Phase-Transfer-Catalyzed Alkylation of Anthrone and 10-Propargylanthrone

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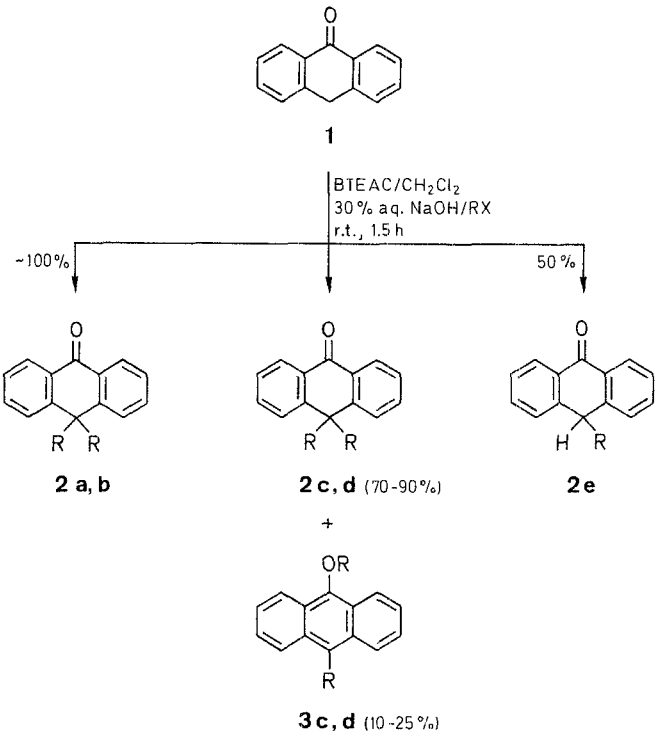
Phase-transfer-catalyzed alkylation of anthrone with a variety of active alkyl halides gave mainly *C,C*-dialkylated products, whereas that of 10-propargylanthrone with dimethyl sulphate and allyl bromide gave *O*-alkylated products.

Alkylation of anthrone, unlike other analogously active benzenoid systems, has been a matter of controversy ever since the first attempts were made. Different groups[2-5] have been frustrated in the attempt to obtain products of *C*-alkylation, *C,C*-dialkylation, or both *C*- and *O*-alkylation, and in many cases an unwanted side product of oxidation, viz. anthraquinone was formed. In recent years, phase-transfer catalysis has been widely used for its apparent selectivity[6,7] in the alkylation of ambident anions and it has been claimed[8] that alkylation of anthrone and acridone with dimethyl sulphate using benzyltriethylammonium chloride as phase-transfer catalyst yielded *O*-alkylated products quantitatively. However, the product with acridone has latter been characterized as *N*-methyl acridone.[9] Phase-transfer-catalyzed alkylation of different ketones has been extensively studied.[10,11] Cyclic ketones with the methylene group activated by the presence of an aromatic ring, e.g. 1-acenaphthenone and 2-tetralone were found to undergo *C,C*-dialkylation irrespective of the alkylating agent.[10,11] These reports on the mode of alkylation prompted us to study the phase-transfer-catalyzed alkylation of anthrone and 10-propargylanthrone with different allylic and acetylenic active halides.



	R		R
2a	$CH_2CH=CH_2$	**2d**	$CH_2C\equiv CCH_2OC_6H_4Cl$-4
2b	$CH_2CH=CHCH_3$	**2e**	$C(CH_3)_2C\equiv CH$
2c	$CH_2C\equiv CCH_3$	**3c**	$CH_2C\equiv CCH_3$
		3d	$CH_2C\equiv CCH_2OC_6H_4Cl$-4

Reaction of anthrone with allyl bromide in dichloromethane in the presence of benzyltriethylammonium chloride (BTEAC) in 30% aqueous sodium hydroxide gave 10,10-diallylanthrone (**2a**) in quantitative yield. With crotyl bromide also only one product was obtained and this was characterized as 10,10-dicrotylanthrone (**2b**). The reaction was then attempted with 1-

Table. Compounds **2**, **3** and **5** Prepared

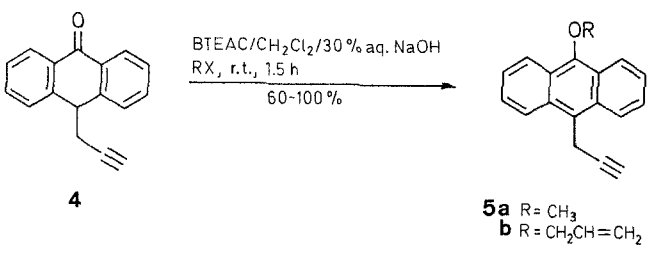
Compound	Yield[a] (%)	mp[b] (°C)	Molecular Formula[c]	UV (EtOH) λ_{max} (nm)[d]	IR (KBr) ν (cm^{-1})[e]	^{1}H-NMR ($CDCl_3$/TMS) δ, J (Hz)
2a	100	86	$C_{20}H_{18}O$ (274.1)	270	1320, 1450, 1605, 1665	2.8–3.2 (d, 4H, J = 6); 4.2–5.2 (m, 6H); 7.3–8.0 (m, 6H); 8.3–8.7 (m, 2H)[f]
2b	100	82	$C_{22}H_{22}O$ (302.2)	270	970, 1325, 1450, 1600, 1650, 2935	1.1–1.4 (d, 6H, J = 6); 2.7–3.2 (d, 4H, J = 6.5); 4.3–5.4 (m, 4H); 7.3–8.1 (m, 6H); 8.3–8.7 (m, 2H)[f]
2c	90	167	$C_{22}H_{18}O$ (298.1)	270	935, 1325, 1450, 1600, 1650, 2240, 2920	1.4–1.6 (t, 6H, J = 2.5); 2.9–3.1 (q, 4H, J = 2.5); 7.4–7.6 (m, 2H); 7.6–8.0 (m, 4H); 8.3–8.6 (m, 2H)[g]
2d	70	114	$C_{34}H_{24}Cl_2O_3$ (551.1)	270	1010, 1240, 1325, 1490, 1600, 1655, 2260, 2940	3.0–3.2 (t, 4H, J = 2.2); 4.2–4.5 (t, 4H, J = 2.2); 6.4–6.7 (m, 4H); 7.0–7.2 (m, 4H); 7.4–7.6 (m, 2H); 7.6–7.8 (m, 4H); 8.3–8.6 (m, 2H)[g]
2e	50	169	$C_{19}H_{16}O$ (260.1)	270	935, 1460, 1595, 1650, 2120, 3290	1.1 (s, 6H); 2.1 (s, 1H); 4.0 (s, 1H); 7.4–7.8 (m, 6H); 8.1–8.4 (m, 2H)[g]
3c	10	110	$C_{22}H_{18}O$ (298.1)	258, 358	970, 1285, 1355	1.7–1.8 (t, 3H, J = 2.6); 1.8–2.0 (t, 3H, J = 2.4); 4.3–4.4 (q, 2H, J = 2.6); 4.8–5.0 (q, 2H, J = 2.4); 7.4–7.8 (m, 4H); 8.2–8.6 (m, 4H)[g]
3d	25	128	$C_{34}H_{24}Cl_2O_3$ (551.1)	259, 358	1290, 1358, 1495	4.4–4.5 (m, 2H); 4.5–4.6 (m, 2H); 4.6–4.7 (m, 2H); 4.9–5.0 (m, 2H); 6.7–6.9 (m, 4H); 7.0–7.4 (m, 4H); 7.4–7.8 (m, 4H); 8.1–8.6 (m, 4H)[g]
5a	100	148	$C_{18}H_{14}O$ (246.1)	258, 358	965, 1090, 1280, 1365, 3260	2.1 (s, 1H); 4.2 (s, 3H); 4.4–4.5 (d, 2H, J = 2.5); 7.4–7.9 (m, 4H); 8.2–8.7 (m, 4H)[f]
5b	60	87	$C_{20}H_{16}O$ (272.1)	258, 358	1100, 1285, 1360, 1400, 3300	2.1 (s, 1H); 4.4–4.5 (d, 2H, J = 2.6); 4.6–4.9 (d, 2H, J = 5.5); 5.2–5.8 (m, 2H); 6.0–6.8 (m, 1H); 7.4–8.0 (m, 4H); 8.3–8.9 (m, 4H)[f]

[a] Yield of pure isolated product.
[b] Recorded on H_2SO_4 bath and are uncorrected.
[c] Satisfactory microanalyses obtained: C ±0.29, H ±0.30.
[d] Recorded on a Hitachi 200-20 spectrometer.
[e] Recorded on a Perkin-Elmer 1330 infrared spectrometer.
[f] Recorded on a Hitachi R-600 NMR spectrometer.
[g] Recorded on a Jeol Fx-100 NMR spectrometer.

bromobut-2-yne and in this case both *C,C*-dialkylated **2c** (90%) and O-alkylated **3c** (10%) products were obtained. With the tertiary halide, 3-bromo-3-methyl-1-butyne, only mono *C*-alkylated product **2e** (50%) was obtained along with an inseparable mixture of products, possibly formed by elimination reactions. Another butynyl halide, namely, 4-(4-chlorophenoxy)-1-bromo-2-butyne also gave both *C,C*-dialkylated product **2d** (70%) and *C*- and *O*-dialkylated product **3d** (25%). All the products were characterized by microanalysis and spectroscopic data (Table).

The nature of alkylation, namely *C*-alkylation **(2e)**, *C,C*-dialkylation **(2a–d)**, and *C*-alkylation followed by *O*-alkylation **(3c, d)** was determined from the absence or presence of carbonyl absorption in the infra-red spectra and/or the absence or presence of dibenzylic proton (at C-10, $\delta = 4.0$) in ^{1}H-NMR spectra. The dialkylated products **2a–d** showed strong carbonyl absorption in the region 1650–1665 cm^{-1} in their infra-red spectra and no dibenzylic proton in their ^{1}H-NMR spectra. However, the mono *C*-alkylated product **2e** showed the presence of both dibenzylic proton at $\delta = 4$ and the carbonyl absorption band at 1650 cm^{-1}. On the other hand, the products 3c, d showed absence of carbonyl absorption in their infra-red spectra and also absence of dibenzylic proton in their ^{1}H-NMR spectra. These products, however, showed UV (EtOH): λ_{max} 258, 358 nm. The position of two aromatic protons (at C-1 and C-8) in the low field region at $\delta = 8.3-8.7$ is also characteristic of *C*-alkylated products (Table).

In the base-catalyzed alkylation of anthrone with methyl iodide, the formation of 10-methylanthracene-9-methyl ether was explained as due to preponderant *C*-alkylation followed by *O*-alkylation of the resulting *C*-alkylated product. However, no attempt has ever been made to alkylate 10-alkylanthrone both under classical and phase-transfer-catalyzed conditions. We undertook the phase-transfer-catalyzed alkylation of 10-propargylanthrone **(4)**, a material already at our disposal.[11] With dimethyl sulphate and allyl bromide using benzyltriethylammonium chloride as catalyst under analogous experimental condition as compared to that of anthrone, 10-propargylanthrone **(4)** reacted to give mainly *O*-alkylated products, 9-methoxy-10-propargylanthracene **(5a)** and 9-allyloxy-10-propargylanthracene **(5b)** (Table).



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5a R = CH_3
b R = $CH_2CH=CH_2$

Alkylation of Anthrone (1) and 10-Propargylanthrone (4); General Procedure:

To a mixture of anthrone (**1**; 1.0 g, 5 mmol) and alkylhalide (RX, X = Br) (15 mmol) in CH_2Cl_2 (25 mL) is added a solution of BTEAC (0.25 g) in 30% NaOH (25 mL) and the mixture is stirred for a period of 1–1.5 h. It is then diluted with water (125 mL) and extracted with CH_2Cl_2 (3 × 25 mL). The combined extract is washed successively with 2N HCl (3 × 25 mL), 5% aqueous $NaHCO_3$ (3 × 25 mL) and brine (3 × 30 mL) and dried (Na_2SO_4). The solvent is removed *in vacuo* and the residual crude mass is purified by chromatography over silica gel (BDH, 60–120 mesh). The compounds are obtained when the column is eluted with the following solvent/solvents: benzene/petroleum ether (60–80°C), 1:1 **(2b)**; benzene **(2c)**; benzene **(2d)**; benzene/petroleum ether (60–80°C) 1:1 **(2e)**; benzene/petroleum ether (60–80°C), 3:1 **(3c)**; petroleum ether (60–80°C) **(3d)**. Compound **2a** is purified by recrystallization from a mixture of $CHCl_3$ and petroleum ether (60–80°C).

For the alkylation of 10-propargylanthrone (**4**; 1.2 g, 5 mmol) Me_2SO_4 (3 g, 23.8 mmol) or allyl bromide (3 g, 25 mmol) is used and the rest of the procedure is the same as given above. The product **5a** is purified by recrystallization of the crude mass from a mixture of $CHCl_3$ and petroleum ether (60–80°C) and **5b** is obtained after chromatography over silica gel (BDH, 60–120 mesh) and eluting the column with benzene/petroleum ether (60–80°C), 3:1. The purity of the products are determined by TLC examination using different solvent systems.

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