyclic product is identified as the all-cis isomer since the four secondary methyls and the two ester methyls appear as a 12-proton doublet and as a 6-proton singlet, respectively. Structure D is preferred over structure G, the all endo isomer, for steric reasons. An interesting feature in the spectrum of D is the virtual coupling of 7.9 Hz observed between H and H' (observed as extra lines in the methyl groups). Such coupling has previously been observed in several disubstituted butanes, and is due to the fact that H and H' are differently coupled

Table 1 NMR Data for Isomeric Bicyclo[2.2.0]hexane Derivatives

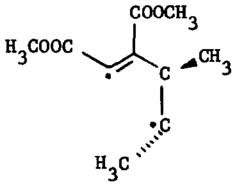
| Compound | $-CH_3$ | $>CH$ | | $-COOCH_3$ |
|---|---|---|---|---|
| A | two doublets<br>.95 δ, 6H<br>1.01 δ, 6H<br>$J_{H,CH_3}$ = 7 Hz | two multiplets<br>2.26 δ, 2H<br>2.50 δ; 2H<br>$J_{H,H'}$ = 9.6 Hz | | one singlet<br>3.62 δ, 6H |
| B | four doublets<br>0.90-1.15 δ, 12H<br>$J_{H,CH_3}$ = 7 Hz | three multiplets<br>2.14 δ, 1H<br>2.38 δ, 2H<br>2.97 δ, 1H<br>$J_{H,H'}$ = 7.5 Hz | | two singlets<br>3.59 δ; 3H<br>3.62 δ, 3H |
| C | two doublets<br>1.07 δ, 6H<br>1.27 δ, 6H<br>$J_{H,CH_3}$ = 7 Hz | two multiplets<br>2.4 δ, 2H<br>2.75 δ, 2H<br>$J_{H,H'}$ = 7.5 Hz | | two singlets<br>3.61 δ, 3H<br>3.59 δ, 3H |
| D | one doublet<br>0.99 δ, 12H<br>$J_{H,CH_3}$ = 7.0 Hz | one multiplet<br>2.65 δ; 4H<br>$J_{H,H'}$ = 7.9 Hz | | one singlet<br>3.61 δ, 6H |
| H | 1.15 δ, 6H, m<br>1.65-1.80 δ, 6H, two d<br>$J_{H,CH_3}$ = 7 Hz | 2.85 δ, 2H, m<br>5.7 δ, 1H, q<br>6.6 δ, 1H, q | olefinic protons | two singlets<br>3.59 δ, 3H<br>3.60 δ, 3H |

to either methyl group.[5] The nmr data of the open chain product H agree well with the assigned structure although the stereochemistry of the 4- and 5-methyl groups is not clear. The formation of bicyclo[2.2.0]hexanes requires the intermediacy of a cyclobutene derivative[6]. This monoadduct could not be detected even in the early stages of the reaction. This suggests that the second addition to the intermediate is faster than the addition to DMAD. The cyclobutene would be expected to absorb light far more strongly than DMAD. The fact that both the cis and trans olefins gave rise to the same isomeric products (see Table II for relative yields) strongly suggests equilibrium of intermediates. Possible equilibration of the olefin prior to addition to DMAD was ruled out as the analysis of the butenes after photolyses showed only 2% isomerization. Thus, it is proposed that the reaction is initiated by the triplet excited state of the ester, and after the formation of the stereoisomeric biradicals (i) and (ii), it is likely that equilibrium is partially established prior to spin inversion and ring closure. The 1,5-diene H appears to be a thermal ring-opened product of one of the isomeric bicyclic products[7], presumably one of the missing ones, perhaps the highly strained E or G.

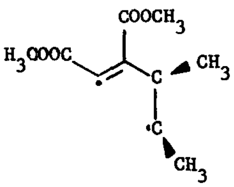
## Table II

| Product | % From trans-2-Butene | % From cis-2-Butene | Retention Time (cm)* |
|---|---|---|---|
| A | 54.5 | 23 | 25.7 |
| B | 18.3 | 39 | 38.0 |
| C | 3.7 | 12 | 38.7 |
| D | 8.0 | 9 | 59.0 |
| H | 10.0 | 13 | 49.0 |

* 6 x 1/4" aluminum column packed with 10% Carbowax 20M on 60 80 mesh chromosorb W. Temp. 135, He flow. 46 ml/min.



(i)



(ii)

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## References

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