단   신

Bicyclo[3, 2, 1]oct-2-en-7-one 에 있어서 광축퇴 자리옮김 반응의 반응속도론적 연구

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A Kinetic Study of the Photo-Degenerate Rearrangement in Bicyclo[3, 2, 1]oct-2-en-7-one

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Thermal degenerate rearrangement of bicyclo [3, 2, 1] oct-2-en-7-one was first studied by Berson, *et. al.*,[1] and singlet-triplet reactivity of the ketone was first investigated by Givens and his co-workers[2]. They reported that (−)-ketone under heating produced (+)-ketone and irradiation of (−)-ketone also gave the same result *via* 1, 3-acyl shift.

In this paper, the kinetics of the ketone racemization[3], especially, the relationship between the quantum efficiency and the first order rate constant will be discussed in detail.

The ketone chosen for study was synthesized and resolved by standard methods[2]. In order to determine the quantum efficiency[4] for the reaction (equation 1), the ketone was irradiated in ether at 300nm after degassing and the optical rotation of (−)-ketone was followed at 15 minute intervals. From the change of the optical rotation at 578nm, the concentration conversion of (−)-ketone to (+)-ketone was calculated.[5] The results are given in *Table* 1. From the results, the quantum yield of the photo-degenerate rearrangement is 0.406 (*Fig.* 1). This, of course, has to be assumed that each absorbed photon converted (−)-ketone to (+)-ketone, *i.e.*, a concerted mechanism. In a common method of quantum yield determination (*Fig.* 1), an accurate optical purity and concentration must be known before irradiation. Since these experimental procedures are time consuming, the first order reaction rate constant was determined and the relationship between the rate constant and quantum efficiency of the racemization was derived as following:
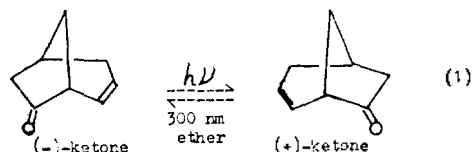
$$\Phi_{rac} = \frac{m \ mol \ (disapperared)}{milli \ Einstein \ (absorbed)} \times \frac{1}{2}$$
$$= \frac{[A_o] - [A_t]}{mE} \times \frac{1}{2}$$

see column (e) in *Table* 1 for multplying $\frac{1}{2}$.

Table 1. The change of optical purity, optical roation and concentration of (−)-Ketone (a)

Time(min.)	mE(b)	optical purity(%)	Optical rotation[α]	[A]$_o$ and[A]$_t$ (m mol)	disappearance of (−)-ketone(e) (mmol)
0	0	20.0	−54.1	0.1688^c	0.000(0.000)
15	0.193(0.035)	16.3	−44.1	0.1376^d	0.016(0.031)
30	0.386(0.064)	14.2	−38.5	0.1199	0.025(0.050)
45	0.580(0.089)	11.7	−31.7	0.0988	0.035(0.070)
61	0.786(0.110)	8.9	−24.0	0.0748	0.047(0.094)
76	0.980(0.126)	7.99	−21.6	0.0675	0.051(0.101)

(a) (−) ketone, 0.8442 mmol (optical purity, 20.0%; 0.1688 mmol of (−)-ketone was used for irradiattion.
(b) Corrected milli Einstein value for levorotatory isomer absorption only. (c) Initial concentration, [A]$_o$.
(d) Concentration at time, t. (e) Disapperarance of levorotatory isomer due to formation of racemic mixture.
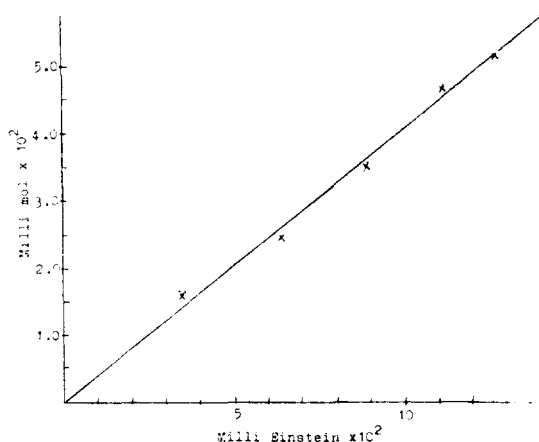
$$= \frac{1}{2mE} ([A_o] - [A_o]e^{-kt})$$

Fig. 1. Millimol racemized as a function of milli Einsteins for the reaction (quantum efficiency (Slope) is 0.406

where $[A_t] = [A_o]e^{-kt}$

$$= \frac{[A_o]}{2mE} (1 - e^{-kt})$$

$$= \frac{[A_o]}{2mE} [1 - (1 - kt + \cdots)]$$

$$\Phi_{rac} \approx \frac{[A_o]}{2mE} \cdot kt \cdot$$

(1) where [A$_o$], initial concentration, (0.8442 m mol), mE; total absorbed light(0.980)mE); t; irradiated time (76×60 sec.), k; 2.07x10^{-4} sec^{-1}

Since the photochemical racemization of (−)-ketone is a unimolecular first order reaction[1],

the rate equation is $\ln\frac{[\alpha_o]}{[\alpha_t]} = kt$.

where $[\alpha_o]$; initial optical rotation, $[\alpha_t]$; optical rotation at time t.

The linear regression of the solution for the rate equation gives k value as $2.07x10^{-4}$ sec^{-1} From the equation (1), quantum yield was calculated as 0.407 which well coincides with the value obtained by the common method for determination of quantum efficiency (*Fig.* 1).

REFERENCES

1. J. A. Berson and L. J. Gardiner, *J. Amer. Chem. Soc.*, **99**, 8509(1977).

2. (a) R. S. Givens and W. K. Chae, *J. Amer. Chem. Soc.*, **100**, 6278. (1978) (b) R. S. Givens and W. K. Chae, *J. Amer. Chem. Soc.*, **104**, 2456 (1982).

3. D. F. Smith, *J. Amer. Chem. Soc.*, **49**, 43 (1927).

4. Quantum yield determination was performed by the following general procedures. A solution of 103mg of the ketone in 10m*l* of ether was placed in a pyrex tube and degassed with purified nitrogen. Irradiation was carried ou with 15 RPR-3000A lamps. Light output was monitored by pot·assium ferrioxalate actinometry according to the method of Hatchard and Parker, *Proc. Roy. Soc., Ser.* A, **235**, 518 (1956).

5. The optical rotations were obtained at 15°C from a Perkin-Elmer 141 polarimeter.