The Influence of Ground State Conformation on the Photochemical Ring-opening of 5-Alkylcyclohexa-1,3-dienes

By CHARLES W. SPANGLER* and RONALD P. HENNIS

(*The Michael Faraday Laboratories, Department of Chemistry, Northern Illinois University, DeKalb, Illinois* 60115)

Summary Photochemical electrocyclic ring-opening of 5-alkylcyclohexa-1,3-dienes may be interpreted in terms of ground-state conformational control of the direction of conrotatory motion.

SEVERAL recent investigations[1-3] have shown the influence of ground-state conformation factors upon the direction of both thermal and photochemical electrocyclic reactions. Although published examples do not allow for direct comparison, a general feature that seems to be consistent can be stated as follows: if two modes of ring-opening or ring-closing are possible, occurring in either a disrotatory or conrotatory manner, the stereoselectivity of the reaction can be explained or predicted from consideration of the ground-state conformer populations. We have investigated the photochemical ring-opening of a series of 5-alkylcyclohexa-1,3-dienes to test this postulate, and have found a remarkable degree of correlation between the stereoselectivity of the reaction and the size of the alkyl group. We interpret our results as a confirmation of the above postulate of ground-state conformational control.

5-Alkylcyclohexa-1,3-dienes (R = Me, Pr^i, Bu^t) were prepared according to a recent procedure which enables the dienes to be obtained free of any double bond isomers.[4] The dienes were irradiated at 253·7 nm in hexane solution (0·03M) at room temperature in a "merry-go-round"† apparatus. Aliquots were removed at various times and examined by g.l.p.c. under conditions which permitted the quantitative resolution and detection of the four possible geometric isomers of the various 1-alkylhexa-1,3,5-trienes formed as primary photoproducts see Table 1.

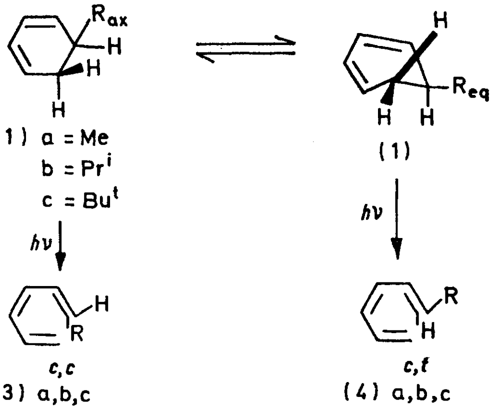
TABLE 1

Photoproducts from 5-*alkylcyclohexa*-1,3-*dienes*

Irradiation time[a] (min)	Sub-stituent	Relative yields (%) Diene	Trienes (**3**) 3*c*, 5*c*	(**5**) 3*t*, 5*c*	(**4**) 3*c*, 5*t*	(**6**) 3*t*, 5*t*
0	5-Me	99·0	—	—	—	—
3	,,	97·0	1·2	—	1·8	—
5	,,	94·9	1·7	trace	2·4	trace
8	,,	86·0	3·1	2·1	4·6	3·2
0	5-Pr^i	99·0	—	—	—	—
2	,,	98·4	0·1	—	0·5	—
3	,,	96·1	0·5	—	2·4	—
5	,,	95·3	0·7	trace	3·0	trace
0	5-Bu^t	99·0	—	—	—	—
3	,,	97·4	0·1	—	1·5	—
5	,,	95·8	0·2	—	3·0	2·3
10	,,	87·0	0·6	—	9·1	5·9

[a] Irradiations were carried out for 30 min in all of the above cases, and in all of the runs extensive photoinduced geometric isomerization was observed after 10 min.

These results clearly show a preference in ring-opening direction as we progress from methyl to t-butyl. This can be explained in terms of the populations of the ground-state conformations by considering the structure of substitued cyclohexa-1,3-dienes. Oberhammer and Bauer[5] have determined, by electron diffraction studies, that most, if not all, cyclohexa-1,3-diene rings must be non-planar as a result of a balance between minimization of bond angle strain, torsional strain, and nonbonded repulsions. This results in conformations which allow a 5-alkyl group to assume either a pseudoaxial or pseudoequatorial position. As a result, conrotatory ring opening of either conformer would generate a different triene geometric isomer.



(1) a = Me
b = Pr^i
c = Bu^t

(1)

c,c
(3) a,b,c

c,t
(4) a,b,c

The initial (**3**) : (**4**) product ratios represent the respective ground-state populations, which can be expressed as the ratio [(**1**)-R_{axial} : (**1**)-$R_{equatorial}$]. These product ratios, if we assume that thermal equilibrium is maintained during the course of reaction, can thus be utilized to calculate approximate isomerization energies for (**1**)-R_{axial} → (**1**)-$R_{equatorial}$, which are listed in Table 2. One potential source of error in the above arguments is the possibility of photochemically induced *cis–trans* isomerization of the product trienes. Table 1 shows that this eventually occurs. In order to establish that this does not contribute to the early stages of the reaction, a mixture of *c,t*-(**4a**) and *t,t*-(**3a**) was photolysed under conditions identical to those employed for the alkylcyclohexa-1,3-diene studies. These results are presented in Table 3.

TABLE 2

Triene product ratios and calculated cyclohexa-1,3-*diene conformational isomerization energies*

Substituent	Ratio ((**3**) : (**4**))[a]	ΔG^{0}_{300} (kcal mol^{-1})
Me	1·5	−0·24
Pr^i	5·0	−0·95
Bu^t	15·0	−2·98

[a] Maximum error in determining product ratio is ± 1%.

TABLE 3

Photoisomerization of Hepta-1,3,5-*triene*

Irradiation time (min)	% Trienes[a] (**3a**); 3*c*, 5*c*	(**4a**); 3*c*, 5*t*	(**5a**); 3*t*, 5*c*	(**6a**); 3*t*, 5*t*
0	—	14·2	—	85·8
30	—	16·0	trace	84·0
60	—	20·5	16·6	62·9
120	—	23·0	55·0	22·0

[a] No 5-methylcyclohexa-1,3-diene was detected.

As can readily be seen by comparing the results in Tables 1 and 3, photochemical triene–triene isomerization is slow compared to the rate of cyclohexadiene–triene conversion. Thus we feel that our initial product ratios (after 5 min) are true product distributions derived from different conformations of the various 5-alkylcyclohexa-1,3-dienes. We also believe that Baldwin's[1] original suggestion that orbital symmetry predicts the possible modes of reaction, but ground-state conformation populations determine which of the allowed modes predominate, is a valid and quite general principle.

(*Received, October 29th,* 1971; *Com.* 1877.)

---

† Rayonet Photochemical Reactor and Merry-go-round accessory, The Southern New England Ultraviolet Co., Middletown, Conn., U.S.A.

[1] J. E. Baldwin and S. M. Krueger, *J. Amer. Chem. Soc.*, 1969, **91**, 6444.

[2] G. A. Doorkian and H. H. Freedman, *J. Amer. Chem. Soc.*, 1968, **90**, 3582.

[3] G. A. Doorkian, H. H. Freedman, R. F. Bryan, and H. P. Weber, *J. Amer. Chem. Soc.*, 1970, **92**, 399.

[4] W. G. Dauben, M. E. Lorber, N. D. Vietmeyer, R. H. Shapiro, J. H. Duncan, and K. Tormer, *J. Amer. Chem. Soc.*, 1968, **90**, 4762.

[5] H. Oberhammer and S. H. Bauer, *J. Amer. Chem. Soc.*, 1969, **91**, 10.