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Bromo-organics. 2. Irradiation-Induced Transformations of Tetrabromocyclopentadienone Dimer[1]

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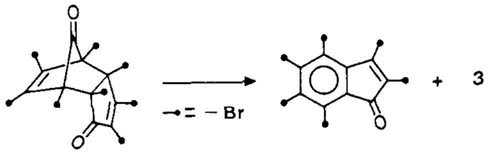
The title compound (1) undergoes on photolysis decarbonylation to perbromoinden-1-one (2) and intramolecular $[_\pi 2 + _\pi 2]$ cycloaddition to the dissymetric perbromobishomocubanedione 3. The results from direct irradiation, sensitization and quenching experiments were taken to indicate that two excited states are involved.

In the framework of a comprehensive study on polybromo organic compounds, we have recently started an investigation of the dimer (1) of tetrabromocyclopentadienone (over 80% bromine content!) and have already reported[1] its peculiar reactivity toward nucleophilic attack. We are now describing its photochemical behavior.

Direct and sensitized irradiations of 1 led to two products in varying yields, dependent on the irradiation conditions: the known perbromoinden-1-one (2)[1,2] and an unknown compound, the IR, UV, and mass spectra of which indicated it to be a saturated isomer of 1. The immediate proposition for the structure of this product was the dissymmetric octabromopentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]deca-6,10-dione (3), following an internal $[_\pi 2 + _\pi 2]$ photocycloaddition in 1 and in analogy with its octachloro[3,4b] and octahydro[4] derivatives which give 4 and 5, respectively. One should not, however, take this for granted since the dicyclopentadienone system may show great versatility.[1-7] Thus, various substituted cyclopentadienone dimers have led, on photolysis, not only to the dissymmetric, internal cycloaddition cage products but also to symmetric ones, be it of symmetry C_{2v} (6) or D_{2h} (7).[5,6]

Since the uniform perbromo substitution does not allow the mass spectrometric approach[6] to be taken, we resorted to ^{13}C NMR spectroscopy in order to prove unequivocally the structural assignment of 3. The rationale was simply that only 3 should exhibit five distinct signals, corresponding to ten pairwise equivalent carbon nuclei, as such a structure with C_2 symmetry implies. The general validity of this approach can be proven, if at all needed, by applying the same criterion to the octachloro analogue 4 of proven structure.[3,5]

The cage diketone 3 is difficult to purify—only by repeated sublimation—due to its tendency to add water and form hydrates. In fact it was easier to isolate and characterize it as the dihydrate 8. As such, it could also be methylated by diazomethane to the corresponding tetramethoxy derivative 9 whose ^1H NMR spectrum exhibits *two* methyl signals (6 H each) by which, in fact, the centrosymmetric structure 7 could have been excluded—but not 6.[3,6] Eventually, the ^{13}C NMR spectra of both the octabromo and octachloro dihydrates (8 and 10, respectively) were measured and the data are assembled in Table I, proving that they, as well as their parent diketones (3 and 4, respectively), are indeed C_2 symmetry structures.



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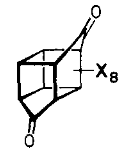
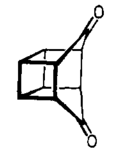


3-X=Br
4-X=Cl
5-X=H



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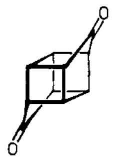

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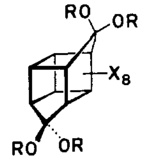

8-X=Br;R=H
9-X=Br;R=Me
10-X=Cl;R=H

Returning to the photochemistry of the dimer (1), its UV spectrum is depicted in Figure 1 and the irradiation results are assembled in Table II. It should be mentioned at the outset that the high-molecular-weight high-melting products and the sensitivity of the starting material (1) towards nucleophiles (e.g., H_2O, ROH)[1] render quantitative work very difficult and forced us to conduct our experiments at high conversion, monitoring them by using low-precision product isolation techniques. Nevertheless, the results are reproducible and conclusive, following a set of carefully planned experiments, including variable-wavelength direct irradiations, as well as sensitization and quenching studies (Table II). We rely on those to put forward a mechanism for the photochemical behavior of 1.

Discussion

To begin with, the formation of perbromoinden-1-one (2) is both interesting and somewhat surprising since it involves decarbonylation–debromination of 1 (be it in a concerted or stepwise process) induced by direct or sensitized irradiation, the latter process being, in fact, the more efficient one. To be sure, norbornen-7-one and its

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(1) Part I: B. Fuchs, R. Lidor, C. Krüger, and C. K. Liu, *Nouv. J. Chim.*, 4, 361 (1980).
(2) R. G. Pews, *Org. Prep. Proced. Int.*, 3, 37 (1971).
(3) G. W. Griffin and A. K. Price, *J. Org. Chem.*, 29, 3192 (1964).
(4) (a) E. Baggiolini, E. G. Herzog, S. Iwasaki, R. Schorta, and K. Schaffner, *Helv. Chim. Acta*, 50, 297 (1967); (b) U. Klinsmann, J. Gauthier, K. Schaffner, M. Pasternak, and B. Fuchs, *ibid.*, 55, 2643 (1972).
(5) (a) B. Fuchs, B. Pazhenchevsky, and M. Pasternak, *Tetrahedron Lett.*, 3051 (1972); (b) B. Pazhenchevsky and B. Fuchs, *ibid.*, 3047 (1972); (c) B. Fuchs, M. Pasternak, and B. Pazhenchevksy, *Tetrahedron*, in press.
(6) B. Fuchs and M. Pasternak, *J. Am. Chem. Soc.*, 100, 6225 (1978).
(7) B. Fuchs, *Isr. J. Chem.*, 20, 203 (1980).

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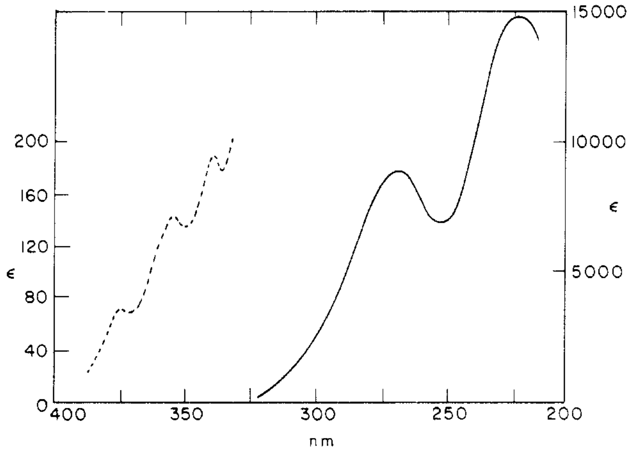

Figure 1. UV spectrum of **1**. The right and left scales are for the full and broken curves, respectively.

Table I. ^{13}C NMR Chemical Shifts[a]

compd	$C(OH)_2$	C-Br			
8	105.93	76.69	74.15	70.84	67.51
10	104.81	80.03	79.00	78.52	75.52

[a] Parts per million in acetone-d_6 with Me_4Si as internal standard.

derivatives are known to photodecarbonylate readily,[4,5,8] but they do that only on direct irradiation at low wavelength (e.g., 254 nm) via singlet excited states.[8] At the same time, the analogous octachloro dimer (**1**-Cl_8) conspicuously fails to photodecarbonylate under any conditions and yields only the cage product **4** via an excited triplet state.[3,4b]

In our case, the decarbonylation–debromination occurs to an appreciable extent either by direct irradiation of the low-wavelength (π,π^*) absorption band of **1** (cf. Figure 1 and Table II, run 1) or by sensitization with relatively high triplet energy sensitizers (runs 5–7). As the triplet energy of the sensitizer decreases, the yield of **2** diminishes, vanishing asymptotically at and below 53 kcal (runs 7–9). Furthermore, complete quenching is achieved by using 1,3-cyclohexadiene or oxygen (runs 10 and 11). Consequently, we assign to the triplet state of **1**, involved in the latter's decarbonylation–debromination, a tentative energy around 60 kcal/mol. We feel compelled to mention a peculiar and still puzzling feature of this process, namely, that no decarbonylation product is isolated, as it is in all other photodissociation processes of norbornen-7-ones.[8] Whether the accompanying debromination is taking place concertedly or as a discrete step is not known to date.

The cage product **3** is apparently formed via a low-energy excited triplet state since it is isolated after direct irradiation at $\lambda \geq 300$ nm (run 2) and in even better yield at $\lambda \simeq 350$ nm (run 3 and 4) by irradiation of the n,π^* absorption band (Figure 1) or by irradiation with low-energy triplet sensitizers (runs 7–9). The lower yields of **3** obtained in the acetone-sensitized experiments (runs 5 and 6) may be due either to the efficient competition of the decarbonylation process in the sensitization process or to some residual direct irradiation below the acetone absorption band (vide infra). Be this as it may, the triplet excited state responsible for the internal cycloaddition process **1** → **3** can be safely assigned an energy around 50 kcal.

The facile intersystem crossing operating in **1** is readily understood for such a heavy atom substituted compound. One cannot, however, exclude the possibility that singlet states also play a role in the above described photochemical behavior, namely, the higher singlet S_2 in the dissociation process to **2** and the lowest excited singlet S_1 in the cage (**3**) formation. Unfortunately, we could not get any information from emission spectroscopy since no emission of **1** could be detected in solution or in glass (MeTHF) at 70 K.

Our conclusion from the existing data is that two triplets operate: a lower one, T_1 ($E_T \simeq 50$), from which the less energy demanding cycloaddition process occurs, is readily reached by intersystem crossing and by energy transfer; a higher one, T_2 ($E_T \simeq 60$), is formed by energy transfer from acetone and may lead to some **3** via internal conversion to T_1, but its main reaction path is molecular dissociation to **2**. The exclusive isolation of **2** by direct irradiation at higher wavelength may be reasonably explained by concomitant rapid photodecomposition due to irradiation into C–Br absorptions, precluding formation and isolation of the cage compound (**3**).

Experimental Section

IR and UV spectra were taken on Perkin-Elmer Models 297 and 337 and Cary 17 spectrophotometers, respectively. ^{13}C and ^1H NMR spectra were measured on a Bruker WH-90 NMR spectrometer in acetone-d_6 with Me_4Si as internal standard. Mass spectra were measured on a Du Pont 21-491 B mass spectrometer at 14-20 eV. Irradiations were performed in Rayonet reactors, using 350- or 300-nm lamps. The starting material (**1**) was prepared according to the literature procedure.[2]

Table II. Product Distribution on Irradiation of 1 under Various Conditions[a]

run	irradiation (λ, nm)	solvent	filter (cut off, nm)	sensitizer/quencher (E_T)	% yield[b] 2[e]	% yield[b] 3
1	direct (300)	MeCN	Corex (280)		21	
2	direct (300)	MeCN	Pyrex (300)		~4	62
3	direct (350)	MeCN	Pyrex (300)		~5	75
4	direct (350)	$CHCl_3$[c]	Pyrex (340)[d]		~4	76
5	sensitized (300)	acetone	Corex (280)	acetone (79)[f]	66	30
6	sensitized (300)	acetone	Pyrex (300)	acetone (79)[f]	40	30
7	sensitized (350)	$CHCl_3$	Pyrex (300)	thioxanthen-9-one (65)[f]	~12	47
8	sensitized (350)	$CHCl_3$	Pyrex (300)	fluoren-9-one (53)[f]	1	48
9	sensitized (350)	$CHCl_3$	Pyrex (300)	benz[*de*]anthracen-7-one (47)[f]	1	51
10	direct (350)[g]	1,4-dioxane	Pyrex (300)	1,3-cyclohexadiene (53)		14
11	direct (350)[g]	1,4-dioxane	Pyrex (300)	O_2 saturated (22)		40

[a] The general procedure is given in the experimental section. [b] Irradiations were performed to full disappearance of starting material; the balance to 100% conversion is made up of ill-defined decomposition products. [c] Similar results were obtained in 1,4-dioxane. [d] Solution cut-off filter below 340 nm.[4b] [e] The accuracy of the hexabromoindenone (**2**) yields may suffer somewhat from the possibility that small amounts of residual dimer could yield **2** following chromatographic workup.[1] [f] In all sensitized irradiations, better than 99% of the light was absorbed by the sensitizer. [g] Same irradiation time as in run 4 (see footnote *c*).

Irradiation of Tetrabromocyclopentadienone Dimer (1) (See Table II). A solution of 1 g of 1 in 450 mL of solvent was swept thoroughly with nitrogen, irradiated for 18 h, and monitored by IR and/or UV spectroscopy until the starting material was practically gone. The solvent was evaporated and the residue chromatographed on silica gel. The hexabromoindenone (2), mp 198 °C dec[2] was eluted with petroleum ether while the cage (3 partly hydrated) emerged with $CHCl_3$/EtOAc (1:1). The data for the new compounds are given below.

Octabromopentacyclo$[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]$deca-6,10-dione (3): purified by sublimation; IR (KBr) ν_{max} 1800 (CO) cm^{-1}; mass spectrum, m/e 712 (M^+ − Br), 684 (−CO), 604 (−Br).

Dihydrate of 3 (8): isolated from wet acetone and recrystallized from chloroform; IR (KBr) ν_{max} 3640–2800 (OH) cm^{-1}; mass spectrum identical with that of **3**; ^{13}C NMR, see Table I. Anal. Calcd for $C_{10}H_4O_4Br_8$: C, 14.51; H, 0.49; Br, 77.26. Found: C, 14.33; H. 0.85; Br, 76.96.

Tetramethyl Diketal of 3 (9). This was obtained by treating 8, suspended in ether, with an ethereal solution of diazomethane. The mixture was stirred overnight and, after evaporation of the solvent in the hood, the residue was chromatographed on neutral alumina. The diketal (9) was eluted with CCl_4 and isolated in 1% yield: IR (KBr) ν_{max} 2980, 2940, 2840 (CH) cm^{-1}; mass spectrum, m/e 803 (M^+ − Br); ^1H NMR ($CDCl_3$, Me_4Si) δ 3.62 (6 H, s), 3.78 (6 H, s).

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Registry No. 1, 31838-43-4; 2, 31838-44-5; 3, 76215-24-2; 8, 76215-25-3; 9, 76215-26-4; 10, 76252-05-6.

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[8] B. Fuchs and G. Scharf, *Isr. J. Chem.*, 16, 335 (1977), and a discussion therein on this subject.

Notes

Structure Analysis by Carbon-13 Nuclear Magnetic Resonance Spectroscopy of Pandicine, a Novel Bisindole Alkaloid from *Pandacastrum saccharatum* Pichon[1]

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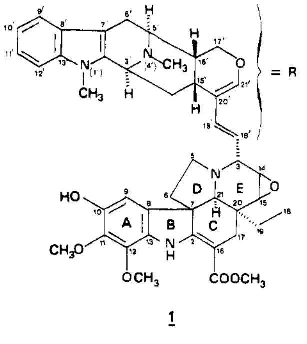
From the leaves of *Pandacastrum saccharatum* Pichon (*Apocynaceae*) we have isolated a novel bisindole alkaloid, pandicine (1), possessing a hitherto unknown highly oxygenated tabersonine skeleton linked at its C(3) position to the C(18′) of a macroline[3] moiety. We report the structure 1 of pandicine, established mainly from an analysis of its ^1H and ^{13}C NMR spectra along with the consideration of its mass spectral fragmentation pattern. Although the chemistry of pandicine was little explored due to paucity of material, its facile oxidation to the iminoquinone 2 was singularly helpful for the structural elucidation.



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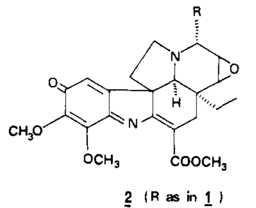
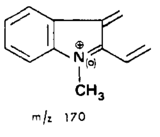


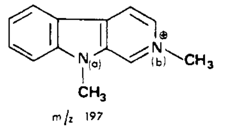
2 (R as in 1)

Pandicine was obtained as a brown amorphous solid which resisted all attempts toward crystallization. Determination of its specific rotation was precluded due to the immediate development of a dark color (coloration may be due to traces of 2 and possibly other oxidation products) whenever pandicine was dissolved in an organic solvent. The mass spectrum of pandicine (1) showed the molecular ion peak at m/z 746.3698, corresponding to the formula $C_{44}H_{50}N_4O_7$ (calcd 746.3679). The UV spectrum of 1 showed maxima (EtOH) at 231, 234, 297, 307, and 342 nm with a shoulder at 250 nm. In acid medium the maxima were observed at 228, 265, 297, 304, and 342 nm while in alkaline medium there was a markedly visible bathochromic shift above 350 nm with broadening of absorption but no appreciable change below 300 nm. Compound 2, which was obtained in quantitative yield by swirling a chloroform solution of 1 with activated MnO_2, showed a very different UV spectrum, having maxima at 233, 260, and 396 nm with a shoulder at 288 nm. The IR spectrum of 1 showed complex C=O and C=C absorptions at 1680, 1640, and 1610 cm^{-1} and a broad NH/OH band at 3400 cm^{-1}. The latter disappeared in the IR spectrum of 2 while strong bands were observed at 1690, 1640, and 1580 cm^{-1}.

The mass spectrum of pandicine (1) displayed fragmentation peaks at m/z 170 and 197 (base peak) typical of the $N_{(a)}$–CH_3 and $N_{(b)}$–CH_3 macroline skeleton.[3] Complementary peaks at m/z 290 and 456 (M − 290) may be attributed to well-known retro-Diels–Alder opening of ring C followed by cleavage of the C(5)–C(6) bond.[4]



m/z 170



m/z 197

The complete structural elucidation of pandicine (1) followed from an analysis of its ^{13}C NMR spectrum. Resonances due to the 44 carbons appeared as distinct

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[1] Part 21 in the series "Plantes Malgaches". For Part 20, see N. Langlois, L. Diatta, and R. Z. Andriamialisoa, *Phytochemistry*, 18, 467 (1979).

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