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A Study Of Claisen Rearrangements Of (1,1-Dimethyl-3-Prop-2-Ynyloxy)-[4H]-1-Benzopyran-4-One Derivatives.*

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Abstract: The Claisen rearrangements of 7-(1,1-dimethyl-3-prop-2-ynyloxy) derivatives of 7-hydroxy-8-methyl-3-phenyl-[4H]-1-benzopyran-4-one[1] (1), 2,8-dimethyl-7-hydroxy-3-phenyl-[4H]-1-benzopyran-4-one[1] (5), 8-(prop-2-enyl)-7-hydroxy-3-phenyl-[4H]-1-benzopyran-4-one[2] (8), 8-(1-phenyl-2-propenyl)-7-hydroxy-3-phenyl-[4H]-1-benzopyran-4-one[3] (11) was carried out to furnish novel products 1,2,3,7-tetrahydro-1,1,3-trimethyl-6-phenylcyclopenta-(2,3-h) [2H, 7H]-benzopyran-2,7-dione (3), (7), and 2,2-dimethyl-7-phenyl-3-(prop-2-enyl)pyrano (2,3-h) (8H)-1-benzopyran-8-one (10) along with expected products (4) and (13). Probable mechanisms of the rearrangements are discussed.

Introduction

Most of the naturally occurring Isoflavones have been shown to possess a prenyl unit either in open chain form or in the form of a pyran ring fused linearly or angularly to the isoflavone ring system, e.g. 2,3-Dehydrokievitone, Alpinum isoflavone, Derron, Parvisoflavone-A and B etc. One of the well established routes developed by Iwai and Ide[4] consisted of rearrangement of 1,1-dimethyl propargyl ether in dimethylaniline. This reaction is a variant of the Claisen allylic rearrangement. Iso-encecalin and encecalin[5] have been prepared by a similar route. Seshadri and coworkers[6] observed that 7-(1, 1-dimethyl-3-prop-2-ynyloxy) derivatives of 5, 7-dihydroxy-2-methyl-[4H]-1-benzopyran-4-one and 5, 7-dihydroxy-4'-methoxy-3-phenyl[4H]-1-benzopyran-4-one in the formation of two isomers irrespective of the group of polyphenols used. The work carried out by Jain et. al.[7,8] on 5,7-dihydroxy-3',4'-dimethoxy-3-phenyl-[4H]-1-benzopyran-4-one and 7-hydroxy-3-phenyl-[4H]-1-benzopyran-4-one supports the above observations but with 7-hydroxy-4'-methoxy-3-phenyl-[4H]-1-benzopyran-4-one only the angular product was obtained.[9] The present work deals with the Claisen rearrangements of 7-(1,1-dimethyl-3-prop-2-ynyloxy)-8-methyl-3-phenyl-[4H]-1-benzopyran-4-one, 7-(1,1-dimethyl-3-prop-2-ynyloxy)-8-(prop-2-enyl)-3-phenyl-[4H]-1-benzopyran-4-one and

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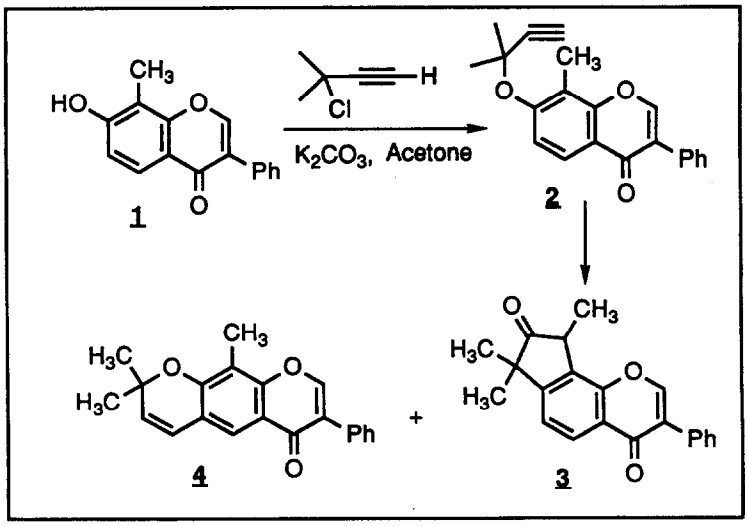
7-(1,1-dimethyl-3-prop-2-ynyloxy)-8-(1-phenyl-2-propenyl)-3-phenyl-[4H]-1-benzopyran-4-one derivatives. Novel products were obtained during these rearrangements.

Results and Discussion

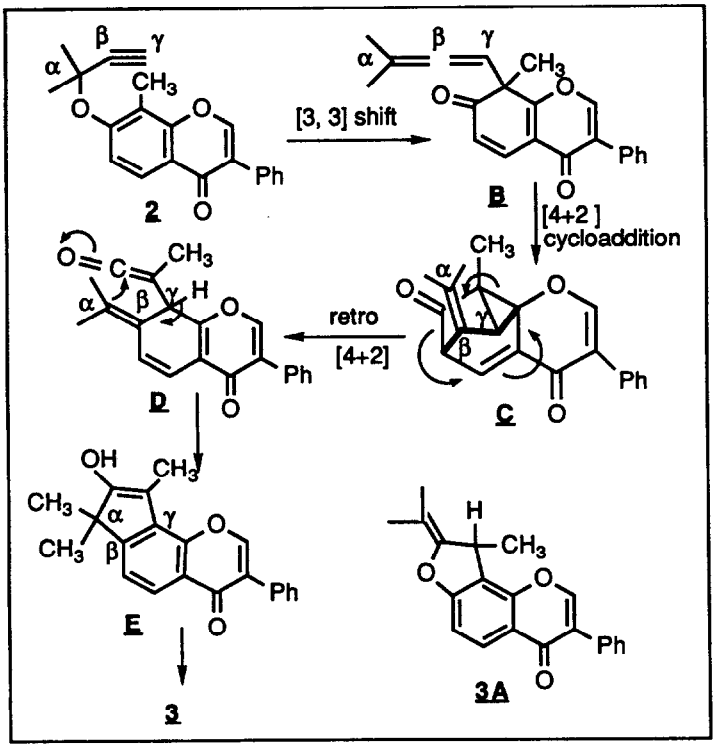
7-Hydroxy-8-methyl-3-phenyl-[4H]-1-benzopyran-4-one (**1**) was condensed with 3-chloro-3-methylbut-1-yne[10] in alkaline medium to obtain 7-(1,1-dimethyl-3-prop-2-ynyloxy)-8-methyl-3-phenyl-[4H]-1-benzopyran-4-one (**2**). (Scheme-I) It was subjected to Claisen rearrangement by refluxing it in N,N-dimethylaniline for 5 h, which gave a mixture of two products. The mixture was separated by column chromatography by eluting first with petroleum ether to furnish (3A). On further elusion with benzene, an impure product (4) was obtained in very poor yields. (4) was further purified by subjecting it to preparative TLC using benzene as a solvent. Pmr ($CDCl_3$) spectrum of (**3A**) exhibited signals at δ 1.38 and 1.4, two



Scheme-I

singlets for two -CH_3 groups at C-2; 1.65, doublet, J 9Hz, 3H, -CH_3 at C-3; 3.8, quartet, J 9Hz, C_3-H, 7.5-7.7, multiplet, 6H, aromatic protons; 8.25,doublet, J 9Hz, C_8-H; 8.0, singlet, C_5-H. On the basis of the above pmr signals the structure 2,2-dimethylmethylene-3-methyl-6-phenyl-2,3,4-trihydrofuro (2,3-h)[2H,7H]-benzopyran-7-one was tentatively assigned for (**3A**).[11] ^{13}C NMR of (**3A**) showed signals ($CDCl_3$) at δ 15.9 and 25.3, quartets for three -CH_3 groups one at C-3 and two at C-1. Doublet for -CH-CH_3 group was observed at 44 and a singlet at 50 was observed for C-1. Singlets for aromatic carbons C-6, C-10, C-11 and C-1' were observed at δ 123.8, 125.4, 126.3 and 131.5 ppm; One downfield doublet and singlet for C-5 and C-11a were observed at δ 152.4 and 153.5 ppm respectively; Other aromatic carbons appeared as doublets at δ 128.1, 128.3 and 128.9 ppm; surprisingly it showed two singlets in the downfield carbonyl region, one at δ 175.8 and the other at 220.8 ppm. The former was assigned to the carbonyl group of pyran ring system, while the latter was assigned to an overcrowded carbonyl group of cyclopentenone ring system. The presence of a second carbonyl group was confirmed by its IR spectrum which showed two bands, one at 1640 cm^{-1} for the

carbonyl group of the pyran ring system and the other at 1740 cm^{-1} for the carbonyl group of the cyclopentenone ring system. Based on these observations, the structure (3A) is now revised to structure 1,2,3,7-tetrahydro-1,1,3-trimethyl-6-phenylcyclopenta (2,3-h) [2H, 7H]-benzopyran-2,7-dione (3). The

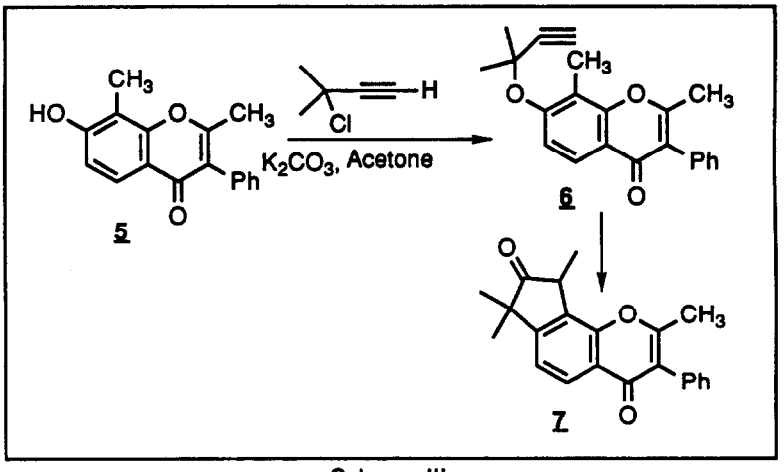


Scheme-II

mechanism for the formation of (3) can be given as shown in (scheme-II). (2), on Claisen rearrangement gives cyclohexadienone structure (B), the propargyl system collapsing into an allene system. This structure can not undergo aromatization as there are no protons on the neighbouring carbon atom. Hence it underwent an intramolecular Diels-Alder reaction to give a tricyclic ring system shown in the structure (C). The cyclopropane ring system in (C), being highly unstable, undergoes an initial ring opening by retro [4+2] to give the intermediate (D) which undergoes 6π electrocyclisation to give (E) and finally tautomerise to compound (3). Thus this mechanism involves four thermally allowed six-electrons concerted reactions. The metamorphosis of the structural changes can be visualized by assigning α, β and γ nomenclature to the carbon atoms of the ether chain. In the final structure, the β and γ carbons of the side chain are now part of the new benzene ring and the γ carbon carrying the gem-dimethyl group becomes the part of cyclopentenone ring system. Similar observations were made by Zsindely and Schmid[12] suggesting the formation of a tricyclic ketone which is thermally unstable and can form 2-indenones but without any details about its formation. Another product was obtained by purification on preparative TLC using benzene as the solvent. It was assigned to be 8,8,10-trimethyl-3-phenylpyrano (2,3-g)[4H]-1-benzopyran-4-one (4), on the basis of pmr ($CDCl_3$) showing signals at 1.6, singlet, 6H, two -CH_3 groups at C-8; 2.5, singlet, 3H, -CH_3 at

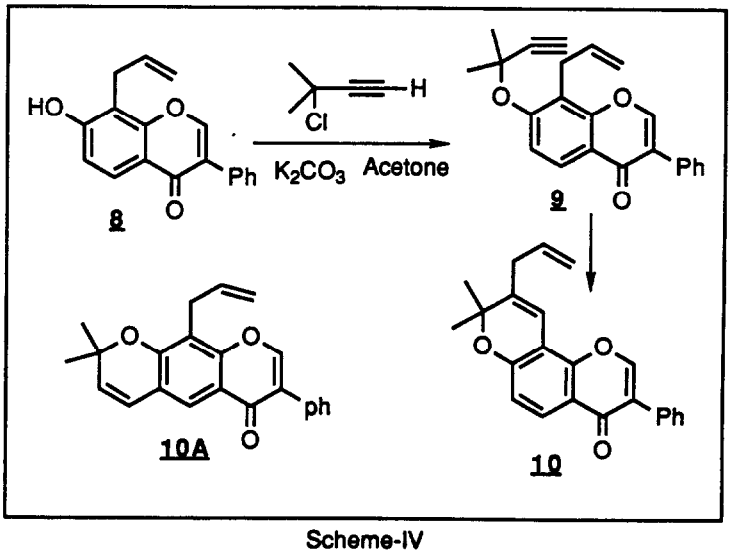
C-10; 5.85, doublet, J 10Hz, C_7-H; 6.5, doublet, J 10Hz, C_8-H. These two doublets at δ 5.85 and 6.5 confirmed the benzopyran nature of the product. 7.3-7.5, multiplet, 5H, Ar-H; 7.85, singlet, C_2-H; 8.1, singlet, C_5-H indicates that ring closure had taken place at C-6 of the isoflavone ring.

2,8-Dimethyl-7-hydroxy-3-phenyl-[4H]-1-benzopyran-4-one (5) was condensed with 3-chloro-3-methyl but-1-yne in the presence of K_2CO_3 and KI refluxing in acetone solvent to give 7-(1,1-dimethyl-3-prop-2-ynyloxy)-2,8-dimethyl-3-phenyl-[4H]-1-benzopyran-4-one (6). (Scheme-III). On refluxing compound (6) in



Scheme-III

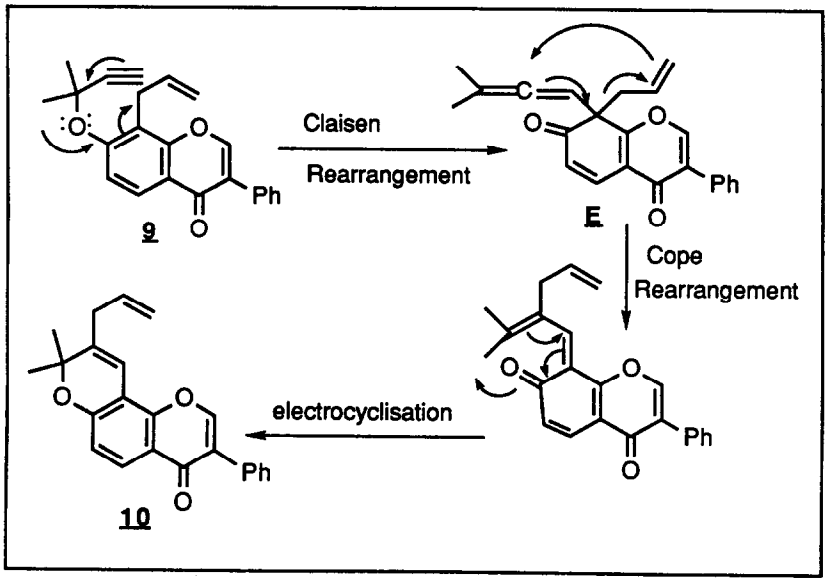
dimethylaniline for 8 h, the product obtained was purified by column chromatography using benzene as eluent. It exhibited pmr ($CDCl_3$) at δ 1.37 and 1.4, two closely spaced singlets for two methyl groups at C-1; 1.65, doublet, J 9Hz, 3H, C_3-CH_3; 2.35, singlet, 3H, C_5-CH_3; 3.8, quartet, J 9Hz, C_3-H; 7.25, multiplet, 5H, Ar-H; 8.1, doublet, J 9Hz, C_8-H. Further (6) showed two bands in the carbonyl region, one at 1620 cm^{-1} for



Scheme-IV

pyran carbonyl group while another at 1750 cm^{-1} for cyclopentenone carbonyl group. Thus on the basis of pmr and IR spectra and also in analogy with compound (**3**), the structure 1,2,3,7-tetrahydro-1,1,3,5-tetramethyl-6-phenylcyclopenta (2,3-h) [2H, 7H]-benzopyran-2,7-dione is assigned to (**7**).

7-Hydroxy-8-(prop-2-enyl)-3-phenyl-[4H]-1-benzopyran-4-one (**8**) was condensed with 3-chloro-3-methyl-but-1-yne in the presence of K_2CO_3 and KI refluxing in acetone, to furnish 7-(1,1-dimethyl-3-prop-2-ynyloxy)-8-(prop-2-enyl)-3-phenyl-[4H]-1-benzopyran-4-one (**9**). (Scheme-IV). It was refluxed in dimethylaniline for 3 h to obtain rearranged product 2,2-dimethyl-7-phenyl-3-(prop-2-enyl)pyrano (2,3-h)[8H]-1-benzopyran-8-one (**10**). Its pmr ($CDCl_3$) exhibited the signals at δ 1.4, singlet, 6H, two $-CH_3$ groups at C-2; 2.85, doublet, J 8Hz, 2H, $-C\underline{H}_2-CH=CH_2$ at C-3; 5.1, multiplet, 2H, $-CH_2-CH=C\underline{H}_2$; 5.8, multiplet, 1H, $-CH_2-C\underline{H}=CH_2$; 6.5, singlet, 1H at C-4; 6.7, doublet, J 9Hz, C_{10}-H; 7.1-7.5, multiplet, 5H, Ar-H; 7.8, singlet, C_6-H; 7.9, doublet, J 9Hz, C_9-H. The expected structure 8,8-dimethyl-10-(prop-2-enyl)-3-phenylpyrano (2,3-g) [4H]-1-benzopyran-4-one (**10A**) is eliminated because it did not show the two doublets around 6.0-7.0, J 10Hz for protons at C6 and C7 and also the downfield singlet of the proton at C-5. The fact that it showed two doublets at δ 7.9 and 6.7 indicates that the migration had taken place at C-8 and not at C-6 of the benzopyrone ring system. The mechanism for the formation of compound (**10**) is shown in scheme-V. Here

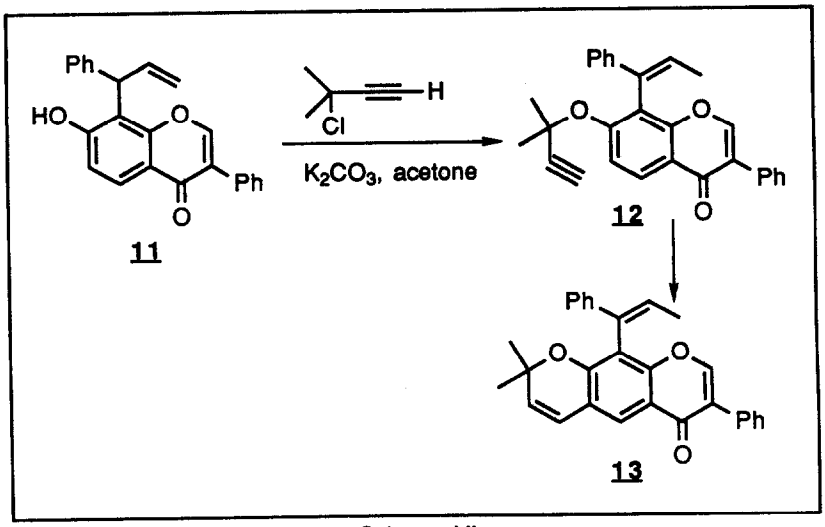


Scheme-V

the Claisen rearrangement first takes place on C-8 position, the acetylenic side chain collapsing to an allenic system to furnish intermediate structure (**E**), which further undergoes a [3, 3] sigmatropic Cope rearrangement, followed by cyclization through the carbonyl group to produce a dimethylpyran ring having allyl side chain at C-3. The structure of compound (**10**) was further confirmed by ^{13}C NMR ($CDCl_3$) showing signals at δ 25.9 ppm, quartet for two $-CH_3$ groups at C-2; 36.3 ppm, triplet for $-\underline{C}H_2-CH=$ at C-3; 80 ppm, singlet, quaternary carbon at C-2; 110.5 ppm, singlet, quaternary carbon at 8a; 111.5 ppm, doublet for vinylic carbon $-\underline{C}H=CH_2$, 114.9 ppm, doublet, C-4; 118.0 ppm, triplet for $-CH=\underline{C}H_2$; 118.4 ppm, singlet for quaternary carbon, C-3; three singlets for aromatic carbons at C-7, C-1' and C-12 were observed at δ 124.9,

131.9 and 140.3 ppm. One downfield doublet for C-6 and two downfield singlets for C-11 and C-12a were observed at δ 152, 156 and 151 ppm respectively. Other aromatic carbons appeared as doublets at δ 125.8, 127.9, 128.3, 128.9 and 134.6 ppm. A singlet for carbonyl carbon appeared at δ 175.6 ppm. IR spectrum confirmed the structure by showing only one band for carbonyl group at 1635 cm^{-1}.

7-Hydroxy-8-(1-phenyl-2-propenyl)-3-phenyl-[4H]-1-benzopyran-4-one (**11**) was condensed with 3-chloro-3-methyl-but-1-yne in the presence of anhyd. K_2CO_3 and KI in the acetone. The product (**12**), is formed as a result of a prototopic rearrangement of double bond present in the propylene side chain. This rearrangement was occurring from the terminal carbon to C-1 carbon atom. Pmr ($CDCl_3$) of (**12**) exhibited two singlets at δ 1.35 and 1.5, gem dimethyl groups at C-8, 1.65, doublet, J 7Hz, 3H, >C=CH-C<u>H</u>$_3$. 2.6,



Scheme-VI

singlet of acetylenic proton; 6.4, multiplet, 1H, >C=C<u>H</u>-CH_3; 7.2-7.8, multiplet for 11H, Ar-H; 7.9, singlet, C_2-H; 8.3, doublet, J 9Hz, C_5-H. The doublet for the methyl group at 1.65 indicated that the terminal double bond present in the 1-phenyl-2-propenyl side chain has isomerized giving rise to terminal methyl group. This reaction occurred due to presence of weak alkali K_2CO_3 in the reaction mixture in which substance was heated for a very long period. (**12**) was further subjected to Claisen rearrangement followed by [1, 5] shift and 6π electrocyclisation by refluxing it in dimethylaniline for 8 h to furnish 2,2-dimethyl-7-phenyl-10-(1-phenyl-prop-1-enyl) pyrano (2,3-g)-1-benzopyran-[6H]-one (**13**). Pmr ($CDCl_3$) exhibited signals at δ 1.1 and 1.35, two singlets for 6H, -CH_3 groups at C-2; 1.65, doublet, J 9Hz, >C=CH-C<u>H</u>$_3$ at C-10; 5.7, doublet, J 9Hz, C_3-H; 6.4, multiplet, 2H, overlapping signals of C_4-H and >C=C<u>H</u>-CH_3; 7.2-7.5, multiplet, 10H, Ar-H; 7.8, singlet, C_8-H; 7.95, singlet, C_5-H. The singlet at 7.95 for the proton at C-5 indicated that the ring closure had taken place at C-6 of the benzopyrone ring and not at C-8 as has been previously observed. (Scheme-VI)

Experimental

All melting points are uncorrected. Pmr spectra are recorded on a 90 MHz spectrometer using TMS as internal standard. The silica gel used for column chromatography had mesh size 60-120.

7-(1,1-Dimethyl-3-prop-2-ynyloxy)-8-methyl-3-phenyl-[4H]-1-benzopyran-4-one (2). A mixture of 7-hydroxy-8-methyl-3-phenyl-[4H]-1-benzopyran-4-one (1) (4.0 g, 0.016 mol), 3-chloro-3-methyl-but-1-yne (2 ml), anhyd. K_2CO_3 (10.0 g) and KI (0.05 g) was refluxed in dry acetone for 72 h. After every 10 h, 1 ml of fresh reagent was added to the reaction mixture. The reaction mixture was poured in cold water. It was filtered, dried and crystallized from benzene to obtain (2), (1.0 g, 20%); m.p. 150°C; (Found: C, 79.3; H,5.5. $C_{21}H_{18}O_3$ requires: C,79.2; H,5.6%). Pmr($CDCl_3$): 1.6 (s, 6H, 2 -CH_3 groups); 2.2 (s, 3H, Ar-CH_3), 2.5 (s, 1H, ≡CH); 7.2-7.6 (m, 6H, Ar-H); 7.9 (s, 1H, C_2-H); 8.0 (d, J 9Hz, 1H, C_5-H); IR spectrum shows band at 3200 cm-1 for terminal alkyne group.

1,2,3,7-Tetrahydro-1,1,3-trimethyl-6-phenylcyclopenta (2,3-h) [2H,7H]-benzopyran-2,7-dione (3) and 8,8,10-trimethyl-3-phenylpyrano (2,3-g) [4H]-1-benzopyran-4-one (4). (2) (1.0 g, 0.0031 mol) was refluxed in dimethylaniline (7 ml) for 5 h. Reaction mixture was cooled and poured into mixture of crushed ice and conc. HCl. It was subjected to column chromatography. Fraction A: Light petroleum ether was eluted to obtain (3) with light yellow fluorescence. It crystallized from benzene + pet. ether (0.125 g, 12.5%); m.p. 165°C; (Found: C, 79.6; H, 5.4. $C_{21}H_{18}O_3$ requires: C, 79.2; H,5.6%). Fraction B: on eluting benzene, (4) was obtained which was further purified by preparative TLC giving product in traces, with bluish white fluorescence. It crystallized from petroleum ether (0.03 g, 3%); m.p. 136-40°C; (Found: C, 78.9; H, 6.0. $C_{21}H_{18}O_3$ requires: C, 79.2; H, 5.7%).

7-(1,1-Dimethyl-3-prop-2-ynyloxy)-2,8-dimethyl-3-phenyl-[4H]-1-benzopyran-4-one (6). A mixture of 2,8-dimethyl-7-hydroxy-3-phenyl-[4H]-1-benzopyran-4-one (5) (6.0 g), 3-chloro-3-methyl-but-1-yne (3 ml), anhyd. K_2CO_3 (15.0 g) and KI (0.05 g) was refluxed in dry acetone for 70-72 h. After each 10 h, 1 ml of fresh reagent was added. Reaction mixture was poured over crushed ice and left overnight. Next day solid was separated and crystallized from benzene to obtain (6) (2.0 g, 22.7%); m.p. 125°C; (Found: C, 79.9; H, 5.8. $C_{22}H_{20}O_3$ requires: C, 79.5; H, 6.0%). Pmr($CDCl_3$): δ 1.75 (s, 6H, CH_3); 2.34 and 2.35 (two closely spaced singlets, 6H, C_2-CH_3 and C_8-CH_3); 2.65 (s, 1H, ≡CH); 7.3 (m, 5H, Ar-H); 7.6 (d, J 9Hz, C_6-H); 8.0 (d, J 9Hz, C_5-H).

1,2,3,7-Tetrahydro-1,1,3,5-tetramethyl-6-phenylcyclopenta-[2H,7H]-benzopyran-2,7-dione (7). (6) (1.0 g) was refluxed with dimethylaniline (7.0 ml) for 8 h. Reaction mixture was cooled and poured over crushed ice and conc. HCl mixture. Solid was separated, filtered and dried. Inspection on TLC gave only one spot. It was purified by column chromatography using benzene as eluent and crystallized from benzene + light petroleum ether (0.3 g, 30%); m.p. 165°C; (Found: C, 79.9; H,5.8. $C_{22}H_{20}O_3$ requires: C, 79.5; H, 6.2%).

7-(1,1-Dimethyl-3-prop-2-ynyloxy)-8-(prop-2-enyl)-3-phenyl-[4H]-1-benzopyran-4-one (9). A mixture of 7-hydroxy-8-(prop-2-enyl)-3-phenyl-[4H]-1-benzopyran-4-one (8) (2.0 gm), 3-chloro-3-methyl-but-1-yne (2.0 ml), anhyd. K_2CO_3 (7.0 g) and KI (0.02 g) in dimethylformamide (8.0 ml) was refluxed with stirring for 25 h. 0.5 ml of fresh reagent was added after interval of 6 h. Reaction mixture was cooled, filtered and excess of solvent was distilled off. It was poured over crushed ice, the product crystallized from benzene (1 g, 40%); m.p. 138°; (Found: C, 80.7; H, 6.0. $C_{23}H_{20}O_3$ requires: C, 80.2; H, 5.8%). Pmr($CDCl_3$): δ 1.75 (s, 6H, CH_3 groups at C-2); 2.7 (s, 1H, -C≡C<u>H</u>); 3.6 (d, J 8Hz, 2H, Ar-CH_2-); 5.0 (m, 2H, -CH_2-CH=C<u>H</u>$_2$); 6.0 (m, 1H, -CH_2-C<u>H</u>=CH_2); 7.4 (m, 5H, Ar-H); 7.65 (d, J 9Hz, C_6-H); 8.05 (d, J 9Hz, C_5-H); 7.9 (s, 1H, C_2-H).

2,2-Dimethyl-7-phenyl-3-(prop-2-enyl)pyrano (2,3-h)[8H]-1-benzopyran-8-one (10). (1.0 g) of (9) was refluxed with dimethylaniline (7.0 ml) for 3 h. Reaction mixture was cooled and poured into mixture of crushed ice and conc. HCl. Solid was separated, filtered and dried. It was purified by passing through the column of silica gel using benzene as eluent. It crystallized from benzene + petroleum ether (0.25 g, 25%); m.p. 165°C; (Found: C, 80.9; H, 5.6. $C_{23}H_{19}O_3$ requires: C, 80.5; H, 5.5%).

7-(1,1-Dimethyl-3-prop-2-ynyloxy)-3-phenyl-8-(1-phenyl prop-2-enyl) benzopyran-[4H]-one (12). A mixture of (11) (2.0 g), 3-chloro-3-methyl-but-1-yne (2.0 ml), anhyd. K_2CO_3 (7.0 g) and KI (0.02 g) was refluxed with stirring in dimethylformamide for 25 h. 0.5 ml of fresh reagent was added after interval of 6 h. Reaction mixture was cooled, filtered and excess of solvent was distilled off. It was poured over crushed ice, solid separated, filtered and dried. It crystallized from benzene (1.2 g, 50%); m.p. 160°C; (Found: C, 82.4; H, 5.6. $C_{29}H_{24}O_3$ requires: C, 82.8; H, 5.7%).

2,2-Dimethyl-7-phenyl-10-(1-phenyl-prop-1-enyl)pyrano (2,3-g) benzopyran-[6H]-one (13). (1.0 g) of (12) was refluxed with dimethylaniline (7.0 ml) for 8 h. Reaction mixture was cooled and poured into mixture of crushed ice and conc. HCl. Solid obtained was filtered, dried and crystallized from benzene (0.4 g, 40%); m.p. 161-2°C; (Found: C, 82.4; H, 5.8. $C_{29}H_{24}O_3$ requires: C, 82.8; H, 5.7%).

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