Vol. 46, No. 24
Dec. 20, 1977]

THE CLAISEN REARRANGEMENT OF 7-CINNAMYLOXY DERIVATIVES OF 3-METHOXYFLAVONE AND 4-METHYL COUMARIN

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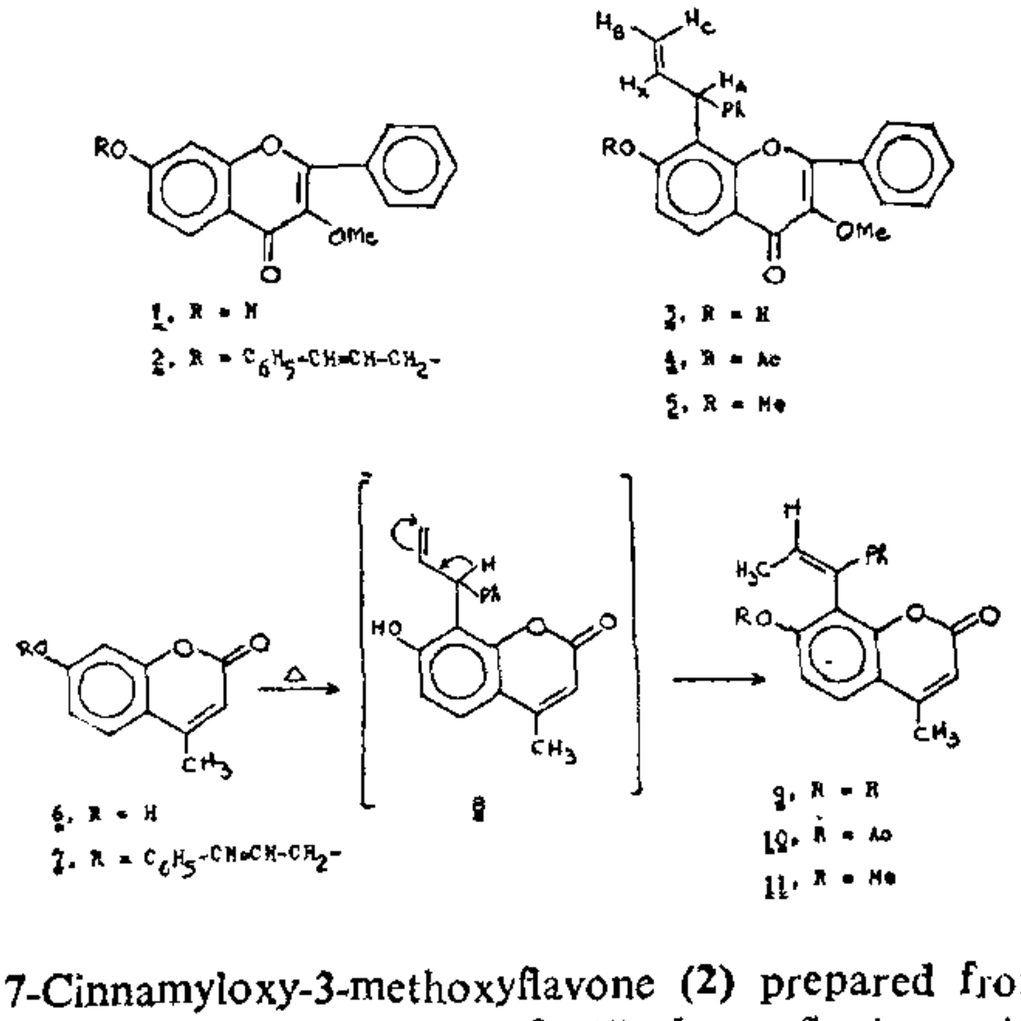
ABSTRACT

The Claisen rearrangement of 7–cinnamyloxy–3–methoxyflavone (**2**) and 4–methyl–7–cinnamyloxycoumarin (**7**) yields 8–(1–phenyl–2–propenyl)–7–hydroxy–3–methoxyflavone (**3**) and 4–methyl–8–(1–phenyl–1–propenyl)–7–hydroxycoumarin (**9**) respectively. The compound (**3**) represents the normal rearranged product and further has structural features similar to those present in some natural neoflavonoids but (**9**) is the abnormal product formed by further allylic rearrangement of the normal one (**8**).

IN continuation of our work on the Claisen rearrangement of cinnamyl ethers of complex polyphenols[1,2], the rearrangement of 7-cinnamyloxy derivatives (**2** and **7**) of 3-methoxyflavone and 4-methylcoumarin respectively have been studied by refluxing them in *N, N*-dimethylaniline. In each case only one product has been isolated. Since the products are different from those reported earlier and one of them has a similar feature as is present in some natural neoflavonoids, results are reported here.



7-Cinnamyloxy-3-methoxyflavone (**2**) prepared from 7-hydroxy-3-methoxy-flavone[3] (**1**) by refluxing with cinnamyl bromide in the presence of potassium carbonate and acetone, crystallized from benzene-light petroleum mixture as colourless crystals, m.p. 121-22° C; R_f 0·61 (Solvent A)[4]; λ_{max} (MeOH): 219, 259 and 314 nm (log ε 4·00, 4·45 and 4·26 respectively) (Found: C, 78·5; H, 5·4. $C_{25}H_{20}O_4$ requires C, 78·1; H, 5·2%); 60 MHz NMR ($CDCl_3$): δ 3·90 (s, 3H, $-OCH_3$), 4·75 (*d*, J = 5Hz, 2H, $-OCH_2$), 6·10 - 6·50 (*m*, 2H, $CH = CH$), 6·73 (*br s*, 1H, *H* - 8), 6·96 (*dd*, J = 10Hz and 3Hz, 1H, *H* - 6), 7·16 - 8·00 (*m*, 10 *H*, $2XC_6H_5$) and 8·14 ppm (*d*, J = 10Hz, 1H, *H* - 5).

The above cinnamyloxy flavone (**2**) when refluxed with *N, N* - dimethylaniline gave a product which crystallised from benzene as colourless crystals, m.p. 209 – 10° C; R_f 0·25 (Solvent B); λ_{max} (MeOH): 221, 256, 316 nm (log ε 4·45, 4·39 and 4·37 respectively). Elemental analysis (Found: C, 78·5; H, 5·6. $C_{25}H_{20}O_4$ requires C, 78·1; H, 5·2%) indicated it to be an isomeric product. Its NMR spectrum showed that it has a 1-phenyl-allyl unit in the position 8. Thus its 60 MHz NMR spectrum in DMSO–d_6 showed resonance signals at δ 3·78 (*s*, 3H, $-OCH_3$), 5·11–5·27 (*m*, 1H, $CH_2 = CH-CHAr_2$), 5·30–5·65 (*m*, 2H, $CH_2 = CH-$), 6·23-6·83 (octet, 1H, $-CH = CH_2$), 7·08 (*d*, J = 10Hz, 1H, *H* - 6), 7·17–7·36 (*m*, 10H, $-2C_6H_5$) and 7·89 ppm (*d*, J = 10Hz, 1H, *H* - 5). Hence it has the structure of 8 - (1 - phenyl - 2 - propenyl) - 7–hydroxy - 3 - methoxyflavone (**3**), in support of which it formed an acetate (**4**) and a methyl ether (**5**). The acetate (**4**) crystallised from benzene-light petroleum mixture as colourless crystals, m.p. 160-61° C; R_f 0·4 (Solvent C); 60 MHz NMR ($CDCl_3$); δ 2·12 (*s*, 3H, $-OCOCH_3$), 3·85 (*s*, 3H, OCH_3), 5·13 (*m*, J_{AX} = 8·0Hz, J_{AB} = 1·6Hz, 1H, $CH_2 = CH-CHAr_2$), 5·31–5·48 (*m*, 2H, $CH_2 = CH-$), 6·12-6·68 (*m*, 1H, $CH_2 = CH - CH<$), 7·13 (*d*, J = 9Hz, 1H, *H*–6), 7·18–7·71 (*m*, 10H, 2 - C_6H_5) and 8·20 ppm (*d*, J = 9Hz, 1H, *H* - 5) (Found: C, 76·2; H, 5·1, $C_{27}H_{22}O_5$ requires C, 76·0; H, 5·2%). The methyl ether (**5**) crystallised from methanol as colourless crystals, m.p. 188° C; R_f 0·6 (Solvent B); ν_{max} (nujol) 1675 cm^{-1} (> C = O); λ_{max} (MeOH) 276 and 222 nm (log ϵ 4·30 and 4·23 respectively) (Found; C, 78·0; H, 5·8. $C_{26}H_{22}O_4$ requires C, 78·0; H, 5·5%); 80 MHz NMR ($CDCl_3$): δ 3·83, 3·90 (2*s*. 6H 2X-OCH_3) 5·03 5·14 (*m*, 1H, $CH_2 = CH-CHAr_2$) 5·15-5·62 (*m*, 2H, $CH_2 = CH-$), 6·10-6·48 (*m*, 1H, $CH-CH = CH_2$) 7·05 (*d*, J = 10Hz, 1H, *H* - 6), 7·12-7 46 (*m*, 10H, 2X-C_6H_5) and 8·9 ppm (*d*, J = 10Hz, 1H, *H* - 5). The formation of **3** represents the normal Claisen rearrangement which is rarely met in such compounds.

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This structural feature is present in some neoflavonoids such as latifolin.

4-Methyl-7-cinnamyloxycoumarin (7), prepared from 4-methyl-7-hydroxy coumarin[3] (6) in the same way as described for (2), crystallised from ethyl acetate as colourless crystals, m.p. 178–79° C, R_f 0·45 (Solvent B); λ_{max} (MeOH): 219, 253 and 320 nm (log ε 4·52, 4·57 and 4·46 respectively) (Found: C, 78·4; H, 5·5. $C_{19}H_{16}O_3$ requires C, 78·1; H, 5·5%); 60 MHz NMR (DMSO-d_6): δ 2·45 (*d*, J = 1Hz, 3H, $-CH_3$), 4·82 (*d*, J = 5Hz, 2H, O–CH_2–), 6·15 (*q*, J = 1Hz, 1H, *H*–3), 6·40–6·64 (*m*, 2H, Ar–*CH* = *CH*–), 6·70 (*d*, J = 2·5 Hz, 1H, *H*–8), 6·95 (*dd*, J = 10 Hz and 2·5 Hz, 1H, *H*–6), 7·20–7·40 (*m*, 5H, C_6H_5) and 7·60 ppm (*d*, J = 10Hz, 1H, *H*–5).

The above cinnamyloxy coumarin (7) on the Claisen rearrangement gave a colourless product which crystallised from ethyl acetate as colourless crystals, m.p. 222–23° C; R_f 0·6 (Solvent A); λ_{max} (MeOH): 220, 250 and 323 nm (log ε 4·54, 4·53 and 4·46 respectively). Its elemental analysis (Found: C, 78·0; H, 5·4. $C_{19}H_{16}O_3$ requires C, 78·1; H, 5·5%) showed that it is an isomeric product. The following resonance signals in its 60 MHz NMR spectrum ($CDCl_3$) established that it is 4–methyl–8–(1–phenyl–1–propenyl)–7–hydroxycoumarin (9): δ 1·68 (*d*, J = 7Hz, 3H, CH_3–CH =), 2·42 (*d*, J = 1Hz, 3H, $-CH_3$ in the 4 position), 6·10 (*q*, J = 1Hz, 1H, *H*–3), 6·68 (*q*, J = 7Hz, 1H, $\rangle C = C\langle^{H}_{CH_3}$) 7·00 (*d*, J=9Hz, 1H, *H*–6). 7·28 (*s*, 5H, C_6H_5) and 7·55 ppm (*d*, J = 9Hz, 1H, *H*–5). In conformity with the structure (9), it formed an acetate (10) which crystallised from ethanol as colourless crystals, m.p. 139–40° C, R_f 0·75 (Solvent B) (Found: C, 75·1; H, 5·8. $C_{21}H_{18}O_4$ requires C, 75·4; H, 5·4%) and methyl ether (11) which crystallised from methanol as colourless needles, m.p. 165° C; R_f 0·78 (Solvent B), λ_{max} (MeOH): 220, 250 and 321 nm (log ε 4·20, 4·18 and 4·14 respectively); 60 MHz NMR ($CDCl_3$): δ 1·61 (*d*, J = 7Hz, 3–H, CH_3–CH =), 2·42 (*d*, J = 1·5Hz, 3H, CH_3 in the 4 position), 3·83 (*s*, 3H, O–CH_3), 6·11 (*q*, J = 1·5Hz, 1H, *H*–3), 6·25–6·60 (*m*, 1H, $\rangle C = C\langle^{H}_{CH_3}$), 6·92 (*d*, J = 9Hz, 1H, *H*–6), 7·18 (*s*, 5H, C_6H_5) and 7·56 ppm (*d*, J = 9Hz, 1H, *H*–5).

The formation of the product (9) can be explained on the basis of the normal Claisen rearrangement followed by allylic rearrangement of the resulting intermediate (8).

ACKNOWLEDGEMENTS

The authors express their sincere gratitude to the C.S.I.R., New Delhi, for the award of JRF to DKT, and to the U.G.C., New Delhi, for the award of JRF to AK and NF to ACJ.

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