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PROTON MAGNETIC RESONANCE ASSIGNMENTS IN DICHLOROKETENE-OLEFIN ADDUCTS BY LANTHANIDE-INDUCED SHIFTS[1]

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Since the discovery[2] that dichloroketene adds readily in situ to reactive olefins to yield α,α-dichlorocyclobutanones, the reaction has found use in a large number of synthetic and mechanistic studies[3]. In spite of these developments, no method for determining the regiochemistry[4] of the adducts directly, without resort to chemical degradation, has been available. Although tentative assignments have been made to the nmr resonances of the two methine protons on the cyclobutanone ring in a number of these systems, these assignments do not, in general, rest on a firm basis in experiment.

In the course of our investigations with dichloroketene, we have synthesized several of its adducts[5] with olefins in which the nmr absorptions of the aforementioned protons may be assigned unequivocably from analysis of coupling constants or from knowledge of regiochemistry gained by chemical methods. We now find that shifts in the nmr resonances of these protons induced by $Eu(fod)_3$, tris (1,1,1,-2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionato)europium (III),[6] are most useful in structure assignment, obviating chemical transformations.

It is now well established[7] that the magnitudes of the paramagnetic shifts induced by lanthanide complexes in the pmr spectra of molecules containing polar functional groups (X) arise from pseudo-contact interactions and thus depend upon the distance (r) of a proton from the metal atom and the internuclear angle (θ=<X-Eu-proton) according to the relationship $\Delta Eu \propto (3\cos^2\theta - 1)r^{-3}$. In a study[8] of

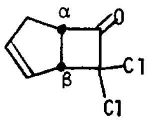
endrin, dieldrin, and photodieldrin, compounds containing only epoxide and chlorine functional groups, Eu(thd)$_3$ was found to complex only with the epoxide oxygen atoms. One would, therefore, expect that, in the case of α,α-dichlorocyclobutanones, the shift reagent would complex through the lone pairs of electrons on the carbonyl oxygen. That this indeed occurs, may be deduced from the data in the accompanying table. Using this method we have assigned the structure of ketone 5 to one of the products resulting from cycloaddition of dichloroketene to 3,3-dimethylcyclopentene.

For every compound examined, the proton α to the carbonyl is shifted farther downfield than the β-proton and Δα/Δβ ranges from 1.5 to 1.9.[9] Although in some cases the shifts are relatively small, they are reproducible and accurate to within ±1 Hz.

Table. Downfield Shifts (ΔEu)^c Induced by Eu(fod)$_3$^{a} in CCl_4

Compound^b	α-H		β-H		Δα/Δβ
	τ(CCl_4)^d	ΔEu(Hz)	τ(CCl_4)^d	ΔEu(Hz)	
1	5.75 (m)	23	5.98 (m)	12	1.9
2	6.33 (d)	12	5.80 (ddd)	8	1.5
3	6.37 (d of m)	9	6.68 (m)	5	1.8
4	6.07 (m)	24	7.08 (ddd)	14	1.7
5	6.45 (d)	21	6.66 (m)	13	1.6
6	6.10 (m)	31	7.05 (d)	18	1.7
7	6.12 (m)	21	7.08 (m)	11	1.9

(a) *ca*. 0.3*M* (b) *ca*. 0.5*M* (c) ΔEu=τ in CCl_4-τ in CCl_4 after addition of Eu(fod)$_3$
(d) m=multiplet, d=doublet, ddd=doublet of doublet of doublets.



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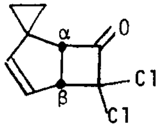

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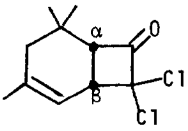

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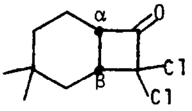

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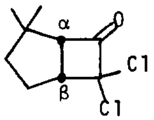

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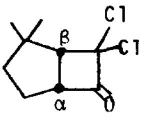

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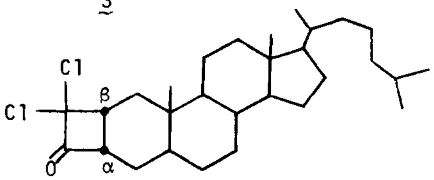

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It is important to note that assignment cannot be made by assuming that the α-proton will always appear downfield from the β-proton absorption. Thus, in compound 2, the α-proton resonance is *upfield*, presumably as a result of shielding by the cyclopropane ring. This method is rapid and should be applicable to assignment and structure determination of other ketene adducts.

Acknowledgement

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References

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3. For recent work and leading references in this area see:
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   (b) L.Ghosez, R. Montaigne, A. Roussel, H. Vanlierde and P. Mollet, *Tetrahedron*, *27*, 615 (1971).
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4. "Regio" is used to describe directional selectivity in bond formation or bond breaking: A. Hassner, *J. Org. Chem.*, *33*, 2684 (1968).

5. Adducts 2 and 4 were prepared in these laboratories by N. Sartoris and D.P.G. Hamon, respectively, while 7 was reported by V.R. Fletcher and A. Hassner, *Tetrahedron Letters*, 1071 (1970).
   The independent chemical structure proof for these molecules, as well as for 3 and 6 were straightforward, and will be published separately.

6. Obtained from Norell Chemical Co.; stored over P_2O_5.

7. J. Briggs, F.A. Hart and G.P. Moss, Chem. Comm., 1506 (1970), for example.

8. L.H. Keith, *Tetrahedron Letters*, 3 (1971).

9. Assuming a geometry for complexation in which the average position of the europium atom lies on the line formed by extending the C=O bond, and a Eu-O distance of 2.5-3.5 Å, Δα/Δβ was calculated from model parameters to be in the range 1.6 to 1.8. The observed ratios are in good agreement with this.