

Preliminary Note

The photochemistry of 4,7-undecanedione: evidence of electronic energy migration

M. V. ENCINA and E. A. LISSI

Departamento de Química, Universidad Técnica del Estado, Santiago (Chile)

F. CASTAÑEDA and A. OLEA

Facultad de Ciencias Químicas, Universidad de Chile, Santiago (Chile)

(Received January 20, 1978)

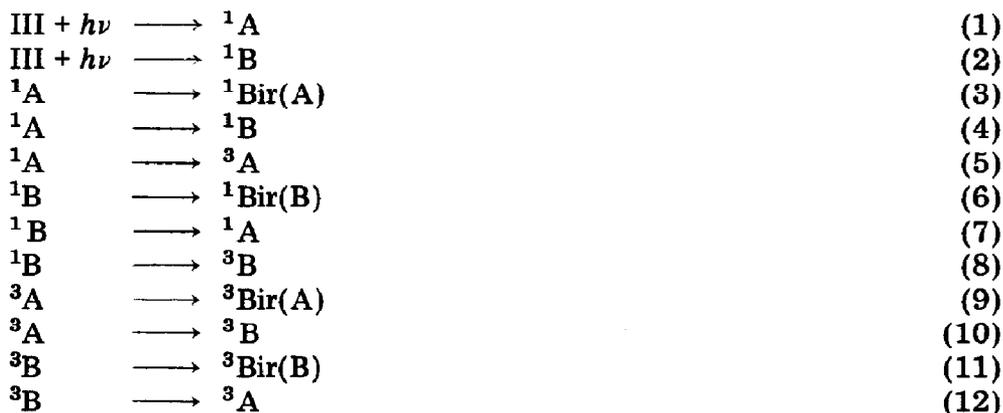
The rate of energy migration between similar chromophores is a matter of current interest. Electronic carbonyl excitation has been shown to migrate rapidly in exothermic intramolecular processes [1, 2], and there is experimental evidence that intramolecular migration takes place among carbonyl groups in polymers [3]. However, studies carried out in solution [4, 5] and in the gas phase [5] show that intermolecular energy hopping between similar carbonyl groups in aliphatic ketones is a rather slow process. The intramolecular energy migration between carbonyl groups located in small aliphatic molecules has not been reported. It was considered interesting to study the photochemistry of aliphatic dicarbonyl compounds in order to establish the importance of energy migration in their photochemical behaviour. These compounds are particularly suitable for such studies since the photochemistry of isolated carbonyl groups is well established [6] and they afford the opportunity of measuring the importance of energy migration in both singlet and triplet excited states. In the present communication we describe the synthesis of asymmetrical 1,4-diketones and show that the photochemistry of 4,7-undecanedione indicates efficient energy migration between both carbonyl groups.

The stability differences between mono- and dicarbanions derived from furan allow selective alkylation in position 2 and 5. Furthermore, it is well known [7] that furan hydrolysis permits an entry to 1,4-dicarbonyl systems.

Metalation of furan with *n*-butyllithium in tetrahydrofuran solution at -20°C produced 2-furyllithium which on condensation with 1-bromobutane gave 2-*n*-butylfuran (I) in 60% yield, b.p. $137 - 139^{\circ}\text{C}$ [8]. The nuclear magnetic resonance (NMR) spectrum (CCl_4) of I showed resonances at 0.90 (3H, triplet (t)), 1.20 - 1.97 (4H, multiplet (m)), 2.60 (2H, t), 5.90 (1H, doublet of doublets (d of d)), 6.20 (1H, d of d) and 7.21 (1H, broad) ppm. Subsequent metalation and alkylation of I with 1-bromopropane formed 2-*n*-butyl-5-*n*-propylfuran (II) in 66% yield, b.p. $196 - 197^{\circ}\text{C}$, which had

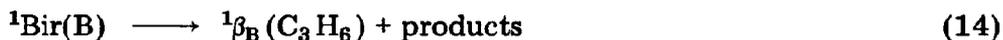
NMR (CCl_4) peaks at 0.90 - 0.98 (6H, 2t), 1.21 - 1.97 (6H, m), 2.58 (4H, singlet (s)) and 5.90 (2H, s) ppm. Careful hydrolysis of the dialkylated intermediate in aqueous acetic acid containing some sulphuric acid provided the expected 4,7-undecanedione (III) in 43% yield, b.p. 110 - 112 °C (10 mmHg)[†]. The NMR spectrum (CCl_4) of III showed resonances at 0.90 (6H, t), 1.20 - 1.90 (4H, t) and 2.57 (4H, s) ppm. Comparisons of the NMR spectrum of III with those of acetonylacetone and some other 1,4-diketones prepared by the same procedure as described earlier were made. As a result, the 2.57 ppm singlet absorption was assigned to the two methylenes located on position 5 and 6, and the 2.40 ppm triplet absorption was assigned to the two methylenes on positions 3 and 8 of III. For the photochemistry, III was purified by redistillation at 105 °C (6 mmHg) and by vapour chromatography using an SE-30 (10 ft \times $\frac{3}{8}$ in) column at 230 °C.

The absorption spectra of 2,5-hexanedione (Fluka) and 2-hexanone (Fluka) show a first band with a maximum at nearly 280 nm. The fluorescence of both compounds is similar, showing a band with maximum at 400 nm. The similarity between the behaviour of the 1,4-diketone and that observed for 2-hexanone can be taken as evidence that both chromophores can be considered as isolated in the ground state and in the first excited state of the dicarbonyl compound. Energy migration between the chromophores can be analysed in terms of a weak interaction model [9] and the experimental data can be treated according to the following reaction scheme:



where A and B represent the ketone with the excited energy localized in $(\text{C}=\text{O})_4$ and $(\text{C}=\text{O})_7$ respectively.

The biradicals (Bir) can decompose according to the following equations:



where the β coefficients indicate the fraction of a given biradical that photo-fragments.

[†]Satisfactory elemental analyses were obtained for isolated compounds.

The following assumptions will be made in order to simplify the kinetic treatment of the data:

$$k_1 = k_2$$

$$k_4 = k_7$$

and

$$k_{10} = k_{12}$$

since the absorption spectra of alkyl ketones and the $n\pi^*$ excitation energy is insensitive to small changes in the alkyl side chains [10]. Furthermore, it will be assumed that

$$k_5 = k_8$$

that the primary photoreactions of A are similar to those of excited 2-pentanone, and that the primary photoreactions of B are similar to those of 2-hexanone. These assumptions are supported by the insensitivity of the intramolecular hydrogen abstraction to structural features other than γ substitution [11].

Depending upon the relation between the lifetimes of A and B and the rate of energy migration, two extreme situations can be envisaged.

(1) No significant intramolecular energy transfer between the chromophores takes place; we call this situation no migration.

(2) The rates of processes (4), (7), (10) and (12) are considerably faster than that of any other process of the excited molecules. We consider that this situation leads to "equilibration" and in the steady state we obtain

$${}^3\text{B} = {}^3\text{A}$$

and

$${}^1\text{B} = {}^1\text{A}$$

If the limiting situation (1) applies, the photochemistry of ketone III must resemble that of an equimolecular mixture of 2-pentanone and 2-hexanone. In the second case, the product distribution and lifetimes will be determined by the reactions of B, since it can be expected [6] that

$$k_6 \approx 7k_3$$

and

$$k_{11} \approx 33k_9$$

The results expected in these two extreme situations are shown in Table 1, together with those experimentally obtained in degassed n-hexane solutions at 20 °C with low intensity radiation of 3130 Å. Quenching experiments and triplet quantum yield measurements were carried out employing *cis*-1,3-pentadiene as a selective triplet quencher. The calculated values of ϕ_{II} given in Table 1 were obtained assuming that the values of β for 4,7-undecanedione are similar to those obtained in the photolysis of 2-pentanone and 2-hexanone.

TABLE 1

	Experimental	No migration	Equilibration
$\phi(\text{C}_2\text{H}_4)_s$	0.005	0.012	0.009
$\phi(\text{C}_3\text{H}_6)_s$	0.03	0.043	0.062
ϕ_T	0.56	0.6	0.53
$\phi(\text{C}_2\text{H}_4)_T$	0.025	0.1	0.004
$\phi(\text{C}_3\text{H}_6)_T$	0.12	0.057	0.14
$k_q\tau_T^a$	154	82	165
τ_T	1.4×10^{-8}	0.74×10^{-8}	1.5×10^{-8}

^aDetermined by quenching the formation of propylene with 1,3-pentadiene.

This assumption can overestimate the values of ϕ_{II} owing to the dependence of β on the size of the alkyl group opposite the chain bearing the unpaired electron [11]. Furthermore, the values of ϕ_T given were obtained assuming a value of $1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ [12] for the quenching rate constant of III. This value disregards the influence of the ketone size and of energy migration upon the quenching rate constant. Comparison between expected and obtained values can then only be qualitative.

The data of Table 1 show that the predictions of both models are not different enough to show conclusively the importance of the singlet energy migration. In contrast, they show conclusively the contribution of energy migration in the triplet state. In particular, the value obtained for $\phi(\text{C}_2\text{H}_4)_T$ indicates that energy migration must be the dominant process for ³A. This result indicates that triplet energy migration from A to B must take place with a rate constant considerably higher than 10^7 s^{-1} .

References

- 1 P. J. Wagner and T. Nakahira, *J. Am. Chem. Soc.*, **95** (1973) 8474.
- 2 D. O. Cowan and A. A. Baum, *J. Am. Chem. Soc.*, **93** (1971) 1153.
- 3 J. E. Guillet, *Pure Appl. Chem.*, **36** (1973) 127.
- 4 G. Schuster and N. J. Turro, *Tetrahedron Lett.*, (1975) 2261.
- 5 E. B. Abuin, M. V. Encina and E. A. Lissi, unpublished results.
- 6 M. V. Encina and E. A. Lissi, *J. Photochem.*, **4** (1975) 321; **5** (1976) 287; **6** (1976/77) 173.
- 7 G. Buchi and H. Wuest, *J. Org. Chem.*, **31** (1966) 977.
- 8 V. Ramanathan and R. Levine, *J. Org. Chem.*, **27** (1962) 1216.
- 9 A. A. Lamola, *Energy Transfer and Organic Photochemistry*, Wiley-Interscience, New York, 1969, p. 17.
- 10 M. O. Sullivan and A. C. Testa, *J. Am. Chem. Soc.*, **92** (1970) 5842; A. C. Somersall and J. E. Guillet, *Macromolecules*, **5** (1972) 410.
- 11 M. V. Encina and E. A. Lissi, *J. Photochem.*, **8** (1977) 131.
- 12 P. J. Wagner and I. Kochevar, *J. Am. Chem. Soc.*, **90** (1968) 2232.