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CATALYTIC DECOMPOSITION OF BRANCHED α'-PHENOXY-α-DIAZO KETONES AFFORDING 2,8H-CYCLOHEPTA[b]FURAN-3-ONE AND 2H-CYCLOHEPTA[b]FURAN-3a(3aH)METHYL-3-ONE

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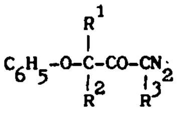
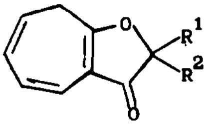
Abstract - The decomposition induced by bis(hexafluoroacetoacetonato)Cu II on branched α-diazo ketones **1** bearing a phenoxy group at the α'-carbon has been investigated. The course of the reactions has been shown to be dependent upon substitution. Mixtures of furanones **2** and chromanones **4** were obtained from α-unsubstituted substrates **1b-d**, as in the case of **1a**. Instead, among the α-mono substituted substrates **1f** and **1g** selectively gave cycloheptatrienes **3f** and **3g**, respectively, while **1e** and **1h** gave mixtures of the corresponding **3** and **4**. Cycloheptatrienes **3** easily rearranged to chromanones **4**. The intermediacy of norcaradienes **5** has been tentatively proposed in the catalytic decomposition of **1**, and in rearrangement of **3e-h** to **4e-h**.

The intramolecular cyclization of α-diazo carbonyl compounds under catalytic conditions has been extensively studied and interpreted according to a mechanism involving the addition of an intermediate carbenoid species to an olefinic or aromatic unsaturated system.[1-9] Participation by neighboring heteroatoms in the reaction of carbenes has also been considered and recently reviewed.[10] However, decomposition of α-diazo ketones bearing an aryloxy substituent at the α'-carbon atom has not been systematically investigated except for **1a** and related unbranched substrates, which afforded a convenient synthesis of 3-chromanones and naphto-3-pyranones.[11] In order to explore the feasibility of the above reaction for the case of branched α-diazo ketones, we investigated the decomposition of **1b-h** under the action of bis(hexafluoroacetoacetonato)Cu II in CH_2Cl_2. This study (see Table) revealed interesting deviations from the selective course observed for unbranched substrates, the title compounds **2** and **3** being obtained alone or along with the corresponding 3-chromanones **4**.



$C_6H_5\text{-O-}\overset{R^1}{\underset{R^2}{C}}\text{-CO-}\underset{R^3}{C}N_2$

1

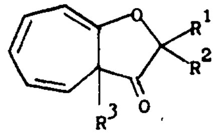


2

1a: $R^1=R^2=R^3=H$
1b: $R^1=CH_3$; $R^2=R^3=H$
1c: $R^1=C_6H_5$; $R^2=R^3=H$
1d: $R^1=R^2=CH_3$; $R^3=H$

1e: $R^1=R^2=H$; $R^3=CH_3$
1f: $R^1=R^3=CH_3$; $R^2=H$
1g: $R^1=C_6H_5$; $R^2=H$; $R^3=CH_3$
1h: $R^1=R^2=R^3=CH_3$

2a: $R^1=R^2=H$
2b: $R^1=CH_3$; $R^2=H$
2c: $R^1=C_6H_5$; $R^2=H$
2d: $R^1=R^2=CH_3$



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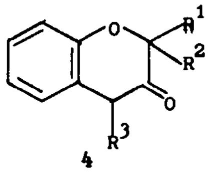

4

3e: R^1=R^2=H; R^3=CH$_3$
3f: R^1=R^3=CH$_3$; R^2=H
3g: R^1=C$_6$H$_5$; R^2=H; R^3=CH$_3$
3h: R^1=R^2=R^3=CH$_3$

4a: R^1=R^2=R^3=H
4b: R^1=CH$_3$; R^2=R^3=H
4c: R^1=C$_6$H$_5$; R^2=R^3=H
4d: R^1=R^2=CH$_3$; R^3=H

4e: R^1=R^2=H; R^3=CH$_3$
4f: R^1=R^3=CH$_3$; R^2=H
4g: R^1=C$_6$H$_5$; R^2=H; R^3=CH$_3$
4h: R^1=R^2=R^3=CH$_3$

RESULTS AND DISCUSSION

Under the action of bis(hexafluoroacetoacetonato)Cu II, α'-phenoxy-α-diazo ketones **1a-h** undergo intramolecular cyclization in good yield, independently from the branching of the side chain. However, the observed product distribution shows that mono- or di-substitution at the α'-carbon (substrates **1b-d**) strongly depresses the formation of chromanones **4** in favour of the furanone derivatives **2**, while substitution at the α-carbon (substrates **1e-h**) afforded the cycloheptatriene derivatives **3**. Remarkably, formation of chromanones was entirely suppressed with **1f,g** in which both the α-carbons bear an extra substituent.

Furanones **2** and chromanones **4** were separated and obtained in pure state by column chromatography over silica gel. This procedure could not be employed for the purification of **3e-h**, owing to their isomerization on SiO$_2$ to the corresponding chromanones **4e-h**. However, they could be purified by distillation in <u>vacuo</u>, followed by chromatography over anhydrous Al$_2$O$_3$.

Table. Catalytic decomposition of α'-phenoxy-α-diazo ketones **1a-h**.

Substrate(*)	Products (relative ratio)	Total yield %
1a	2a, 4a (1:9)	95
1'a	2'a, 4'a (3:7)	95
1b	2b, 4b (2:3)	80
1'b	2'b, 4'b (3:2)	80
1c	2c, 4c (1:1)	75
1d	2d, 4d (1:1)	86
1e	3e, 4e (2:3)	65
1f	3f	95
1g	3g	88
1h	3h, 4h (9:1)	95

The structure of 2,8H-cyclohepta[b]furan-3-one was assigned to compounds **2a-d** mainly on the basis of spectroscopical evidence. The ^{1}H NMR spectrum shows that the methylene group in the seven membered ring is flanked only by one vinylic proton, ruling out therefore the isomeric structures 2,5H, 2,6H, and 2,7H. ^{13}C NMR experiments in the presence of Yb(fod)$_3$ and the IR absorption at

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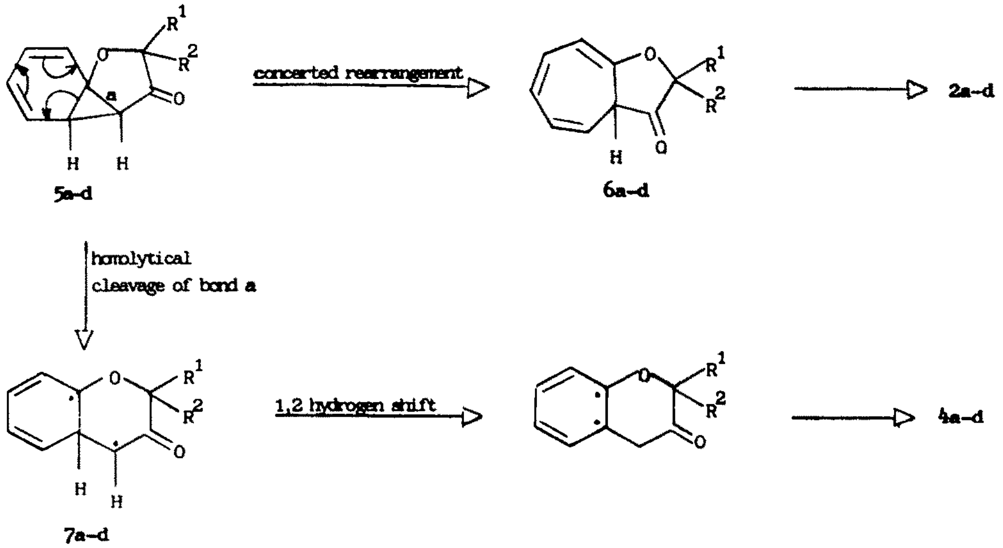
(*) Substrates **1'a** and **1'b** were deuteriated in the aromatic ring.

1695 cm^{-1} demonstrated that the methylene group must be located at the 8, rather than at the 4 position.[2] The structures of cycloheptatriene derivatives **3** and chromanones **4** were in turn unambigously assigned on the basis of their ^1H NMR spectra (see Experimental).

As for the stereochemistry of the reaction, cycloheptatriene **3f** was obtained only in the cis configuration, while **3g** and chromanones **4f** and **4g** were obtained as diastereomeric mixtures.(*) Mechanistically, the reactions of alleged metal-carbene complexes derived from the interaction of an α-diazocarbonyl system with a transition-metal salt or chelate have been assimilated to those of the free carbenes.[12] The selective cyclization of **1a** and the results obtained with the branched substrates suggest that cycloheptatriene derivatives 2 and 3 and chromanones **4** might all originate from a common norcaradiene intermediate. In the hypothesis that the latter may rearrange through non ionic pathways,[13] the above results may be interpreted according to the reaction mechanism illustrated in the Scheme.

SCHEME



Enlargement of the six-membered ring of **5a-d** might occur through a concerted process leading first to cycloheptatrienes **6a-d**, which then isomerize to the thermodynamically more stable tautomers **2a-d**.[7] Instead, homolytical cleavage of bond a of **5a-d** may be involved in the enlargement of the five membered ring, resulting into chromanones **4a-d**.

Catalytic decomposition of substrates **1'a** and **1'b** (pentadeuteriated in the aromatic ring) gave a product distribution significantly different from that obtained from the undeuteriated substrates **1a** and **1b** (see Table). These results are in agreement with the mechanism illustrated by the Scheme: since a 1,2 deuterium shift is involved in the aromatization leading to chromanones, in the deuteriated series the formation of the latter, as expected, was depressed in favour of the furanones. Structures **2'a,b** and **4'a,b** were assigned to the deuteriated products on the basis of the ^1H NMR spectra: cycloheptatriene derivatives **2'a,b** showed in fact a singlet (IH) for the C_8 methylene at 3.13 and 3.12 δ respectively; analogously, chromanones **4'a,b** showed a singlet (1H) for the C_4 methylene at 3.46 and 3.55 δ respectively.

The catalytic decomposition of α-substituted α-diazo ketones **1e-h** may also be interpreted according to the reaction mechanism illustrated in the Scheme. Cycloheptatrienes **3e-h** and chromanones **4e-h** might in fact originate from the two concurrent rearrangements of the initially formed norcaradienes

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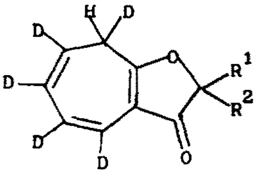
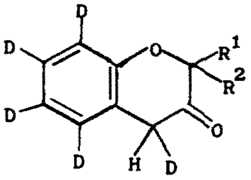
(*) The cis configuration was assigned on the basis of the ^1H NMR 2D NOESY spectrum (see Experimental).



2'a: $R^1=R^2=H$

2'b: $R^1=CH_3$; $R^2=H$

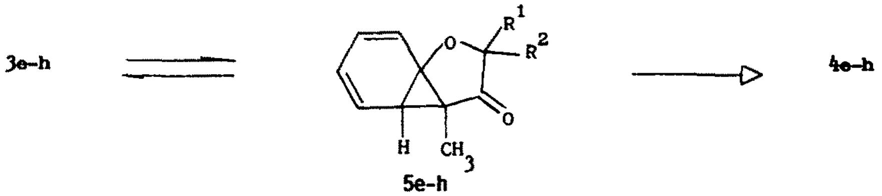


4'a: $R^1=R^2=H$

4'b: $R^1=CH_3$; $R^2=H$

5e-h.

The mechanism of the isomerization of **3e-h** to **4e-h** has not been investigated; however, it seems reasonable that the SiO_2 induced rearrangement proceeds <u>via</u> a reversed formation of the norcaradiene intermediates **5e-h**, the latter being the precursors of the final chromanones.[14-16]



5e-h

Clearly, in the decomposition of α-diazo ketones **1a-d**, with no substituent on the α-carbon, such equilibrium should not be operating, the intermediate norcaradienes **5a-d** undergoing irreversible rearrangement to the corresponding furanones and/or chromanones.

The mechanism at work in the decomposition of α-diazo ketones **1** under the action of bis(hexafluoroacetoacetonato)Cu II cannot be completely cleared until the role played by the copper catalyst will be understood. In this connection, the hypothesis can be made that the catalyst initially coordinate to the substrate carbonyl; however, it is not clear at all how substitution at the carbons adjacent to the carbonyl may result in the observed product distributions.

EXPERIMENTAL

Microanalyses were obtained with a Perkin-Elmer CHN elemental analyzer. IR spectra were measured as liquid films using a Perkin-Elmer 1310 infrared spectrometer. ^1H NMR spectra were recorded with Varian T60 and Bruker CXP-300 spectrometers using TMS as the internal standard. ^{13}C NMR spectra for the LIS (Lantanide Induced Shift) measurements were obtained with a Varian XL-100 instrument. The ^1H NMR 2D NOESY spectra were obtained with WP-80-SY Bruker instrument. GLC analyses were performed with a Perkin-Elmer F30 chromatograph (6 ft x 1/8 in. column of 10% SE 30 on Chromosorb W at 180°).

<u>Substrates</u>. α-Diazo ketones **1a-d** are known compounds.[17] The remaining substrates were prepared by reacting the appropriate acyl chlorides with a 0.2 M ether solution of CH_2N_2 or CH_3CHN_2 (mole ratio 1:4 and 1:3 respectively). After evaporation of the solvent, the oily residues were purified by column chromatography on SiO_2 (eluant light petroleum ether-ethyl ether 95:5).

<u>1-Diazo-3-pentadeuteriophenoxy-2-propanone</u>, **1'a**. Yellow oil. ^1H NMR ($CDCl_3$) δ: 5.66 (1H,s); 4.45 (2H,s).

<u>1-Diazo-3-pentadeuteriophenoxy-2-butanone</u>, **1'b**. Yellow oil. ^1H NMR ($CDCl_3$) δ: 5.27 (1H,s); 4.48 (1H,d,J=5Hz); 1.45 (3H,d,J=5Hz).

<u>3-Diazo-1-phenoxy-2-butanone</u>, **1e**. Yellow oil, b.p. 94-95° 0.25 mmHg; (Found: C, 63.36; H, 5.49; N, 14.61. $C_{10}H_{10}N_2O_2$ requires C, 63.15; H, 5.29; N, 14.73%); ^1H NMR ($CDCl_3$) δ: 7.36-6.70 (5H,m); 4.66 (2H,s); 1.96 (3H,s).

<u>2-Diazo-4-phenoxy-3-butanone</u>, **1f**. Yellow oil, b.p. 84-85° 0.15 mmHg; (Found: C, 64.85; H, 6.01; N, 13.54. $C_{11}H_{12}N_2O_2$ requires C, 64.70; H, 5.88; N, 13.72%); ^1H NMR ($CDCl_3$) δ: 7.33-6.70 (5H,m); 4.81 (1H,q,J=5Hz); 1.73 (3H,s); 1.56 (3H,d,J=5Hz).

<u>3-Diazo-1-phenyl-1-phenoxy-2-butanone</u>, **1g**. Yellow crystals, m.p. 59-60°; (Found: C, 72.18; H, 5.36; N, 10.41. $C_{16}H_{14}N_2O_2$ requires C, 72.18; H, 5.26; N, 10.52%); ^1H NMR ($CDCl_3$) δ: 7.56-6.83 (10H,m); 4.10 (1H,s); 1.83 (3H,s).

2-Diazo-4-methyl-4-phenoxy-3-pentanone, **1h**. Yellow oil, b.p. 100-101° 0.25 mmHg ; (Found: C, 64.58; H, 5.80; N, 13.66. $C_{11}H_{12}N_2O_2$ requires C, 64.70; H, 5.88; N, 13.72%); ^{1}H NMR ($CDCl_3$) δ: 7.36-6.58 (5H,m); 1.90 (3H,s); 1.55 (6H,s).

Catalytic decomposition of α-diazo ketones, **1a-d**. A solution of the substrate (2.5 mmol) in CH_2Cl_2 (5 ml) was treated with bis(hexafluoroacetoacetonato)Cu II (0.08 mmol) keeping the temperature between 15° and 25°. Once the N_2 evolution ceased (3-5 min), the solution was passed through a short column of neutral Al_2O_3 and evaporated to dryness. The residue was submitted to GLC and NMR analyses; product distribution and yields are reported in the table. Column chromatography over SiO_2 (eluant light petroleum ether-ethyl ether 9:1) gave pure **4a-d** and **2a-d**. Compounds **4a-d** were generally eluted first.

2,8H-Cycloepta[b]furan-3-one, **2a**. ^{1}H NMR ($CDCl_3$) δ: 6.36-6.00 (3H,m); 5.32-5.12 (1H,m); 4.55 (2H,s); 3.13 (2H,d,J=5Hz).

2-Methyl-2,8H-cyclohepta[b]furan-3-one, **2b**. Oil, b.p. 100-101° 0.1 mmHg ; (Found: C, 73.81; H, 6.35. $C_{10}H_{10}O_2$ requires C, 74.06; H, 6.21%); $\nu_{C=O}$ 1695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 6.53-5.88 (3H,m); 5.53-5.10 (1H,m); 4.50 (1H,q,J=6Hz); 3.12 (2H,d,J=6Hz); 1.43 (3H,d,J=6Hz).

2-Phenyl-2,8H-cyclohepta[b]furan-3-one, **2c**. Oil, b.p. 82-83° 0.01 mmHg ; (Found: C, 80.49; H, 5.54. $C_{15}H_{12}O_2$ requires C, 80.35; H, 5.35%); $\nu_{C=O}$ 1697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 7.26 (5H,s); 6.38-5.95 (3H,m); 5.56-5.21 (1H,m); 5.40 (1H,s); 3.23 (2H,d,J=5Hz).

2,2-Dimethyl-2,8H-cyclohepta[b]furan-3-one, **2d**. Oil, b.p. 64-65° 0.1 mmHg ; (Found: C, 75.18; H, 6.70. $C_{11}H_{12}O_2$ requires C, 75.00; H, 6.81%). $\nu_{C=O}$ 1697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 6.53-5.90 (3H,m); 5.40-5.10 (1H,m); 3.10 (2H,d,J=6Hz); 1.38 (6H,s). The LIS experiments were performed on **2d** by ^{13}C NMR measurements in the presence of Yb(fod)$_3$. With a molar ratio lantanide: substrate equal to 0.15 in $CDCl_3$ solution, the following Δδ were observed: 11.7 for the carbonyl (the site of coordination), 4.4 for the sp^2 hybridized C_4, 2.5 for the C_8 methylene.

3-Oxo-3,4-dihydro-2H-1-benzopyran, **4a**.[18]

2-Methyl-3-oxo-3,4-dihydro-2H-1-benzopyran, **4b**. Oil, b.p. 110-111° 0.3 mmHg ; (Found: C, 74.22; H, 6.35. $C_{10}H_{10}O_2$ requires C, 74.06; H, 6.21%); $\nu_{C=O}$ 1725 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 7.28-6.83 (4H,m); 4.28 (1H,q,J=6Hz); 3.55 (2H,s); 1.46 (3H,d,J=6Hz).

2-Phenyl-3-oxo-3,4-dihydro-2H-1-benzopyran, **4c**[19]

2,2-Dimethyl-3-oxo-3,4-dihydro-2H-1-benzopyran, **4d**.[20]

Decomposition of α-diazo ketone, **1'a**. The reaction was run following the above general procedure, but the final mixture, before treatement on Al_2O_3, was submitted to GLC and NMR analyses which gave the following composition: 30% of 2,8H-4,5,6,7,8-pentadeuterio cyclohepta[b]furan-3-one, **2'a**, $\nu_{C=O}$ 1695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 4.40 (2H,s); 3.13 (1H,s) and 70% of 3-oxo-3,4-dihydro-2H-1-(5,6,7,8-tetradeuteriobenzo)-4-deuteriopyran, **4'a**, $\nu_{C=O}$ 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 4.22 (2H,s); 3.46 (1H,s). The CH_2Cl_2 solution, when eluted over Al_2O_3 and then submitted to NMR analysis showed the complete H/D scrambling at C_4, δ: 3.46 (2H,s) of **4'a** while no scrambling was observed for **2'a**.

Decomposition of α-diazo ketone, **1'b**. The reaction was performed as for **1'a**. The final mixture, before elution on Al_2O_3, had the following composition: 60% of 2-methyl-2,8H-4,5,6,7,8-pentadeuterio-cyclohepta[b]furan-3-one, **2'b**, $\nu_{C=O}$ 1695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 4.50 (1H,q,J=7Hz); 3.12 (1H,s); 1.43 (3H,d,J=7Hz); and 40% of 2-methyl-3-oxo-3,4-dihydro-2H-1-(5,6,7,8-tetradeuteriobenzo)-4-deuteriopyran, **4'b**, $\nu_{C=O}$ 1725 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 4.28 (1H,q,J=6Hz); 3.55 (1H,s); 1.46 (3H,d,J=6Hz). Treatement of the CH_2Cl_2 solution with Al_2O_3 gave unaltered **2'b** and the H/D scrambling at C_4 of **4'b**, δ: 3.55 (2H,s).

Catalytic decomposition of α-diazo ketones, **1e-h**. The reaction was performed as for **1a-d**; however, in order to avoid isomerization of the cycloheptatriene derivatives **3e-h** into the corresponding chromanones, more rigourous anhydrous conditions were required for both the reaction medium and the purification procedure. In particular, separation of the products could be achieved by chromatography over neutral, anhydrous Al_2O_3, previously heated at 400° for 24 h. Chromatography of the reaction mixtures over SiO_2 (light petroleum ether as eluant) lead to complete isomerization of **3e-h** to **4e-h**.

3a-Methyl-2,3aH-cyclohepta[b]furan-3-one, **3e**. The structure can only be provisionally assigned because the product was obtained as a slighty impure oil of **4e**. $\nu_{C=O}$ 1760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 6.25-5.98 (3H,m); 5.90-5.73 (1H,m); 5.13-5.05 (1H,m); 4.61, 4.10 (2H, AB system, J=18Hz); 0.98 (3H,s).

2,3a-Dimethyl-2,3aH-cyclohepta[b]furan-3-one, **3f**. Oil, b.p. 84-85° 0.1 mmHg ; (Found: C, 75.12; H, 6.98. $C_{11}H_{12}O_2$ requires C, 75.00; H, 6.81%); $\nu_{C=O}$ 1760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 6.33-6.03 (3H,m); 5.95-5.71 (1H,m); 5.33-5.03 (1H,m); 4.25 (1H,q,J=6Hz); 1.50 (3H,d,J=6Hz); 0.95 (3H,s). In the ^{1}H NMR 2D NOESY spectrum a cross-peak was observed between the singlet at 0.95 δ and the doublet at 1.50 δ (due to the C_{3a}-methyl and to the C_2-methyl respectively) indicating a dipolar magnetization exchange between such groups; instead no cross-peak was present between the resonance of the C_{3a} methyl and the quartet at 4.25 δ due to methynic proton.

2-Phenyl-3a-methyl-2,3aH-cyclohepta[b]furan-3-one, **3g** was obtained as an oil (b.p. 115-116° 0.3 mmHg) in which the two diastereoisomers were present in 3:2 ratio; (Found: C, 80.80; H, 6.01. $C_{16}H_{14}O_2$ requires C, 80.67; H, 5.88%); $\nu_{C=O}$ 1760 cm^{-1}; ^{1}H NMR of the preponderant isomer: $(CDCl_3)$ δ: 7.26 (5H,s); 6.30-5.78 (4H,m); 5.50-5.20 (1H,m); 5.14 (1H,s); 0.90 (3H,s). ^{1}H NMR of the other diastereoisomer: $(CDCl_3)$ δ: 7.26 (5H,s); 6.30-5.78 (4H,m); 5.63 (1H,s); 5.50-5.20 (1H,m); 5.14 (1H,s); 0.90 (3H,s).

2,2,3a-Trimethyl-2,3aH-cyclohepta[b]furan-3-one, **3h**. Obtained in pure state after chromatography over neutral anhydrous Al_2O_3. Oil, b.p. 75-76° 0.4 mmHg; (Found: C, 75.60; H, 7.48. $C_{12}H_{14}O_2$ requires C, 75.78; H, 7.36%); $\nu_{C=O}$ 1760 cm^{-1}; ^{1}H NMR $(CDCl_3)$ δ: 6.33-5.68 (4H,m); 5.33-5.03 (1H,m); 1.46 (3H,s); 1.30 (3H,s); 0.99 (3H,s).

4-Methyl-3-oxo-3,4-dihydro-2H-1-benzopyran, **4e**. Oil, b.p. 102-103° 0.2 mmHg; (Found: C, 74.16; H, 6.31. $C_{10}H_{10}O_2$ requires C, 74.06; H, 6.21%); $\nu_{C=O}$ 1720 cm^{-1}; ^{1}H NMR $(CDCl_3)$ δ: 7.23-6.73 (4H,m); 4.53,4.21 (2H, AB system, J=18Hz); 3.56 (1H,q,J=6Hz); 1.46 (3H,d,J=6Hz).

2,4-Dimethyl-3-oxo-3,4-dihydro-2H-1-benzopyran, **4f**[21] was obtained as an oily mixture of diastereoisomers in 1:1 ratio. The ^{1}H NMR spectrum gave for the more abundant diastereoisomer the following signals: $(CDCl_3)$ δ: 7.20-6.66 (4H,m); 4.20 (1H,q,J=6Hz); 3.50 (1H,q,J=6Hz); 1.40 (3H,d,J=6Hz); 1.44 (3H,q,J=6.5Hz). The less abundant stereoisomer was characterized by the following signals: $(CDCl_3)$ δ: 7.20-6.66 (4H,m); 4.31 (1H,q,J=7Hz); 3.50 (1H,q,J=6.5Hz); 1.34 (3H,d,J=7Hz); 1.36 (3H,d,J=6.5Hz).

4-Methyl-2-phenyl-3-oxo-3,4-dihydro-2H-1-benzopyran, **4g**. Oil, mixture of diastereoisomers in 3:2 ratio, b.p. 120° 0.3 mmHg; (Found: C, 80.83; H, 5.99. $C_{16}H_{14}O_2$ requires C, 80.67; H, 5.88%); $\nu_{C=O}$ 1720 cm^{-1}. The more abundant stereoisomer was characterized by the following signals in the ^{1}H NMR spectrum: $(CDCl_3)$ δ: 7.60-6.80 (4H,m); 5.20 (1H,s); 3.75 (1H,q,J=5Hz); 1.59 (3H,d,J=5Hz). The ^{1}H NMR spectrum of the other stereoisomer differed only for the H-(C_2) which was at 5.3 δ (1H,s).

2,2,4-Trimethyl-3-oxo-3,4-dihydro-2H-1-benzopyran, **4h**. Oil, b.p. 111-112° 0.3 mmHg ; (Found: C, 75.80; H, 7.50. $C_{12}H_{14}O_2$ requires C, 75.78; H, 7.36%); $\nu_{C=O}$ 1720 cm^{-1}; ^{1}H NMR $(CDCl_3)$ δ: 7.23-6.76 (4H,m); 3.60 (1H,q,J=6Hz); 1.46 (3H,d,J=6Hz); 1.30 (3H,s); 0.99 (3H,s).

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