Tetrahedron Letters No.18, pp. 1377-1380, 1971. Pergamon Press. Printed in Great Britain.

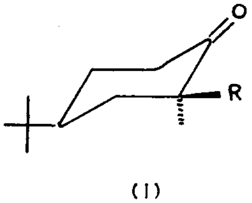
THE USE OF FLUORESCENCE SPECTRA AS A PROBE TO MOLECULAR STRUCTURE.[1] A CORRECTION OF THE STRUCTURAL ASSIGNMENTS OF THE cis AND trans 2-ALKYL-2-METHYL-4-t-BUTYLCYCLOHEXANONES.

K. Dawes and N.J. Turro
Department of Chemistry, Columbia University, New York, N.Y. 10027

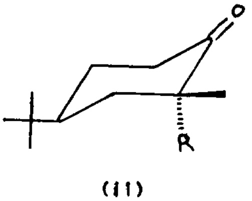
J.M. Conia
Laboratoire des Carbocycles, Universite de Paris-Sud, 91-Orsay

(**Received in USA 22 March 1971; received in UK for publication 30 March 1971**)

As part of a photochemical study we required some pairs of epimers of cis and trans 2-alkyl-2-methyl-4-t-butylcyclohexanones (I) and (II), and these were synthesized by the alkylation of 2-methyl-4-t-butylcyclohexanone or by the methylation of the corresponding 2-alkyl-4-t-butylcyclohexanone (2). It is known that such alkylations are not stereospecific and lead to a mixture of epimers (2) and that the main product has been reported to occur from equatorial, and not axial alkylation (3). The exact stereochemistry was based on the ozonolysis of eipmer pairs (e.g., the methallyl ketones (Ic, IIc) to acetonyl ketones (If, IIf) and the alkyl ketones (Ib, IIb) to the keto-acids (Ie, IIe), and then alkaline and acid cyclization of these derivatives to bicyclic enones and diones. However, the resulting stereochemical assignments were found to be in disagreement with NMR solvent effects on the C-2-methyl signals (3). It was suggested that a non-chair conformation existed for all these ketones. From the examination of the NMR spectra of cis and trans-2-methyl, 2,2-dimethyl, and 2-methyl-2-methyl-d_3-derivatives of 4-t-butylcyclohexanones, Caine (4) suggested that the original assignments should be reversed, and that the chemical evidence (3) was not unequivocal.



(I)



(II)

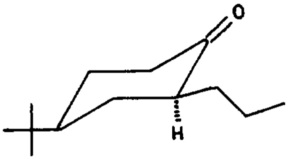
a R = CH_3
b $CH_2\text{-}CH\text{=}CH_2$
c $CH_2\text{-}C(CH_3)\text{=}CH_2$
d $CH_2\text{-}CH(CH_3)_2$
e $CH_2\text{-}COOH$
f $CH_2\text{-}CO\text{-}CH_3$

In fact, a preliminary study of the photochemistry of compounds (Ic) and (IIc) leads us to believe that the original assignments should be reversed, since on irradiation in benzene (Ic) was converted into (IIc) whereas (IIc) gave products not yet characterized but no conversion to

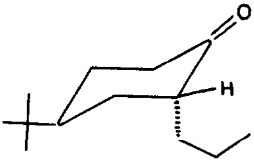
(Ic) was observed. The fluorescence spectra of (Ic) and (IIc) also gave unexpected results, since (Ic) fluoresced about three times more efficiently than (IIc). As a consequence of our earlier work, we predicted that deactivation of the S_1 state would occur more readily when the C=C group was accessibly positioned in the plane of the carbonyl, as with the fluorescence quenching of alkyl ketones with electron rich olefins (5).

We wish to report the use of fluorescence spectra as a probe to molecular structure, which leads to an unambiguous assignment of the structures of (Ic) and (IIc).

Work in these laboratories (6) with the two epimers of 2-n-propyl-4-t-butylcyclohexanones (III) and (IV) has shown that (IV) fluoresces much more strongly than (III), i.e., the singlet lifetime of the *cis* epimer is shorter than that of the *trans* epimer (IV) due to the more facile deactivation of the S_1 state of the cyclic ketone by intramolecular γ-hydrogen abstraction in the plane of the carbonyl. We have used this evidence to assign the structures of (Ic) and (IIc) by use of the hydrogenation products (Id) and (IId). Measurement of the fluorescence spectra showed that (Id) fluoresced about five times more efficiently than (IId), i.e., according to the original assignments, and this is the reverse of what would be expected on previous evidence. Therefore, *we suggest that the original assignments (2,3) should be reversed*, since the equatorial isobutyl group should lead to a shorter singlet lifetime. Table I summarizes our results, using the new assignments.

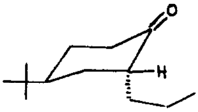
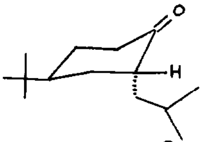
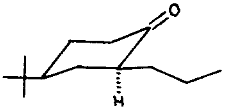
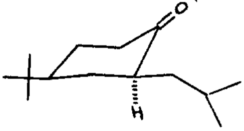


(III)



(IV)

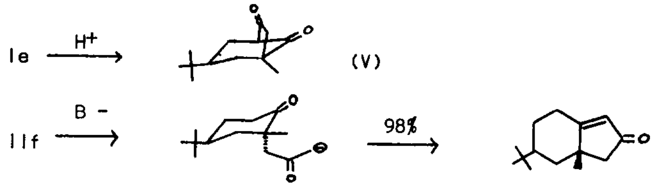
TABLE I[a]

	$\emptyset_f^{rel}$ [b]		$\emptyset_f^{rel}$
	1.00		1.00
	0.28		0.19

(a) 0.1M solution in spectrograde n-hexane, $\emptyset_f^{rel}$ based on the peak heights of emission at 405 nm., excitation at 313 nm. (b) From reference 6.

We feel that the use of comparative fluorescence spectra of two epimers will serve as a method of providing further evidence of the assignments for 2,2-dialkylcyclohexanones for the cases in which only one of the alkyl groups possesses a hydrogen atom γ to the carbonyl.

If the correction of the first structural assignments of all epimeric ketones III (3) is taken into account, it is clear that (4): (a) the signal of an axial C-2-methyl group resonates at lower field (δ 1.07 to 1.15 ppm) than that for an equitorial one (δ 0.99 to 0.98 ppm) in CCl_4, and they are respectively shielded and deshielded in C_6H_6; (b) all the C_6 rings assume the chair form; (c) in all cases the product from axial alkylation is predominant. Furthermore, it is now clear that the structures of the products from cyclization of the ketones (Ie), (IIe) and (If, (IIf) (3) should be reassigned. The keto-acid (Ie) undergoes cyclization in preference to (IIe), Ie giving the bicyclic dione (V) under acidic conditions. The acetonyl ketone (IIf) gives a higher yield (98%) of cyclization product under basic conditions than If (48%). This result is possibly due to easier axial attack of the anion from IIf to yield VI.



(V)

(VI)

We also studied the photochemistry of the ketones (Id) and (IId) in the hope that one could also prove the structures using the fact that there is a stereoelectronic requirement for the Type II photoelimination (6,7) and, therefore, only the compound with an equatorial isobutyl group would give rise to Type II elimination. The reactions were conducted in neat piperylene (to quench T_1 reaction). However, photoisomerization still occurred and the Type II product (2-methyl-4-t-butylcyclohexanone) was formed from both epimers. This is interesting, since it means that the α-cleavage of the cyclohexanone is coming from the S_1 state or a very short-lived T_1 excited state. Yang (8) has recently reported that he could only partially quench the photoisomerization of the cis and trans-9-methyl-1-decalones.

REFERENCES

1. Molecular Photochemistry XLIII. Paper XLII: J.C. Dalton and N.J. Turro, J. Am. Chem. Soc., in press. The authors at Columbia thank the Air Force Office of Scientific Research (Grant AFOSR-70-1848) for its generous support of this work. K.D. thanks the SRC for a NATO Postdoctoral Fellowship.
2. J.M. Conia and P. Briet, Bull Soc. Chim. Fr., 3881 (1966).
3. J.M. Conia and P. Briet, ibid., 3888 (1966).
4. B. Huff, F. Tuller and D. Caine, J. Org. Chem., **34**, 2070 (1969).
5. N.J. Turro, J.C. Dalton, G. Farrington, M. Niemczyk and D.M. Pond, J. Am. Chem. Soc., **92** 6978 (1970).
6. K. Dawes, J.C. Dalton and N.J. Turro, Mol. Photochem., in press.
7. N.J. Turro and D.S. Weiss, J. Am. Chem. Soc., **90**, 2185 (1968).
8. N.C. Yang and R.H.-K. Chen, Ibid., **93**, 530 (1971).