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Photochemistry of cyclic vicinal tricarbonyl compounds Photolysis of alloxan in the presence of olefins containing allylic hydrogen

M.T. Silva, D.F. Gomes, A.M. Cardoso da Silva, J.C. Netto-Ferreira*

Departamento de Química, Universidade Federal Rural do Rio de Janeiro, Antiga Rio-São Paulo km 47, Seropédica, 23851-970 Rio de Janeiro, Brazil

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Abstract

UV irradiation of an acetone solution of alloxan (**1**) in the presence of olefins containing allylic hydrogen leads to the formation of 5-hydroxy-5-alkenyl barbituric acids (**2**) resulting from an initial hydrogen abstraction process. On the other hand, photolysis of **1** with ethyl-1-propenyl ether yields [2 + 2] (oxetanes) and [4 + 2] (dioxenes) photocycloaddition products, beside the corresponding hydrogen abstraction products. When the irradiation was performed with olefins containing electron-acceptor substituents, product formation could not be observed.

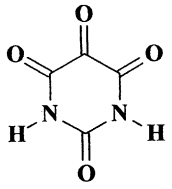
Keywords: Photochemistry; Alloxan; Polycarbonyl compound

1. Introduction

The photochemical behavior of polycarbonyl compounds has been recently reviewed [1]. The photochemical reaction of open chain triketones results in a complex mixture of products with very low quantum yield for disappearance of the starting material [2]. When diphenyl triketone is photolyzed in the presence of an electron donor, such as DABCO, the reaction proceeded with higher quantum yield and produced benzil as a single product. A study of the photochemistry of 1,2,3-indanetrione shows that this cyclic vicinal tricarbonyl compound is highly inert towards UV light since only 5% conversion to products was observed after 250 h irradiation [3,4]. However, when the irradiation of 1,2,3-indanetrione is performed in the presence of olefins, a quantum yield of approximately one was observed. In this case, products derived from photocycloaddition (Paternò–Bücchi reaction) and/or hydrogen abstraction processes, depending on the olefin structure, were formed [5,6].

Alloxan (**1**) was one of the first cyclic vicinal tricarbonyl compound for which a photochemical reaction has been reported [7]. Irradiation of ethanol [7] or *iso*-propanol [8] solutions of **1** yielded alloxantin and acetaldehyde. The irradiation of aqueous solutions of alloxan with a high-pressure mercury lamp yielded the same product, i.e. alloxantin [9–11]. However, it is worth noting that in these solvents alloxan exists almost completely as the hydrate (in water) or the hemiketal (in alcohols) form.

In this communication we show that the photochemical behavior of alloxan (**1**) in the presence of olefins is similar to that previously observed for 1,2,3-indanetrione, resulting in the formation of products derived from both hydrogen abstraction and photocycloaddition processes.



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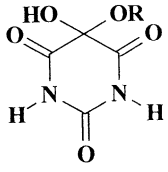

1a: R=H
1b: R=alkyl

2. Results and discussion

Photochemical irradiation of alloxan (**1**) in acetone in the presence of olefins containing allylic hydrogen, such as 2,5-dimethyl-2,4-hexadiene, 2,4,4-trimethyl-1-pentene, 2-methyl-2-butene, 2-methyl-1-butene and 1-methyl-1-cyclopentene, leads exclusively to the formation of products formed by an initial hydrogen abstraction reaction from

* Corresponding author.
E-mail address: jcnetto@ufrrj.br (J.C. Netto-Ferreira).

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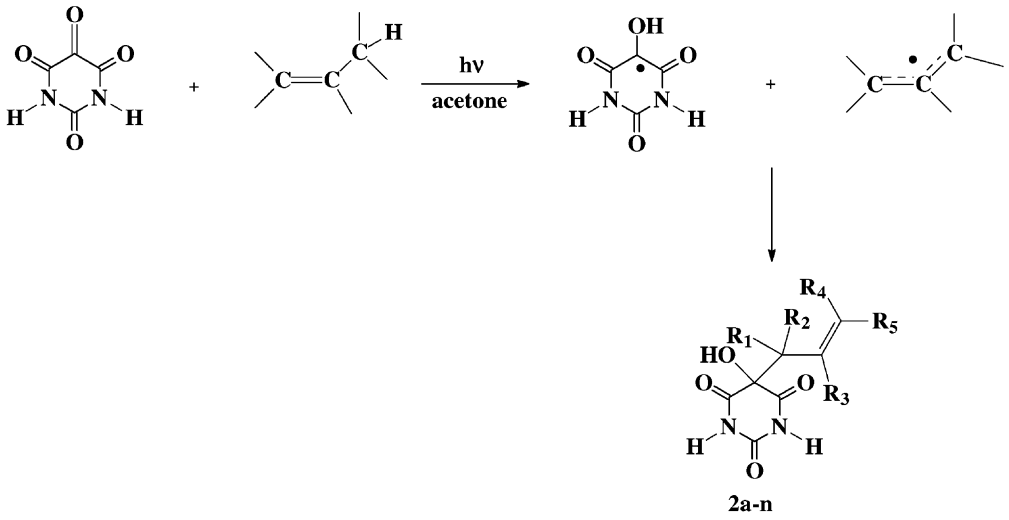
Table 1
Product distribution in the photolysis of alloxan (**1**) with olefins containing allylic hydrogen in acetone

Olefin	Compound no.	Product	Yield (%)[a]
2,5-Dimethyl-2,4-hexadiene	**2a**	$R_1 = R_4 = R_5 = H$; $R_2 = CH = C(CH_3)_2$; $R_3 = CH_3$	87
	2b	$R_1 = R_2 = R_4 = H$; $R_3 = CH_3$; $R_5 = CH = C(CH_3)_2$	13
2,4,4-Trimethyl-1-pentene	**2c**	$R_1 = R_2 = R_4 = R_5 = H$; $R_3 = CH_2C(CH_3)_3$	100
2-Methyl-2-butene	**2d**	$R_1 = R_2 = R_3 = H$; $R_4 = R_5 = CH_3$	35
	2e	$R_1 = R_2 = CH_3$; $R_3 = R_4 = R_5 = H$	8
	2f	$R_1 = R_2 = R_4 = H$; $R_3 = R_5 = CH_3$	20
	2g	$R_1 = R_2 = R_5 = H$; $R_3 = R_4 = CH_3$	17
	2h	$R_1 = R_4 = R_5 = H$; $R_2 = R_3 = CH_3$	20
2-Methyl-1-butene	**2f**	$R_1 = R_2 = R_4 = H$; $R_3 = R_5 = CH_3$	[b]
	2g	$R_1 = R_2 = R_5 = H$; $R_3 = R_4 = CH_3$	[b]
	2h	$R_1 = R_4 = R_5 = H$; $R_2 = R_3 = CH_3$	9
	2i	$R_1 = R_2 = R_4 = R_5 = H$; $R_3 = CH_2CH_3$	9
1-Methyl-1-cyclopentene	**2j**	$R_1 = R_5 = H$; $R_3 = CH_3$; R_2, $R_4 = CH_2CH_2$	30
	2k	$R_1 = R_3 = H$; $R_2 = R_4 = CH_2CH_2$; $R_5 = CH_3$	33
	2l	$R_1 = CH_3$; R_2, $R_4 = CH_2CH_2$; $R_3 = R_5 = H$	10
	2m	$R_1 = R_2 = R_4 = H$; R_2, $R_5 = CH_2CH_2CH_2$	10
	2n	$R_1 = R_4 = R_5 = H$; R_2, $R_3 = CH_2CH_2CH_2$	17
Ethyl-1-propenyl ether[c]	**2o**		[d]
	2p		[d]
	3a		6
	3b		Traces
	4a		35
	4b		21

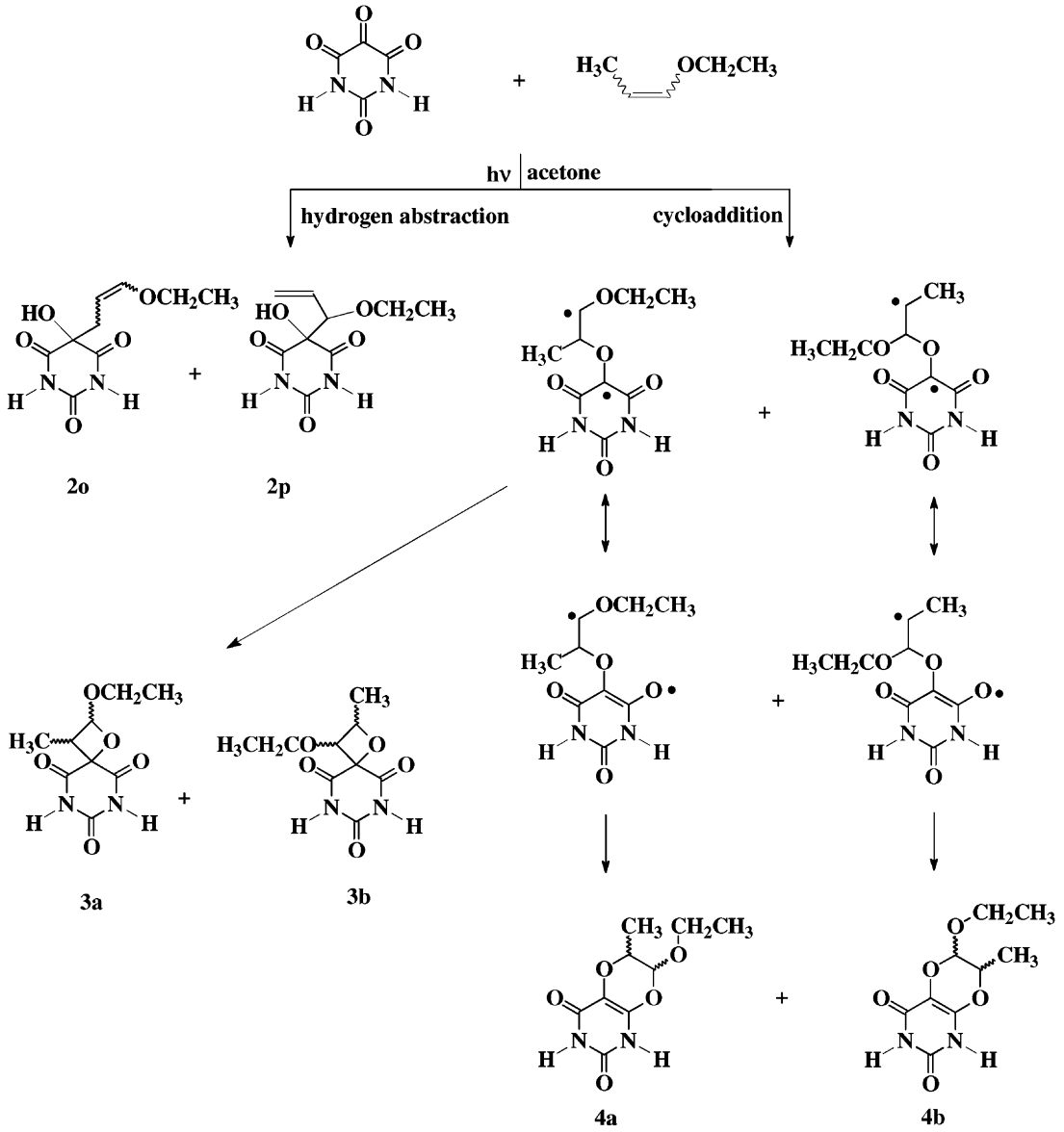
[a] Yields were obtained from integration of representative protons on NMR spectra.
[b] A yield of 82% was obtained for ***2***f + ***2***g.
[c] See Scheme 2.
[d] Allylic hydrogen abstraction accounted for 38% of total products.

the olefin (**2a**–**n**, Table 1). When the irradiation was performed with ethyl-1-propenyl ether a complex mixture of products derived from both hydrogen abstraction and photocycloaddition processes was observed. The oxetane **3** and the dioxene **4** probably arise from the initial 1,4-biradical formed by attack of the electrophilic excited carbonyl oxygen to the olefin double bond. Scheme 1 shows probable mechanisms for the formation of these different products.

In general, alkyl vinyl ethers lead to a complex mixture of products, including polymeric co-products, which cannot be separated. However, the characterization and the unambiguous assignment of the products resulting from



Scheme 1.



Scheme 2.

the reaction of alloxan with ethyl-1-propenyl ether, i.e. **3a** (6%), **4a** (35%) and **4b** (21%), were made through analysis of one-dimensional (1D) and two-dimensional (2D: homonuclear $^{1}H \times {}^{1}H$-COSY and heteronuclear $^{1}H \times {}^{13}C$-COSY-$^{n}J_{CH}$ ($n = 1$–3, COLOC)) ^{1}H and ^{13}C NMR spectra. Due to the complexity of the NMR spectra, it was not possible to make a detailed assignment for the products resulting from the allylic hydrogen abstraction reaction, i.e. **2o** and **2p** (accounting for 38% yield overall), as well as for the spirooxetane **3b** (traces) (Table 1, Scheme 2).

Photolysis of **1** in the presence of olefins containing electron-acceptor substituents, such as maleic anhydride or dimethyl fumarate did not lead to the formation of any product. A similar result was found with dimethyl acetylenedicarboxylate, 1,1-diphenylethylene or acenaphthylene. However, when the irradiation was performed with diastereoisomerically pure *cis*- or *trans*-stilbene, olefin isomerization could be observed. In this case, the same *cis*/*trans* ratio was obtained, independently of the starting isomer. It is well known that the triplet energy of cyclic vicinal tricarbonyl compounds is well bellow 50 kcal/mol [3,12]. Thus, direct energy transfer from triplet alloxan to either *cis*- or *trans*-stilbene is highly endothermic and, consequently, an excited complex must be involved in the quenching process [13–15].

Only $n\pi^*$ singlet excited state ($n\pi^{*1}$) forms oxetanes with electron deficient substrates [16–19], with the oxetane formation from $n\pi^{*1}$ being completely stereospecific. Thus, the non-stereospecific nature of the product mixture resulting from the reaction of **1** with the olefins employed in this work is in agreement with the involvement of the alloxan triplet state showing $n\pi^*$ character.

The general topological features of the surfaces for the perpendicular approach required in the π–n orbital interaction, which results in oxetane (or dioxene) formation, is the same as those for hydrogen abstraction. Thus, it has been postulated that these processes occur through an excited complex which decays either to give a 1,4-biradical, precursor of the [2 + 2] and [4 + 2] photocycloaddition products, or to form a radical pair by an intramolecular hydrogen abstraction, which ultimately leads to the photoreduction of the alloxan central carbonyl [16,20,21].

The rate constant for direct hydrogen abstraction by a nπ* state reaches a limit of $\sim 10^6\,M^{-1}\,s^{-1}$ and then partial electron transfer begins to dominate the quenching process. Thus, it is expected that hydrogen abstraction will not compete favorably with oxetane formation when the olefin is a good quencher ($k_q > 10^7\,s^{-1}$) of nπ* states, but hydrogen abstraction may be competitive when $k_q < 10^6\,s^{-1}$ [22]. Previous studies on other cyclic vicinal tricarbonyl compounds indicate that rate constants for the reaction of their triplet with alkenes range from 10^5 to $10^7\,M^{-1}\,s^{-1}$. Photocycloaddition products start to be formed when the ionization potential of the olefin approaches 8.7 eV [5,6,23]. The photochemical reaction of **1** in the presence of olefins can then be explained by a primary interaction between **1** and the olefin, through an excited complex containing some charge transfer character. Like the photochemical reaction of 1,2,3-indanetrione [6] in the presence of enol ethers, photolysis of **1** with these considerably electron rich olefins leads predominantly to the formation of photocycloaddition products.

The low selectivity shown by alloxan in its reaction with ethyl-1-propenyl ether is probably consequence of its high reactivity towards olefins. Like other cyclic vicinal tricarbonyl compounds, the enhanced reactivity of the central carbonyl is probably due to the presence of the two other coplanar carbonyl groups. In such respect, these compounds may be regarded as superenophiles [24,25].

The product observed in the photolysis of **1** with 2,4,4-trimethyl-1-pentene through a hydrogen abstraction reaction does not involve the most stable allylic radical and thus the product derived from the hydrogen abstraction of the allylic secondary hydrogen was not observed. As shown in Fig. 1, the intermolecular approach (a) between alloxan and 2,4,4-trimethyl-1-pentene should be favored over approach (b) towards hydrogen abstraction from the primary allylic center for steric reasons. This result is similar to that obtained for 1,2,3-indanetrione [6].

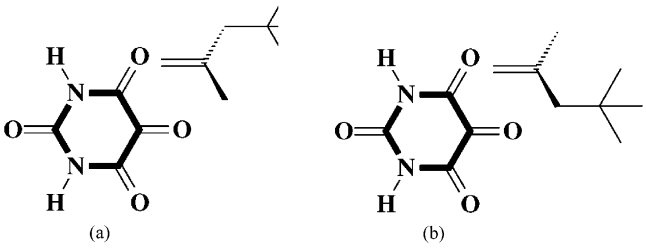


Fig. 1. Possible approximations for the interaction between alloxan triplet and 2,4,4-trimethyl-1-pentene.

A comparison between products obtained in the reaction of 1,2,3-indanetrione and alloxan with some olefins, such as 2,5-dimethyl-2,4-hexadiene [23], 2-methyl-1-butene [23], 2-methyl-2-butene [6], and 2,3-dimethyl-2-butene [5], shows that different steric effects are involved in these two cases. In general, alloxan is less regiospecific than 1,2,3-indanetrione to the initial hydrogen abstraction process, but a more pronounced steric effect was found in the radical pair recombination for the former, probably due to changes in its ring conformation. This leads to a net result that these reactions are strongly dependent on steric factors.

Finally, it is worth noting that the photochemical reaction of alloxan with olefins containing allylic hydrogen is extremely useful in the synthesis of 5-hydroxy-5-alkenyl barbituric acids. Similar products were reported in a very elegant work by Bryon Gill and Idris, which shows that alloxan reacts thermally with olefins, at high temperatures, through an ene-addition reaction [24]. However, the photochemical reaction of alloxan in the presence of electron-rich olefins, such as alkyl vinyl ethers, can yield a new class of barbituric acid derivatives, namely 5,5-spirooxetane barbituric acids.

3. Experimental

3.1. Materials

The solvents employed were Aldrich Spectrograde and were used as received. The olefins were purchased from Aldrich. Alloxan (**1**) was prepared by sublimative dehydration of alloxan monohydrate (Aldrich). After preparation, the orange crystals were kept in sealed ampoules under reduced pressure.

3.2. General techniques

Gas chromatography (GC) analyses were carried out on a Varian model 2400 capillary gas chromatograph employing a 15 m T&W bonded phase vitreous silica FFAP column, under the following conditions: T_{column} from 50 to 200 °C, at 40 °C/min; $T_{detector} = 300$ °C; $T_{injector} = 250$ °C. GC–mass spectra (MS) analyses were carried out on a Hewlett-Packard model 5970/5890 employing a 50 m J&L bonded phase vitreous silica HP-54 column. Mass spectra of main chromatogram peaks were obtained by electron impact with the spectrometer operating at 70 eV. Infrared spectra (IR) were obtained in a model 1420 Perkin-Elmer spectrophotometer in CCl_4 liquid film and using a NaCl cell. 1D and 2D (homonuclear $^1H \times {}^1H$-COSY and heteronuclear $^1H \times {}^{13}C$-COSY-$^nJ_{CH}$ (n = 1–3, COLOC)) ^1H and ^{13}C NMR spectra were recorded in a Bruker AC 200 (^1H: 200 MHz; ^{13}C: 50.3 MHz) and in a Avance DRX-300 (^1H: 300 MHz;

^{13}C: 75.5 MHz) spectrometer in $(CD_3)_2CO$ using tetramethylsilane (TMS) as the internal standard.

3.3. Steady-state photolysis and product analysis

Irradiations were done in a Rayonet with nine RPR-3000 lamps, at room temperature. Typical samples were 100 ml of a 10^{-2} M solution of **1** in dry acetone containing a large excess of the olefin (10^{-1} M). In spite of a reasonable absorption at the irradiation wavelength (300 nm), acetone was chosen due to the larger solubility of alloxan in this solvent. However, a control experiment in which an acetone solution of alloxan, and the olefin 2,4,4-trimethyl-1-pentene, was irradiated at 350 nm wavelength in which acetone has no absorption, shows that product distribution and chemical yield are the same at both wavelengths. Samples were contained in Pyrex tubes and deaerated by bubbling dry oxygen-free nitrogen in a dark room, due to the high photochemical reactivity of **1**. The solution containing **1** and the olefin was irradiated until the yellow color of the original solution disappears (less than 1 h irradiation). The products, colorless or slightly yellow solids, were not isolated. After irradiation, the products were purified by preparative thin-layer chromatography (silica, and chloroform:acetone 8:2 as eluent) to eliminate the starting material, mainly alloxan hydrate formed during sample manipulation. Alloxan readily reacts with water forming the corresponding alloxan hydrate. Thus, chemical yields are not reported since, for a same reaction, a considerable variation on the yield was observed, depending on the time employed on sample preparation. After purification, the product mixture was analyzed by IR, GC–MS, ^{1}H and ^{13}C NMR spectra.

3.4. Spectroscopic and spectrometric data for *2*

2a: ^{1}H NMR (200 MHz, $(CD_3)_2CO$): δ (ppm): 10.68 (OH), 5.95 (bd, CH, $J = 9.8$), 5.30 (m, CH_2), 4.06 (bd, CH, $J = 9.8$), 2.20 (bs, CH_3), 2.15 (bs, CH_3), 2.04 (bs, CH_3). ^{13}C NMR (50.3 MHz, $(CD_3)_2CO$): δ (ppm): 170.31 (C=O), 150.00 (C=O), 143.36, 136.26, 118.94, 115.00, 79.76, 55.77, 25.83, 20.58, 17.44. IR (KBr, ν (cm^{-1})): 3407, 1721. MS *m/z* (relative intensity): 252 ($M^{\bullet+}$, absent), 184 (15), 142 (27), 141 (21), 109 (46), 85 (100), 67 (35), 44 (50), 43 (73).

2b: ^{1}H NMR (200 MHz, $(CD_3)_2CO$): δ (ppm): 6.40 (m, CH), 6.23 (m, CH), 3.22 (s, CH_2), 2.20 (bs, CH_3), 2.15 (bs, CH_3), 1.66 (bs, CH_3). ^{13}C NMR (50.3 MHz, $(CD_3)_2CO$): δ (ppm): 170.67 (C=O), 148.76 (C=O), 142.59, 134.90, 127.26, 119.04, 79.78, 51.46, 29.79, 20.58, 17.44. IR (KBr, ν (cm^{-1})): 3376, 1723. MS *m/z* (relative intensity): 252 ($M^{\bullet+}$, absent), 142 (23), 141 (19), 85 (81), 55 (27), 44 (100), 43 (65).

2c: ^{1}H NMR (200 MHz, $(CD_3)_2CO$): δ (ppm): 9.56 (OH), 4.21 (bs, CH_2, 1H), 4.15 (bs, CH_2, 1H), 2.04 (bs, CH_2), 1.32 (bs, CH_2), 0.14 (bs, CH_3). ^{13}C NMR (50.3 MHz, $(CD_3)_2CO$): δ (ppm): 171.73 (C=O), 149.99 (C=O), 141.02, 119.13, 76.46, 50.03, 48.99, 32.04, 29.80. IR (KBr, ν (cm^{-1})): 3412, 1722. MS *m/z* (relative intensity): 254 ($M^{\bullet+}$, 42), 198 (10), 111 (13), 69 (35), 57 (100), 55 (38).

2d: ^{1}H NMR (200 MHz, $(CD_3)_2CO$): δ (ppm): 4.96 (m, CH), 2.60 (d, CH_2, $J = 8.1$), 1.55 (d, CH_3, $J = 0.9$), 1.47 (d, CH_3, $J = 1.0$). ^{13}C NMR (50.3 MHz, $(CD_3)_2CO$): δ (ppm): 171.81 (C=O), 149.99 (C=O), 138.84, 115.62, 76.93, 40.40, 26.07, 17.89. IR (KBr, ν (cm^{-1})): 3376, 1723. MS *m/z* (relative intensity): 212 ($M^{\bullet+}$, absent), 179 (4), 144 (8), 69 (100), 53 (6), 41 (81).

2e: ^{1}H NMR (200 MHz, $(CD_3)_2CO$): δ (ppm): 5.84 (dd, CH, $J = 17.1, 10.6$), 5.00 (m, CH_2, 1H), 4.97 (m, CH_2, 1H), 1.04 (s, CH_3). ^{13}C NMR (50.3 MHz, $(CD_3)_2CO$): δ (ppm): 170.56 (C=O), 149.99 (C=O), 141.60, 115.41, 80.88, 46.17, 21.99. IR (KBr, ν (cm^{-1})): 3376, 1723. MS *m/z* (relative intensity): ($M^{\bullet+}$, absent), 144 (8), 69 (100), 53 (6), 41 (81).

2f: ^{1}H NMR (200 MHz, $(CD_3)_2CO$): δ (ppm): 5.21 (bq, CH, $J = 6.7$), 2.55 (bs, CH_2), 1.42 (d, CH_3, $J = 6.7$), 1.52 (m, CH_3). ^{13}C NMR (50.3 MHz, $(CD_3)_2CO$): δ (ppm): 171.81 (C=O), 149.99 (C=O), 129.30, 126.26, 76.93, 51.44, 17.14, 13.79. IR (KBr, ν (cm^{-1})): 3376, 1723. MS *m/z* (relative intensity): 212 ($M^{\bullet+}$, absent), 144 (8), 69 (96), 53 (8), 41 (100).

2g: ^{1}H NMR (200 MHz, $(CD_3)_2CO$): δ (ppm): 5.33 (bq, CH, $J = 6.8$), 2.67 (s, CH_2), 1.42 (d, CH_3, $J = 6.8$), 1.59 (m, CH_3). ^{13}C NMR (50.3 MHz, $(CD_3)_2CO$): δ (ppm): 171.81 (C=O), 149.99 (C=O), 129.07, 126.75, 76.23, 43.83, 25.19, 14.05. IR (KBr, ν (cm^{-1})): 3376, 1723. MS *m/z* (relative intensity): 212 ($M^{\bullet+}$, absent), 144 (8), 69 (96), 53 (8), 41 (100).

2h: ^{1}H NMR (200 MHz, $(CD_3)_2CO$): δ (ppm): 4.70 (m, CH_2), 2.70 (q, CH, $J = 7.1$), 1.62 (m, CH_3), 1.06 (d, CH_3, $J = 7.1$). ^{13}C NMR (50.3 MHz, $(CD_3)_2CO$): δ (ppm): 171.81 (C=O), 149.99 (C=O), 145.12, 115.10, 79.85, 51.54, 20.54, 13.28. IR (KBr, ν (cm^{-1})): 3376, 1723. MS *m/z* (relative intensity): 212 ($M^{\bullet+}$, absent), 144 (8), 69 (96), 53 (8), 41 (100).

2i: ^{1}H NMR (200 MHz, $(CD_3)_2CO$): δ (ppm): 10.29 (OH), 4.87–4.79 (m, CH_2), 2.75–2.71 (m, CH_2), 2.12–2.04 (m, CH_2), 0.94 (t, CH_3, $J = 7.3$). ^{13}C NMR (50.3 MHz, $(CD_3)_2CO$): δ (ppm): 171.93 (C=O), 150.17 (C=O), 145.11, 114.33, 76.65, 47.39, 30.19, 12.44. IR (KBr, ν (cm^{-1})): 3382, 1724. MS *m/z* (relative intensity): 212 ($M^{\bullet+}$, 15), 144 (31), 70 (27), 69 (100), 55 (73), 41 (96).

2j: ^{1}H NMR (200 MHz, $(CD_3)_2CO$): δ (ppm): 5.50 (bs, CH), 3.10 (m, CH), 2.20–2.04 (m, CH_2), 1.78 (s, CH_3). ^{13}C NMR (50.3 MHz, $(CD_3)_2CO$): δ (ppm): 171.62 (C=O), 150.35 (C=O), 138.35, 131.29, 78.84, 59.23, 31.24, 26.86, 16.78. IR (KBr, ν (cm^{-1})): 3392, 1720. MS *m/z* (relative intensity): 224 ($M^{\bullet+}$, 2), 144 (5), 81 (100), 80 (14), 79 (31), 41 (20).

2k: ^{1}H NMR (200 MHz, $(CD_3)_2CO$): δ (ppm): 5.16 (bs, CH), 3.27 (m, CH), 2.20–2.11 (m, CH_2), 2.20–2.04 (m, CH_2), 1.68 (s, CH_3). ^{13}C NMR (50.3 MHz, $(CD_3)_2CO$): δ (ppm): 172.34 (C=O), 150.35 (C=O), 146.78, 121.43, 80.58, 57.30, 36.70, 24.81, 16.78. IR (KBr, ν (cm^{-1})): 3392, 1720.

MS *m*/*z* (relative intensity): 224 ($M^{\bullet+}$, 2), 144 (5), 81 (100), 80 (14), 79 (31), 41 (20).

2l: ^{1}H NMR (200 MHz, $(CD_3)_2CO$): δ (ppm): 5.16 (bs, CH), 5.50 (bs, CH), 2.20–2.11 (m, CH_2), 1.24 (s, CH_3). ^{13}C NMR (50.3 MHz, $(CD_3)_2CO$): δ (ppm): 170.95 (C=O), 150.35 (C=O), 131.44, 121.53, 81.59, 37.54, 22.55. IR (KBr, ν (cm^{-1})): 3392, 1720. MS *m*/*z* (relative intensity): 224 ($M^{\bullet+}$, 2), 144 (5), 81 (100), 80 (14), 79 (31), 41 (20).

2m: ^{1}H NMR (200 MHz, $(CD_3)_2CO$): δ (ppm): 5.50 (bs, CH), 2.80 (s, CH_2), 2.20–2.11 (m, CH_2), 1.78 (m, CH_2). ^{13}C NMR (50.3 MHz, $(CD_3)_2CO$): δ (ppm): 171.73 (C=O), 150.35 (C=O), 137.38, 131.44, 76.35, 42.68, 36.34, 32.99, 24.30. IR (KBr, ν (cm^{-1})): 3392, 1720. MS *m*/*z* (relative intensity): 224 ($M^{\bullet+}$, 2), 144 (5), 81 (100), 80 (14), 79 (31), 41 (20).

2n: ^{1}H NMR (200 MHz, $(CD_3)_2CO$): δ (ppm): 5.03 (bs, CH_2, 1H), 4.83 (bs, CH_2, 1H), 3.1 (m, CH), 2.20–2.11 (m, CH_2). ^{13}C NMR (50.3 MHz, $(CD_3)_2CO$): δ (ppm): 171.62 (C=O), 150.35 (C=O), 110.75, 79.01, 53.93. IR (KBr, ν (cm^{-1})): 3392, 1720. MS *m*/*z* (relative intensity): 224 ($M^{\bullet+}$, 2), 144 (5), 81 (100), 80 (14), 79 (31), 41 (20).

2o and **2p:** Evidences for the formation of these products are ^{1}H NMR (200 MHz, $(CD_3)_2CO$): δ (ppm): 9.43 and 9.40 (OH), 7.99–7.42 (m), 3.00–9.90 (m), 2.49 (q, J = 7.1). ^{13}C NMR (50.3 MHz, $(CD_3)_2CO$): δ (ppm): 170.37 and 170.26 (C=O), 152.45, 152.38, 151.53 (C=O), 100.20, 100.02, 86.26, 80.70, 73.67, 70.98.

Products **2d**, **2f–i** and **2m** were already reported by Bryon Gill and coworkers [24,25] upon thermal reaction of alloxan and 3-methyl-1-butene (**2d**), 2-methyl-1-butene (**2f**, **2g** and **2i**), 2-methyl-2-butene (**2h**) and methylenecyclopentane (**2m**).

*3.5. Spectroscopic and spectrometric data for **3** and **4***

3.5.1. General features

Owing to the presence of the 5,5-spirooxetane moiety in the barbituric acid derivatives **3**, NMR signals within the following ranges were observed: δ_C (ppm): 172–170 (C-4,6), 151–149 (C-2) and 85–82 (C-5). For the dioxene moiety in **4** signals within the following ranges were observed: δ_C (ppm): 178–176 (C-6), 170–167 (C-4,5), 153–152 (C-2).

3a: ^{1}H NMR (200 MHz, $(CD_3)_2CO$): δ (ppm): 5.72 (m, CH), 3.95 (m, CH_2), 2.52–2.43 (m, CH), 2.04 (m, CH_3), 1.11 (m, CH_3). ^{13}C NMR (50.3 MHz, $(CD_3)_2CO$): δ (ppm): 170.00 (C=O), 150.00 (C=O), 102.97/102.78, 82.73, 36.30, 33.33. IR (KBr, ν (cm^{-1})): 1713, 1310–934. MS *m*/*z* (relative intensity): 228 ($M^{\bullet+}$, absent), 173 (6), 100 (21), 86 (79), 58 (41), 43 (100).

4a: ^{1}H NMR (200 MHz, $(CD_3)_2CO$): δ (ppm): 4.83 (d, CH, J = 3.5)/4.72 (d, CH, J = 3.1), 4.20–4.00 (m, CH), 3.52–3.50 (m, CH_2), 1.20–1.00 (m, CH_3). ^{13}C NMR (50.3 MHz, $(CD_3)_2CO$): δ (ppm): 168.24 (C=O), 152.21 (C=O), 96.91/96.20, 66.96/66.90, 16.65, 9.00. IR (KBr, ν (cm^{-1})): 1712, 1306–1056. MS *m*/*z* (relative intensity): 228 ($M^{\bullet+}$, 26), 86 (100), 58 (71), 57 (32).

4b: ^{1}H NMR (200 MHz, $(CD_3)_2CO$): δ (ppm): 4.60–4.70 (m, CH), 3.90–3.82 (m, CH)/3.70–3.52 (m, CH), 3.52–3.50 (m, CH_2), 1.20–1.00 (m, CH_3). ^{13}C NMR (50.3 MHz, $(CD_3)_2CO$): δ (ppm): 169.71 (C=O), 152.21 (C=O), 98.72, 86.26, 64.61/64.33, 16.85, 7.27. IR (KBr, ν (cm^{-1})): 1712, 1306–1056. MS *m*/*z* (relative intensity): 228 ($M^{\bullet+}$, 26), 86 (100), 58 (71), 57 (32).

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