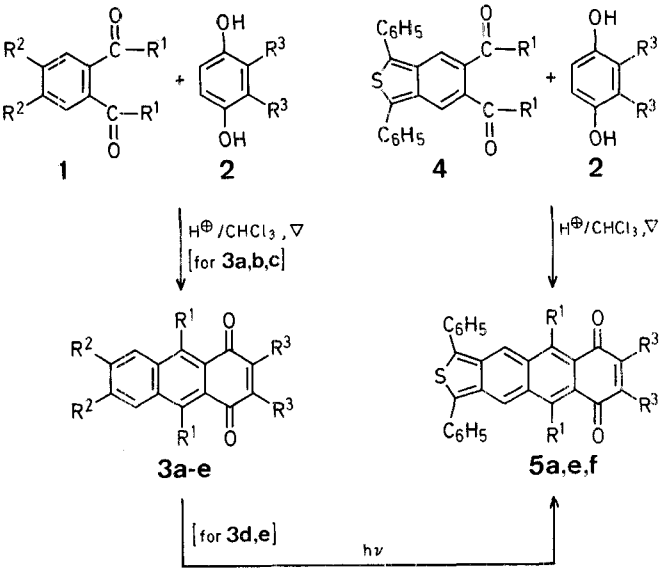
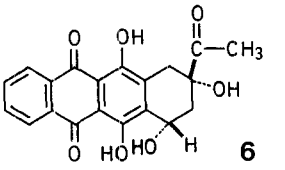
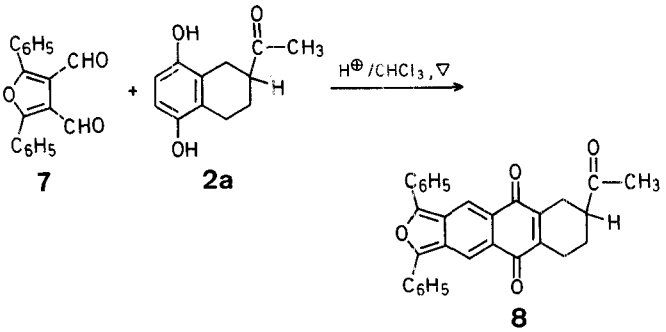
was found to be a suitable condensing agent. The dibenzoyl-substituted quinones **3d** and **3e** were obtained by photolytic cleavage of compounds **5a** and **5e**; alternatively, quinones **3d** and **3e** were prepared by trapping of the *o*-quinodimethane (*o*-bis[bromomethylene]-cyclohexadiene) produced from 4,5-dibenzoyl-1,2-bis[dibromomethyl]-benzene with 6-acetyl-5,6,7,8-tetrahydronaphthoquinone[8] or 1,4-naphthoquinone according to Ref.[9].







Synthesis of Polycyclic Quinones Including Some Furo- and Thieno-Fused Polycyclic Quinones

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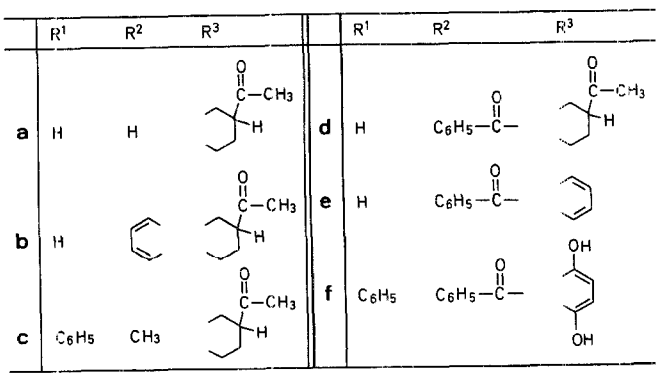
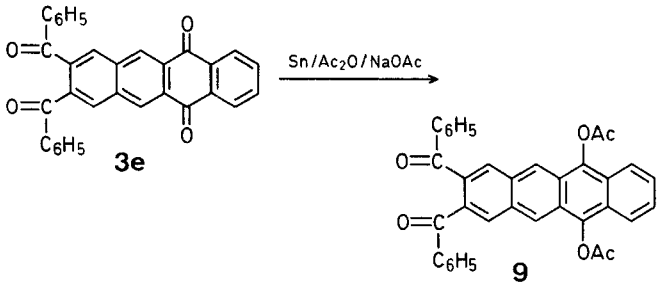
The 1,2,3,4-tetrahydronaphthacene-5,12-quinone **3a**[1] is a precursor of (±)-4-demethoxydaunomycinone **(6)**[2]. We report here convenient syntheses of the polycyclic quinones **3** and of the related thieno- and furo-fused polycyclic quinones **5** and **8**. The new quinones **3b, 3d, 5a,** and **8** are potential intermediates (after protection of reactive sites) for the synthesis of 4-demethoxydaunomycinone derivatives.

Fused quinones are easily obtained by the cyclocondensation of hydroquinones with 1,4-dialdehydes under various conditions[3,4]. For the synthesis of the fused quinones **3a, b, c, 5a, e, f,** and **8** from hydroquinones **2** and dicarbonyl compounds **1, 4,** and **7**, respectively, *p*-toluenesulfonic acid in chloroform

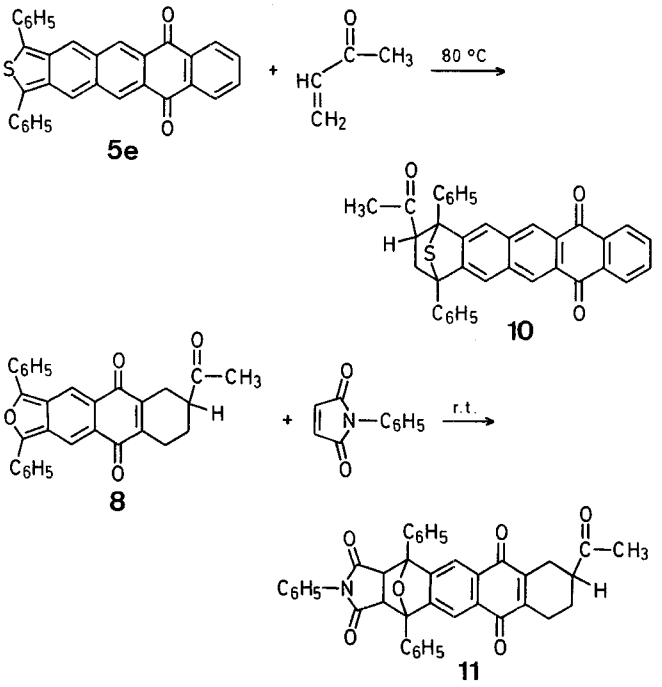


0039-7881/82/1032-0882 $ 03.00

Reduction of 8,9-dibenzoylnaphthacene-5,12-quinone **(3e)** with tin/acetic anhydride affords 5,12-diacetoxy-8,9-dibenzoylnaphthacene **(9)** in 90% yield.



The thieno- and furo-fused polycyclic quinones **5e** and **8** react with dienophiles (e.g., butenone and *N*-phenylmaleimide) to give Diels-Alder adducts of the types **10** and **11**, respectively. This reaction permits the protection of the reactive naphtho[2,3-*c*]thiophene and 2-benzofuran moieties in quinones **5e** and **8** in the transformation of these quinones into daunomycine-type compounds.



I.R. spectra were determined with a Perkin-Elmer Model 297 spectrophotometer. U.V.-Vis. spectra were determined with a Beckmann Model 25 spectrophotometer. ^{1}H-N.M.R. spectra were determined with a Varian Model E.M. 360 spectrograph. Microanalyses were performed by M. J. Leger (Laboratoire R. Bellon).

2-Acetyl-5,8-dihydroxy-1,2,3,4-tetrahydronaphthalene (2a)[10]:
A mixture of 6-acetyl-5,6,7,8-tetrahydro-1,4-naphthoquinone[8] (4 g, 19.6 mmol), sodium dithionite (8 g), ether (200 ml), and water (80 ml) is stirred for 30 min at room temperature. The ether layer is washed with water (10 ml). Ether is evaporated in vacuo, the crystalline product is washed with ether, and recrystallised from water; yield: 2 g (50%); m.p. 138 °C.

$C_{12}H_{14}O_3$	calc.	C 69.88	H 6.84
(206.2)	found	69.88	7.00

I.R. (KBr): $\nu = 3400$ cm^{-1} (OH); 1705–1680 cm^{-1} (C=O).

U.V. (CH_2Cl_2): $\lambda_{max} = 287$ nm ($\log\varepsilon = 3.58$).

^{1}H-N.M.R. ($CDCl_3$/TMS_{int}): $\delta = 2.25$ (s, 3H); 1.5–3 (m, 7H); 4.45 (s, 1H, OH); 4.55 (s, 1H, OH); 6.5 ppm (s, 2H_{arom}).

Condensation of 1,4-Dicarbonyl Compounds 1, 4, and 7 with Hydroquinones 2; General Procedure:
A mixture of the dicarbonyl compound **1, 4,** or **7** (2 mmol), the hydroquinone **2** (2 mmol), and *p*-toluenesulfonic acid (0.75 g) in chloroform (100 ml) is heated at reflux temperature for 4 h (with **1c**, 6 h; with **4c**, 64 h), then washed with hot water (2 × 30 ml), and dried with sodium sulfate. The chloroform is evaporated in vacuo and the crystalline product washed with ether. Compound **5f** is purified by column chromatography on silica gel 40 Merck (0.063–0.2 mm) using benzene as eluent.

Quinones 3d, e from Quinones 5a, e by Photooxidation:
A solution of quinone **5a** or **5e** (1 mmol) in chloroform (250 ml) is irradiated with a Philips SP 500 lamp using a sodium nitrite filter for ~ 1 h (disappearance of the characteristic color of the educt). The solution is then concentrated and the crystalline product is washed with ether containing a few drops of acetone.

2-Acetyl-8,9-dibenzoyl-1,2,3,4-tetrahydronaphthacene-5,12-quinone **(3d);** yield: 32%; m.p. 283–284 °C (from dimethylformamide).

$C_{34}H_{24}O_5$	calc.	C 79.67	H 4.72
(512.5)	found	79.55	4.83

I.R. (KBr): $\nu_{C=O} = 1665$, 1710 cm^{-1}.

U.V.-Vis. (CH_2Cl_2): $\lambda_{max} = 271$ ($\log\varepsilon = 4.81$); 402 nm (3.84).

8,9-Dibenzoylnaphthacene-5,12-quinone **(3e);** yield: 78%; m.p. 363–365 °C (subl.).

$C_{32}H_{18}O_4$	calc.	C 82.39	H 3.89
(466.5)	found	82.25	3.98

I.R. (KBr): $\nu_{C=O} = 1660$, 1680 cm^{-1}.

U.V.-Vis. (CH_2Cl_2): $\lambda_{max} = 275$ ($\log\varepsilon = 4.86$); 385 (shoulder; 3.83); 398 nm (3.88).

Quinones 3d, e by Trapping of 1,2-Bis[bromomethylene]-4,5-dibenzoyl-3,6-cyclohexadiene:

1,2-Bis[dibromomethyl]-4,5-dibenzoylbenzene: A mixture of 1,2-dibenzoyl-4,5-dimethylbenzene[6] (15 g, 47.8 mmol), *N*-bromosuccinimide (34 g, 0.19 mol), dibenzoyl peroxide (0.34 g, 2.2 mmol), and tetrachloromethane (340 ml) is heated under reflux for 15 h. The succinimide is filtered and washed with two portions of chloroform. The filtrate is washed with hot water (3 × 50 ml), the organic solution is dried with sodium sulfate, and evaporated to give an oily product which crystallises when stirred with ether; yield: 26 g (85%); colorless crystals, m.p. 188 °C (from ethyl acetate).

$C_{22}H_{14}Br_4O_2$	calc.	C 41.94	H 2.24	Br 50.74
(630)	found	42.27	2.27	50.91

I.R. (KBr): $\nu = 1660$, 1680 cm^{-1} (C=O).

Table 1. Condensation of 1,4-Dicarbonyl Compounds **(1, 4, 7)** with Hydroquinones **(2)**

Reagents	Product	Yield [%]	m.p. [°C]	Molecular formula or m.p. [°C] reported
1a + **2a**	**3a**	73	195°	189–192°[1]
1b[5] + **2a**	**3b**	98	305° (DMF)	$C_{24}H_{18}O_3$ (354.4)
1c[6] + **2a**	**3c**	64	270° (xylene)	$C_{34}H_{28}O_3$ (484.6)
4a[7] + **2a**	**5a**	98	275° (xylene)	$C_{34}H_{24}O_3S$ (512.5)
7[3] + **2a**	**8**	66	284° (DMF)	$C_{30}H_{22}O_4$ (446.5)
4a + **2e**[b]	**5e**	95	352° (xylene)	$C_{32}H_{18}O_2S$ (466.5)
4c + **2f**[c]	**5f**	25	347° (xylene)	$C_{44}H_{26}O_4S$ (648.6)

[a] The microanalyses showed the following maximum deviations from the calculated values: C, ±0.27; H, ±0.23; S, ±0.31.

[b] 1,4-Dihydroxynaphthalene[12].

[c] 1,4,5,8-Tetrahydroxynaphthalene ⇌ 5,8-Dihydroxytetralin-1,4-dione[11].

Table 2. Spectral Data of Compounds **3**, **5**, and **8**

Compound	I.R. (KBr) $\nu_{C=O}$ [cm^{-1}]	U.V.-Vis. (CH_2Cl_2) λ_{max} [nm] (logε)	^{1}H-N.M.R. ($CDCl_3$/TMS_{int}) δ [ppm]
3b	1705, 1660	262 (4.90); 313 (shoulder; 4.05); 326 (4.33); 341 (4.48); 382 (3.60); 405 (3.67); 465 (3.93)	2.3 (s, 3H, $COCH_3$); 1.5–3 (m, 7H, CH_2 and CH); 7.4–8.3 (m, 4H_{arom}); 8.65 (s, 2H_{arom}); 8.85 (s, 2H_{arom})
3c	1710, 1662	245 (4.69); 280 (4.38); 296 (shoulder; 4.41); 306 (4.44); 412 (3.80)	2.2 (s, 3H); 2.3 (s, 6H); 1.5–3 (m, 7H); 7.2–7.7 (m, 12 H_{arom})
3d	1710, 1665	271 (4.81); 402 (3.84)	2.3 (s, 3H); 1.5–3 (m, 7H); 7.3–7.9 (m, 10H); 8.2 (s, 2H); 8.7 (s, 2H)
3e	1680, 1660	275 (4.86); 385 (shoulder; 3.83); 398 (3.88)	insufficiently soluble
5a	1705, 1660, 1645	260 (4.53); 293 (4.60); 352 (4.59); 556 (4.20)	2.3 (s, 3H); 1.5–3 (m, 7H); 7.3–7.8 (m, 10H); 8.3 (s, 2H); 8.4 (s, 2H)
5e	1670, 1655	262 (4.56); 300 (4.68); 357 (4.66); 530 (4.06)	insufficiently soluble
5f	1620	262 (4.56); 309 (4.77); 363 (4.54); 555 (4.32)	insufficiently soluble
8	1710, 1660, 1645	282 (4.67); 315 (shoulder; 4.31); 475 (4.18); 520 (shoulder; 4.01)	2.25 (s, 3H); 1.5–3 (m, 7H); 7.3–8 (m, 10H); 8.45 (s, 2H)

Quinones **3d, e** (cf. Ref.[9]): A mixture of 4,5-dibenzoyl-1,2-bis[dibromomethyl]benzene (8 g, 12,7 mmol), quinone (13 mmol), sodium iodide (16 g, 106 mmol), and dimethylformamide (80 ml) is heated at 70 °C for 15 h; the mixture is poured into water (300 ml) with sodium hydrogen sulfite (30 ml).

2-Acetyl-8,9-dibenzoyl-1,2,3,4-tetrahydronaphthacene-5,12-quinone **(3d).** The crystalline product is washed with acetone; yield: 2.47 g (36%); m.p. 283–284 °C.

8,9-Dibenzoylnaphthacene-5,12-quinone **(3e).** The crystalline product is washed with ether and extracted with chloroform (200 ml) in a Soxhlet apparatus; yield: 2.5 g (52%); m.p. 363–365 °C.

5,12-Diacetoxy-8,9-dibenzoylnaphthacene (9):
A mixture of 8,9-dibenzoylnaphthacene-5,12-quinone (**3e**; 1 g, 2.15 mmol), anhydrous sodium acetate (1 g), tin (powder; 4 g), and acetic anhydride (40 ml) is heated at reflux temperature for 90 min and is then filtered into water (500 ml). The red crystalline product is isolated by suction and washed with acetone; yield: 0.9 g (90%); m.p. 301 °C (from acetic acid).

$C_{36}H_{24}O_6$	calc.	C 78.25	H 4.38	
(552.5)	found	77.94	4.50	

I.R. (KBr): ν = 1660, 1740 cm^{-1} (C=O).

U.V.-Vis. (CH_2Cl_2): λ_{max} = 274 (logε = 4.82); 294 (4.76); 307 (4.65); 400 (3.50); 424 (3.62); 435 (shoulder; 3.59); 470 (3.72); 501 nm (3.66).

^{1}H-N.M.R. ($CDCl_3$/TMS_{int}): δ = 2.7 (s, 6H); 7.3–8.1 (m, 10H); 8.25 (s, 2H); 8.7 ppm (s, 2H).

10-Acetyl-8,11-diphenyl-8,11-epithio-8,9,10,11-tetrahydronaphthacene-5,12-quinone (10):
A mixture of 1,3-diphenylnaphthaceno[2,3-*c*]thiophene-6,11-quinone (**5e**; 1 g, 2.14 mmol) and butenone (2 ml, 24 mmol) is heated at 80 °C in the dark for 20 h. Water (20 ml) is then added, the mixture extracted with ethyl acetate (3 × 60 ml), the extract washed with water (20 ml), and evaporated in vacuo. The residue crystallises upon addition of a few drops of an ether/acetone mixture to give yellow **10**; yield: 0.46 g (40%); m.p. 251–252 °C (dec, from acetone).

$C_{36}H_{24}O_3S$	calc.	C 80.58	H 4.51	S 5.96
(538.6)	found	80.36	4.67	5.60

I.R. (KBr): ν = 1675, 1715 cm^{-1} (C=O).

U.V.-Vis. (CH_2Cl_2): λ_{max} = 269 (logε = 4.73); 310 (4.40); 390 nm (3.26).

***N*-Phenyl-2-acetyl-7,10-diphenyl-7,10-epoxy-1,2,3,4,7,8,9,10-octahydronaphthacene-5,12-quinone-8,9-dicarboximide (11):**
A solution of 7-acetyl-1,3-diphenyl-6,7,8,9-tetrahydroanthra[2,3-*c*]furan-5,10-quinone (**8**; 400 mg, 0.89 mmol) and *N*-phenylmaleimide (160 mg, 0.92 mmol) in chloroform (40 ml) is allowed to stand at room temperature in the dark for ~48 h. The yellow solution is evaporated in vacuo and the yellow crystalline product is washed with ether; yield: 0.55 g (99%); m.p. 190 °C (dec) (from acetone).

$C_{40}H_{29}O_6N$	calc.	C 77.53	H 4.72	N 2.26
(619.6)	found	76.77	4.99	2.21

I.R. (KBr): ν = 1665, 1715, 1780 cm^{-1}.

U.V. (CH_2Cl_2): λ_{max} = 252 (logε = 4.42); 258 (4.44); 274 (shoulder; 4.14); 326 nm (3.51).

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[10] This compound was only mentioned without data by F. Suzuki, R. D. Gleim, S. Trenbeath, C. J. Sih, *Tetrahedron Lett.* **1977**, 2306.
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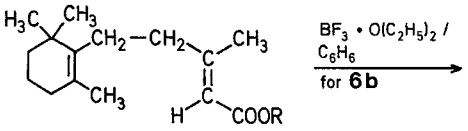
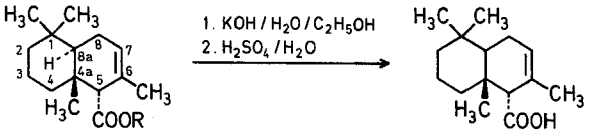
C. Schmidt, N. H. Chishti, T. Breining, *Synthesis* **1982** (5), 391-393:
The formula scheme for the reaction **6**→**7** (p. 391) should be:



6a R = H
6b R = CH_3
6c R = C_2H_5



7b R = CH_3 **7a** R = H

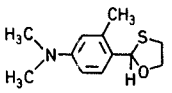
B. A. Arbuzov, N. N. Zobova, *Synthesis* **1982** (6), 433-450:
The correct name for compound **15** (p. 436) is *N'*-benzoyl-*N,N*-dimethyl-2-phenyl-2-butenamidine and for compound **30b** (p. 439) is 4-trifluoroacetylimino-2-trifluoromethyl-4*H*, 9a*H*-pyrido[2,1-*b*]-1,3,5-oxadiazine.

Chen-Chu Chan, Xian Huang, *Synthesis* **1982** (6), 452-454:
The last sentence on page 452 should read: However, under the normal conditions [20% aqueous sodium hydroxide in the presence of benzyltriethylammonium chloride (TEBA)] the ring underwent cleavage and the main product was dimethylmalonic acid in the case of methylation.

P. Molina, A. Arques, A. Ferao, *Synthesis* **1982** (8), 645-647:
Compounds **3,4,** and **6** are substituted pyrido[2,1-*b*][1,3,4]thiadiazinium salts.

Abstract 6431, *Synthesis* **1982** (9), 801
The correct name for the title compounds **3** is 2-oxoalkanehydroximic chlorides.

B. Burczyk, Z. Kortylewicz, *Synthesis* **1982** (10), 831-832:
In Table 1 (p. 832) the b.p. of product **6a** should be 113-114°C/0.3 torr; the structure and molecular formula of product **7d** should be



and $C_{12}H_{17}NOS$ (223.2); the b.p. and n_D^{20} of product **8a** should be 114-116°C/60 torr and 1.5346, respectively. In Table 2 (p. 832) the second term in the ^{1}H-N.M.R. spectrum of product **7b** should be 1.90 (s, 3H, CH_3).

K. D. Deodhar, A. D. D'Sa, S. R. Pednekar, D. S. Kanekar, *Synthesis* **1982** (10), 853-854:
The correct name for compounds **4a,b** (p. 854) is (*E*)- and (*Z*)-6-benzylidene-3-oxo-2,3,4,6-tetrahydro[1,2,4]triazino[3,4-*a*]isoindoles.

L. Lepage, Y. Lepage, *Synthesis* **1982** (10), 882-884:
The correct name for compound **10** (p. 884) is 2-acetyl-1,4-diphenyl-1,2,3,4-tetrahydro-1,4-epithiopentacene-7,12-quinone.

R. R. Schmidt, A. Wagner, *Synthesis* **1982** (11), 958-962:
It should be noted that the numbers in the products **5**-**16c** in Table 1 refer only to the ^{1}H-N.M.R. data in Table 2 and are not identical with the numbering used for the systematic nomenclature of the products.

T. Takajo, S. Kambe, W. Ando, *Synthesis* **1982** (12), 1080-1081:
The compounds **7** should be named 2,4,6,12-tetraaryl-2,5,6,7-tetrahydro-4*H*-3,6a-methanoindeno[1,2-*f*][1,3,5]triazocines.