

PHOTOXYGENATION STUDIES ON 2-OXAZOLIN-5-ONES

S. S. CHIBBER, S. K. DUTT AND SANGEETA PANDITA

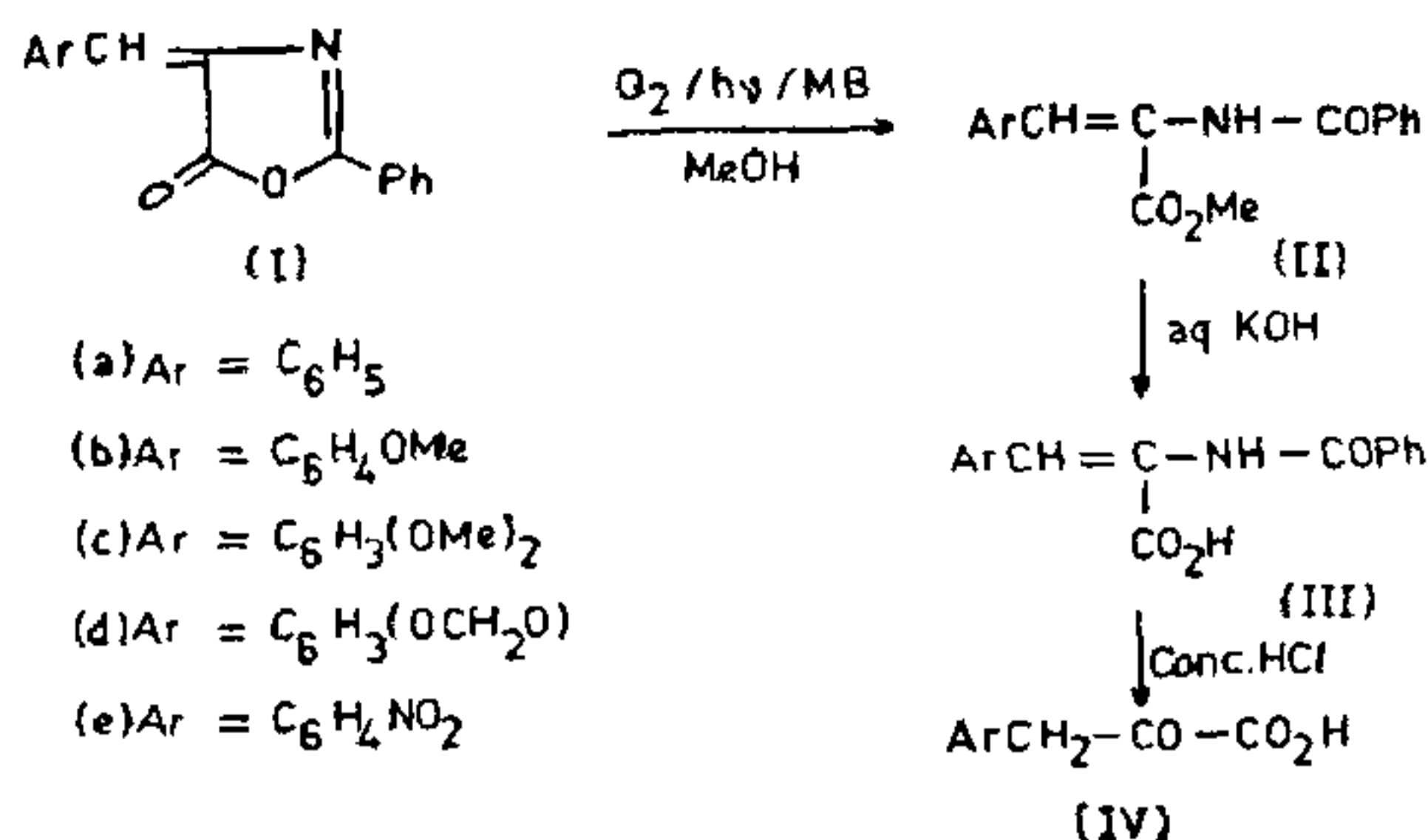
Department of Chemistry, University of Delhi, Delhi 110 007, India.

SINGLET oxygen in its reaction with heterocyclic compounds, is known to bring about novel types of transformations¹⁻⁵. The present study reports the reaction of singlet oxygen with a number of 2-oxazolin-5-ones containing a 4-arylidene group (unsaturated azlactones).

Azlactones, Ia⁶, Ib⁷, Ic⁸, Id⁹, and Ie¹⁰, prepared by the condensation of hippuric acid with different aromatic aldehydes were taken up for study. Each azlactone (100 mg) was dissolved in methanol containing a catalytic amount of the sensitizer (Methylene blue). The solutions, irradiated with a 100 W-tungsten lamp, were subjected to continuous air supply. The progress of each reaction was checked by TLC and stopped after the products reached a steady state. The reaction mixture was then worked up first by concentrating under reduced pressure and subsequently by extracting the residue with ether and ethyl acetate. The extracts were combined, concentrated and subjected to preparative-TLC (solvent system: benzene-ethyl acetate (1:1)) to obtain the products in pure, crystalline forms. It was found that each of the substrates (Ia-e) yielded a single photo-product (IIa-e). The time taken for each reaction varied from 6-10 hr.

4-Benzylidene-2-phenyloxazolin-5-one (Ia) gave photo-product (IIa) in 60% yield after 10 hr. It analysed for C₁₇H₁₅NO₃, m.p. 140°. Its mass spectrum showed M⁺ peak at m/e 281, which was 32 mass units greater than that of the parent azlactone (M⁺ 249). Its IR spectrum showed that the characteristic absorption bands of the azlactone disappeared viz 1800 cm⁻¹ for the carbonyl and 1650 cm⁻¹ for the C=N bond. Instead, it showed absorptions at 1710 and 1640 cm⁻¹ due to an α,β-unsaturated ester and secondary amide group, respectively. The NMR spectrum of the compound showed two additional peaks besides the characteristic peaks of the azlactone. A three-proton-singlet at δ3.79 was assigned to a methoxyl group, while a singlet at δ7.43 integrating for one proton indicated the presence of an amido (-CONH) proton.

The identity of compound IIa was confirmed by its saponification to give compound IIIa, m.p. 224°, which on acidification gave a compound, m.p. 155°, identified as phenylpyruvic acid (IVa). The above series of reactions (depicted in scheme I) indicated IIIa to



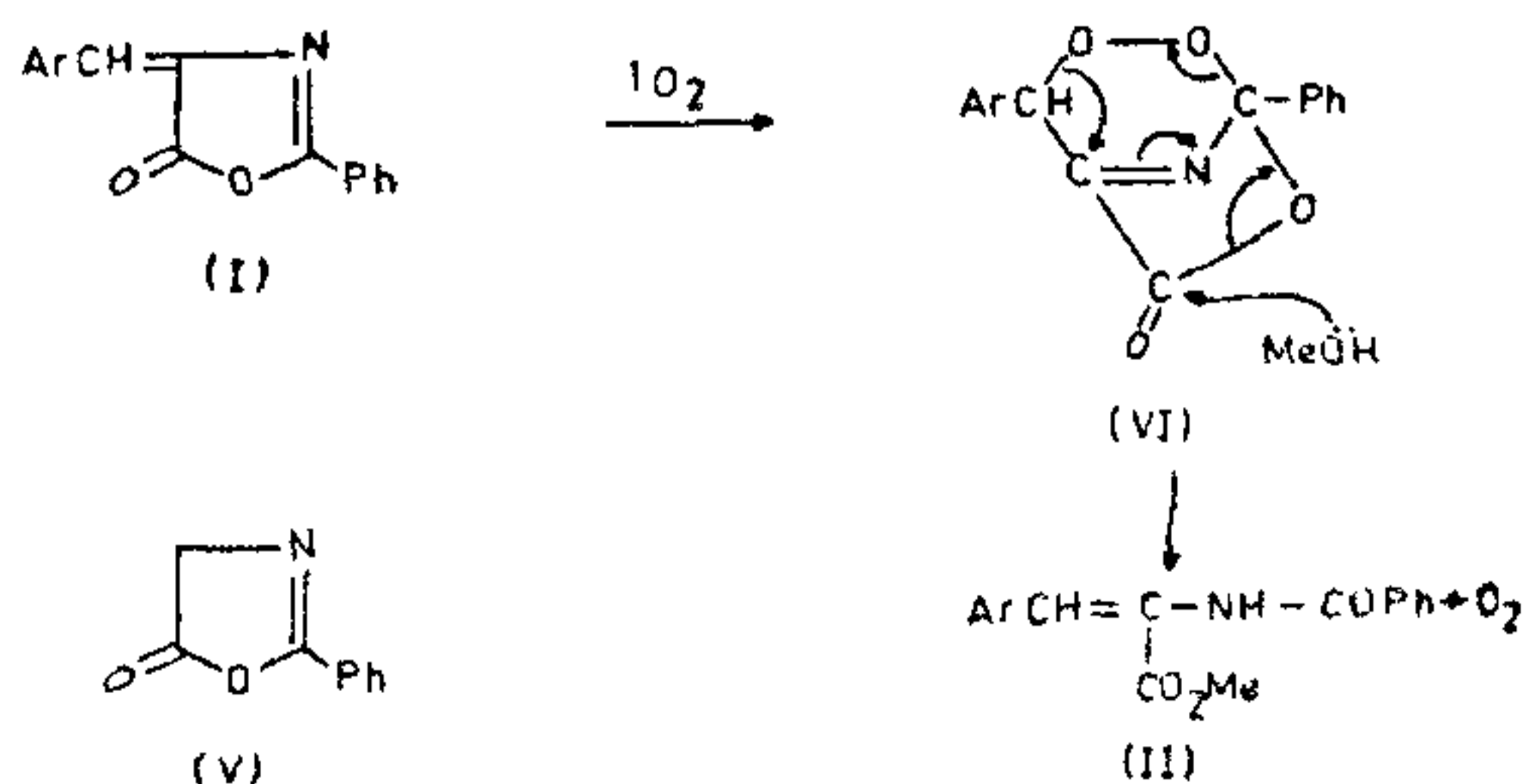
Scheme I

be α-benzamidocinnamic acid and photo-product IIa to be α-benzamidocinnamic acid methyl ester. The latter was finally confirmed by its comparison (m.p., m.m.p., co-TLC and co-IR) with a synthetic sample¹¹ obtained by condensation of hippuric acid methyl ester and benzaldehyde.

Examination of the spectroscopic values of the products obtained from the above azlactones indicated that they were analogous to one another. It was found that all the products showed absorptions for α,β-unsaturated ester (1710-1720 cm⁻¹) and secondary amide group (1640-1645 cm⁻¹) in their IR spectra. The NMR spectrum in each case showed characteristic peaks for methoxyl (δ3.67-3.79) and amido proton (δ7.35-7.43). Based on the above argument, structures similar to IIa were envisaged for photo-products (IIb-e) formed from azlactones (Ib-e). The structures of IIb¹², IIc and IId⁹ and IIe¹³ were confirmed by their syntheses from hippuric acid methyl ester and the appropriate aldehyde in the presence of pyridine.

The involvement of ¹O₂ in the reaction is shown by its quenching by DABCO¹⁴. Moreover, the azlactone did not undergo ring opening when any one of the three essential conditions for photooxygenation, i.e. visible light, air and sensitizer, was eliminated.

Whereas hippuric azlactone (V) undergoes ring opening on methanolysis, the unsaturated azlactones



Scheme II

do not. This can be attributed to resonance stabilization which decreases the double bond character of the carbonyl group. Keeping in view that singlet oxygen plays a part in the reaction, the following mechanism is postulated (scheme II). This envisages the formation of an intermediate (VI) devoid of any resonance stabilization, thereby facilitating ring opening by methanolysis.

Generally, the greater the electron density at the benzylic carbon, the more favoured is the formation of the intermediate and the faster is the rate of the reaction.

SKD is thankful to the CSIR for financial assistance.

18 December 1982

1. Wasserman, H. H. and Lipshutz, B. H. in *Singlet oxygen*, (ed.) H. H. Wasserman and R. W. Murray, Academic Press, 1979, 430.
2. Chawla, H. M. and Chibber, S. S., *Tetrahedron Lett.*, 1976, 2171.
3. Chawla, H. M., Chibber, S. S. and Sharma, A., *Tetrahedron Lett.*, 1978, 2713.
4. Chibber, S. S. and Sharma, R. P., *Indian J. Chem.*, 1979, B18, 538.
5. Sharma, A., Chibber, S. S. and Chawla, H. M., *Indian J. Chem.*, 1980, B19, 905.
6. Gillespie, H. B. and Snyder, H. R., *Organic synthesis*, 1934, 14, 81.
7. Dakin, H. D., *J. Biol. Chem.*, 1910, 8, 11.
8. Buck, J. S. and Ide, W. S., *Organic Synthesis*, 1933, 13, 8.
9. Kropp, W. and Decker, H., *Ber.*, 1909, 42, 1184.
10. Baltazzi, E. and Davis, E. A., *Chem. Ind.*, 1962, 929.
11. Buckles, R. E., Filler, R. and Hilfman, L., *J. Org. Chem.* 1952, 17, 233.
12. Erlenmeyer, E. and Wittenberg, W., *Ann.*, 1904, 337, 297.
13. *Beilsteins' Handbuch der Organischen Chemie*, 1969, 10, 3020.
14. Ouannes, T. and Wilson, C., *J. Am. Chem. Soc.*, 1968, 90, 6528.

TANNIN CONTENT AT DIFFERENT STAGES OF GRAIN DEVELOPMENT IN SOME BIRD SUSCEPTIBLE AND RESISTANT SORGHUMS

S. P. YADAV* AND B. S. RANA†

University of Nairobi, Nairobi and UNDP/FAO, Kenya Sorghum and Millet Development Project, Busia, Kenya.

* Present address: Department of Biochemistry, University of Sokoto, Sokoto, Nigeria.

† Present address: All India Coordinated Sorghum Improvement Project, IARI-Regional Station, Rajendranagar, Hyderabad 500 030, India.

THE *Quelea quelea* are migratory birds in East Africa which feed on the exposed grain cereals. The damage caused to sorghum by these birds is extremely ravaging as compared to residential birds. Brown grain varieties are grown in these areas which are nutritionally inferior. The birds show a high degree of selectivity between sorghum lines differing in polyphenol content¹. Therefore, some bird susceptible and resistant varieties were analyzed to establish the genotypic difference in tannin content at different stages of grain development.

The material comprised five bird susceptible varieties (CSH-5, CSH-6, 2Kx17, Lulu D, Muvemba Local), three moderately resistant varieties (E525 HR, V2 and V70) and three resistant varieties (Serena, Hijak and Sabina). Except CSH-5 and CSH-6 hybrids of Indian origin, the rest of the varieties originated in East Africa. The trial was conducted at Alupe Agricultural Research Station, Busia (Western Kenya) in an equatorial climate (Latitude 0° 28'N, Longitude 34° 07'E) during 1980 long rains (March-July) with three replications. The varieties were grown at a spacing of 60 cm × 15 cm.

Five normal earheads were selected from each variety at four different stages (S) of grain development. First earhead sample was taken after 6 days of anthesis and the rest of the samples at 12 day intervals. The observation on 6, 18, 30 and 42 days after anthesis represented milk stage (S₁), soft dough stage (S₂), dough stage (S₃) and maturity (S₄) respectively. The composite samples of each variety were analysed. The tannin content was expressed as catechin equivalent mg/100 mg of sorghum grain².

Variability among varieties:

The tannin content per 100 mg grain varied from 0.236-1.2 mg in S₁, 0.18-1.267 mg in S₂, 0.227-0.793 mg in S₃ and 0.21-0.607 mg in S₄ (table I). The differences among varieties were significant at all the stages. The Indian white grain hybrids, CSH-5 and