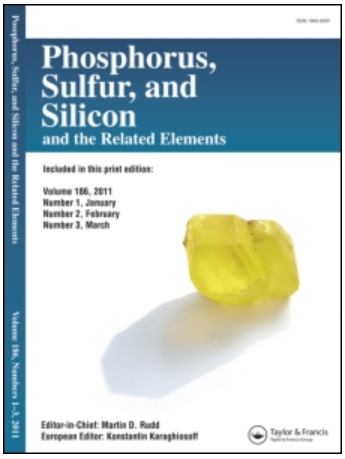

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PTC-ALKYLATION AND MICHAEL ADDITION OF INDANONES; SYNTHESIS OF 2-SUBSTITUTED INDANONES

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PTC-ALKYLATION AND MICHAEL ADDITION OF INDANONES; SYNTHESIS OF 2-SUBSTITUTED INDANONES

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The reactivity of indan-1-one (**1a**) and/ or indan-1,3-dione (**1b**) towards alkylation in the absence or presence of carbon disulphide under phase transfer catalysis (PTC) conditions has been investigated to give indanone derivatives **2–9**. Michael addition of (**1a,b**) to α,β-unsaturated carbonyl compounds under the same PTC conditions yielded the adducts **10–16**.

In continuation of our previous work[1,3] in the field of phase transfer catalysis (PTC), we have reported here the study of O-vs-C-alkylation[4] of indanones (**1a,b**) by some organohalogen compounds in the absence or presence of carbon disulphide. Also Michael type addition of (**1**) to some α,β-unsaturated carbonyl compounds under PTC reaction conditions was investigated as one of the most important techniques in organic synthesis[5,6]. The present work was presented orally at PTC' 97 conference in Nagoya[7].

In this investigation we used K_2CO_3/benzene or ether as the solid/ liquid phases and tetrabutyl ammonium bromide (TBAB) as a catalyst in the alkylation of (**1a**), while NaOH (30%)/ CH_3CN as liquid / liquid phases and benzyltriethylammonium chloride (TEBA) as a catalyst in Michael addition of (**1a,b**) at 25°C as the optimum conditions to give the best yields in a short reaction time.

Treatment of equimolar amounts of 1-indanone (**1a**) and benzyl chloride in dry ether and K_2CO_3 in the presence of (TBAB) at 25°C afforded 2,2-(bisbenzyl)indan-1-one (**2**) in 62% yield whereas, 1,3-dibromopropane underwent simultaneous C- and 0-alkylation to give 2,3-dihydroindeno[3,2-b]pyran (3) in 54% yield under the same PTC conditions

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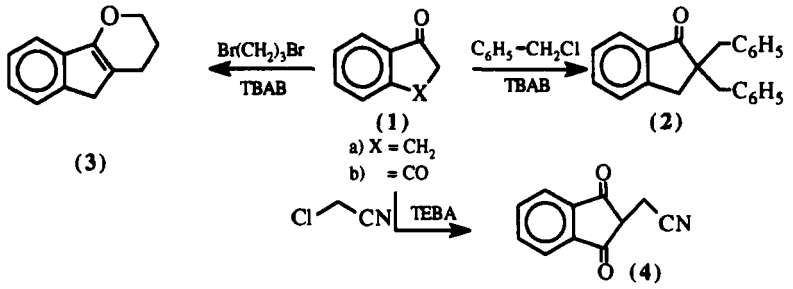
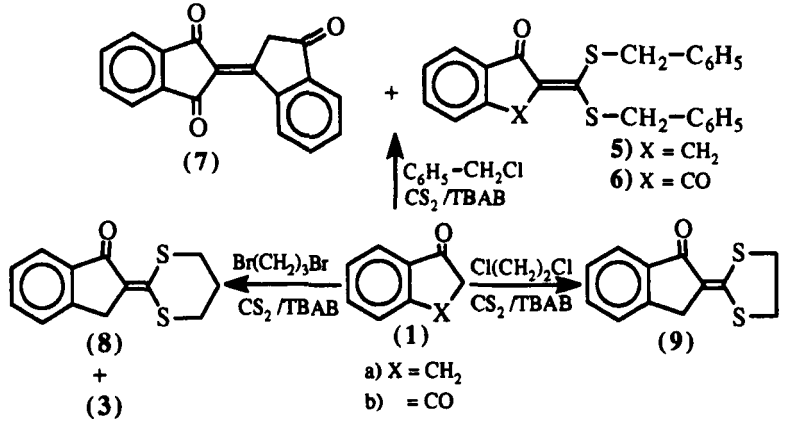
(Scheme 1). Also, PTC-alkylation of indan-1,3-dione (**1b**) by chloroacetonitrile in CH_3CN/NaOH (30%) in the presence of (TEBA) as catalyst gave (1,3-dioxoindan-2-yl)acetonitrile (**4**) in 60% yield (Scheme 1).



SCHEME 1

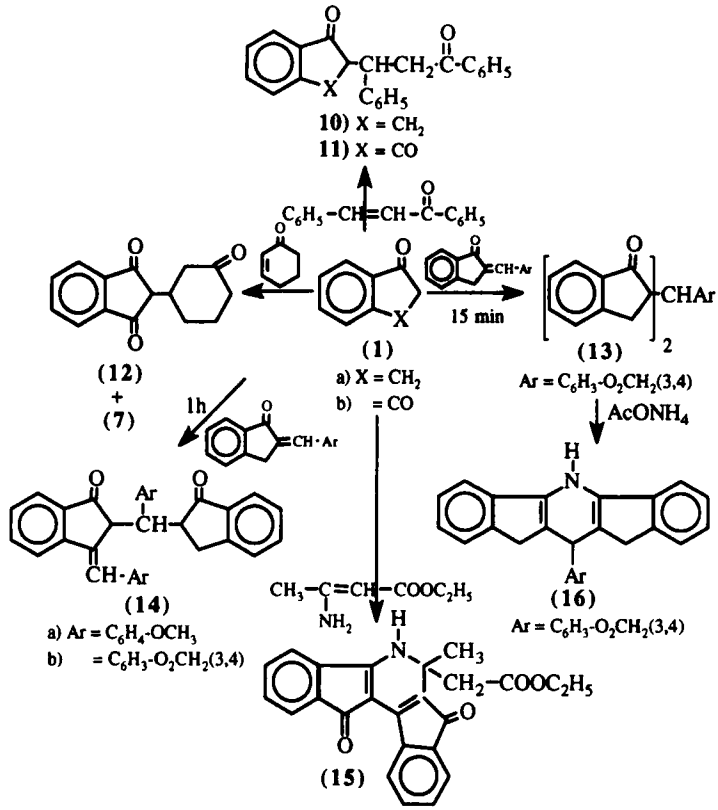
Reaction of active methylene compounds with carbon disulphide in the presence of base followed by alkylation of the dithiolate anions has been studied[2,8]. Treatment of indanones (**1a**) with benzyl chloride in the presence of carbon disulphide in dry ether and anhydrous K_2CO_3 and in the presence of TBAB at 25°C yielded 2-(bisbenzylthio)methyleneindan-1-one (**5**) in 72% yield, whereas with indane-1,3-dione (**1b**) produced a mixture of 2-(bisbenzylthio)methyleneindan-1,3-dione (**6**) and 2-(1-oxo-indan-3,3-diyl)indan-1,3-dione (**7**) were obtained in 50% and 22% yields, respectively (Scheme 2).



SCHEME 2

Furthermore, PTC reaction of indan-1-one (**1a**) with 1,3-dibromo propane in the presence of carbon disulphide afforded a mixture of (**3**) and 2-(1′-oxo-indan-2′-yliden)-1,3-dithiane (**8**) in 10% and 65% yield respectively (Scheme 2), while with 1,2-dichloroethane yielded 2-(1′-oxo-indan-2′-yliden)-1,3-dithiolane (**9**) in 53% yield (Scheme 2).

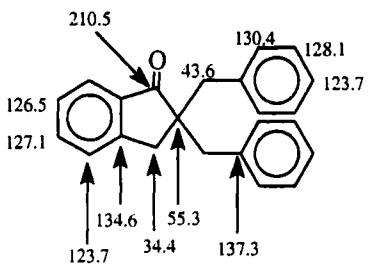
On the other hand, Michael type addition of the indanones (**1a,b**) as active methylene compounds to some α,β-unsaturated carbonyl compounds such as, benzylidene acetophenone, cyclohex-2-en-1-one, 2-arylidene indan-1-ones and ethyl 3-aminocrotonate under PTC reaction conditions using CH_3CN/NaOH (30%) as liquid/liquid phases and TEBA as catalysts at 25°C afforded the expected Michael adducts (**10–15**) in 60–90% yields (Scheme 3) within short time.



SCHEME 3

Fusion of (**13**) with ammonium acetate at 160–170°C gives 7-(3,4-methylenedioxy)phenyl-bisindeno[3,2-b:2′,3′-e]-1,4-dihydropyridine **(16)** (Scheme 3).

The structures of the products have been confirmed by elemental analysis, IR, ^{1}H-NMR, ^{13}C-NMR and mass spectra.



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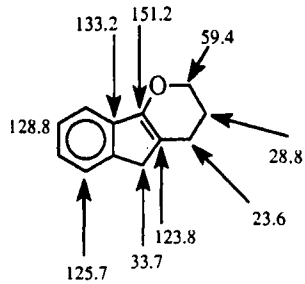

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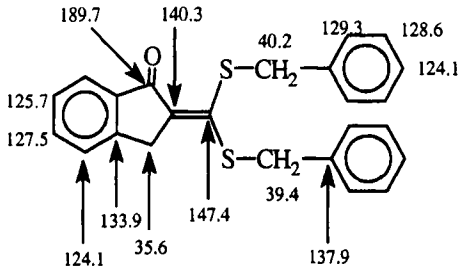

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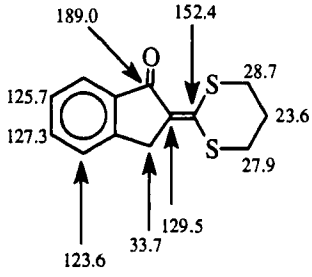

(8)

EXPERIMENTAL

Melting points recorded are uncorrected. Physical data and reaction conditions are listed in Table I. IR spectra were recorded (in KBr) on Pye unicam Sp 200G, Perkin-Elemer 2000 and FT-IR spectrometers. ^{1}H-NMR spectra were determined on a Varian (FT-90 and Gimini 200 MHz) and Brucker Ac-200 spectrometers. ^{13}C.NMR spectra were measured with 135/90 Dept experiment on a Brucker AMX. 300 spectrometer. All chemi-

cal shifts (δ) are expressed in ppm. using TMS as internal standard. Mass spectra were determined with HP model MS-5988 at 70 eV. Elmental analyses were determined by Perkin-Elmer 2400, CHN elemental analyzer. Starting materials and most of commercial reagents were Aldrich products.

ALKYLATION IN ABSENCE OR PRESENCE OF CARBON DISULPHIDE

To a solution of 1-indanone **(1a)** and / or 1,3 -indandione **(1b)** (0.01 mol) in dry ether or benzene (50mL), anhydrous potassium carbonate (0.02 mol) and halogen compounds, namely benzyl chloride, 1,3-dibromo propane, chloroacetonitrile and / or 1,2-dichloro ethane (0.02mol) were added in absence or presence of carbon disulphide (0.1mol), then tetrabutylammonium bromide (TBAB) (0.003mol) was added to the reaction mixture. The reaction mixture was stirred at 25°C over a period of time (Table I). At the end of the reaction the organic layer was separated and the solvent was removed under reduced pressure, then the residue obtained was triturated and finally crystallized by the proper solvents (Table I) to give the products 2–9 as yellow crystals.

MICHAEL ADDITION OF INDANONES (1) TO α,β-UNSATURATED CARBONYL COMPOUNDS: FORMATION OF ADDUCTS 10–15

General procedure

To a solution of indanones **(1a,b)** (0.01 mol) in acetonitrile (30 mL) and sodium hydroxide (10 mL, 30%), the α,β-unsaturated compounds like, benzylidene acetophenone (trans-chalcone), 2-cyclohexen -1-one, 2-arylidene indan –1-ones (0.01mol) and ethyl 3-amino crotonate were added in one portion. The reaction mixture was stirred over a periods of time at 25°C (Table I) under TLC control. The reaction mixture was diluted with water (50mL) and then neutralized with dilute hydrochloric acid (till pH 7). The solid separated was collected,washed with water (2 × 10mL), dried and crystallized from proper solvent (Table I) to give adducts **14, 15** as yellow crystals and adducts **(10–13)** as colourless crystals.

TABLE I Physical data of compounds prepared

Compd. no	*mp°C Solvent of cryn*	*Time (hr)*	*M.Formula (M.wt)*	*Analysis Calcd/Found*		
				C	*H*	*N%*
2	120–122	72	$C_{23}H_{20}O$	88.43	6.45	–
	Pet 60–80		(312.41)	88.56	6.59	
3	100–102	120	$C_{12}H_{12}O$	83.69	7.03	–
	Pet 60–80		(172.23)	83.43	6.92	
4	167–169	72	$C_{11}H_7NO_2$	71.35	3.81	7.56
	Bz		(185.18)	71.55	3.91	7.61
5	98–100	72	$C_{24}H_{20}OS_2$	74.19	5.19	–
	Pet 40–60		(388.55)	74.32	5.12	
6	142–143	18	$C_{24}H_{18}O_2S_2$	71.61	4.51	–
	Bz		(402.54)	71.51	4.69	
7	206–208	18	$C_{18}H_{10}O_3$	78.83	3.68	–
	Bz-E		(274.27)	78.62	3.96	
8	130–131	120	$C_{13}H_{12}OS_2$	62.87	4.87	–
	T		(248.37)	62.72	5.02	
9	90–92	36	$C_{12}H_{10}OS_2$	61.51	4.30	–
	Pet 60–80		(234.34)	61.30	4.22	
10	214–216	24	$C_{24}H_{20}O_2$	84.68	5.92	–
	$CHCl_3$		(340.42)	84.77	5.82	
11	122–124	6	$C_{24}H_{18}O_3$	81.34	5.12	–
	Pet.80-100		(354.40)	81.09	5.42	
12	88–90	6	$C_{15}H_{14}O_3$	74.37	5.82	–
	Pet.40–60		(242.27)	74.21	5.78	
13	250 dec	15min	$C_{26}H_{20}O_4$	78.77	5.09	–
	Pet 60–80		(396.44)	78.63	4.93	
14a	182–184	1	$C_{34}H_{28}O_4$	81.58	5.64	–
	Bz		(500.59)	81.47	5.86	
14b	148–150	1	$C_{34}H_{24}O_6$	77.26	4.58	–
	M		(528.56)	77.42	4.32	
15	220–222	2	$C_{24}H_{19}NO_4$	74.79	4.99	3.63
	E		(385.42)	74.81	5.10	3.72
16	329–331	–	$C_{26}H_{19}NO_2$	82.74	5.07	3.71
	E		(377.44)	82.53	5.12	3.83

Petr. = Petroleum ether M = Methanol Bz= Benzene T = Toluene E = Ethanol

TABLE II Spectral data of compound prepared

Compd. n°. NMR(Solvent)	*IR ν Cm^{-1}*	*^{1}H-NMR δ ppm*	*MS(m/z %)*
2 ($CDCl_3$)	1690 (C=O)	2.84 (d,2H, CH_2), 3.05 (s,2H, C3-H_2), 3.22 (d,2H; CH_2), 7.12–7.63 (m, 14H, Ar-H).	
3 ($CDCl_3$)	1655 (enolic ether)	2.20 (t,2H,C4-H_2), 3.05 (destorted pent., 2H, C3-H_2), 3.22(t, 2H, C2-H_2), 3.68 (s, 2H, C5-H_2), 7.30–7.82 (m,	
4 (DMSO-d_6)	2220(C≡N)	4H,Ar-H). 3.15(d,2H,CH_2),4.05(t, 1H,C2-H), 7.40	
5 ($CDCl_3$)	1720,1705(C=O) 1680 (C=O)	(s_{br}, 2H, Ar-H), 8.00 (s_{br}, 2H, Ar-H). 3.65 (s,2H,C3-H_2), 4.11(s,2H, S-CH_2), 4.28 (s, 2H,S-CH_2), 7.26–7.73(m, 14H,	
6 ($CDCl_3$)	1670(C=O)	Ar-H). 4.31 (s, 4H, 2XS-CH_2), 7.28 (s, 10H, 2XC_6H_5), 7.70 (m,2H, Ar-H), 7.90 (m,	
7 (DMSO-d_6)	1725,1690(C=O)	2H, Ar-H). 4.16(s, 2H, CH_2), 7.70–8.05 (m, 7H,	
8 ($CDCl_3$)	1680 (C=O)	Ar-H), 9.69 (d, 1H, Ar-H). 2.26 (p, 2H, C5-H_2), 3.05 (m, 4H, C4- H_2+C6-H_2), 3.67(s, 2H, C'3-H_2), 7.28- 7.81 (m, 4H, Ar-H).	
9 ($CDCl_3$)	1660 (C=O)	3.47(t, 2H, S-CH_2), 3.56(t, 2H, S- CH_2), 3.69 (S, 2H, C3-H_2), 7.26–7.83	
10	3425 (OH enol) 1710,1700(C=O)	(m,4H, Ar-H)	
11 ($CDCl_3$)	1745, 1710 (C=O)	3.52(d, 1H, C2-H), 3.64(d, 1H, C2-H), 4.15(d, 1H, C2-H), 4.36 (m, 1H, C3- H), 7.3–8.01 (m, 14H, Ar-H)	
12 ($CDCl_3$)	1750, 1715, 1700(C=O)	1.20–2.90(m,10H,cyclohexyl-H), 7.80(s_{br},2H,Ar-H), 7.89 (s_{br},2H,Ar-H)	

Compd. n°. NMR(Solvent)	*IR ν Cm^{-1}*	*^{1}H-NMR δ ppm*	*MS(m/z %)*
13	1700(C-=O)	–	M^+(396, 15%), M^+-2 (394,83%), 378 (37%), 265 (67%), 248 (32%), 178(26%), 135(100%), 115 (28%)
14a (DMSO-d_6)	1710, 1690 (C=O)	3.03(d,2H,C3-H_2),3.67(s,3H, OCH_3), 3.70 (s, 3H, OCH_3), 3.82 (dd, 1H, Ar-CH), 4.03 (d,1H, C2-H), 4.48 (m, 1H, C2-H), 6.70–7.70 (m, 17H, Ar-H + =CH),	M^+ (500, 18%), 482 (3%), 379 (100%), 251 (29%), 178 (21%), 121 (17%).
14b	1712, 1685(C=O)	–	M^++1 (529, 24%), 394 (100%), 264 (37%), 168 (20%), 135 (21%).
15	3340(NH) 1725,1710, 1680 (C=O)	1.26 (t, 3H, CH_3), 1.80 (s, 3H,CH_3), 2.94(d,1H, CH_2), 3.62 (d, 1H, CH_2), 4.22 (q, 2H, CH_2), 7.35–7.68 (m, 7H, Ar-H), 8.38 (s_{br}, 1H, NH), 8.57 (d, 1H, Ar-H).	
16 (DMSO-d_6)	3600 (NH)	3.92 (s, 4H,2XCH_2), 4.55 (s, 1H, NH), 6.22 (s, 2H, O- CH_2-O), 7.15–8.24(m, 11H, Ar-H)	M^+ (377, 8%), M^+-2 (375, 100%), 341 (11%), 316 (27%), 290 (5%), 254 (7%), 173 (15%), 157 (35%)

^{13}C-nm ($CDCl_3$) spectra of compounds **2, 3, 5** and **8** showed signals at δ (ppm) which are listed on each of the corresponding carbons on the structures (page 4)

Cyclization of 13 with ammonium acetate. Formation of 16

A mixture of **13** (1 g) and ammonium acetate (2 g) was heated at 160°-170°C without solvent for 3h. After cooling, the residue was treated with warm water (20mL). The solid separated was filtered, washed with water (2 × 15mL), dried and crystallized from ethanol to give **16** as yellow crystals.

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