

STUDIES IN CLAISEN REARRANGEMENTS

CLAISEN REARRANGEMENT OF BISPROPARGYL ETHERS

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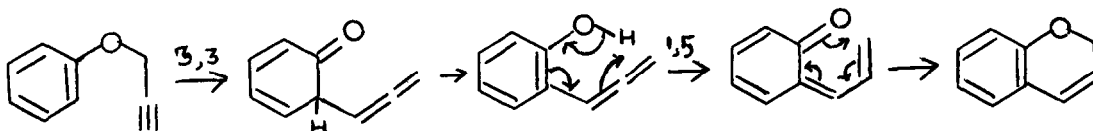
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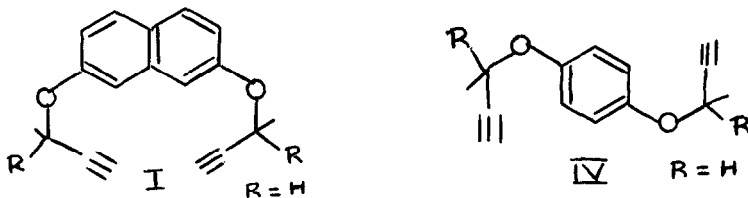
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In recent years there has been a lot of interest in the study of multiple and sequential Claisen rearrangements^{1 - 5} and Claisen rearrangement of aryl propargyl ethers^{6 - 16} and other related oxygen systems^{17 - 23} from synthetic and mechanistic view points. The mechanism that has been arrived at by Schmid *et al*^{11, 13, 14} for the thermal rearrangement of aryl propargyl ethers to chromenes is illustrated below:

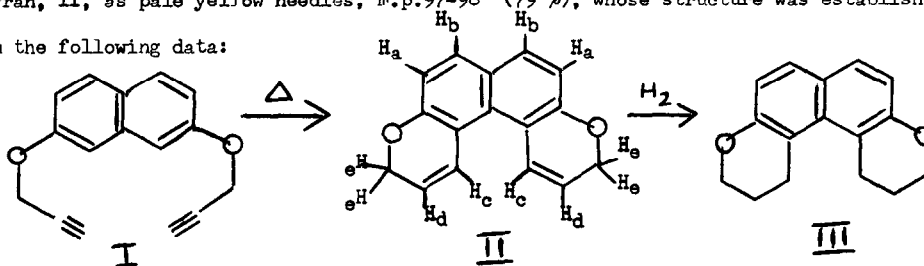


In connection with our work in this area, we were interested in studying the thermal rearrangement of bispropargyl ethers such as I, IV etc., with a view to obtain some information regarding (i) the course and synchronous nature of the two migrations, (ii) the regiospecificity and (iii) the degree of stereoselectivity in the case of rearrangement of ethers where $R \neq H$. While the Claisen rearrangement of bisallyl ethers of dihydroxybenzenes and dihydroxynaphthalenes are known^{24 - 25} there seems to be no report in literature about the rearrangement of corresponding acetylenic ethers. In this communication we wish to report a facile double Claisen migration of the bispropargyl ethers I and IV to novel benzodipyran derivatives.



When 2,7-bis(2'-propynyloxy)naphthalene, I, m.p. 93-94° [M/e at 236; U. V. $\lambda_{max}^{CCl_4}$ 247 m μ]

I. R. (nujol) 3280, 3300, 2130, 1220, 1015, 1625 and 1605 cm^{-1} ; NMR (CDCl_3) δ 2.5 (2H, t, $J = 1.5 \text{ Hz}$, $\equiv\text{CH}$), δ 4.7 (4H, d, $J = 1.5 \text{ Hz}$, $-\text{OCH}_2-$), δ 6.95 (2H, d, $J = 10 \text{ Hz}$, H_3 & H_6), δ 7.6 (2H, d, $J = 10 \text{ Hz}$, H_4 & H_5) and δ 7.1 (2H, s, superimposing with one limb of the doublet at δ 6.95, H_1 & H_8) was refluxed in *N,N*-diethylaniline in a nitrogen atmosphere in five minutes itself, complete disappearance of the starting material was observed as indicated by TLC and NMR analyses. Usual work up afforded a neutral viscous dark liquid (85 %), I. R. (CCl_4) 1635, 1240, 1025 and 1005 cm^{-1} and no $\equiv\text{CH}$ band; U.V. $\lambda_{\text{max}}^{\text{CCl}_4}$ 253, 364^{sh} and 380^{sh} m μ . The NMR spectrum showed no signals due to olefinic methyl or any other methyl group. These data clearly indicate the absence of any monorearrangement product or any methylnaphthofurans in the above rearranged product. Column chromatography of the above product over silica gel furnished naphtho(2,1-b:7,8-b) dipyran, II, as pale yellow needles, m.p. 97-98° (79 %), whose structure was established from the following data:

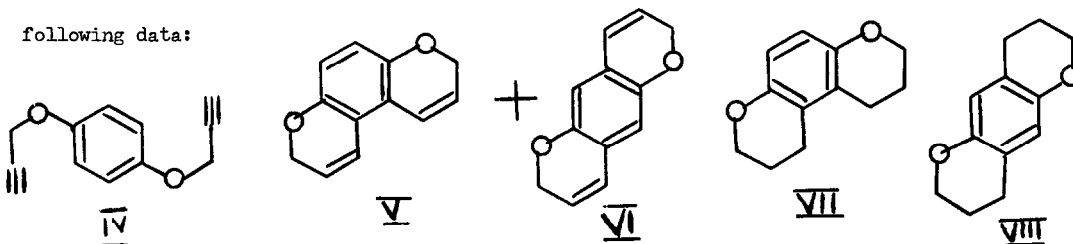


It analysed for $\text{C}_{16}\text{H}_{12}\text{O}_2$ and showed the molecular ion peak at 236. It readily decolourised bromine in CCl_4 or neutral aqueous potassium permanganate solution. The Ultraviolet absorption maximum shifted to bathochromic comparing with that of the starting material. Its Infrared spectrum showed a new band at 1635 cm^{-1} (I.R. CCl_4 : 1635, 1240, 1025 and 1005 cm^{-1}) and its NMR spectrum showed an A_2B_2 quartet (δ 7.05, 2H d, $J_{\text{H}_a\text{H}_b} = 9.5 \text{ Hz}$, H_a ; δ 7.6, 2H, d, $J_{\text{H}_b\text{H}_a} = 9.5 \text{ Hz}$, H_b), a doublet at δ 7.1 (2H, $J_{\text{H}_c\text{H}_d} = 10 \text{ Hz}$, H_c), a quintet at δ 5.75 (2H, H_d) and a quartet at δ 4.75 (4H, $J_{\text{H}_e\text{H}_d} = 5 \text{ Hz}$ and $J_{\text{allylic}} = 1.5 \text{ Hz}$, $-\text{OCH}_2-$). The above data clearly rule out the other possible structures, viz., naphtho(2,3-b:7,6-b)dipyrane and naphtho(2,1-b:7,6-b)dipyrane shown below:



Catalytic hydrogenation of the dipyran II furnished the tetrahydroderivative III, m.p. 193° (Molecular ion at 240; I.R. KBr 1610, 1245, 1235, 1220, 1205 and 1000 cm^{-1} ; U.V. $\lambda_{\text{Max}}^{\text{CCl}_4}$ 248 $\text{m}\mu$; NMR CDCl_3 δ 1.9 (4H, quintet, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$), δ 3.25 (4H, t, CH_2-CH_2-) δ 4.2 (4H, t, $J = 5.5\text{ Hz}$, $-\text{OCH}_2-$), an A_2B_2 quartet (δ 6.8, 2H, d, $J = 9.5\text{ Hz}$ and δ 7.4, 2H, d, $J = 9.5\text{ Hz}$). The fact that the NMR spectrum of the tetrahydro compound exhibits only an AB quartet (integrating for four protons only) in the aromatic region unequivocally establishes the assigned structure. The regiospecific migration of the propargyl groups to 1 and 8 positions contrasts with that reported recently for the double Fries rearrangement of 2,7-diacetoxynaphthalene to 1,6-diacetyl-2,7-dihydroxynaphthalene²⁶.

Refluxing a solution of 1,4-bis(2'-propynyloxy)benzene, IV, m.p. 46° [(molecular ion at 186; I.R. Nujol 3320, 3280, 2120, 1230 and 1020 cm^{-1} ; U.V. $\lambda_{\text{Max}}^{\text{CCl}_4}$ 249 and 287 $\text{m}\mu$; NMR CDCl_3 δ 6.9 (4H, s), δ 4.55 (4H, d, $J = 2\text{ Hz}$) and δ 2.5 (2H, t, $J = 2\text{ Hz}$)] in *N,N*-diethyl-aniline for 3 hrs. furnished a neutral dark liquid (76 %) consisting of a 1 : 1 mixture of benzo(1,2-b;4,3-b)dipyran V and benzo(1,2-b;4,5-b)dipyran VI, as inferred from the following data:



It showed two very close moving spots in TLC (1 : 4 benzene-hexane) and infrared spectrum showed no $\equiv\text{CH}$ band. Its NMR spectrum showed a very closely spaced sextet at δ 4.65 due to different $-\text{OCH}_2-$ groups, a multiplet at δ 5.83 due to coupled olefinic protons, two tall singlets in between a multiplet at δ 6.4 - 6.56 due to aromatic protons and a multiplet at δ 6 to 6.15 due to pyran ring protons ($=\text{CH}-$). Catalytic reduction of the above crude mixture afforded a white crystalline solid melting over a range, m.p. $80-120^{\circ}$ (86 %). This solid also showed two very close moving spots in TLC (1 : 1 benzene-hexane) and its NMR spectrum showed two singlets (a sharp one at δ 6.42 and a little broader one at δ 6.27) in a ratio of 1 : 1 (totally 2H), a multiplet at δ 4 (4H, $-\text{OCH}_2-$), a multiplet at δ 2.5 (4H, CH_2-) and a multiplet at δ 2 (4H, $-\text{CH}_2-\text{CH}_2-\text{O}$). Fractional crystallisation of the above solid from hexane afforded two crystalline solids, m.p. $119-120^{\circ}$ (Molecular ion at 190; I.R. KBr 2950, 2870, 1600, 1250, 1200, 1050, and 1010 cm^{-1} ; U.V. $\lambda_{\text{Max}}^{\text{CCl}_4}$ 256 & 301 $\text{m}\mu$)

and m.p. 78-80°. The NMR spectrum of the higher melting isomer showed a sharp singlet at δ 6.48 (2H), a triplet at δ 4 (4H, $J = 6$ Hz, $-\text{OCH}_2-$), a triplet at δ 2.55 (4H, $J = 6$ Hz, OCH_2-) and a quintet at δ 2 (4H, $-\text{CH}_2-\text{CH}_2-\text{O}-$, $J = 6$ Hz). The NMR spectrum of the low melting isomer displayed close similarity to that of the higher melting isomer in the nonaromatic region and indicated that it is still contaminated with 25% of the higher melting isomer. We are tentatively assigning structures VII and VIII respectively to the higher melting and lower melting solids on the basis of the smaller NMR signal width of the aromatic protons of the higher melting solid.

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