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pH DEPENDENT PHOTOTRANSFORMATION OF ATROPINE

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ABSTRACT

Photolysis of atropine by UV light at different pH gave different products. At pH 3, it gave carbon dioxide, ditropane (II) and 1,4–dihydroxy–2,3–diphenylbutane (III); at pH 9 it gave a α–diketone (IV) and tropane peroxide (V) and at pH 7, it gave tropine (VI), phenyl acetaldehyde (VII) and carbon monooxide. The structure of all the products have been confirmed by spectral data and elemental analysis.

Key words: Atropine, Phototransformation, pH Dependent

INTRODUCTION

Photochemistry of organic compounds has been a vast field of research. Phototransformation of almost all classes of compounds has been studied, but very few reports are there in the literature on the phototransformation of alkaloids[1–7]. Atropine is an important alkaloid with medicinal value. Therefore, in the present paper, we report the photochemical behaviour of atropine at different pH.

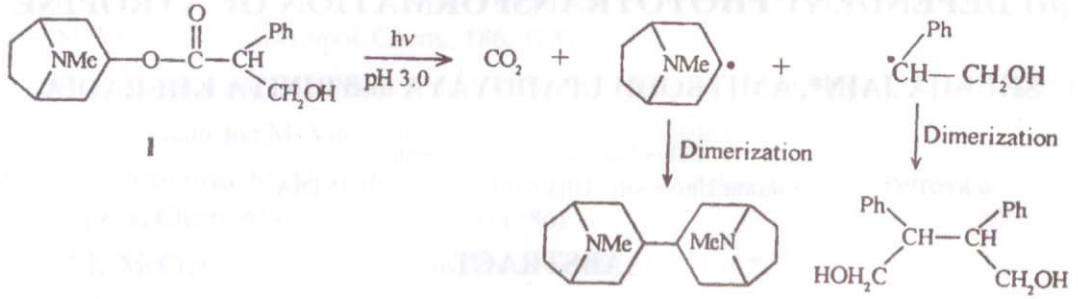
EXPERIMENTAL

An ethanolic solution of atropine (2 g) was taken in an all quartz immersion well photoreactor (SAIC make). Benzophenone (0.01 g) was added as sensitizer. The solution was then irradiated by 125 W medium pressure mercury vapour lamp fitted in the reactor. The progress of the reaction was monitored by TLC using butanol : acetic acid : water (9 : 3 : 5 v/v) solvent system. The irradiation was continued till the spot of atropine disappeared. Dil. HC1 and ethanolic NaOH solution were used to make the medium acidic and alkaline. The time of irradiation was 40 hr. at pH 7 and 50 hr. at pH 3 and 9.

RESULTS AND DISCUSSION

Irradiation of atropine by UV light in acidic medium (pH 3) gave ditropane (**II**) and 1,4–dihydroxy–2,3–diphenylbutane (**III**) and carbon dioxide as follows:

The spectral data of (II) are reported here :

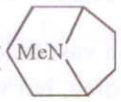


I II III

IR : 2970 and 2929 cm^{-1} (C–H stretching), 1450, 1379 cm^{-1} (C–H bending), 1083 cm^{-1} (C–N stretching) etc.

^{1}H NMR : δ 1.2–3.6 (series of multiples, alicyclic protons), and δ 3.8 (s, NCH_3 protons).

^{13}C NMR : δ 26–63 (alicyclic and N–CH_3 C atoms).

Mass : m/z 248 (M^+ peak), 233 ($M^+ - CH_3$), 219 (233–N), 191 (219–CH_2=CH_2), 165 (191–C_2H_2), 124 (

)

Spectral data of the product III are :

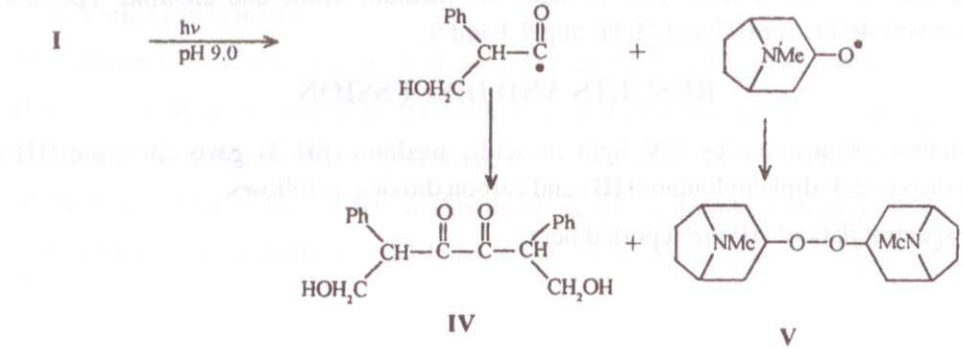
IR : 3438 cm^{-1} (OH stretching), 3030 cm^{-1} (C–H stretching aromatic), 2981 cm^{-1} (C–H stretching aliphatic), 1045, 875, cm^{-1} (C–H bending)

^{1}H NMR : δ 3.3 (m, CH protons), δ 3.6 (d, CH_2 protons), δ 4.0 (–OH protons) and δ 7.5–8.0 (aromatic protons).

^{13}CNMR : δ 45 (CH carbon), δ 60 (CH_2 carbon) and δ 120–125 (aromatic carbons).

Mass : m/z 242 (M^+ peak), 211 (M^+–CH_2OH), 210 (211–H), 225 (M^+–OH), 224 (M^+–H_2O), 121 ([$PhCHCH_2OH$]$^+$), 165 (M^+–Ph), 88(165–Ph)

UV irradiation of atropine in alkaline medium (pH 9.0) gave (**IV**) and (**V**) as follows:



IV V

Product IV gave following spectral data –

IR : 3423 cm^{-1} (O–H stretching), 3030 cm^{-1} (arom. C–H stretching), 2923, 2852 cm^{-1} (C–H stretching), 1700 cm^{-1} (C=O stretching), 1620 cm^{-1} (aromatic C=C str.).

^{1}H NMR : δ 3.2 (t, CH protons), δ 3.6 (d, CH_2 protons), δ 4.1 (–OH protons) and δ 7.1–7.5 (m, aromatic protons).

^{13}C NMR : δ 60 (CH carbon), δ 64 (CH_2 carbon), δ 125–130 (aromatic carbon) and δ 170 (carbonyl carbon).

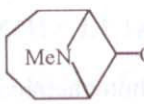
Mass : m/z 298 (M^+ peak), 281 (M^+ –OH), 280 (M^+ – H_2O), 268 (M^+–CH_2O), 267 (M^+–CH_2OH), 266 (267–H), 149 ([$PhCH(CH_2OH)CO]^+$), 148 (149–H), 120 (148–CO) etc.

Product (V) gave the following spectral data:

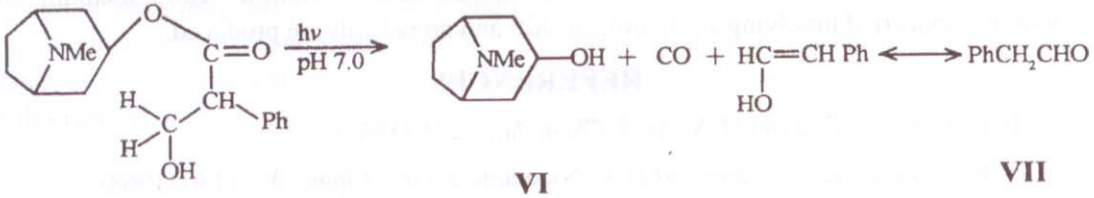
IR : 2925, 2856 cm^{-1} (aliphatic C–H stretch), 1150 cm^{-1} (C–O stretch), 880 cm^{-1} (O–O stretch).

^{1}H NMR : δ 1–2.8 (series of multiples for alicyclic protons) and 3.6 (s, NCH_3 protons).

^{13}C NMR : δ 22–58 (alicyclic carbons) and δ 62 (N–CH_3 carbon).

Mass : m/z 280 (M^+peak), 140 (), 124 (140–O), 112 (140–CO), 97 (112–CH_3), 96 (97–H), 82 (96–CH_2).

Atropine, when irradiated in neutral medium gave tropine (**VI**), phenylacetaldehyde (**VII**) and carbon monooxide as follows:



VI **VII**

Tropine (VI) gave following spectral data –

IR : 3219 cm^{-1} (O–H str.); 1265 and 1160 cm^{-1} (O–H bending and CO str.).

^{1}H NMR : δ 1.1–3.3 (m, alicyclic protons), 3.5(s, N–CH_3 protons) and 3.8 (–OH proton).

^{13}C NMR : δ 18–53 (alicyclic carbons), 55 (COH carbon) and 56 (–NCH_3 carbon).

Mass : m/z 141 (M^+ peak), 140 (M^+–H), 124 (M^+–OH or 140–CH_3), 112 (140–CO), 97 (124–HCN), 96 (124–CH_2CH_2).

Spectral data for phenyl acetaldehyde (VII) is as follows –

IR : 3000 cm^{-1} (C–H str. arom.), 2952 cm^{-1} (CH str. aliph.), 2833 and 2700 cm^{-1} (aldehyde C–H stretching), 1700 cm^{-1} (C=O stretch).

^1H NMR : δ 2.8 (CH_2 protons), δ 8.2–8.5 (aromatic protons) and 9.2 (CHO proton).

^{13}C NMR : δ 58 (CH_2 carbon), δ 125–130 (aromatic carbon atoms), δ 190 (carbonyl carbon).

The results of elemental analyses, yields and melting points of all the products are given in table 1.

Table 1.

Product	M.P.	Yield	% (C, H, N)	
			Calcd.	Found
II	Viscous Oil	0.5 g	C 77.42, H 11.29, N 11.29	C 77.58, H 11.39, N 11.20
III	25°C	0.4 g	C 79.34, H 7.44	C 79.44, H 7.64
IV	Viscous Oil	0.5 g	C 72.48, H 6.04	C 72.19, H 6.00
V	Viscous Oil	0.5 g	C 68.57, H 10.00, N 10.00	C 68.49, H 9.86, N 9.91
VI	Viscous Oil	0.6 g	C 68.09, H 10.64, N 9.93	C 67.99, H 10.52, N 9.83
VII	32°C	0.5 g	C 80.66, H 6.67	C 79.80, H 6.57

CONCLUSION

From the results, it is clear that the photochemical behaviour of atropine is different at different pH. It seems to be more susceptible at neutral pH as compared to acidic or alkaline pH as the time required for phototransformation is less in former condition as compared to latter. In all the three conditions, the molecule undergoes cleavage, in acidic and alkaline medium, it cleaves to produce radicals, which then undergo dimerization whereas in neutral medium, the reaction is concerted involving 1,4 hydrogen shift and no radicals are produced.

REFERENCES

1. F. R. Stermitz, Pua and H. Vyas, *J. Chem. Soc.*, 216 (1967).
2. F. R. Stermitz, R. P. Seiber and D. E. Nicodem, *J. Org. Chem.*, **33**, 1136 (1968).
3. G. Behnsen, L. Kuchn and R. Craft, *Pharmezie*, **27**, 734 (1972).
4. T. Majima and S. Arai, *J. Syn. Org. Chem. (Japan)*, **42**, 10, 912 (1984).
5. S. J. Atherton and B.B. Gaig, *Chem. Phy. Lett.*, **127**, 1, 7 (1986).
6. M. Hoshimo and H. Shezuka, *J. Phys. Chem.*, **91**, 714 (1987).
7. L. J. Johnston, J. Lobagh and V. Wintgens, *J. Phys. Chem.*, **93**, 7370 (1989).

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