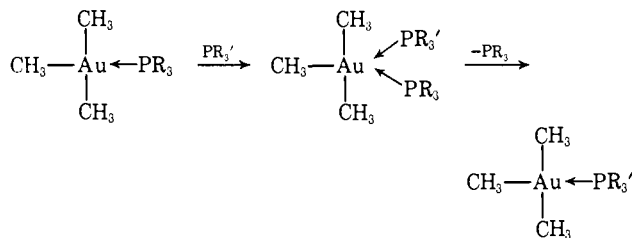


Thus, compound **2** may be converted into the corresponding triethylphosphine complex simply by mixing it with excess $(C_2H_5)_3P$. After 1 day at 50° , $(CH_3)_3AuP(C_2H_5)_3$ is obtained in 80% yield. The most likely mechanism^{8,9} for this reaction is again an associative process, now involving a *pentacoordinate* intermediate with gold in a dsp^3 state.



The difference in reaction rates for compounds **1** and **2** is probably due to the variation in the Au-P bond energies. It is also significant that $|J(^1H C^{31}P)|$ appears to be greater for compound **2** than for compound **1**, confirming a stronger Au-P interaction in the former. Finally, in ir spectra reported by Coates, *et al.*,⁶ the Au-P stretching frequencies show a higher value for Au^{III} than for Au^I compounds. According to molecular models, steric factors are not likely to play a decisive role.

(8) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965, p 18.

(9) C. D. Falk and J. Halpern, *J. Amer. Chem. Soc.*, **87**, 3003 (1965); F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, N. Y., 1968, p 357 ff.

(10) Visiting scholar supported by UBE Industries Ltd., Tokyo, Japan.

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Stereoselectivity in the Photochemical Rearrangement of 3,4-Dimethyl-4-trichloromethyl-2,5-cyclohexadienone^{1,2}

Sir:

It was reported some years ago that the photochemical rearrangement of 4-methyl-4-trichloromethyl-2,5-cyclohexadienone (**1a**) in a variety of solvents gave only one of the two possible stereoisomeric lumiketones **IIa**.³ In the absence of the second diastereomer, no definite assignment of stereochemistry to the product was possible, although structure **IVa** was preferred on the basis of spectral data.³ The presence of the larger substituent in the *endo* orientation as in **IVa** would be consistent with observations made in several other dienone-lumiketone photorearrangements,^{4,5} for which a rationalization has been provided by Rodgers and Hart.⁵

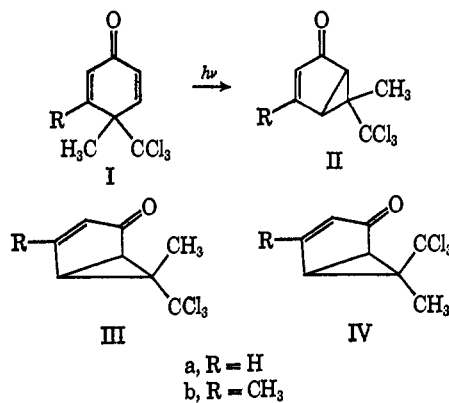
(1) Part XXIX of a series on the photochemistry of unsaturated ketones in solution. Part XXVIII: D. I. Schuster and B. M. Resnick, *J. Amer. Chem. Soc.*, **92**, 7502 (1970).

(2) This research was supported at New York University by the National Science Foundation under Grants GP-7433 and GP-10828.

(3) D. I. Schuster and D. J. Patel, *J. Amer. Chem. Soc.*, **88**, 1825 (1966); D. J. Patel and D. I. Schuster, *ibid.*, **90**, 5137 (1968).

(4) (a) T. Matsuura, *Bull. Chem. Soc. Jap.*, **37**, 564 (1964); (b) B. Miller and H. Margulies, *J. Amer. Chem. Soc.*, **89**, 1678 (1967); (c) B. Miller, *ibid.*, **89**, 1690 (1967); (d) K. Ogura and T. Matsuura, *Bull. Chem. Soc. Jap.*, **43**, 2891 (1970).

(5) T. R. Rodgers and H. Hart, *Tetrahedron Lett.*, 4845 (1969).



The photochemistry of the methyl homolog of **1a**, cyclohexadienone **1b**, has now been studied, and it is found that both stereoisomeric lumiketones **IIIb** and **IVb** are formed. The stereochemistry of these bicyclic ketones has been unequivocally established on the basis of spectral data, and ultimately X-ray crystallographic analysis of one of the isomers. Photolysis of **1b** at 2537 \AA in *tert*-butyl alcohol, followed by chromatography on silica gel, led to isolation of **IIIb**, mp $69-71^\circ$, and **IVb**, mp $91-93^\circ$. Analysis of the crude photolysate by glpc indicated they are formed initially in the ratio of 15:1, respectively. The isomers have similar mass spectra, except for the relative intensity of some peaks and the absence of a molecular ion at m/e 238 in the case of **IIIb**;⁶ in both cases the base peak was at m/e 203 ($M - Cl$). Their ir spectra are similar, featuring a carbonyl band at 1710 cm^{-1} in both cases. Whereas **IIIb** showed uv absorption (EtOH) at 257 ($\log \epsilon$ 3.57) and 208 nm ($\log \epsilon$ 3.79), that for **IVb** was slightly shifted to 266 ($\log \epsilon$ 3.56) and 212 nm ($\log \epsilon$ 3.79). From their nmr spectra a stereochemical assignment is possible. Whereas both isomers show resonances for the vinyl proton at δ 5.64 ppm (broad multiplet) and a vinyl methyl at δ 2.14 ppm (d), the other methyl group is shielded in **IIIb** (δ 1.54) compared with **IVb** (δ 1.62),⁷ while the cyclopropyl-H resonances are correspondingly deshielded (δ 2.74, m) in **IIIb** compared with **IVb** (δ 2.42, m). In addition, the *endo*-methyl resonance in **IIIb** is broadened compared with **IVb**, consistent with long-range coupling with the cyclopropane protons according to the familiar W plan.⁸

No interconversion of the lumiketones **IIIb** and **IVb** is observed on heating or irradiation of either stereoisomer.⁹ Such treatment leads, as in the parent case,³ to other compounds whose structures are currently being elucidated.

The configuration of **IIIb** has been established absolutely by X-ray crystallographic analysis. The compound crystallized in the monoclinic space group

(6) The elemental composition of **IIIb** is based on a satisfactory elemental analysis as well as the mass spectral fragmentation.

(7) Shielding of *endo*-relative to *exo*-6-methyl groups in bicyclo[3.1.0]-hexenones has been suggested earlier^{4,5} and used to assign stereochemistry. See also D. W. Swatton and H. Hart, *J. Amer. Chem. Soc.*, **89**, 5075 (1967).

(8) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, New York, N. Y., 1969, p 334 ff.

(9) In other investigations,¹⁰ interconversion of epimeric lumiketones was also not observed. This appears to be a general observation in these systems.

(10) (a) H. E. Zimmerman and J. O. Grunewald, *J. Amer. Chem. Soc.*, **89**, 5163 (1967); (b) D. I. Schuster and W. V. Curran, *J. Org. Chem.*, **35**, 4192 (1970).

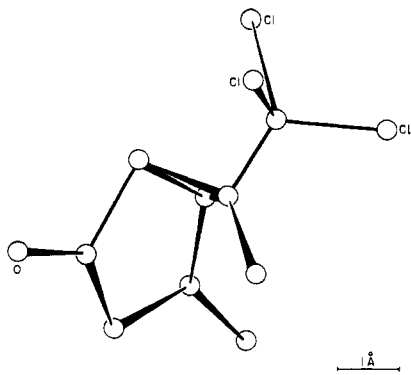
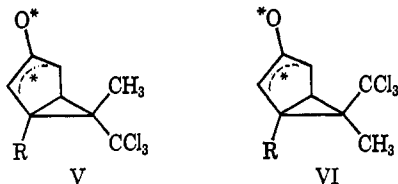


Figure 1. Crystal structure of 4-methyl-endo-6-methyl-exo-6-trichloromethylbicyclo[3.1.0]hex-3-en-2-one. The view is down the C^* axis perpendicular to the xy plane.

$P2_1/c$ with cell dimensions $a = 13.11$, $b = 8.00$, $c = 11.90$ Å, $\beta = 115.9^\circ$. Figure 1 is drawn from the final parameters obtained for the structure when the agreement factor, R , has been reduced to 0.14. Full details of the solution will be reported separately elsewhere. This absolute structure determination provides a firm foundation for the spectroscopic analyses given above and in related investigations.^{4,5,7,10b}

The factors influencing the stereochemistry of the dienone-lumiketone photorearrangement have been discussed in detail elsewhere.^{5,10b,11} Briefly, this is the result of the stereoselectivity associated with (1) electrocyclic ring closure to a 3,5-bonded intermediate V or VI, and (2) the stereochemistry of the final [1,4]-sigmatropic shift.^{11a-c} If step 2 occurs with inversion



of configuration, by analogy with established ground-state reactions,¹¹⁻¹⁴ then the selective formation of IIIb must be due to preferential formation of intermediate Vb as opposed to VIb. This is contrary to the prediction⁵ based only on the steric size of the substituents at C-4, but is consistent with repulsion of the C-O and C-CCl₃ dipoles in the ring closure leading to VI.

(11) (a) H. E. Zimmerman and D. S. Crumrine, *J. Amer. Chem. Soc.*, **90**, 5612 (1968); (b) H. E. Zimmerman, D. S. Crumrine, D. Döpp, and P. S. Huyffer, *ibid.*, **91**, 434 (1969); (c) H. E. Zimmerman, *Angew. Chem., Int. Ed. Engl.*, **8**, 1 (1969); (d) R. B. Woodward and R. Hoffmann, *ibid.*, **8**, 781 (1969).

(12) T. M. Brennan and R. K. Hill, *J. Amer. Chem. Soc.*, **90**, 5614 (1968); R. F. Childs and S. Winstein, *ibid.*, **90**, 7146 (1968); H. Hart, T. R. Rodgers, and J. Griffiths, *ibid.*, **91**, 754 (1969).

(13) This assumes that deactivation from the electronic excited state precedes rearrangement, which has not been unequivocally established [see D. I. Schuster and D. J. Patel, *ibid.*, **90**, 5145 (1968), and ref 10b]. The stereochemistry of the final sigmatropic rearrangement can be established experimentally by study of a chiral cyclohexadienone, which is in progress in these laboratories.

(14) In ref 4d, it is claimed that a dienone-lumiketone phototransformation has been observed in which the final [1,4]sigmatropic rearrangement occurs with retention of configuration, *i.e.*, by a pivotal motion involving exo-endo interconversion of substituents on proceeding from the 3,5-bonded intermediate to the product. However, the assignment of configuration to the intermediate in this case is dubious,^{4d} since it ignores precisely those stereochemical factors which were pointed out by Rodgers and Hart.⁵

In the light of these observations and the near identity of the chemical shift of the 6-methyl (δ 1.55) for the lumiketone from dienone Ia and the 6-methyl in IIIb (δ 1.54), we now propose that structure IIIa be assigned to the lumiketone derived from dienone Ia, rather than IVa as tentatively suggested earlier.³ The effect of the added methyl group in Ib is to introduce some steric interference in the route to Vb,⁵ and to divert some of the reaction *via* VIb to IVb. Thus both steric and electronic effects must be considered in rationalizing and predicting the course of these photochemical rearrangements.

(15) Alfred P. Sloan Research Fellow, 1967-1969.

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Segmental Motion in Liquid 1-Decanol. Application of Natural-Abundance Carbon-13 Partially Relaxed Fourier Transform Nuclear Magnetic Resonance¹

Sir:

In a previous report² we showed that carbon-13 spin-lattice relaxation times (T_1), measured by means of partially relaxed Fourier transform (PRFT) nmr,²⁻⁴ could be used to monitor segmental motion of biopolymers in solution. Such measurements on smaller molecules also yield detailed information about relative rotational mobility in carbon chains. In general, the ¹³C spin-lattice relaxation of a protonated carbon is overwhelmingly dominated by dipole-dipole interactions with the attached protons,⁵ and T_1 is given by⁶

$$1/T_1 = N\hbar^2\gamma_C^2\gamma_H^2r_{CH}^{-6}\tau_C \quad (1)$$

where γ_C and γ_H are the gyromagnetic ratios of ¹³C and ¹H, N is the number of directly bonded hydrogens, r_{CH} is the C-H distance, and τ_C is the effective correlation time for rotational reorientation. Equation 1 applies in the "extreme narrowing" limit, when $1/\tau_C$ is much greater than the resonance frequencies of the ¹³C and ¹H nuclei, and is thus usable for small molecules in liquids of low viscosity.

Individual carbon-13 T_1 values in liquid 1-decanol were determined from the peak intensities in partially relaxed frequency-domain spectra obtained by Fourier transformation of accumulated time-domain signals following 180°- τ -90° pulse sequences.^{3,7} Details have

(1) Carbon-13 Fourier Transform Nuclear Magnetic Resonance. IV. For part III see ref 2.

(2) A. Allerhand, D. Doddrell, V. Glushko, D. W. Cochran, E. Wenkert, P. J. Lawson, and F. R. N. Gurd, *J. Amer. Chem. Soc.*, **93**, 544 (1971).

(3) R. L. Vold, J. S. Waugh, M. P. Klein, and D. E. Phelps, *J. Chem. Phys.*, **48**, 3831 (1968).

(4) R. Freeman and H. D. W. Hill, *ibid.*, **53**, 4103 (1970).

(5) K. F. Kuhlmann, D. M. Grant, and R. K. Harris, *ibid.*, **52**, 3439 (1970).

(6) H. G. Hertz, *Progr. Nucl. Magn. Resonance Spectrosc.*, **3**, 159 (1967).

(7) A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, London, 1961, p 64.