Synthesis and Evaluation as a Visible-Light Polymerization Photoinitiator of a New Eosin Ester with an *O*-Benzoyl-α-oxooxime Group

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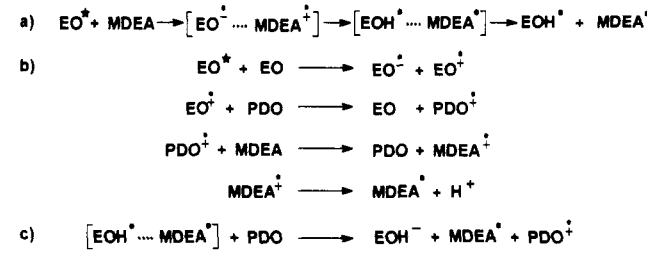
Introduction. The use of dyes as light-absorbing components in photoinitiator systems for radical polymerization under visible-light irradiation is of interest to many research groups.[1-6] These systems are safer when compared with those sensitive to ultraviolet light and in many cases offer clear economic and technological advantages. For example, systems sensitive to visible light allow the use of modern commercial lasers emitting above 400 nm, because most dyes described as photoinitiators exhibit very high molar absorption coefficients at these wavelengths. In addition, it is easy to adjust the system to specific sensitivity ranges by the appropriate choice of the visible-absorbing compound or mixture of compounds. Nevertheless, examination of the available literature on the actual applications of these visible "photopolymer systems" indicates that they have not received widespread attention. However, they have been successfully employed for the obtention of holographic optical elements[7] and for real-time holographic interferometry[8] because, in some cases, they can reach high diffraction efficiencies and high signal-to-noise ratios.[9]

Halogenated xanthene dyes such as Eosin or Rose Bengal, in combination with electron donors such as an iodonium salt or an amine, act as efficient visible-light photoinitiators for the polymerization of acrylic monomers.[1,5,6] Mixtures of these dyes, electron donors, and monomers are active at the emission frequencies of commercial Ar^+ and He–Ne lasers and can be used as photoinitiators even in the presence of oxygen. During the process the dye usually bleaches so that fading of the color can be related to the degree of polymerization. The accepted primary photochemical mechanism includes an electron–proton transfer from the donor to the excited dye which gives rise to active donor radicals which can actually initiate chain polymerizations.

In recent years, it has been observed that photopolymer systems containing xanthene dyes show an increase in their polymerization rates when irradiated with visible light in the presence of aromatic carbonyl compounds such as benzophenones, benzoins, or benzils. These compounds are currently used as type I UV photoinitiators. The mechanism of this interesting effect is not fully understood. Working with mixtures of Eosin (EO), *N*-methyldiethanolamine (MDEA), and the UV photoinitiator ethyl 1-phenyl-1-oxopropan-2-iminyl carbonate (PDO), Fouassier and Chesneau[10] found rates that were 2–3 times those observed upon irradiation of the same system but in the absence of PDO. They proposed that this sensitivity enhancement is a consequence of an increase in the production of amine initiator radicals, MDEA•, suggesting

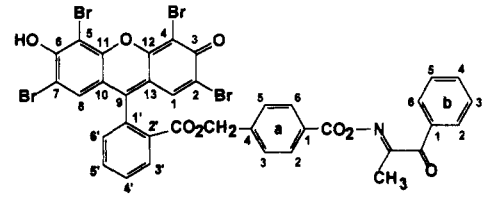
Scheme 1



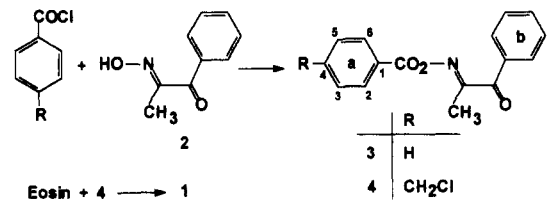
that, in the presence of PDO, besides the accepted electron-proton transfer from amine to dye (reaction a, Scheme 1), there is another process in which this carbonate behaves as an intermediate in the transfer, an electron passing first from the PDO to the semioxidized dye and then another from the amine to the semioxidized PDO (reaction b). A critical analysis of these results prompted Neckers and Valdes-Aguilera[5] to propose that the reaction between the radical pair (semireduced dye...semioxidized amine) and PDO (reaction c) must be an additional source of initiating amine radicals.

To obtain more information about the role played by the carbonyl compound in the irradiated mixture, a different approach would be to evaluate a molecule containing both chromophores: that of the xanthene dye and that of the *O*-acyl-α-oxooxime. Such a compound would produce higher polymerization rates than the 1:1 mixture dye/acyloxime when irradiated in the presence of a monomer and under comparable conditions, because intramolecular electron–proton transfer between both chromophores must be much faster than the corresponding intermolecular reaction.

In this paper, we report the synthesis of a new Eosin ester possessing an *O*-benzoyl-α-oxooxime group in the C-2′ carboxylate (1).



COMPOUND 1



The parent Eosin benzyl ester can be easily obtained by the reaction of the dye (disodium salt) with benzyl chloride.[11] The behavior of the new ester 1 as a photoinitiator for the polymerization of 2-hydroxyethyl methacrylate (HEMA) has been studied using differential scanning photocalorimetry (DSPC). A photopolymerizable mixture containing the dye 1, HEMA, MDEA, and ethylene glycol dimethacrylate (EGDMA) has also been evaluated as a photosensitive recording material for holography.

Results and Discussion. The comparative study of the photoinitiators was mainly carried out by DSPC. Solutions of each dye in HEMA with total absorption at

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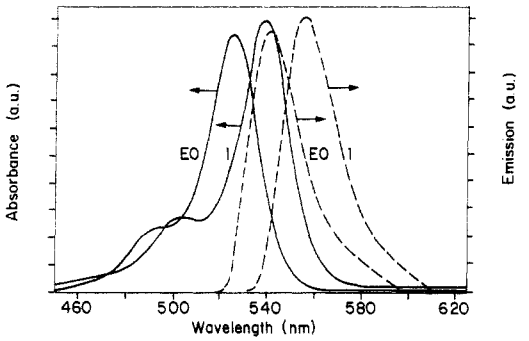

Figure 1. Absorption (—) and uncorrected emission (– –) spectra of Eosin (EO) and its ester 1, in acetonitrile solution (arbitrary concentrations) at room temperature.

Table 1. Polymerization Rates (R_p) of Visible Photoinitiator Systems, Determined by DSPC (Solutions in HEMA; Dye Concentration *ca.* 5×10^{-4} M; Irradiation with 525-nm Light; Total Absorption)

	$R_p \times 10^4$ (M·s^{-1})[a]	
initiator	without MDEA	with MDEA[b]
EO	2.2	3.6
EO+3 (1:1)	4.6	6.3
1	4.9	16.3

[a] Average values of at least two experiments, estimated error ±0.2 × 10^{-4} M·s^{-1}. [b] [MDEA] = 5×10^{-3} M.

525 nm were irradiated under identical conditions. Although both Eosin and its ester 1 have maximum absorption in solution in the monomer HEMA at 531 and 541 nm, respectively (in acetonitrile at 527 and 540 nm; Figure 1), they also present high absorptions at 525 nm, the wavelength of maximum transmittance of the filter used in the DSPC experiments. The polymerization rates obtained are shown in Table 1. As can be observed, compound 1 behaves as a faster photoinitiator when compared to EO or the 1:1 mixture EO+3, both in the absence and in the presence of an excess of MDEA. The polymerization rates obtained with EO+3 are approximately double those of EO alone, thus in accordance with the results already cited.[10] As expected, the presence of MDEA always produces an increase in the polymerization rate, which is remarkably higher in the case of compound 1.

These DSPC results provide information about the primary photochemical mechanism involved. It is interesting to note that EO behaves as a photoinitiator even in the absence of benzoyloxime or amine, indicating that the monomer HEMA takes part in the mechanism of primary free-radical generation, as was observed in previous work with the same monomer and the dye succinylfluorescein by our group[12] and in similar systems by other groups.[2] In the absence of amine, the mixture EO+3 behaves almost like ester 1 (Table 1), demonstrating that the proximity in the same molecule of Eosin and *O*-benzoyl-α-oxooxime groups hardly influences the polymerization rate. If the primary photoreaction were an electron transfer from the benzoyloxime chromophore to the semioxidized Eosin group, a much higher rate would be expected for ester 1. Moreover, the shapes of the absorption and fluorescence emission spectra of 1 are similar to those of the corresponding spectra of both EO (Figure 1) and the mixture EO+3, suggesting that possible intramolecular charge-transfer complexes are not formed in the ground state nor upon excitation. However, as the presence of free or bound *O*-benzoyl-α-oxooxime does increase the R_p value, it is reasonable to think that this chromophore favors the generation of initiating radicals

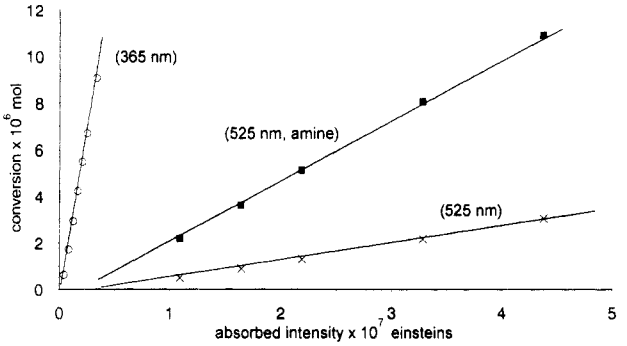

Figure 2. Evaluation of ester 1 as a photoinitiator by differential scanning photocalorimetry (DSPC), under irradiation with 365 or 525 nm and in the presence or the absence of the amine MDEA (see Table 1). Conversions <10%.

by a still unknown mechanism where the distance between the two chromophores does not seem to be the limiting condition.

The primary mechanism must be different in the presence of amine. In this case ester 1 generates radicals at a higher rate than the mixture EO+3 under comparable conditions. Assuming that the reaction rates of the excited dyes EO and 1 with MDEA are similar, the important increase in the R_p value obtained with ester 1 must be a consequence of the *proximity* of the two chromophores. This fact strongly supports the existence of a primary photoreaction between the excited dye and the amine, giving a radical pair which, in the presence of the benzoyloxime chromophore, in the medium, or, better, in the same molecule, gives rise to more initiating amine radicals, in accordance with the mechanism previously proposed (reaction c, Scheme 1).[5]

Compound 1 also photoinitiates the polymerization of HEMA under irradiation with UV light (365 nm) and in the absence of amine. In these conditions, its polymerization quantum yield (Φ_m), determined from DSPC data (Figure 2), is 300 ± 50 mol·einstein^{-1}, while that obtained under visible (525-nm) irradiation, also in the absence of amine, is much lower, 6 ± 2 mol·einstein^{-1} (23 ± 2 mol·einstein^{-1} in the presence of the amine MDEA). Thus compound 1 is a more efficient photoinitiator under UV irradiation. Nevertheless, benzoyloxime 3 remains the best photoinitiator under irradiation with 365-nm light and in the absence of amine, with a Φ_m value of 2500 ± 400 mol·einstein^{-1}. On the other hand, since in HEMA solution the molar absorption coefficient at 365 nm of ester 1 (2540 mol·L^{-1}·cm^{-1}) is much higher than that of benzoyloxime 3 at the same wavelength (54 mol·L^{-1}·cm^{-1}), with the former it is possible to reach polymerization rates similar to those achieved with the latter, but working with lower concentrations. The dual behavior of ester 1 as an UV and visible photoinitiator allows for its use in panchromatic processes of potential utility.

The former photoinitiator systems, with ester 1 and with the mixture EO+3, were also tested as photopolymer recording materials for holography. The results obtained (Figure 3 and Table 2) also indicate that, in the presence of MDEA, compound 1 is a much better photoinitiator than EO or the mixture EO+3. Working with compound 1, a maximum diffraction yield of 72% was obtained, a value similar to those reached with the other two systems but achieved in less time, thus employing less energy (E). The inhibition time (t_i), or time during which the diffraction yield of the irradiated mixture is null, is inversely related to the efficiency of the system in the elimination of the dissolved oxygen, through direct reaction with the generated radicals or through the formation of singlet

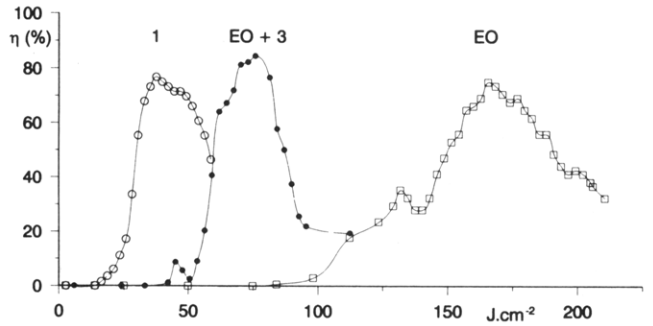

Figure 3. Evaluation of visible-light-sensitive photopolymers as holographic recording systems. Change of the diffraction yield (η) with the absorbed energy (E) (see Table 2).

Table 2. Holographic Evaluation of Visible Photoinitiator Systems (Solutions in 1:1 (v/v) HEMA–EGDMA; Dye Concentrations, 1.5×10^{-3} M (EO) and 2×10^{-3} M (Ester 1); Molar Ratio MDEA/dye 10:1; Irradiation with 514-nm Light; t_i = Initiation Time; E = Recording Energy for Maximum Diffraction Yield; η_{max} = Maximum Diffraction Yield)

initiator	t_i (min)	E (J·cm^{-2})	η_{max} (%)
EO	30	166	71
EO+3 (1:1)	15	76	78
1	7	37	72

molecular oxygen and subsequent reaction with the unsaturated monomers in the medium.[13] The new photoinitiator 1 is more sensitive than EO or the mixture EO+3: about 4 times or double, respectively. An additional advantage is the comparatively higher stability of the final gratings recorded with ester 1. Final diffraction yields of 41% (ester 1) and 17% (EO+3) (Figure 3) dropped, after 90 days of storage in the dark, to 22% and 7%, respectively.

In conclusion, the results obtained with ester 1 indicate that this compound is a very efficient visible-light photoinitiator and that systems containing it can be used for the formulation of new and very promising "photopolymers" as recording materials for holography.

Experimental Section. Materials. Commercial samples (Aldrich) of Eosin (EO) and (*E*)-1-phenyl-2-(hydroxyimino)-1-propanone (2) were used without further purification. Monomers HEMA (Alcolac) and EGDMA (Merck) were vacuum-distilled under nitrogen. *N*-Methyldiethanolamine (MDEA; Aldrich) was dried and distilled.

Spectroscopy. Absorption and emission spectra were measured respectively on a Perkin-Elmer Lambda-2 spectrophotometer and on a SLM 8000D digital fluorimeter. IR spectra were recorded in a Perkin-Elmer 681 spectrophotometer. Mass spectra (MS) were obtained on a VG 12-250 spectrometer with an electron impact at 70 eV or on a high-resolution VG AutoSpec (HRMS) apparatus for fast atom bombardment (FAB, beams of Cs) in a *m*-nitrobenzyl alcohol matrix. Nuclear magnetic resonance (NMR) spectra were registered on a Varian-Gemini spectrometer (200 MHz) with tetramethylsilane as the internal reference.

Differential Scanning Photocalorimetry (DSPC). Bulk photopolymerizations were studied in a homemade DSPC apparatus previously described.[14,15] The monomer HEMA was used because the photoinitiator systems under study are soluble in this ester and because at the working temperature (40 °C) its vapor pressure is very low. Solutions (30 μL) in HEMA of each dye (5×10^{-4} M, total absorption at 525 nm for a path length of 1 mm) in the absence, or in the presence, of MDEA (molar ratio MDEA/dye 10:1) were irradiated at 40 °C under a nitrogen atmosphere using visible cold light from a Schott KL-1500 source, filtered by a Schott VG 9 filter (maximum transmission at 525 nm). For UV irradiations, the light from a Hanovia Uvitron irradiation system containing a Hanovia OX-1 filter (maximum transmission at 365 nm) was used. In both cases, the light intensities reaching the samples were in the range 1.2×10^{-9}–2.0×10^{-9} einsteins·s^{-1}. The DSPC technique provides direct information on the rate of heat emission during polymerization by irradiation. The temporal change of the degree of monomer polymerization was obtained by integration, using suitable software, of the calorimetric trace in the range 15–120 s, a time zone in which the rate is constant (conversions <10%), and by taking into account the heat for total HEMA polymerization (11.9 kcal·mol^{-1}).[16] Polymerization rates were calculated from the slope of the profiles conversion *vs* time, using a least-squares approach. Polymerization quantum yields (Φ_m, ratio of polymerized molecules/absorbed photons) can also be determined when the light absorbed by the samples is known.

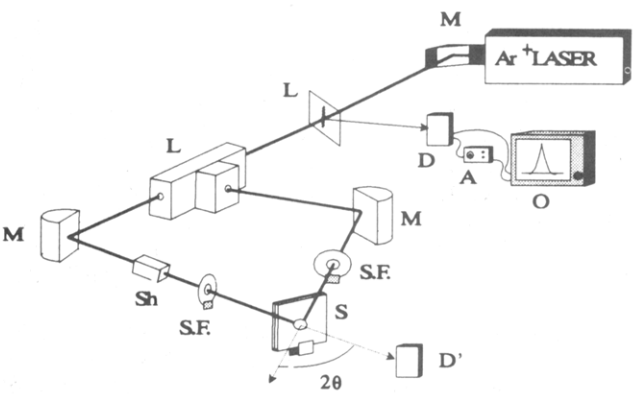

Figure 4. Experimental setup for recording diffraction gratings. M, mirror; L, beam splitter; D, scanning interferometer; A, amplifier; O, oscilloscope; Sh, shutter; S.F., spatial filter; S, sample; D′, detector.

Holography. Solutions of 1, or of the 1:1 mixture EO+3 (dye concentration in the range 1.5×10^{-3}–2.0×10^{-3} M), in the 1:1 (v/v) monomer mixture HEMA–EGDMA (the presence of EGDMA allows for higher refractive index changes), with coinitiator MDEA (molar ratio MDEA–dye 10:1), were placed between two 10 × 10 cm square glass plates with a separator ($\approx$45 μm) and fixed on an antivibrating table. The solutions (70% transmittance at 514 nm) were irradiated with light intensities in the range 1.3×10^{-7}–1.9×10^{-7} einsteins·s^{-1} as shown in the holographic system in Figure 4.[12,13] The light (514 nm) from an Ar^+ laser (Spectra Physics 2030; 20 W, coherence length > 4 m) was divided by a beam splitter (L) into two identical beams, which were made to interfere in the mixture under study. The stability coherence length during the exposure was evaluated with a scanning interferometer. The light of one of the beams diffracted in the direction of the detector D′ was measured in real time when a shutter closed the other beam. The photopolymerization progress is expressed as the diffraction yield (η), defined as the ratio between the intensities of diffracted and incident lights.

Synthesis of (*E*)-1-Phenyl-2-[(benzoyloxy)imino]-1-propanone (3).[17] Benzoyl chloride (11 mmol) was added dropwise to a stirred solution of the monooxime 2 (10 mmol) and triethylamine (11 mmol) in dry acetone (20 mL) at 0 °C. The reaction mixture was then left at room temperature for 2 h and, after vacuum evaporation, the residue was crystallized in hexane. Mp: 71–72 °C. Yield:

87%. IR (KBr): ν_{max} 1760 (vs), 1680 (s) cm^{-1}. MS: *m/z* (%) 267 (M^+, <1), 226 (6), 198 (20), 105 (100). UV (CH_3CN): λ_{max} (ϵ) 243 nm (19 200 $M^{-1}\cdot cm^{-1}$). ^1H NMR ($CDCl_3$): δ 2.44 (s, 3H, CH_3), 7.51–7.53 (m, 4H, H-3a/H-5a and H-3b/H-5b), 7.63 (m, 1H, H-4a or H-4b), 7.66 (m, 1H, H-4b or H-4a), 8.13 and 8.20 (m, 4H, H-2a/H-6a and H-2b/H-6b). ^{13}C NMR ($CDCl_3$): δ 13.1 (CH_3), 128.3 (C-1a), 128.5, 128.7, 129.8, 131.0 (C-2a/C-6a, C-2b/C-6b, C-3a/C-5a, and C-3b/C-5b), 133.8, 133.9 (C-4a and C-4b), 134.9 (C-1b), 162.0, 163.1 (*C*=N and *C*O ester), 189.9 (*C*O ketone).

Synthesis of (*E*)-1-Phenyl-2-[[*p*-(chloromethyl)benzoyloxy]imino]-1-propanone (4). It was similarly obtained from the reaction between monooxime 2 and freshly prepared *p*-(chloromethyl)benzoyl chloride (from *p*-methylbenzoyl chloride and phosphorus pentachloride).[18] It was purified by crystallization in hexane. Mp: 98–99 °C. Yield: 97%. Anal. Calcd for $C_{17}H_{14}ClNO_3$: C, 64.67; H, 4.47; N, 4.44; Cl, 11.23. Found: C, 64.31; H, 4.60; N, 4.71; Cl, 11.54. IR (KBr): ν_{max} 1740 (vs), 1665 (s). MS: *m/z* (%) 315 (M^+, <1), 280 (6), 155 (96), 153 (100), 105 (95) UV (CH_3CN): λ_{max} (ϵ) 248.5 nm (27 300 $M^{-1}\cdot cm^{-1}$). ^1H NMR ($CDCl_3$): δ 2.43 (s, 3H, CH_3), 4.64 (s, 2H, CH_2Cl), 7.47–7.57 (m, 4H, H-3a/H-5a and H-3b/H-5b), 7.62 (m, 1H, H-4b), 8.11 and 8.18 (m, 4H, H-2a/H-6a and H-2b/H-6b). ^{13}C NMR ($CDCl_3$): δ 13.2 (CH_3), 45.1 (CH_2Cl), 128.1, 128.5, 128.8, 130.2, 131.0 (C-1a, C-2a/C-6a, C-2b/C-6b, C-3a/C-5a, and C-3b/C-5b), 134.0 (C-1b), 134.7 (C-4b), 143.2 (C-4a), 162.1, 162.6 (*C*=N and *C*O ester) and 189.9 (*C*O ketone).

Synthesis of Eosin (*E*)-*p*-[[(1-Phenyl-1-oxopropan-2-iminyl)oxy]carbonyl]benzyl Ester (1). A solution of ester 4 (1 mmol) and Eosin (0.8 mmol) in *N,N*-dimethylformamide (20 mL) was maintained with stirring for 4 days at 50 °C under an inert atmosphere and darkness. The subsequent workup yielded a solid which was purified by flash chromatography (silica gel, methylene chloride–ethanol 95:5 (v/v) as eluent). The final solid (red crystals) was washed with hexane and dried in vacuum. Mp: >300 °C. Yield: 60%. The dye was used without further purification because some decomposition occurred on heating. It gave a single spot on thin layer chromatography plates with several eluents. Their solutions were handled under poor, diffuse illumination or almost in the dark. IR (KBr): ν_{max} 3400 (m), 1755 (vs), 1720 (vs), 1685 (s), 1555 (s). MS (FAB): *m/z* 972 $[M + 2Na-H]^+$, 950 $[M + Na]^+$. UV (CH_3CN): λ_{max} (ϵ) 540.6 nm (138 700 $M^{-1}\cdot cm^{-1}$). ^1H NMR (acetone-d_6): δ 2.54 (s, 3H, CH_3), 5.10 (s, 2H, CH_2), 7.17 (d, J = 8.3 Hz, 2H, H-3a/H-5a), 7.26 (s, 2H, H-1/H-8), 7.54–7.60 (m, 3H, H-6′, H-3b/H-5b), 7.71 (t, J = 7.4 Hz, 1H, H-4b), 7.86–8.00 (m, 4H, H-4′, H-5′, and H-2a/H-6a), 8.21 (dd, J = 8.2 and 1.3 Hz, 2H, H-2b/H-6b) and 8.38 (dd, J = 7.0 and 1.7 Hz, 1H, H-3′). ^{13}C NMR (acetone-d_6): δ 13.7 (CH_3), 67.2 (CH_2), 100.79 (C-4/C-5), 110.61 (C-2/C-7), 119.65 (C-10/C-13), 128.9, 129.1, 129.2, 129.8, 130.2, 130.7, 131.2, 131.6, 131.7, 131.9, 133.7, 134.6, 135.0, 136.2 (C-1/C-8, carbons of "a" nucleus plus C-2b/C-6b, C-3b/C-5b, C-4b, and C-1′ to C-6′), 141.6 (C-1b), 151,4 (C-9), 154.1 (C-11/C-12), 163.0, 163.5, 166.0, 169.7 (C-3/C-6, *C*=N, CO_2C, and CO_2N) and 191.1 (*C*O ketone).

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