

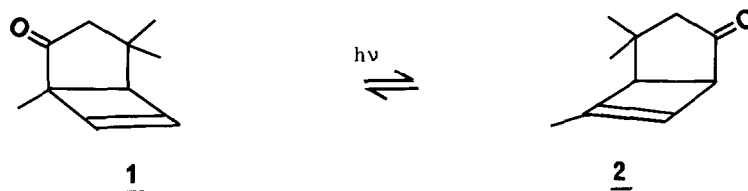
USE OF CMR SPECTROSCOPY AND PHOTOCHEMICAL TRANSFORMATIONS IN
STRUCTURE ASSIGNMENTS TO BICYCLO [3.2.0] HEPT-6-EN-2-ONES¹

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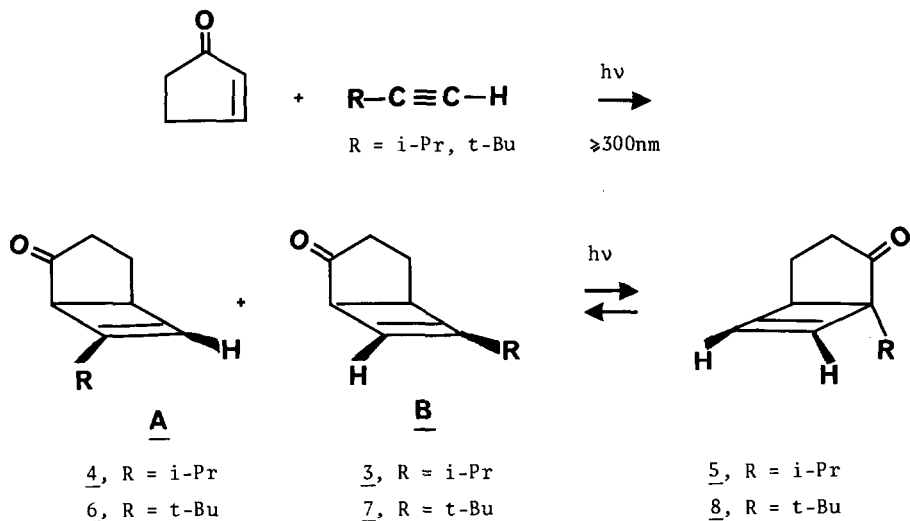
Abstract: Isomeric bicyclo [3.2.0] hept-6-en-2-ones, differing in the position of substituents at C_β and C_γ, can be distinguished by their photochemical behavior and by CMR spectroscopy.

The photochemistry of β,γ-unsaturated ketones is dominated by [1,2]- and [1,3]-sigmatropic acyl shifts, as documented in several recent reviews.² The first reported example of the latter process was the conversion of (1) to (2).³ An interest in determining the effect of substituents on

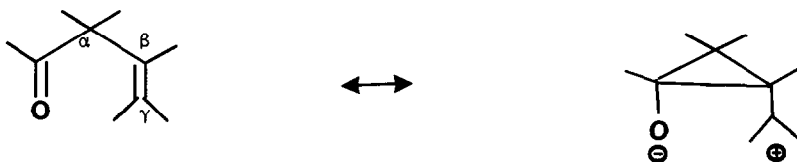


the quantitative aspects of these reactions (i.e., quantum yields and rate constants) prompted us to prepare several other bicyclo [3.2.0] hept-6-en-2-ones by the well known photocycloaddition of acetylenes to cyclopentenone. Structure assignments to the isomeric adducts derived from unsymmetrical acetylenes turned out not to be completely straightforward, and is the subject of this note.

Thus, cycloaddition of 3-methyl-1-butyne to cyclopentenone afforded isomeric adducts A and B which were isolated by preparative glpc (1/4" x 6 ft. column of 10% carbowax 20 M on chromasorb P). Although the products could be positively identified as the desired adducts from their spectral properties, it was difficult to decide which was which. The only distinguishing feature in the PMR spectra of A and B was the signal for the olefinic proton, which appeared at δ 5.95 for A and 5.75 for B. Inductive electron withdrawal by the carbonyl group should deshield a proton at the β-carbon relative to that at C_γ, while homoallylic interactions as shown below, analogous to electronic interactions in conjugated carbonyl compounds, should result in selective



deshielding of the protons on the α -carbon. Thus, no definitive structural assignments could be made based on these PMR data.



Irradiation of isomer A in hexane at wavelengths above 300 nm did not result in formation of any new products, as revealed by glpc or PMR analysis. On the other hand, irradiation of isomer B under the same conditions gave a single isomeric product which could readily be identified as (5) from its PMR spectrum, which showed two olefinic proton doublets at δ 6.4 and 6.1 with $J = 3$ Hz. On the assumption that (5) is the result of a [1,3]-acyl shift, by analogy with the photochemical behavior of (1) and many other β, γ -enones,^{2,3} structure (3) can be assigned to B and structure (4) is then assigned to A. The lack of reactivity of A (4) on exposure to UV light is then readily rationalized, since the [1,3]-acyl shift in this case represents an enantiomerization process, which of course would not be detected using GLPC and spectral analysis.

In order to confirm these results, compounds (6) and (7) were prepared by photoaddition of tert-butylacetylene to cyclopentenone. Once again, one of these compounds was "unreactive" on exposure to UV light while the other was readily converted to a photoisomer (8). The unreactive isomer (6) again had an olefinic proton at δ 5.95 in its PMR spectrum, while the reactive isomer (7)

had a corresponding signal at 5.75 ppm. Thus, it appears that in these ketones the olefinic proton which experiences greater deshielding is attached to the γ -carbon, suggesting that the homoallylic electronic interactions shown above dominate over inductive effects. Since such interactions ought to have more pronounced effects in CMR than in PMR spectra, CMR spectral analysis of these compounds was undertaken in the hope that CMR might be more useful in spectral differentiation of isomers in these systems.

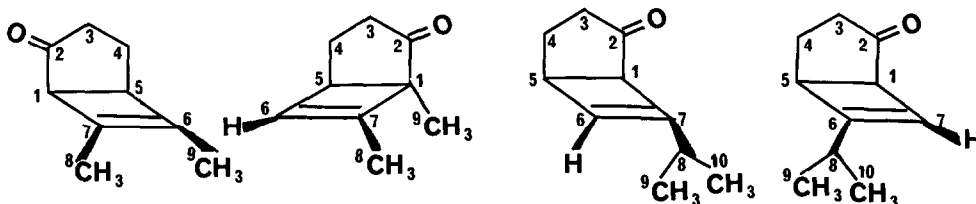
The strategy used was to choose a standard enone where the chemical shifts could be assigned to each carbon unambiguously, and then to assign shifts to carbons in the isomeric pairs of enones by analogy. Enone (9) was chosen as the standard, since its structure had been established in the literature⁴ and it had the requisite substitution to differentiate various positions in the molecule. The complete CMR spectrum of 9 is given in Table I. The two olefinic carbons at δ 149.70 and 130.66 ppm (all shifts relative to TMS) could be readily distinguished in SFORD spectra where the former appears as a singlet and the latter as a doublet, assigned therefore to C_7 and C_6 , respectively.^{5,6} Similarly, C_1 and C_5 appear as singlets and doublets, respectively, in SFORD spectra. The two methylene carbons (triplets in the SFORD spectrum) at 34.73 and 20.88 ppm are assigned to C_3 and C_4 , respectively, assuming normal electronic deshielding by the carbonyl group. Similarly, the methyl group attached to C_7 was assigned a downfield shift based on its position in the corresponding PMR spectrum.

In CMR spectra of the pair of isomers (3) and (4), the unsubstituted olefinic carbon appeared at 129.74 in isomer A and 123.79 in isomer B. In the spectrum of the standard enone (9), the unsubstituted olefinic carbon at the γ -position to the carbonyl has a shift of 130.66 ppm. Therefore, structure 4 can be assigned to that isomer (A) with the resonance at 129.74. The other carbon shifts were assigned using SFORD spectra and by analogy with the assignments for (9). Similar considerations permit the assignments for enone (3) given in Table I, as well as for (10), the precursor to (9).⁴ Unfortunately, sufficiently pure samples of the other enones discussed above were not available for CMR spectral analysis.

Both the PMR and CMR spectra indicate that homoconjunctive interactions are important in the ground states of bicyclo [3.2.0] hept-6-en-2-ones, leading to selective decrease in electron density at the γ -carbons.

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TABLE 1
CMR CHEMICAL SHIFTS OF CARBON ATOMS IN SUBSTITUTED
BICYCLO [3.2.0]-HEPT-6-EN-2-ONES (ppm relative to TMS = 0)



	(10)	(9)	(4)	(3)
C ₁	53.72	58.41	53.47	49.45
C ₂	not seen	216.52	214.42	215.08
C ₃	34.08	34.73	34.12	33.70
C ₄	20.36	20.88	22.62	18.78
C ₅	42.59	47.40	39.21	43.12
C ₆	141.45	130.66	129.74	160.17
C ₇	135.51	148.70	153.94	123.79
C ₈	15.15	12.64	28.98	28.42
C ₉	11.80	12.25	19.84	20.49
C ₁₀	-	-	19.13	19.99

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