Zeolite-Induced Heterodomino Reaction. Regioselective Synthesis of 2*H*-1-Benzopyrans from Phenols and α-Alkynols

Franca Bigi, Silvia Carloni, Raimondo Maggi, Chiara Muchetti, and Giovanni Sartori*

Dipartimento di Chimica Organica e Industriale dell'Università, Viale delle Scienze, I-43100 Parma, Italy

Received April 16, 1997

Introduction

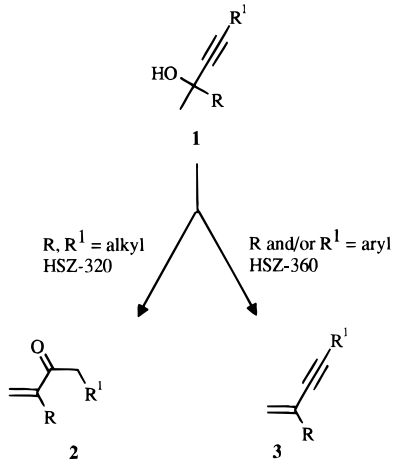
The development of "one-pot reactions" represents a great challenge in organic synthesis today. Indeed this strategy allows the construction of highly complex molecules from relatively simple reagents under economically favorable conditions. Moreover the combination of the "one-pot strategy" with the use of environmentally friendly solid acid catalysts is now the best tool for preparation of specific target compounds with minimum production of pollutants as well as reduction of the cost.[1]

As part of a program designed to develop new selective and preparatively useful methodologies based on the use of solid acids as promoters for fine chemicals preparation, previous studies from these laboratories have described the rearrangement−dehydration of α-alkynols to α,*β*-unsaturated ketones or conjugated enynes over zeolite catalyst.[2] Thus, heating a slurry of zeolite HSZ-360[3] and α-alkynols **1** at 130 °C in chlorobenzene led to α,*β*-unsaturated ketones **2** or conjugated enynes **3** depending on R and R^1 being alkyl or aryl groups (Scheme 1).

In light of these results it was thought that enynes **3** produced from α-alkynols **1** would offer the potential for subsequent bisalkylation of phenol substrates leading to the construction of 2*H*-1-benzopyrans **5** with proper regiochemical control (Scheme 2, route A) following a chemical behavior similar to that previously observed with conjugated dienes[4] (Scheme 2, route B).

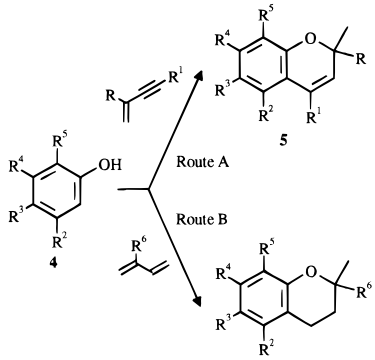
The 2*H*-1-benzopyran ring system constitutes the basic skeleton of a variety of natural compounds showing interesting biological activities. Different synthetic approaches to these compounds are reported in the literature, including addition of Grignard reagents to coumarins and chromanones, Dieckmann and aldol-type condensation of convenient aromatic carbonyl compounds or thermal rearrangement of propargyl phenyl ethers.[5] Acid-catalyzed reaction of phenols with α-alkynols was also attempted, but yields reported are less than 10%.[6]

Scheme 1



v: R=CH_3, R^1=H; **w**: R=C_2H_5, R^1=CH_3
x: R=C_6H_5, R^1=H, **y**: R=CH_3, R^1=C_6H_5
z: R=C_6H_5, R^1=CH_3

Scheme 2



We have thus reinvestigated this reaction under zeolite catalysis. Here we show the results of these studies.

Results and Discussion

We have first pursued evidence for the feasibility and the regioselective control of the reaction of enynes with phenols under solid acid catalysis. Indeed, although many examples of bisalkylation of phenols with dienes to produce chromans or benzofurans are known,[7] to the best of our knowledge the same reaction with enynes was not reported.

Treatment of *p*-methoxyphenol (**4c**) with 3-phenyl-3-buten-1-yne (**3x**) in the presence of zeolite HSZ-360 [commercial faujasitic-type zeolite with 13.9 SiO_2/Al_2O_3 molar ratio, pore size 8 Å, surface area 500 ± 10 m^2/g[8], and acidity 0.51 mequiv H^+/g[9]] in chlorobenzene at reflux

(1) (a) Tietze, L. F.; Beifuss, U. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 131. (b) Grigg, R.; Sridharan, V. *Comprehensive Organometallic Chemistry*; 2nd ed.; Abel, E., Wikinson, G., Stone, F. G. A., Eds., Pergamon Press: New York, 1995; Vol. 12, Chapter 3,6. (c) Padua, A. *Chem. Rev.* **1996**, *96*, 223. (d) Grigg, R.; Putnikovic, B.; Urch, C. *Tetrahedron Lett.* **1996**, *37*, 695. (e) Grigg, R.; Sridharan, V.; Terrier, C. *Tetrahedron Lett.* **1996**, *37*, 4221. (f) Negishi, E.; Coperet, C.; Ma, S.; Liou, S. Y.; Liu, F. *Chem. Rev.* **1996**, *96*, 365. (g) Denmark, S. E.; Senanayake, C. B. W. *Tetrahedron*, **1996**, *52*, 11579.

(2) Sartori, G.; Pastorio, A.; Maggi, R.; Bigi, F. *Tetrahedron* **1996**, *52*, 8287.

(3) HSZ-360 acidic zeolite was purchased by Tosoh Corp.

(4) Bolzoni, L.; Casiraghi, G.; Casnati, G.; Sartori, G. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 684.

(5) (a) Schweizer, E. E.; Meeder-Nycz, D. 2*H*- and 4*H*-1-Benzopyrans. In *Heterocyclic Compounds. Chromenes, Chromanones and Chromanes*, Ellis, G. P., Ed., John Wiley and Sons: NY, 1977; pp 11−139. (b) North, J. T.; Kronenthal, D. R.; Pullockaran, A. J.; Real, S. D.; Chen, H. Y. *J. Org. Chem.* **1995**, *60*, 3397.

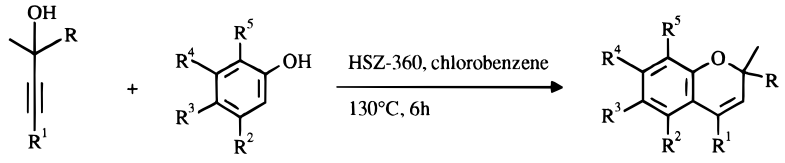
(6) (a) Cardillo, G.; Merlini, L. *Gazz. Chim. Ital.* **1968**, *98*, 191 (*Chem. Abstr.* **1968**, *69*, 43735*k*). (b) Hoffman, F. *Br. Patent* 877,960, 1960 (*Chem. Abstr.* **1962**, *56*, 7282). (c) Pendse, H.; Ruegg, R.; Ryser, G. U.S. Patent 3,004,040, 1960 (*Chem. Abstr.* **1962**, *56*, 8693d).

(7) (a) Dauben, W. G.; Cogen, J. M.; Behar, V. *Tetrahedron Lett.* **1990**, *31*, 3241. (b) Pochini, A.; Marchelli, R.; Bocchi, V. *Gazz. Chim. Ital.* **1975**, *195*, 1245. (c) Mohamed, S. E. N.; Thomas, P.; Whiting, D. A. *J. Chem. Soc., Chem. Commun.* **1983**, 738. (d) Laan, J. A. M.; Geisen, F. L. L.; Ward, J. P. *Chem. Ind.* **1989**, 354. (e) Wehrli, P. A.; Fryer, R. I.; Metlesics, W. *J. Org. Chem.* **1971**, *36*, 2910. (f) Molyneux, R. J.; Jurd, L. *Tetrahedron* **1970**, *26*, 4743.

(8) Determined in our laboratory by the BET method: Brunauer, S.; Emmett, P. H.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309.

S0022-3263(97)00690-7 CCC: $14.00

Table 1. Synthesis of some 2*H*-1-Benzopyrans 5



entry	R	R^1	R^2	R^3	R^4	R^5	product	yield (%)	selectivity (%)
1	C_6H_5	H	H	H	H	H	**5ax**	40	90
2	C_6H_5	H	H	OH	H	H	**5bx**	75	95
3	C_6H_5	H	H	OCH_3	H	H	**5cx**	60	90
4	C_6H_5	H	H	$-OCH_2O-$		H	**5dx**	50	85
5	C_6H_5	H	$-CH=CHCH=CH-$		H	H	**5ex**	75	95
6	C_6H_5	H	H	H	$-CH=CHCH=CH-$		**5fx**	66	95
7	C_6H_5	H	CH_3	OH	CH_3	CH_3	**5gx**	50	85
8	CH_3	C_6H_5	H	OCH_3	H	H	**5cy**	70	90
9	CH_3	C_6H_5	$-CH=CHCH=CH-$		H	H	**5ey**	60	95
10	CH_3	C_6H_5	H	H	$-CH=CHCH=CH-$		**5fy**	65	94
11	CH_3	C_6H_5	CH_3	OH	CH_3	CH_3	**5gy**	25	95
12	C_6H_5	CH_3	H	OCH_3	H	H	**5cz**	70	98
13	C_6H_5	CH_3	H	H_3	OCH_3	H	**5hz**	60	90

for 3 h afforded the expected product **5cx** in 65% yield and 92% selectivity. Further experiments performed in the absence of any catalyst gave no reaction; use of Lewis acids (previously utilized in similar reactions with dienes)[7] gave mixtures of products.

The reaction could be carried out in a more rapid fashion by using 3-phenyl-1-butyn-3-ol (**1x**), the precursor of **3x**, with only a slight decrease in efficiency (60% yield, 90% selectivity) (Table 1, entry 3).

To investigate the generality of this process, the α-alkynols **1x**−**z** and phenols **4a**−**h** were subjected to similar reaction conditions allowing the easy synthesis of 2*H*-1-benzopyrans **5ax**−**hz** (Table 1).

The key step of the present process is a typical electrophilic substitution, since the presence of electron-donating groups on the phenol ring results in a more facile and more efficient production of compounds **5** (Table 1, entries 2−5). However, the process suffers from some steric hindrance. Indeed, trimethyl hydroquinone (**4g**) reacts with 3-phenyl-1-butyn-3-ol (**1x**) [R′ = H], affording the product **5gx** in 50% yield, whereas the reaction with 3-methyl-1-phenyl-1-butyn-3-ol (**1y**) [R′ = C_6H_5] produces compound **5gy** in 25% yield (Table 1, entries 7 and 11).

The regiochemical outcome of the present reaction appears to be the same with all α-alkynols and phenols utilized since in all cases the sole products arise from interaction of the phenol oxygen with the olefinic double bond and the *ortho*-carbon of the phenol ring with the acetylenic framework of the enyne intermediate.[10] The process shows also complete *ortho*-regiospecificity with respect to the phenol ring (Table 1, entry 1).

On the basis of our previous studies concerning the dehydration of α-alkynols to conjugated enynes[2] and the *ortho*-regioselective alkenylation of phenols and aromatic amines with alkynes under zeolite catalysis,[11] we believed that enynes **3** might be the actual alkylating reagents.

To this purpose we studied the reaction of *p*-methoxyphenol (**4c**) with α-alkynols **1v** (R = CH_3, R^1 = H) and **1w** (R = C_2H_5, R^1 = CH_3) which in the presence of zeolite HSZ gave α,*β*-unsaturated ketones **2v** and **2w** instead of conjugated enynes *via* a Rupe rearrangement.[2] Under the conditions used in the previous experiments, compounds **2v** and **2w** were recovered in 40% and 62% yield, respectively, as the sole products. Guided by these results and previous studies from literature,[12] we envisaged two possible modes by which the enyne might react with the phenol: a direct attack of the carbon−carbon triple bond on the *ortho*-position of the aromatic ring (Scheme 3, route A) or prior aryl propargyl ether formation followed by a Claisen-like rearrangement (Scheme 3, route B). However we argue against the last formulation, because attempts to isolate the aryl propargyl ether in the reaction of 2,4,6-trimethylphenol (**4i**) with 3-phenyl-1-butyn-3-ol (**1x**) resulted in the complete recovering of **4i** accompanied by 3-phenyl-3-buten-1-yne (**3x**) in 92% yield.[13]

The moderately acidic zeolite HSZ-360 first promotes the dehydration of **1** to **3**, which then regioselectively adds to the phenol substrate **4** to yield dienic compound **7**; further isomerization of **7** to tautomers **8** or **9** followed by an electrocyclic rearrangement affords the target compound **5**, in agreement with previously reported studies.[12]

In conclusion, zeolite HSZ-360 allows both dehydration of α-alkynols to conjugated enynes and their successive regiospecific reaction with phenols, giving 2*H*-1-benzopyrans in good yields with a minimum number of synthetic steps according to a typical heterodomino process.[14]

Experimental Section

General. Melting and boiling points are uncorrected. ^{1}H NMR spectra were recorded at 400 and 300 MHz. Mass spectra were obtained in EI mode at 70 eV. Microanalyses were carried

(9) Determined in our laboratory by temperature programmed desorption of ammonia gas (NH_3-TPD): Berteau, P.; Delmon, B. *Catal. Today* **1989**, *5*, 121.

(10) Confirmed by ^{1}H NMR NOESY experiment showing, for example, a strong cross-peak correlation between the H-5 naphtholic hydrogen and the H-4 olefinic hydrogen in compound **5fx**.

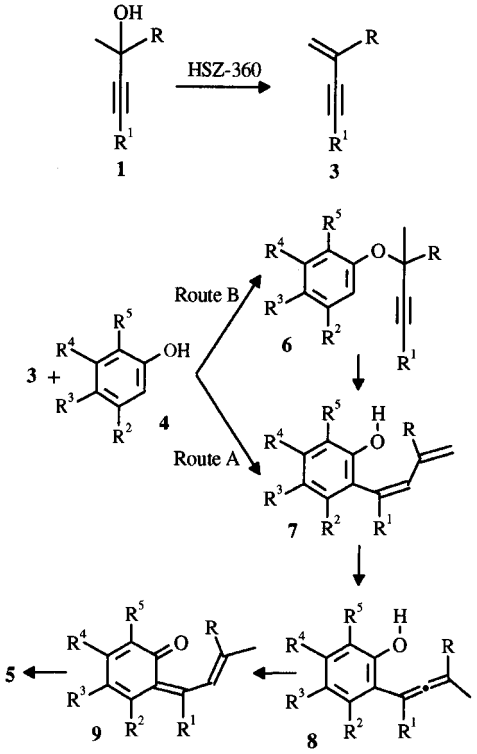
(11) (a) Sartori, G.; Bigi, F.; Pastorio, A.; Porta, C.; Arienti, A.; Maggi, R.; Moretti, N.; Gnappi, G. *Tetrahedron Lett.* **1995**, *50*, 9177. (b) Arienti, A.; Bigi, F.; Maggi, R.; Marzi, E.; Moggi, P.; Rastelli, M.; Sartori, G.; Tarantola, F. *Tetrahedron* **1997**, *53*, 3795.

(12) (a) Richey, H. G., Jr.; Philips, J. C.; Renmick, L. E. *J. Am. Chem. Soc.* **1965**, *87*, 1381. (b) Zsindely, J.; Schmid, H. *Helv. Chem. Acta* **1968**, *51*, 1510. (c) Harfenist, M.; Thom, E. *J. Org. Chem.* **1972**, *37*, 841. (d) Rao, U.; Balasubramanian, K. K. *Tetrahedron Lett.* **1983**, *24*, 5023. (e) Tsukayama, M.; Utsumi, H.; Kunugi, A. *J. Chem. Soc., Chem. Commun.* **1995**, 615.

(13) It is important to emphasize that the rearrangement of aryl propargyl ethers requires high temperatures (220−240 °C), whereas the present reaction occurs at 130 °C.

(14) Tietze, L. F. *Chem. Rev.* **1996**, *96*, 115.

Scheme 3



out by Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica dell'Università di Parma, Italy. TLC analyses were performed on Merck 60 PF_{254} silica gel plates using mixtures of hexane−ethyl acetate (5−25%). The solvents were dried on 4 Å molecular sieves. All the reagents were of commercial quality from freshly opened containers. Zeolite HSZ-360 (Tosoh Corp.) was utilized without previous thermal or chemical treatment.

Synthesis of α-alkynols 1. General Procedure. The α-alkynols were synthesized as reported in the literature starting from convenient acetylenic compounds (100 mmol) and ketones (100 mmol).[15]

3-Methyl-1-phenyl-1-butyn-3-ol (1y): yield 15.9 g (99%), pale yellow solid; mp 53−54 °C (Et_2O); ^1H NMR (300 MHz, $CDCl_3$) δ 7.5−7.2 (5 H, m), 2.2 (1 H, br s), 1.61 (6 H, s); IR (KBr) 3278, 2320 cm^{-1}; MS *m*/*z* (M^+) 160 (23), 145 (30), 115 (18). Anal. Calcd for $C_{11}H_{12}O$: C, 82.5; H, 7.6. Found: C, 82.3; H, 7.8.

2-Phenyl-3-butyn-2-ol (1z): yield 14.4 g (90%), white solid, mp 41−42 °C (lit.[2] mp 41−42.5 °C).

Synthesis of 2*H*-1-Benzopyrans 5. General Procedure. The selected alkynol (10 mmol), the selected phenol (10 mmol), and zeolite HSZ-360 (1 g) in chlorobenzene (10 mL) were heated at reflux for 6 h. After cooling to rt, the catalyst was removed by filtration and washed with diethyl ether (100 mL); the solvents were distilled off and the crude was chromatographed on silica gel column with hexane−ethyl acetate mixtures to give the products.

2-Methyl-2-phenyl-2*H*-1-benzopyran (5ax): yield 0.9 g (40%), pale yellow liquid; bp 71−73 °C/0.05 mmHg; ^1H NMR (300 MHz, $CDCl_3$) δ 7.50 (2 H, d, *J* = 7.3 Hz), 7.31 (2 H, t, *J* = 7.3 Hz), 7.22 (1 H, t, *J* = 7.3 Hz), 7.11 (1 H, td, *J* = 7.3 and 1.4 Hz), 6.96 (1 H, dd, *J* = 7.3 and 1.4 Hz), 6.87 (1 H, d, *J* = 7.3 Hz), 6.81 (1 H, t, *J* = 7.3 Hz), 6.44 (1 H, d, *J* = 9.8 Hz), 5.91 (1 H, d, *J* = 9.8 Hz), 1.79 (3 H, s); MS *m*/*z* (M^+) 222 (10), 207 (100), 145 (25). Anal. Calcd for $C_{16}H_{14}O$: C, 86.5; H, 6.4. Found: C, 86.7; H, 6.2.

6-Hydroxy-2-methyl-2-phenyl-2*H*-1-benzopyran (5bx): yield 1.8 g (74%), pale red liquid; bp 100−102 °C/0.05 mmHg; ^1H NMR (300 MHz, $CDCl_3$) δ 7.7−7.1 (5 H, m), 6.74 (1 H, d, *J* = 8.6 Hz), 6.56 (1 H, dd, *J* = 8.6 and 2.9 Hz), 6.44 (1 H, d, *J* = 2.9 Hz), 6.36 (1 H, d, *J* = 9.7 Hz), 5.96 (1 H, d, *J* = 9.7 Hz), 4.7 (1 H, br s), 1.74 (3 H, s); IR (NaCl) 3375 cm^{-1}; MS *m*/*z* (M^+) 238 (23), 223 (100), 161 (26). Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.7; H, 5.9. Found: C, 80.9; H, 6.2.

6-Methoxy-2-methyl-2-phenyl-2*H*-1-benzopyran (5cx): yield 1.5 g (60%), pale yellow liquid; bp 113−115 °C/0.05 mmHg; ^1H NMR (300 MHz, $CDCl_3$) δ 7.51 (2 H, d, *J* = 7.5 Hz), 7.32 (2 H, t, *J* = 7.5 Hz), 7.25 (1 H, t, *J* = 7.5 Hz), 6.83 (1 H, d, *J* = 8.7 Hz), 6.69 (1 H, dd, *J* = 8.7 and 3.0 Hz), 6.55 (1 H, d, *J* = 3.0 Hz), 6.43 (1 H, d, *J* = 9.7 Hz), 5.99 (1 H, d, *J* = 9.7 Hz), 3.74 (3 H, s), 1.77 (3 H, s); MS *m*/*z* (M^+) 252 (21), 237 (100), 175 (19). Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.9; H, 6.4. Found: C, 80.7; H, 6.3.

2-Methyl-6,7-(methylenedioxy)-2-phenyl-2*H*-1-benzopyran (5dx): yield 1.3 g (50%), pale yellow solid; mp 58−59 °C (Et_2O); ^1H NMR (300 MHz, $CDCl_3$) δ 7.45 (2 H, dm, *J* = 7.1 Hz), 7.25 (2 H, tm, *J* = 7.1 Hz), 7.15 (1 H, tt, *J* = 7.1 and 2.3 Hz), 6.46 (1 H, s), 6.38 (1 H, s), 6.25 (1 H, d, *J* = 9.7 Hz), 5.75 (1 H, d, *J* = 9.7 Hz), 5.70 (1 H, d, *J* = 11.6 Hz), 5.69 (1 H, d, *J* = 11.6 Hz), 1.69 (3 H, s); MS *m*/*z* (M^+) 266 (17), 251 (100), 189 (15). Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.7; H, 5.3. Found: C, 76.9; H, 5.2.

3-Methyl-3-phenyl-3*H*-naphtho[2,3-*b*]pyran (5ex): yield 2.0 g (75%), pale orange liquid; bp 75−78 °C/0.05 mmHg; ^1H NMR (300 MHz, $CDCl_3$) δ 8.09 (1 H, d, *J* = 8.2 Hz), 7.89 (1 H, d, *J* = 8.2 Hz), 7.84 (1 H, d, *J* = 8.2 Hz), 7.8−7.7 (2 H, m), 7.62 (1 H, ddd, *J* = 8.3, 7.0 and 1.3 Hz), 7.6−7.4 (4 H, m), 7.41 (1 H, d, *J* = 8.8 Hz), 7.32 (1 H, d, *J* = 9.9 Hz), 6.21 (1 H, d, *J* = 9.9 Hz), 2.04 (3 H, s); MS *m*/*z* (M^+) 272 (17), 257 (100), 195 (38), 128 (24). Anal. Calcd for $C_{20}H_{16}O$: C, 88.2; H, 5.9. Found: C, 88.0; H, 6.2.

2-Methyl-2-phenyl-2*H*-naphtho[1,2-*b*]pyran (5fx): yield 1.8 g (66%), pale orange liquid; bp 80−82 °C/0.05 mmHg; ^1H NMR (300 MHz, $CDCl_3$) δ 8.32 (1 H, d, *J* = 8.0 Hz), 7.72 (1 H, d, *J* = 8.0 Hz), 7.55 (2 H, d, *J* = 7.8 Hz), 7.5−7.2 (5 H, m), 7.20 (1 H, tm, *J* = 7.2 Hz), 7.11 (1 H, d, *J* = 8.3 Hz), 6.55 (1 H, d, *J* = 9.7 Hz), 5.97 (1 H, d, *J* = 9.7 Hz), 1.87 (3 H, s); MS *m*/*z* (M^+) 272 (22), 257 (100), 195 (18). Anal. Calcd for $C_{20}H_{16}O$: C, 88.2; H, 5.9. Found: C, 88.1; H, 6.0.

6-Hydroxy-2,5,7,8-tetramethyl-2-phenyl-2*H*-1-benzopyran (5gx): yield 1.4 g (50%), pale brown liquid; bp 116−118 °C/0.05 mmHg; ^1H NMR (300 MHz, $CDCl_3$) δ 7.48 (2 H, d, *J* = 7.3 Hz), 7.29 (2 H, t, *J* = 7.3 Hz), 7.20 (1 H, tm, *J* = 7.3 Hz), 6.65 (1 H, d, *J* = 10.1 Hz), 6.00 (1 H, d, *J* = 10.1 Hz), 4.18 (1 H, s), 2.23 (3 H, s), 2.14 (6 H, s), 1.72 (3 H, s); IR (NaCl) 3432 cm^{-1}; MS *m*/*z* (M^+) 280 (40), 235 (91), 207 (100). Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.4; H, 7.2. Found: C, 81.6; H, 7.2.

6-Methoxy-2,2-dimethyl-4-phenyl-2*H*-1-benzopyran (5cy): yield 1.9 g (70%), yellow liquid; bp 83−86 °C/0.05 mmHg; ^1H NMR (300 MHz, $CDCl_3$) δ 7.6−7.1 (5 H, m), 6.82 (1 H, d, *J* = 8.7 Hz), 6.71 (1 H, dd, *J* = 8.7 and 3.0 Hz), 6.57 (1 H, d, *J* = 3.0 Hz), 5.64 (1 H, s), 3.66 (3 H, s), 1.43 (6 H, s); MS *m*/*z* (M^+) 266 (11), 251 (100). Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.2; H, 6.8. Found: C, 81.4; H, 6.7.

3,3-Dimethyl-1-phenyl-3*H*-naphtho[2,3-*b*]pyran (5ey): yield 1.8 g (64%), yellow solid; mp 114−116 °C (Et_2O); ^1H NMR (300 MHz, $CDCl_3$) δ 7.70 (2 H, d, *J* = 8.6 Hz), 7.4−7.1 (7 H, m), 7.09 (1 H, d, *J* = 8.4 Hz), 7.01 (1 H, ddd, *J* = 8.0, 6.5 and 1.1 Hz), 5.69 (1 H, s), 1.49 (6 H, s); MS *m*/*z* (M^+) 286 (17), 271 (100), 135 (14). Anal. Calcd for $C_{21}H_{18}O$: C, 88.1; H, 6.3. Found: C, 87.9; H, 6.2.

2,2-Dimethyl-4-phenyl-2*H*-naphtho[1,2-*b*]pyran (5fy): yield 1.9 g (65%), pale orange oil; bp 165−166 °C/0.05 mmHg; ^1H NMR (300 MHz, $CDCl_3$) δ 8.3−7.3 (9 H, m), 7.29 (1 H, d, *J* = 8.5 Hz), 7.55 (1 H, d, *J* = 8.5 Hz), 5.63 (1 H, s), 1.57 (6 H, s); MS *m*/*z* (M^+) 286 (12), 271 (100). Anal. Calcd for $C_{21}H_{18}O$: C, 88.1; H, 6.3. Found: C, 88.0; H, 6.5.

6-Hydroxy-2,2,5,7,8-pentamethyl-4-phenyl-2*H*-1-benzopyran (5gy): yield 0.7 g (25%), pale yellow solid; mp 123−124 °C (Et_2O); ^1H NMR (300 MHz, $CDCl_3$) δ 7.4−7.1 (5 H, m), 5.68 (1 H, s), 4.23 (1 H, s), 2.20 (6 H, s), 1.62 (3 H, s), 1.41 (6 H, s); IR (KBr) 3494 cm^{-1}; MS *m*/*z* (M^+) 294 (19), 279 (100). Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.6; H, 7.5. Found: C, 81.9; H, 7.4.

6-Methoxy-2,4-dimethyl-2-phenyl-2*H*-1-benzopyran (5cz): yield 1.9 g (70%), yellow liquid; bp 85−88 °C/0.05 mmHg; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (2 H, dd, *J* = 7.3 and 1.4 Hz), 7.33 (2 H, t, *J* = 7.3 Hz), 7.24 (1 H, tt, *J* = 7.3 and 1.4 Hz), 6.9−6.7 (2 H, m), 5.84 (1 H, q, *J* = 1.5 Hz), 3.77 (3 H, s), 2.09 (3 H, d, *J* = 1.5 Hz), 1.76 (3 H, s); MS *m*/*z* (M^+) 266 (10), 251 (100),

(15) Midland, M. M. *J. Org. Chem.* **1975**, *40*, 2250.

189 (20). Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.2; H, 6.8. Found: C, 80.9; H, 6.9.

6,7-Dimethoxy-2,4-dimethyl-2-phenyl-2*H*-1-benzopyran (5hz): yield 1.8 g (60%), pale yellow solid; mp 80−82 °C (Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.6−7.1 (5 H, m), 6.66 (1 H, s), 6.53 (1 H, s), 5.62 (1 H, q, J = 1.5 Hz), 3.85 (3 H, s), 3.81 (3 H, s), 2.04 (3 H, d, J = 1.5 Hz), 1.72 (3 H, s); MS m/z (M^+) 296 (15), 281 (100), 219 (30). Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.0; H, 6.8. Found: C, 76.9; H, 6.6.

Acknowledgment. The authors acknowledge the support of the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST) "Progetto Nazionale Sintesi e Reattività Organica" (ex 40%) and the Consiglio Nazionale delle Ricerche (CNR), Italy. The authors are grateful to the Centro Interfacoltà Misure (CIM) for the use of NMR and mass instruments.

Supporting Information Available: ^{1}H NMR data of all compounds with peak assignments included (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the Journal and can be ordered from the ACS; see any current masthead page for ordering information.

JO970690Y