9,9-Diphenyl-1,9,10,10a-tetrahydro-2*H*-phenaleno[1,9-*bc*]pyrans

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Reaction between some naphtho[2,1-*b*]pyrans and 1,1-diphenylethene affords 9,9-diphenyl-1,9,10,10a-tetrahydro-2*H*-phenaleno[1,9-*bc*]pyrans.

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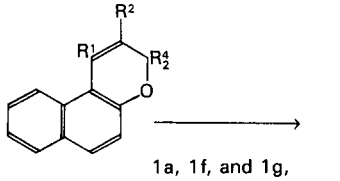
Equimolar proportions of 3*H*-naphtho[2,1-*b*]pyran (**1a**) [1] or 2,3-dihydro-1*H*-naphtho[2,1-*b*]pyran-1-ol (**2a**) and 1,1-diphenylethene in acetic acid containing a small amount of sulphuric acid gave 9,9-diphenyl-1,9,10,10a-tetrahydro-2*H*-phenaleno[1,9-*bc*]pyran (**3a**) whose pmr spectrum was complex and could not be analyzed. However, the following related derivatives, 1,1-dideuterio-9,9-diphenyl-1,9,10,10a-tetrahydro-2*H*-phenaleno[1,9-*bc*]pyran (**3b**), 10a-deuterio-9,9-diphenyl-1,9,10,10a-tetrahydro-2*H*-phenaleno[1,9-*bc*]pyran (**3c**), 1,1-dideuterio-2,2-dimethyl-9,9-diphenyl-1,9,10,10a-tetrahydro-2*H*-phenaleno[1,9-*bc*]-pyran (**3d**), and 10a-deuterio-2,2-dimethyl-9,9-diphenyl-1,9,10,10a-tetrahydro-2*H*-phenaleno[1,9-*bc*]pyran (**3e**) were obtained from the appropriate deuterio derivatives **2b** and **2c** of 2,3-dihydro-1*H*-naphtho[2,1-*b*]pyran-1-ol and **2d** and **2e** of 2,3-dihydro-3,3-dimethyl-1*H*-naphtho[2,1-*b*]pyran-1-ol and 1,1-diphenylethene. The pmr spectra of these adducts **3b-e** could be analyzed and they supported the proposed structure for **3a-e**.

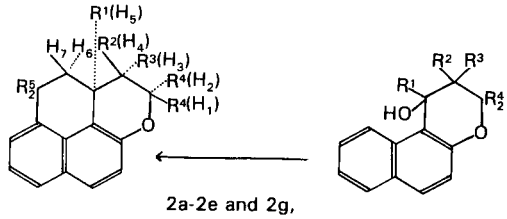
The 2,2-dialkyl-9,9-diaryl-1,9,10,10a-tetrahydro-2*H*-phenaleno[1,9-*bc*]pyrans **3f-h** were obtained on reacting the appropriate 3,3-dialkylnaphthopyran **1f** and **g** [2] with the necessary 1,1-diarylethene under acid conditions.



1a, 1f, and 1g, $Ph_2C=CH_2$, H^+

1h, $(4\text{-}MeOC_6H_4)_2C=CH_2$, H^+

1

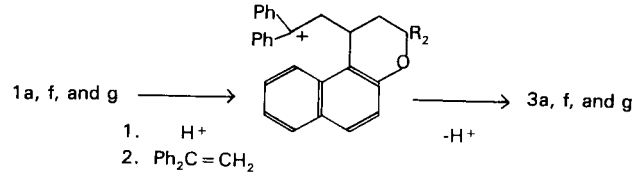


2a-2e and 2g, $Ph_2C=CH_2$, H^+

3 2

1-3	R¹	R²	R³	R⁴	R⁵
1a	H	H		H	
2a	H	H	H	H	
3a	H	H	H	H	Ph
2b	H	D	D	H	
3b	H	D	D	H	Ph
2c	D	H	H	H	
3c	D	H	H	H	Ph
2d	H	D	D	Me	
3d	H	D	D	Me	Ph
2e	D	H	H	Me	
3e	D	H	H	Me	Ph
1f	H	H		Me	
3f	H	H	H	Me	Ph
1g	H	H		Et	
2g	H	H	H	Et	
3g	H	H	H	Et	Ph
3h	H	H	H	Me	4-$MeOC_6H_4$

The formation of the diphenyltetrahydrophenalenopyrans **3** can be explained by protonation of the olefinic double bond of the naphthopyrans **1**, followed by addition to a molecule of diphenylethene to yield ion **4**, which ring closes at position 8 of the naphthalene ring with loss of a

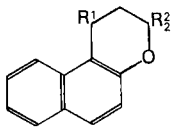


4

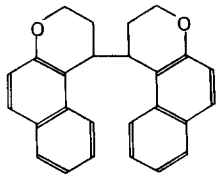
4	R
a	H
f	Me
g	Et

proton. This contrasted with the mechanism of the acid-catalyzed reaction of 2,2-diaryl-2*H*-benzo[*b*]pyrans or 3,3-diaryl-3*H*-naphtho[2,1-*b*]pyrans with 1,1-diphenylethene [3]. It was shown that the site of attack of the proton was the ring oxygen and not the olefinic bond. The subsequent steps involved ring opening to give a cation which reacted with diphenylethene to give a further carbonium ion. The products 4-(2,2-diarylvinyl)-3,4-dihydro-2,2-diphenyl-2*H*-benzo[*b*]pyrans and 1-(2,2-diarylvinyl)-2,3-dihydro-2,2-di-

phenyl-1*H*-naphtho[2,1-*b*]pyrans, respectively, were given by recyclization and loss of a proton.



5



6

5	R^1	R^2
a	Br	Me
b	OH	Me
c	$CH(CO_2Et)_2$	Me
d	$CH(CO_2H)_2$	Me
e	CH_2CO_2H	Me
f	CH_2CPh_2OH	Me
g	CH_2CPh_2OH	H
h	Br	H

The structure of the adducts **3** was shown to be correct by the following unambiguous synthesis. 1-Bromo-2,3-dihydro-3,3-dimethyl-1*H*-naphtho[2,1-*b*]pyran (**5a**) was obtained by the treatment of 2,3-dihydro-3,3-dimethyl-1*H*-naphtho[2,1-*b*]pyran-1-ol (**5b**) [4] with phosphorus tribromide in benzene. Bromo derivative **5a** was reacted with diethyl monosodiomalonate and the resulting diethyl 2,3-dihydro-3,3-dimethyl-1*H*-naphtho[2,1-*b*]pyran-1-malonate (**5c**) hydrolyzed with boiling aqueous ethanolic potassium hydroxide to afford 2,3-dihydro-3,3-dimethyl-1*H*-naphtho[2,1-*b*]pyran-1-malonic acid (**5d**). Decarboxylation of the diacid **5d** yielded 2,3-dihydro-3,3-dimethyl-1*H*-naphtho[2,1-*b*]pyran-1-acetic acid (**5e**), which on esterification, followed by reaction with phenylmagnesium bromide gave 2,3-dihydro-3,3-dimethyl-1-(2,2-diphenyl-2-hydroxyethyl)-1*H*-naphtho[2,1-*b*]pyran (**5f**). Compound **5f** on boiling with acetic acid gave 2,2-dimethyl-9,9-diphenyl-1,9,10,10a-tetrahydro-2*H*-phenaleno[1,9-*bc*]pyran (**3f**).

Attempts to obtain 2,3-dihydro-1-(2,2-diphenyl-2-hydroxyethyl)-1*H*-naphtho[2,1-*b*]pyran (**5g**) either by reacting the Grignard reagent from 1-bromo-2,3-dihydro-1*H*-naphtho[2,1-*b*]pyran (**5h**) and magnesium with diphenylacetaldehyde or by first treating 1-bromo-2,3-dihydro-1*H*-naphtho[2,1-*b*]pyran (**5h**) with diethyl monosodiomalonate were unsuccessful, thus preventing the synthesis of adduct **3a**. The former reaction afforded 1,1-bis(2,3-dihydro-1*H*-naphtho[2,1-*b*]pyran) (**6**), and the latter gave 3*H*-naphtho[2,1-*b*]-pyran (**1a**).

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. The ir spectra were determined in carbon tetrachloride, and the pmr spectra at 100 MHz for **3b** and **3c** at the Physico-Chemical Unit, Harwell, and at 60 MHz for **3d** and **3e**. Mass spectra were determined at the Physico-Chemical Unit, Harwell.

3*H*-Naphtho[2,1-*b*]pyran (**1a**).

3*H*-Naphtho[2,1-*b*]pyran-3-one (4.0 g) [2] was added to an excess of lithium aluminium hydride in ether (200 ml) and set aside overnight. Addition of dilute sulphuric acid, followed by isolation with ether, and crystallization from benzene yielded 3-(2-hydroxy-1-naphthyl)prop-2-en-1-ol, as needles, 3.0 g (73%), mp 124-125°; ir 3540, 3590.

Anal. Calcd. for $C_{13}H_{12}O_2$: C, 78.0; H, 6.0. Found: C, 77.8; H, 6.0.

The diol (3.0 g) and acetic acid were boiled for 0.75 hours. Addition of water, followed by isolation with ether, and recrystallization from light petroleum (bp < 40°) gave platelets, 2.4 g (88%), mp 41-42° (lit [1] mp 41-42°).

3,3-Diethyl-3*H*-naphtho[2,1-*b*]pyran (**1g**).

3*H*-Naphtho[2,1-*b*]pyran-3-one (9.8 g) [2] in benzene (200 ml) was added during 1 hour to a stirred Grignard solution from ethyl bromide (13.8 ml), magnesium (3.93 g), and ether (100 ml). The solution was boiled for 0.75 hour, set aside overnight, and decomposed with 22% ammonium chloride solution. The benzene ether layer was separated, dried (sodium sulfate), and the solvent removed to give a gum, which was dissolved in ethanol (75 ml) and cooled in a solid carbon dioxide/acetone bath to afford a solid. When the container reached room temperature the solid was separated and recrystallized from benzene-light petroleum (bp 60-80°) to give 1,1-diethyl-3-(2-hydroxy-1-naphthyl)prop-2-en-1-ol, as needles, 2.02 g (15%), mp 113-114°; ir: 3530, 3600.

Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.7; H, 7.8. Found: C, 79.8; H, 7.8.

Concentration of the ethanolic mother liquor furnished a solid, which on recrystallization from ethanol gave 2,3-dihydro-1-ethyl-1*H*-naphtho[2,1-*b*]pyran-3-one (formed by 1,4-addition of ethylmagnesium bromide to 3*H*-naphtho[2,1-*b*]pyran-3-one) as granules, 7.89 g (61%), mp 67-68°; ir: 1670; ms: (70 eV, electron impact) m/z (%) 226 (M^+, 32), 198 (14), 197 (100), 169 (11), 141 (11), 115 (7), 98 (4).

1,1-Diethyl-3-(2-hydroxy-1-naphthyl)prop-2-en-1-ol (1.28 g) and acetic acid (30 ml) were boiled for 0.75 hour and poured into water. Isolation with ether followed by distillation afforded **1g**, 980 mg (81%), bp 180-184/15 mm (lit [2] bp 180-182°/15 mm).

2,2-Dideuterio-2,3-dihydro-1*H*-naphtho[2,1-*b*]pyran-1-ol (**2b**).

2,3-Dihydro-1*H*-naphtho[2,1-*b*]pyran-1-one (200 mg) [5], deuterated water, and phosphorus pentoxide were boiled for several hours to give 2,2-dideuterio-2,3-dihydro-1*H*-naphtho[2,1-*b*]pyran-1-one, which was isolated with ether and added to lithium aluminium hydride in ether. Addition of dilute sulphuric acid, followed by isolation with ether gave **2b**. Similarly 2,2-dideuterio-2,3-dihydro-3,3-dimethyl-1*H*-naphtho[2,1-*b*]pyran-1-ol (**2d**) was obtained from 2,3-dihydro-3,3-dimethyl-1*H*-naphtho[2,1-*b*]pyran-1-one [2,6].

1-Deuterio-2,3-dihydro-1*H*-naphtho[2,1-*b*]pyran-1-ol (**2c**).

2,3-Dihydro-1*H*-naphtho[2,1-*b*]pyran-1-one (100 mg) in ether was reacted with lithium aluminium deuteride (25 mg). Dilute sulphuric acid was added and a solid isolated with ether to yield **2c**, 96 mg (94%). Similarly 1-deuterio-2,3-dihydro-3,3-dimethyl-1*H*-

naphtho[2,1-*b*]pyran-1-ol (**2e**) was obtained from 2,3-dihydro-3,3-dimethyl-1*H*-naphtho[2,1-*b*]pyran-1-one.

Formation of Adducts, Diphenyltetrahydrophenalenopyrans **3a-e,g,h**.

The 3*H*-naphtho[2,1-*b*]pyran (4 mmoles) or the 2,3-dihydro-1*H*-naphtho[2,1-*b*]pyran-1-ol (4 mmoles), 1,1-diarylethene (4 mmoles), acetic acid (15 ml), and sulphuric acid (5 drops) were aside for 1 to 2 days to give a solid. Separation and recrystallization from a suitable solvent afforded the diphenyltetrahydrophenalenopyran.

9,9-Diphenyl-1,9,10,10a-tetrahydro-2*H*-phenaleno[1,9-*bc*]pyran (**3a**).

This compound was obtained from **1a** or **2a** and 1,1-diphenylethene as cubes (ethyl acetate), mp 209-210° (66%); ms: (70 eV, electron impact) m/z (%) 362 (M^+, 100), 334 (1), 333 (4), 285 (37), 283 (29), 256 (16.5), 207 (50).

Anal. Calcd. for $C_{27}H_{22}O$: C, 89.5; H, 6.2. Found: C, 89.3; H, 6.2.

1,1-Dideuterio-9,9-diphenyl-1,9,10,10a-tetrahydro 2*H*-phenaleno-[1,9-*bc*]pyran (**3b**).

This compound was obtained from **2b** and 1,1-diphenylethene as cubes (ethyl acetate), mp 205-206° (66%); pmr (deuteriochloroform): δ 6.85-7.44 (m, 15H, aromatic protons), 4.0 (d, H_1, $J_{H_1H_2}$ = 10.5 Hz), 3.37 (d, H_2), 2.35 (H_5, $J_{H_5H_6}$ = 3.5 Hz, $J_{H_5H_7}$ = 12.3 Hz), 2.54 (H_6, $J_{H_6H_7}$ = 12.3 Hz), 2.57 (H_7); ms: (70 eV, electron impact) m/z (%) 364 (M^+, 100), 334 (1), 333 (3), 287 (40), 285 (40), 256 (20), 209 (57).

10a-Deuterio-9,9-diphenyl-1,9,10,10a-tetrahydro-2*H*-phenaleno-[1,9-*bc*)pyran (**3c**).

This compound was obtained from **2c** and 1,1-diphenylethene as cubes (ethyl acetate), mp 205-206° (30%); pmr (deuteriochloroform): δ 6.7-7.99 (m, 15H, aromatic protons), 4.03 (H_1, $J_{H_1H_2}$ = 10.5 Hz), 3.5 (H_2, $J_{H_2H_3}$ = 3.5 Hz, $J_{H_2H_4}$ = 11.5 Hz), 1.37 (H_3, $J_{H_3H_1}$ = 2.1 Hz, $J_{H_3H_4}$ = 12.5 Hz), 1.54 (H_4, $J_{H_4H_1}$ = 4.0 Hz), 2.4 (d, H_6, $J_{H_6H_7}$ = 12.1 Hz), 2.57 (d, H_7); ms: (70 eV, electron impact) m/z (%) 363 (M^+, 100), 335 (1.5), 334 (4), 286 (30), 283 (22), 257 (15), 207 (42.5).

1,1-Dideuterio-2,2-dimethyl-9,9-diphenyl-1,9,10,10a-tetrahydro-2*H*-phenaleno[1,9-*bc*]pyran (**3d**).

This compound was obtained from **2d** and 1,1-diphenylethene as needles (ethyl acetate), mp 205-206° (45%); pmr (deuteriochloroform): δ 6.68-7.80 (m, 15H, aromatic protons), 1.09 (s, 3H, Me), 1.41 (s, 3H, Me), 2.65 (m, H_5, H_6, H_7); ms: (70 eV, electron impact) m/z (%) 392 (M^+, 100), 335 (36.5), 334 (28.5), 333 (28.5), 315 (7), 313 (28.5), 257 (85.5), 256 (21.5), 237 (28.5).

10a-Deuterio-2,2-dimethyl-9,9-diphenyl-1,9,10,10a-tetrahydro-2*H*-phenaleno[1,9-*bc*]pyran (**3e**).

This compound was obtained from **2e** and 1,1-diphenylethene as needles (ethyl acetate), mp 204-205° (40%); pmr (deuteriochloroform): δ 6.68-7.72 (m, 15H, aromatic protons), 1.09 (s, 3H, Me), 1.41 (s, 3H, Me), 1.06 (d, H_3, $J_{H_3H_4}$ = 1.30 Hz), 1.82 (d, H_4), 2.6 (d, H_6, $J_{H_6H_7}$ = 12.5 Hz), 2.74 (d, H_7); ms: (70 eV, electron impact) m/z (%) 391 (M^+ 100), 336 (18.5), 335 (7.5), 334 (7.4), 314 (3.5), 311 (5.5), 258 (11), 257 (59.5), 256 (26), 255 (26), 236 (18.5).

2,2-Diethyl-9,9-diphenyl-1,9,10,10a-tetrahydro-2*H*-phenaleno-[1,9-*bc*]pyran (**3g**).

This compound was obtained from **1g** or **2g** and 1,1-diphenylethene as needles [light petroleum (bp 60-80°)], mp 176-177° (69 and 51%, respectively); ms: (70 eV, electron impact) m/z (%) 418 (M^+, 100), 336 (19), 335 (65), 334 (8), 333 (8), 257 (43), 256 (10), 239 (8).

Anal. Calcd. for $C_{31}H_{30}O$: C, 89.0; H, 7.2. Found: C, 88.6; H, 7.2.

9,9-Di(4-methoxyphenyl)-2,2-dimethyl-1,9,10,10a-tetrahydro-2*H*-phenaleno[1,9-*bc*]pyran (**3h**).

This compound was obtained from **1h** and 1,1-di(4-methoxyphenyl)ethene as needles (ethyl acetate), mp 189-190° (48%).

Anal. Calcd. for $C_{31}H_{30}O_3$: C, 82.7; H, 6.7. Found: C, 82.5; H, 6.9.

2,2-Dimethyl-9,9-diphenyl-1,9,10,10a-tetrahydro-2*H*-phenaleno-1,9-*bc*]pyran (**3f**).

Method 1.

3,3-Dimethyl-3*H*-naphtho[2,1-*b*]pyran (500 mg) [2], 1,1-diphenylethene (430 mg), and 98% formic acid (20 ml) were boiled for 0.5 hour and set aside for 2 days to give a crystalline solid, which was separated and recrystallized as needles from ethyl acetate to yield 210 mg (23%), mp 206-207°.

Anal Calcd. for $C_{29}H_{26}O$: C, 89.2; H, 6.7. Found: C, 88.9; H, 6.6.

Method 2.

2,3-Dihydro-3,3-dimethyl-1*H*-naphtho[2,1-*b*]pyran-1-ol (**5b**) (1.8 g) [4] and phosphorus tribromide (1.8 g) were stirred in ether (50 ml) at room temperature for 16 hours. Removal of the solvent and crystallization from light petroleum (bp 40-60°) gave 1-bromo-2,3-dihydro-3,3-dimethyl-1*H*-naphtho[2,1-*b*]pyran (**5a**) (2.0 g, 85%), mp 77-78°.

Anal. Calcd. for $C_{15}H_{15}BrO$: C, 61.8; H, 5.2; Br, 27.4. Found: C, 61.8; H, 5.3; Br, 27.5.

After completion of the reaction between ethanol (230 mg) and sodium (115 mg), diethyl malonate (860 mg) was added and the mixture heated on a water bath for 0.25 hour. Removal of the solvent gave diethyl monosodiomalonate, which was boiled with *5a* (1.5 g) in benzene (15 ml) for 6 hours. The solvent was removed and the residue was boiled with potassium hydroxide (12 mg) in ethanol for 4 hours and poured into water. Acidification and isolation with ether afforded a gum, which on shaking with 10% sodium carbonate solution (15 ml) left a solid. Recrystallization from light petroleum (bp $<40°$) gave 2,3-dihydro-3,3-dimethyl-1-ethoxy-1*H*-naphtho[2,1-*b*]pyran, as platelets (710 mg, 55%), mp 87-88°.

Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.6; H, 7.8. Found: C, 79.8; H, 8.0.

The sodium carbonate washings on acidification and extraction with ether gave an oil, which on heating at 170-175° yielded a solid. Recrystallization from light petroleum (bp 60-80°) gave 2,3-dihydro-3,3-dimethyl-1*H*-naphtho[2,1-*b*]pyran-1-acetic acid (**5e**), as needles (350 mg, 27%), mp 170-175°; ir: 1750, 3450; ms: Calcd. for $C_{17}H_{18}O_3$: M^+, 270; Found: M^+, 270. To a solution of **5e** (350 mg) in ether (20 ml) was added a solution of diazomethane in ether (20 ml) and the mixture set aside for 2 hours. Isolation with ether gave methyl 2,3-dihydro-3,3-dimethyl-1*H*-naphtho[2,1-*b*]-pyran-1-acetate (200 mg), as a gum; ir: 1750. The gum was dissolved in ether and added to a stirred Grignard solution, prepared from bromobenzene (314 mg), magnesium (48 mg), and ether (15 ml) and the mixture stirred overnight. Decomposition of the Grignard complex with 22% ammonium chloride solution

and isolation with ether gave a gum, which was boiled with acetic acid (3 ml) for 0.75 hour and set aside overnight to afford a solid. The solid was separated and recrystallized from light petroleum (bp 60-80°) to yield 60 mg (12%) of **3d**, as needles, mp and mixed mp 205-207°.

1,1-Bis(2,3-dihydro-1*H*-naphtho[2,1-*b*]pyran) (**6**).

2,3-Dihydro-1*H*-naphtho[2,1-*b*]pyran-1-ol (2 g) and phosphorus tribromdie (2 g) in ether (50 ml) were stirred overnight. Removal of the solvent yielded a gum, which on crystallization from light petroleum (bp 40-60°) gave 1-bromo-2,3-dihydro-1*H*-naphtho[2,1-*b*]pyran, as needles, 1.28 g (76%), mp 75-76°.

Anal. Calcd. for $C_{13}H_{11}BrO$: C, 59.3; H, 4.2; Br, 30.4. Found: C, 59.4; H, 4.3; Br, 31.0.

1-Bromo-2,3-dihydro-1*H*-naphtho[2,1-*b*]pyran (0.952 g) in ether (10 ml) was added to magnesium (0.096 g) in ether (5 ml). Following the addition of 1,1-diphenylacetaldehyde (0.784 g) the mixture was stirred overnight and poured into a 22% solution of ammonium chloride. Isolation with ether and crystallization from ethyl acetate gave **6** as cubes, 0.45 g (61%), mp 246-247°.

Anal. Calcd. for $C_{26}H_{22}O_2$: C, 85.2; H, 6.0. Found: C, 85.0; H, 5.9.

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