chain), 2.10 (2H, t, methylene protons at C-4), 3.70 (4H, m, deshielded methylene protons of ethoxy groups), 3.75 (1H, m, methine proton at C-3), 4.25 (2H, d, methylene protons at C-15) and 5.9–6.6 (6H, m, vinylic protons at C-7, C-8, C-10, C-11, C-12 and C-14) ; M^+ value at *m/z* 358, $C_{24}H_{38}O_2$.

3-Ethoxyretinyl ethyl ether was converted into the corresponding hydroxy compound[6]. This compound also showed λ_{max} at 328 nm (light petroleum) ; the $SbCl_3$ reaction product gave λ_{max} 670 nm ; ν_{max} 3 320br cm^{-1} (OH).

It has been observed that a number of compounds is formed when 3-dehydroretinol is treated with dry ethanolic hydrogen chloride[1-5]. The compound reported here has been proved to be 3-ethoxyretinyl ethyl ether (7). Its stronger adsorbability than that of 3-ethoxyanhydroretinol (4) suggests the presence of more than one ethoxy group in the compound. The absence of any band characteristic of hydroxy group in the ir spectrum rules out the possibility of the presence of free hydroxy group but a strong band at 1 105 cm^{-1} strongly supports the presence of ethoxy group. The uv spectrum of the compound is similar to that of 3-hydroxyretinol diester[7] with an single maximum at 328 nm and its $SbCl_3$ product shows similar band at 670 nm. The ^1H nmr spectrum (60 MHz ; CCl_4) showed signals for all the protons including the deshielded methylene protons. Besides the weak molecular ion peak M^+ at *m/z* 358, the mass spectrum showed peaks at *m/z* 316 (M^+-46) and 266 (base peak, M^+-92) confirming the presence of two ethoxy groups. However, the lower fragmentation patterns are not clear. The hydroxy compound (8) derived from 7 showed a strong broad ir band at 3 320 cm^{-1} attributable to the hydroxy group. Available evidences indicate that the hydroxy compound is 3-hydroxyretinol (8). Further experimental evidences are essential to confirm the identity of 7 with that of 3-hydroxyretinol diester isolated from fish liver oils[7].

Henbest *et al.*[4] suggested the scheme **1→4** for the formation of 3-ethoxyanhydroretinol (4). A reasonable pathway for the formation of 3-ethoxyretinyl ethyl ether (7) involves the steps : **1→2→5→6→7**. The intermediate (5) is protonated at C-4 to give a carbonium ion at C-3 (6) which is finally converted to 7 by solvent ethanol.

References

1. E. M. Shantz, *Science*, 1948, **108**, 417.
2. K. R. Farrar, J. C. Hamlet, H. B. Henbest and E. R. H. Jones, *J. Chem. Soc.*, 1952, 2657.
3. S. Balasundaram, M. S. Bamji, H. R. Cama, P. R. Sundaresan and T. N. R. Varma, *J. Biol. Chem.*, 1958, 233, 827.
4. H. B. Henbest, E. R. H. Jones, T. C. Owen and V. Thaller, *J. Chem. Soc.*, 1955, 2768.
5. K. K. Das and A. K. Saikia, *Chem. Ind. (London)*, 1968, 52.
6. R. K. Barua and P. G. Nayar, *Curr. Sci.*, 1963, **32**, 257.
7. A. B. Barua, R. C. Das and K. Verma, *Biochem. J.*, 1977, **168**, 557.

PMR Spectral Study of Steroidal Oxazolidinones

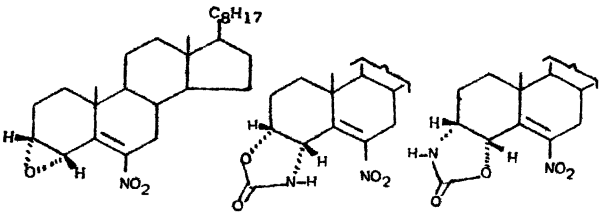
SHAFIULLAH*, D. M. BASHA and SHAHID A. ANSARI

Steroid Research Laboratory, Department of Chemistry, Aligarh Muslim University, Aligarh-202 002

Manuscript received 26 October 1988, accepted 6 January 1989

OXAZOLIDINONES have been shown to possess various biological activities[1]. This prompted us to undertake the synthesis and structural study of the steroidal diasteromeric oxazolidinones.

Reaction of 3α,4α-epoxy-6-nitrocholest-5-ene (**1**)[2] in *N,N*-dimethyl formamide when refluxed with urea gave 6-nitrocholest-5-eno[4α, 3α-*d*]oxazolidin-2'-one (**2**) and 6-nitrocholest-5-eno[3α, 4α-*d*]oxazolidin-2'-one (**3**)[3]. The structures of these diastereomeric oxazolidinones were established on the basis of pmr spectral study.



1 **2** **3**

The ir spectra of the oxazolidinones (**2** and **3**) exhibited characteristic bands at 3 420–3 490 and 1 715–1 725 cm^{-1} for oxazolidinone moiety[4]. In pmr spectra of **2** and **3**, the NH proton appeared as slightly broad singlet at δ 7.74–8.01. The distinction between the two isomeric oxazolidinones **2** and **3** was made comparing the peak positions of C_3 and C_4 protons. Both $C_4\beta$-proton (pseudo-axial) in **3** and $C_3\beta$-proton (equatorial) in **2** are attached to oxygen-bearing carbon atoms, but $C_4\beta$-proton in **3** though being axial (pseudo) appears downfield (δ 5.48)[5] as compared to equatorial $C_3\beta$-protons (δ 5.15) in **2**. This is a reversal of the usual axial-equatorial relationship reported for a wide variety of six-membered ring system[5]. Similar observation was made regarding $C_4\beta$-proton in **2** (pseudo-axial, δ 4.27) appearing at low-field than $C_3\beta$-proton in **3** (equatorial, δ 3.98), both being attached to nitrogen-bearing carbon atoms. The low-field appearance of the pseudo-axial protons at C_4 can be attributed to its allylic nature and to the electron-withdrawing nitro group at C_6.

Experimental

All melting points are uncorrected. Ir spectra (KBr) were determined on a Perkin-Elmer 237 spectrophotometer, and pmr spectra ($CDCl_3$) on a Varian A60 instrument with tetramethyl silane as the internal standard. Tlc plates were prepared from silica gel G and sprayed with 20% aqueous perchloric acid. Light petroleum refers to a fraction

of b.p. 60–80°. Anhydrous sodium sulphate was used as drying agent.

Reaction of epoxide **1** *with urea :* 3α,4α-Epoxy-6-nitrocholest-5-ene (**1**)[2] (1.5 g, 3.77 mmol) in *N,N*-dimethyl formamide (25 ml) was refluxed with urea (1.5 g) for about 6 h. It was then poured in ice-cold water and extracted with ether. The ethereal solution was washed with water and dried over anhydrous sodium sulphate. Evaporation of the solvents provided an oil (1.35 g) which was chromatographed over a column of silica gel (30.0 g). Elution with petroleum ether–ether (8 : 1) gave 6-nitrocholest-5-eno[4α,3α-*d*]oxazolidin-2'-one (**2**) which was recrystallised from petroleum ether (0.4 g, 26.67%), m.p. 120° (Found : C, 71.09 ; H, 9.32 ; N, 5.88. $C_{28}H_{44}N_2O_4$ requires : C, 71.18 ; H, 9.32 ; N, 5.92%) ; ν_{max} (KBr) 3 490 (NH), 1 715 (oxazolidinone moiety)[4], 1 640 (C=C), 1 535 and 1 375 cm^{-1} (C–NO_2) ; δ ($CDCl_3$) 7.94 (1H, brs, NH exchangeable with deuterium), 5.15 (1H, mc, $W_{1/2}$ 7 Hz, $C_3\beta$–H, equatorial), 4.27 (1H, d, *J* 3 Hz, $C_4\beta$–H, pseudo-axial)[5], 1.21, 0.93, 0.83 and 0.68 (angular and sidechain methyl protons) ; and elution with petroleum ether–ether (4 : 1) furnished 6 nitrocholest-5-eno-[3α,4α-*d*]oxazolidin-2'-one (**3**) which was recrystallised from petroleum ether (0.3 g, 20%), m.p. and m.m.p.[3] 137° (Found : C, 71.30 ; H, 9.25 ; N, 5.80. $C_{28}H_{44}N_2O_4$ requires : C, 71.18 ; H, 9.32 ; N, 5.93%) ; ν_{max} (KBr) 3 420 (NH), 1 725 (oxazolidinone moiety)[4], 1 650 (C=C), 1 525 and 1 365 cm^{-1} (C–NO_2) ; δ ($CDCl_3$) 8.01 (1H, brs, NH exchangeable with deuterium), 5.48 (1H, d, *J* 3 Hz, $C_4\beta$–H, pseudo-axial)[3,5], 3.98 (1H, mc, $W_{1/2}$ 7 Hz, $C_3\beta$–H, equatorial), 1.20, 0.88, 0.78 and 0.66 (angular and side chain methyl protons).

Acknowledgement

The authors are indebted to Prof. M. S. Ahmad and Prof. S. M. Osman, Chairman, Department of Chemistry, for facilities and to U.G.C., New Delhi for financial support.

References

1 R. B. Fugitt and R. W. Luckenbaugh, *Chem. Abstr.*, 1982, **97**, 109990 ; W. Eckhardt, W. Kunz and A. Hubele, *Chem. Abstr.*, 1981, **95**, 150642 ; T. Takematsu, T. Hisada, T. Motegi, H. Tsuchiya and M. Furushima, *Chem. Abstr.*, 1975, **83**, 2319 ; H. Igarashi, T. Kurihara and H. Takeda, *Chem. Abstr.*, 1974, **81**, 99445, ; G. Huguenet, C. Fauran, C. Douzon, R Colette and C. Gouret, *Chem. Abstr.*, 1975, **82**, 112058.

2. Shafiullah, S. Husain and M. R. Ansari, *Indian J. Chem., Sect. B*, 1985, **24**, 662.

3. Shafiullah, S. Husain, D. M. Basha and I. H. Siddiqui, *J. Indian Chem. Soc.*, 1986, **63**, 849.

4. L. J. Bellamy, "Advances in Infrared Group Frequencies", Chapman and Hall, London, 1968, p. 165.

5. N. S. Bhacca and D. H. Williams, "Application of NMR Spectroscopy in Organic Chemistry", Holden Day, San Francisco, 1964, pp. 47 49, 73.

Synthesis of n-Alkyl Substituted-pyrazoles using Vilsmeier–Haack Reaction†

R. A. PAWAR* and A. P. BORSE

S. S. V. P. S' Late Karmveer Dr. P. R. Ghogarey Science College, Dhule-424 002

Manuscript received 20 June 1988, accepted 12 October 1988

THERE is considerable interest in Vilsmeier–Haack reaction and its synthetic applications[1]. In continuation of our interest in Vilsmeier–Haack reaction[2], we report here syntheses of 4-n-alkylsubstituted pyrazoles (Scheme 1) from phenylhydrazones, semicarbazones and azines of 2-n-acyl-5-chlorophenols by monoformylation and cyclisation using one mole of the Vilsmeier–Haack reagent ($DMF/POCl_3$). A general mechanistic scheme for this reaction is also suggested.

Synthesis and spectroscopic properties of 2-n-acyl-5-chlorophenols (**1a–d**) and their phenylhydrazones (**2a–d**) have been described by us earlier[3]. The phenylhydrazones (**2a–d**) and one mole of the reagent ($DMF/POCl_3$) were stirred for 6 h and the reaction mixture was then neutralised with NaOH giving 1-phenyl-3-(2'-hydroxy-4'-chlorophenyl)-4-n-alkylpyrazoles (**3a–d**) (Table 1). Structures of the compounds were established by elemental analysis, ir and nmr spectral data. Ir spectra of **3a–d** showed characteristic bands for pyrazole ring[4] at 1 597, 1 553, 1 480 and 1 310 cm^{-1} and nmr spectra, e.g. of **3d** (60 MHz, CCl_4, TMS) showed chemical shifts at δ 1.00 (3H, t, CH_3), 1.5 (4H, m, $(CH_2)_2$), 2.7 (2H, t, CH_2), 10.8 (1H, s, D_2O exchangeable strongly H-bonded OH) and 7.8 (9H, m, ArH).

Table 1—Physical and Analytical Data of Compounds 3

Compd. taken no.	Pyrazole formed			N% : Found/ (Calcd.)
	No.	M.p. °C	Yield %	
2a	3a	138	30	9.47 (9.82)
2b	3b	93	26	9.13 (9.36)
2c	3c	109	20	8.62 (8.95)
2d	3d	107	20	8.21 (8.57)

Plausible mechanism for the above cyclisation is presented in Chart 1. Phenylhydrazone in tautomeric form (**II**) acts as a nucleophile towards a reactive intermediate obtained from $DMF/POCl_3$ to give **III**. Addition of $\bar{O}POCl_2$ to carbon–carbon double bond of **III** affords **IV**. This step is facilitated due to ease in formation of five-membered ring. Activated complex **IV** is then converted by base-induced elimination reaction to pyrazole **V**.

† Presented at the National Symposium on Recent Advances in Organic Chemistry, University of Poona.