gave the ketone (0.15 g.), m.p. 144–145°, undepressed on admixture of natural sintaxanthin, and both samples displayed the same thin layer chromatographic behavior: λ_{max} in n-hexane at 425 (sh), 448, and 473 mμ, in benzene (at 436 (sh), 462, and 485 (sh) mμ. The n.m.r. spectrum (signals at τ 7.72, 8.01, 8.10, 8.27, and 8.97) is in full accord with structure III. The infrared spectrum was superimposable on that of the natural sample.

Anal. Calcd. for $C_{31}H_{42}O$: C, 86.45; H, 9.83. Found: C, 86.5; H, 9.72.

The oxime had m.p. 203–204°. The substance did not depress the melting point of oxime of natural sintaxanthin.

Reduction of Natural Sintaxanthin.—Reduction of the naturally occurring sintaxanthin (40 mg.) in the usual manner[7] with sodium borohydride, removal of the catalyst and solvent, and chromatography of the carotenoid mixture on a column of Microcel C afforded the reduced product, m.p. 117–118°, undepressed on admixture of synthetic sample, and both samples exhibited the same thin layer chromatographic behavior. The visible, n.m.r., and infrared spectra were identical with those of the synthetic sample (II).

Iodine Catalysis of Natural Sintaxanthin.—A solution of sintaxanthin (0.1 mg.) in n-hexane (5 ml.) containing a trace of iodine, was irradiated under a 100-w. lamp for 1 hr. The mixture was washed with 5% sodium thiosulfate solution and water and dried over anhydrous sodium sulfate, and the visible spectrum was determined. A hypsochromic shift of *ca.* 4 mμ in the absorption maxima, accompanied by 16% decrease in extinction value of the main absorption peak, was observed.

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Photochemical Hydrogen Abstraction by the Nitro Group

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The lowest lying singlet and triplet excited states of simple aromatic nitro compounds have been shown to have their origin in an $n \rightarrow \pi^*$ transition.[1,2] This suggests that the photochemistry of these compounds might prove to be analogous to the reactions observed for ketones having lowest lying n–π^* excited states.

One photochemical process which is particularly well documented as characteristic of such ketones is the abstraction of a hydrogen atom by the carbonyl oxygen. There is, in fact, considerable evidence in the literature which suggests that the nitro group, upon irradiation, also can abstract hydrogen atoms. Thus, the photochromic nature of nitro aromatics has been extensively studied[3] and spectral data presented implicating *aci*-nitro tautomers as the colored species. In addition, a number of photochemical rearrangements of nitro compounds have been rationalized by postulating an initial hydrogen abstraction step.[4] Despite the considerable volume of data, however, a definitive, chemical demonstration of hydrogen abstraction by the nitro group has been lacking; the frequency with which such a step is invoked in mechanistic rationales makes such an unambiguous demonstration all the more desirable. It was towards this goal that the experiments below were directed.

o-Nitrotoluene, dissolved in a mixture of deuterium oxide and p-dioxane, was irradiated through a Pyrex filter for 48 hr. The solvent was removed and starting material was recovered by molecular distillation and preparative v.p.c. The infrared spectrum of the recovered material was characterized by the appearance of a new doublet centered at 4.3 μ (C–D stretch) and by the marked decrease in intensity of a peak at 11.7 μ. Examination of the n.m.r. spectrum revealed that an average of 1.6 deuterium atoms/molecule had been incorporated into the methyl group. The mass spectrum gave the following isotopic composition: no deuteration, 10%; monodeuterated, 33%; dideuterated, 40%; and trideuterated, 17%.

No exchange was observed in the dark under comparable conditions. Furthermore, the possibility of exchange owing to some photolytically produced catalyst was eliminated by irradiating the o-nitrotoluene for 24 hr., removing half of the solution, and allowing the remainder to stand in the dark for 48 hr. Work-up of both solutions gave o-nitrotoluene with identical incorporation (0.79 deuterium atoms/molecule). Finally, the intramolecular nature of the abstraction process was demonstrated by irradiating p-nitrotoluene in a deuterium oxide–p-dioxane solution for 48 hr. The recovered starting material was examined by infrared, n.m.r., and mass spectroscopy; the spectra obtained gave no evidence for any incorporation of deuterium.

Experimental Section

All photolyses were conducted under an atmosphere of nitrogen using a 450-w. Hanovia high-pressure immersion lamp and a cylindrical Pyrex filter. Infrared spectra were obtained from a Beckman IR-8, n.m.r. spectra from a Varian A-60 using tetramethylsilane as an internal standard. Mass spectra were recorded on a Bendix time-of-flight mass spectrometer.

Photolysis of o-Nitrotoluene.—A solution of o-nitrotoluene (1.0 g.) in 10.0 ml. of D_2O (Columbia Organic Chemical Co., 99.5%) and 110 ml. of p-dioxane (Matheson Coleman and Bell, Spectrograde) was irradiated for 48 hr. The solvent was removed and the residue, upon molecular distillation (80° and 0.6 mm.), afforded 0.35 g. of o-nitrotoluene. Further purification was effected by preparative v.p.c. on a Carbowax 20M 10 ft. × $^3/_8$ in. column at 200°. The o-nitrotoluene thus prepared was shown to be 98.5% pure by v.p.c. N.m.r. absorptions were at δ 2.57, 7.38, and 7.88 (relative area, 1.4:3.0:0.8). The mass spectrum had peaks at 137, 138, 139, and 140 (relative areas, 1.0:3.4:4.0:1.8).

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