

REACTIONS OF 2-(1-NAPHTHYL)-1,3-INDANEDIONE  
AND 2-(4-NITRO-1-NAPHTHYL)-1,3-INDANEDIONE ANIONS  
WITH SUBSTITUTED BENZYL BROMIDES

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Received November 4th, 1975

The reaction of 2-(1-naphthyl)-1,3-indanedione and 2-(4-nitro-1-naphthyl)-1,3-indanedione anions with X-substituted benzyl bromides in acetone and dimethylformamide was studied. The anion of 2-(1-naphthyl)-1,3-indanedione affords both C-benzyl and O-benzyl derivatives whereas the 4-nitro anion gives only C-benzyl derivatives. A linear relationship was found between  $\log C/O$  and  $\sigma^+$  constants for *para*-substituted benzyl bromides. Steric hindrance was observed in the reaction of *meta*-substituted benzyl bromides with the "soft" nucleophilic center of the ambidental anion. All the studied X-benzyl bromides afford more C-derivatives in dimethylformamide than in acetone.

There are relatively few papers dealing with the effect of the electronic factors of the group R on the reactivity of a compound R—X with a soft or hard nucleophilic center of an ambidental ion. In order to study how the softness or hardness of an electrophilic center R—X affects the ratio of the C-substituted to O-substituted products, C/O, we investigated the reactions of 2-(1-naphthyl)-1,3-indanedione and 2-(4-nitro-1-naphthyl)-1,3-indanedione anions with *para*- and *meta*-substituted X-benzyl bromides. This paper is a continuation of our earlier investigation<sup>1</sup> in which we found that in the reaction of the anion of dimedone with substituted X-benzyl bromides the C/O products ratio depends to a great extent on the character of the substituent.

The reaction of 2-(1-naphthyl)-1,3-indanedione anion with substituted benzyl bromides was carried out in two aprotic solvents: in dimethylformamide and in acetone. We have found earlier<sup>2</sup> that in these solvents the reaction of 2-(1-naphthyl)-1,3-indanedione anion with halogeno hydrocarbons affords relatively high yields of products. Moreover, these solvents differ sufficiently in their dielectric constant which makes it possible to investigate the effect of solvent polarity on the ratio of the formed C- and O-derivatives. The anion of 2-(1-naphthyl)-1,3-indanedione was generated by anhydrous potassium carbonate. All reactions were carried out under the same conditions ( $40 \pm 1^\circ\text{C}$ , 4 hours). The chosen reaction time corres-

ponds to the complete reaction of 2-(1-naphthyl)-1,3-indanedione anion with *p*-nitrobenzyl bromide. The isolation procedure for reactions in both solvents was identical.

The reaction of the 2-(1-naphthyl)-1,3-indanedione anion with all X-benzyl bromides employed afforded in both solvents a mixture of C-benzyl derivatives *Ia–Ik* (2-(1-naphthyl)-2-X-benzyl-1,3-indanediones) and O-benzyl derivatives *IIa* to *IIk* (1-(X-benzyloxy)-2-(1-naphthyl)-1-inden-3-ones). The amount of the C-benzyl derivatives was invariably greater in dimethylformamide than in acetone (Table I). These results agree with the finding<sup>1–5</sup> that in the reaction of anions of cyclic  $\beta$ -diketones the C/O ratio is greater for polar than for less polar solvents.

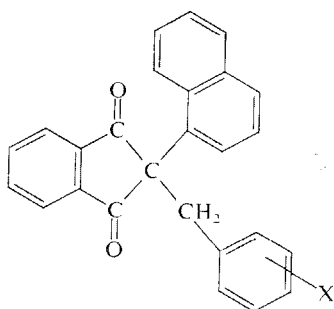
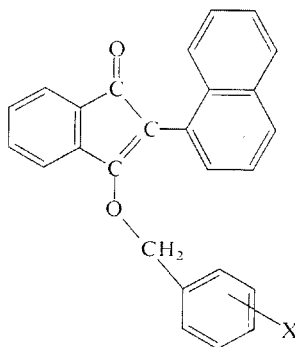
*Ia–Ik**IIa–IIk*

TABLE I

Yields (%) of the Reaction of 2-(1-Naphthyl)-1,3-indanedione Anion with Substituted X-Benzyl Bromides in Acetone and Dimethylformamide

X	Acetone			Dimethylformamide		
	total	C-derivative	O-derivative	total	C-derivative	O-derivative
<i>p</i> -NO <sub>2</sub>	9·14	76·8	23·2	84·0	80·1	19·9
<i>m</i> -Cl	8·41	68·5	31·5	91·0	71·5	28·5
<i>m</i> -I	95·1	55·5	44·5	93·9	61·4	38·6
<i>p</i> -Br	83·0	65·5	34·5	91·4	68·4	31·6
<i>p</i> -Cl	83·6	63·7	36·3	90·8	67·3	32·7
<i>p</i> -I	93·4	63·3	36·7	94·8	67·2	32·8
<i>m</i> -OCH <sub>3</sub>	70·9	55·5	44·5	74·2	62·2	37·8
H	75·5	59·2	40·8	85·1	63·6	36·4
<i>m</i> -CH <sub>3</sub>	57·4	52·1	47·9	69·7	56·8	43·2
<i>p</i> -CH <sub>3</sub>	52·7	48·4	51·6	76·3	53·9	46·1
<i>p</i> -OCH <sub>3</sub>	62·5	40·4	59·6	62·7	44·4	55·6

As seen from Table I, the C/O product ratio in both solvents depends on the character of the substituent in X-benzyl bromide which in both solvents changes in the same way as do the  $\sigma$  substituent constants. A statistical evaluation revealed that for *para*-substituted derivatives  $\log C/O = f(\sigma^+)$ . The reaction of *meta*-substituted derivatives afforded a smaller amount of C-derivatives than expected from the linear Hammett relationship with  $\sigma$  constants. An increase in the van der Waals radius of the *meta* substituent in the benzyl bromide leads to a greater amount of the O-derivative and the deviation from the correlation  $\log C/O = f(\sigma^+)$  thus increases. The results indicate that in the reaction of *meta*-substituted benzyl bromides with the 2-(1-naphthyl)-1,3-indanedione anion there is a steric hindrance at the less accessible soft nucleophilic center of this anion. Therefore, we did not include the  $\log C/O$  values for the *meta*-substituted benzyl bromides in the correlation. An analogous steric hindrance was observed also in the introduction of the second X-benzyl in the reaction of anion of dimedone with X-benzyl bromides whereas the results obtained for the monobenzylation fitted the correlation also in the case of *meta*-substituted benzyl bromides<sup>1</sup>.

In acetone,  $\log C/O = 0.457\sigma_p^+ (\pm 0.029) + 0.173 (\pm 0.03)$ ,  $r = 0.980 \pm 0.083$ , in dimethylformamide  $\log C/O = 0.460\sigma_p^+ (\pm 0.016) + 0.246 (\pm 0.041)$ ,  $r = 0.987 \pm 0.0197$ . Since the slopes of these correlations are identical within the experimental error (Fig. 1), it can be judged that in both solvents the reaction proceeds by the same mechanism. The C/O values for both solvents are given in Table II. It follows from the character of the solvents employed that the reactions in them proceed by a bimolecular mechanism ( $S_N2$ ). The decrease in the portion of the C-derivative in going from electron-accepting to electron-donating substituents can be explained by the Kornblum rule<sup>6</sup>. If, *e.g.* benzyl bromide is substituted in the *para*-position with a nitro group, the inductive as well as the mesomeric effect of this group acts against the formation of the carbocation and the character of the transition state

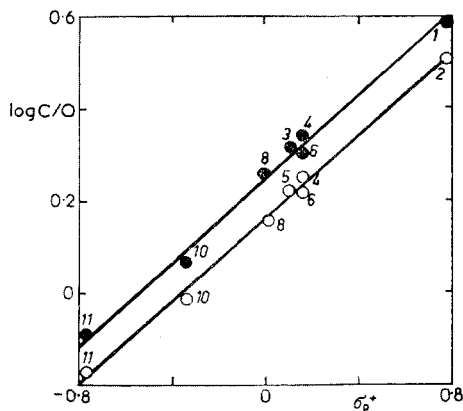


FIG. 1

Plot of  $\log C/O$  against  $\sigma_p^+$  Substituent Constants for the Reaction of 2-(1-Naphthyl)-1,3-indanedione Anion with X-Substituted Benzyl Bromides

● In dimethylformamide, ○ in acetone (for the numbering of the compounds see Table II).

TABLE II

Ratio of C- to O-Derivatives (C/O) in the Reaction of 2-(1-Naphthyl)-1,3-indanedione Anion with X-Benzyl Bromides

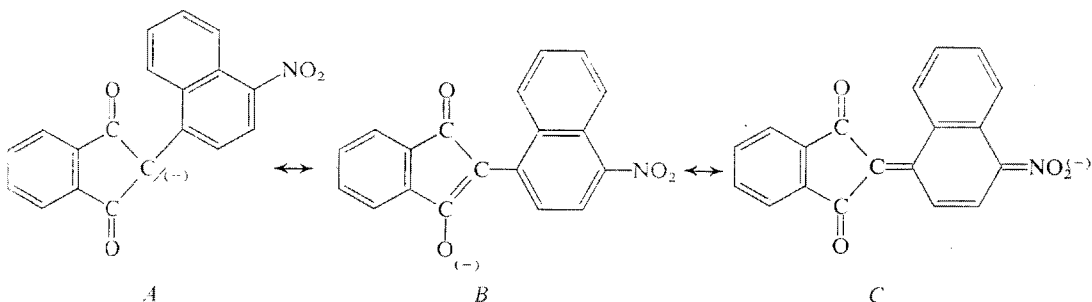
No	X	$\sigma$	$\sigma^+$	Acetone C/O	Dimethylformamide C/O
1	<i>p</i> -NO <sub>2</sub>	0.78	0.79	3.30	4.02
2	<i>m</i> -Cl	0.39	—	2.18	2.51
3	<i>m</i> -I	0.35	—	1.25	1.59
4	<i>p</i> -Br	0.23	+0.15	1.90	2.16
5	<i>p</i> -Cl	0.22	+0.11	1.76	2.06
6	<i>p</i> -I	0.19	+0.14	1.73	2.05
7	<i>m</i> -OCH <sub>3</sub>	0.12	—	1.25	1.67
8	H	0.00	0	1.45	1.75
9	<i>m</i> -CH <sub>3</sub>	-0.09	—	1.09	1.32
10	<i>p</i> -CH <sub>3</sub>	-0.17	-0.31	0.94	1.17
11	<i>p</i> -OCH <sub>3</sub>	-0.27	-0.78	0.68	0.8

is therefore shifted to the S<sub>N</sub>2 reaction. On the contrary, in the case of a reaction with *p*-methoxybenzyl bromide the positive mesomeric effect of the methoxy group makes the formation of the carbocation easier by the polarisation of the C—Br bond and shifts the transition state character toward the S<sub>N</sub>1 mechanism. However, this shift of the transition state character, caused by the electronic properties of the substituent (as shown by the observed linear plot log C/O vs  $\sigma^+$  constants), is continuous and the reaction type does not change, being S<sub>N</sub>2 even in the case of *p*-methoxybenzyl bromide.

In order to check the validity of the Pearson's theory of hard and soft acids and bases in the reaction of 2-(1-naphthyl)-1,3-indanedione anion with substituted benzyl bromides we calculated the electron densities at the electron-accepting carbon in benzyl chloride using CNDO/2 method. It was assumed that the change of the electron density with substituent should be the same for benzyl bromide as for benzyl chloride. The calculated values show that the electron density at the carbon —CH<sub>2</sub>—Cl in substituted benzyl chloride increases in going from *p*-OCH<sub>3</sub> to *p*-NO<sub>2</sub>, *i.e.* the electrophilic carbon in *p*-nitrobenzyl chloride is the softest of the employed benzyl chlorides whereas in *p*-methoxybenzyl chloride it is the hardest<sup>7</sup>. If the substituents effect the electron density at the CH<sub>2</sub>—Br carbon analogously as calculated for benzyl chlorides, then the obtained results agree with the Pearson's theory<sup>8-10</sup> since the CH<sub>2</sub>Br carbon in *p*-nitrobenzyl bromide is the softest carbon and therefore it reacts most readily with the soft nucleophilic center of the ambidental anion; on the other hand, *p*-methoxybenzyl bromide contains the hardest electrophilic center and

therefore it exhibits the greatest affinity to the hard nucleophilic center. Streitwieser and Jesaitis<sup>11</sup> calculated the energy difference for the dissociation of substituted toluenes. We have found that these energy differences ( $\Delta E$ ) can be correlated with the values of  $\log C/O$  observed for the reaction of 2-(1-naphthyl)-1,3-indanedione anion with substituted benzyl bromides, in accord with the theory of Pearson.

Similarly as in the case of 2-(1-naphthyl)-1,3-indanedione anion, we intended to follow the substituent effects also in the reaction of substituted benzyl bromides with the anion of 2-(4-nitro-1-naphthyl)-1,3-indanedione. We have found, however, that this anion affords only C-derivatives, even with such benzyl bromides which would be expected to afford the greatest amount of the O-derivative. This behaviour of the 2-(4-nitro-1-naphthyl)-1,3-indanedione anion may possibly be explained by the preference of the structure *A* over the structure *B* caused by the electron-accepting properties of the nitro group (Scheme 1).



SCHEME 1

The fact that the ambident anion with an attached nitro group reacts to a greater extent at the soft nucleophilic center than does an anion without this group, is not general. Thus, *e.g.* it was shown<sup>12</sup> that in the alkylation of K and Cs salts of ethyl X-benzoylacetates the greatest proportion of O-derivative is formed when X = NO<sub>2</sub>. The structure of the anion of X-benzoylacetates is, however, different from that of 2-(4-nitro-1-naphthyl)-1,3-indanedione and therefore also the nitro group has a different effect on the nucleophilic centers. It is known that for acyclic  $\beta$ -dicarbonyl compounds the reaction course is substantially affected by the formation of cyclic chelates. According to the assumption of Brändström<sup>13,14</sup>, the C-alkylation proceeds *via* an energetically advantageous six-membered transition state.

In order to prove the structure of the formed C- and O-benzyl derivatives we measured their IR spectra. In the carbonyl region the C-derivatives exhibit bands at 1700 to 1710 cm<sup>-1</sup> (stronger and wider) and at 1735–1745 cm, corresponding to symmetric and asymmetric C=O vibrations. The spectra of the O-derivatives display only one C=O band at 1690–1700 cm<sup>-1</sup> the intensity of which is lower than that of the band due to asymmetric C=O vibration in the corresponding C-derivatives.

TABLE III

Analytical Values and Melting Points for 2-(1-Naphthyl)-2-(X-benzyl)-1,3-indanediones (*Ia—Ik*) and 1-(X-Benzoyloxy)-2-(1-naphthyl)-1-inden-3-ones (*IIa—IIIk*)

X	Compound	Formula (mol. w.)	M.p., °C	Calculated/Found			$\nu(\text{C}=\text{O})\text{cm}^{-1}$ $\nu(\text{C}=\text{C})$
				% C	% H	% X	
NO <sub>2</sub>	<i>Ia</i>	C <sub>26</sub> H <sub>17</sub> NO <sub>4</sub> (407·4)	217—219	76·66	4·18	3·44	1 709, 1 743
				76·60	4·17	3·40	—
NO <sub>2</sub>	<i>IIa</i>	C <sub>26</sub> H <sub>17</sub> NO <sub>2</sub> (407·4)	152—153	76·66	4·18	3·44	1 969
				76·85	4·23	3·45	1 620
<i>p</i> -Cl	<i>Ib</i>	C <sub>26</sub> H <sub>17</sub> ClO <sub>2</sub> (396·9)	199—201	78·68	4·28	8·95	1 707, 1 743
				78·62	4·31	9·18	—
<i>p</i> -Cl	<i>IIb</i>	C <sub>26</sub> H <sub>17</sub> ClO <sub>2</sub> (396·5)	135—137	78·68	4·28	8·95	1 694
				78·36	4·36	8·82	1 617
<i>p</i> -Br	<i>Ic</i>	C <sub>26</sub> H <sub>17</sub> BrO <sub>2</sub> (441·3)	205—207	70·74	3·85	18·14	1 708, 1 746
				70·52	3·96	18·48	—
<i>p</i> -Br	<i>IIc</i>	C <sub>26</sub> H <sub>17</sub> BrO <sub>2</sub> (441·3)	133—136	70·74	3·85	18·14	1 693
				70·54	3·83	18·20	1 617
<i>p</i> -I	<i>Id</i>	C <sub>26</sub> H <sub>17</sub> IO <sub>2</sub> (488·3)	204—206	63·93	3·48	25·02	1 707, 1 746
				63·58	3·55	25·10	—
<i>p</i> -I	<i>IIId</i>	C <sub>26</sub> H <sub>17</sub> IO <sub>2</sub> (488·3)	138—141	63·93	3·48	25·02	1 692
				63·80	3·43	24·69	1 618
H	<i>Ie</i>	C <sub>26</sub> H <sub>18</sub> O <sub>2</sub> (362·4)	202—204	84·18	4·97	—	1 702, 1 736
				84·35	5·15	—	—
H	<i>IIe</i>	C <sub>26</sub> H <sub>18</sub> O <sub>2</sub> (362·4)	147—150	84·18	4·97	—	1 697
				83·92	5·26	—	1 621
<i>p</i> -CH <sub>3</sub>	<i>If</i>	C <sub>27</sub> H <sub>20</sub> O <sub>2</sub> (376·5)	174—175	85·70	5·42	—	1 703, 1 736
				85·60	5·21	—	—
<i>p</i> -CH <sub>3</sub>	<i>IIIf</i>	C <sub>27</sub> H <sub>20</sub> O <sub>2</sub> (376·5)	127—130	85·70	5·42	—	1 695
				85·44	5·19	—	1 619
<i>m</i> -Cl	<i>Ig</i>	C <sub>26</sub> H <sub>17</sub> ClO <sub>2</sub> (396·9)	171—173	78·68	4·28	8·95	1 708, 1 745
				78·53	4·33	8·57	—
<i>m</i> -Cl	<i>IIg</i>	C <sub>26</sub> H <sub>17</sub> ClO <sub>2</sub> (396·9)	164—167	78·68	4·28	8·95	1 693
				78·42	4·84	9·12	1 629
<i>m</i> -I	<i>Ih</i>	C <sub>26</sub> H <sub>17</sub> IO <sub>2</sub> (488·3)	201—203	63·93	3·48	25·02	1 704, 1 741
				63·76	3·77	25·17	—
<i>m</i> -I	<i>IIIh</i>	C <sub>26</sub> H <sub>17</sub> IO <sub>2</sub> (488·3)	151—153	63·93	3·48	25·02	1 694
				64·16	3·61	24·85	1 691
<i>m</i> -CH <sub>3</sub>	<i>Ii</i>	C <sub>27</sub> H <sub>20</sub> O <sub>2</sub> (376·5)	163—164	85·70	5·32	—	1 702, 1 736
				85·53	5·56	—	—

TABLE III  
(Continued)

X	Com- pound	Formula (mol.w.)	M.p., °C	Calculated/Found			$\nu(\text{C}=\text{O})\text{cm}^{-1}$
				% C	% H	% X	$\nu(\text{C}=\text{C})$
<i>m</i> -CH <sub>3</sub>	<i>Ili</i>	C <sub>27</sub> H <sub>20</sub> O <sub>2</sub> (376.5)	155–155	85.70	5.32	—	1 696
				85.24	5.35	—	1 619
<i>p</i> -OCH <sub>3</sub>	<i>Ij</i>	C <sub>27</sub> H <sub>20</sub> O <sub>3</sub> (329.2)	156–157	82.47	4.25	—	1 701, 1 732
				83.25	4.36	—	—
<i>p</i> -OCH <sub>3</sub>	<i>Iij</i>	C <sub>27</sub> H <sub>20</sub> O <sub>3</sub> (392.5)	152–153	82.97	4.25	—	1 693
				82.73	4.15	—	1 618
<i>m</i> -OCH <sub>3</sub>	<i>Ik</i>	C <sub>27</sub> H <sub>20</sub> O <sub>3</sub> (392.5)	226–228	82.97	4.25	—	1 702, 1 733
				82.69	4.52	—	—
<i>m</i> -OCH <sub>3</sub>	<i>Iik</i>	C <sub>27</sub> H <sub>20</sub> O <sub>3</sub> (392.5)	163–166	82.97	4.25	—	1 693
				83.15	3.98	—	1 620

The spectrum also exhibits a strong band at 1 615–1 625 cm<sup>-1</sup> due to C=C stretching vibration in the five-membered ring.

### EXPERIMENTAL

The infrared spectra were measured on a "Specord" spectrophotometer in the region 700–2 000 cm<sup>-1</sup>, using an NaCl prism. The instrument was calibrated with a polystyrene foil. The samples were measured as suspension in Nujol and the Nujol spectrum was compensated.

#### Reaction of 2-(1-Naphthyl)-1,3-indanedione Anion with X-Substituted Benzyl Bromides

A mixture of 2-(1-naphthyl)-1,3-indanedione (0.68 g; 2.5 mmol), an appropriate solvent (30 ml), dried potassium carbonate (0.64 g) and substituted benzyl bromide (5 mmol) was heated to 40 ± 1°C for 4 hours. The reaction mixture was extracted five times with warm benzene (50 ml), the combined extracts were concentrated and chromatographed on alumina (Brockmann II, Reanal, Budapest). A mixture of benzene and ethyl acetate (20 : 1) was used as eluant for compounds where X = Cl, Br or I, benzene-chloroform (1 : 1) for X = NO<sub>2</sub> and benzene for other benzyl derivatives. The C-benzyl derivatives were eluted first, followed by the yellow O-benzyl derivatives. The unreacted compound remained at the start. The eluate containing C-derivative was concentrated to 2 ml and light petroleum (20 ml) was added. Upon heating to the boil the cooled solution deposited the C-derivative. The eluate containing the O-derivative was concentrated almost to dryness, the residue was treated with light petroleum (20 ml), warmed and on cooling the O-derivative separated. The overall yields and the yields of C- and O-derivatives are given in Table I; the analytical data are listed in Table III.

TABLE IV

Analytical Values for 2-(4-Nitro-1-naphthyl)-2-(X-benzyl)-1,3-indanediones (*IIIa--IIIe*)

Compound X	Formula (mol. w.)	M.p., °C	Calculated/Found		$\nu(\text{C}=\text{O}),$ $\text{cm}^{-1}$
			% C	% H	
<i>IIIa</i>	$\text{C}_{26}\text{H}_{16}\text{NO}_6$	144 <sup>a</sup>	73.45	3.72	1 710
<i>p</i> -NO <sub>2</sub>	(452.5)		73.63	3.62	1 745
<i>IIIb</i>	$\text{C}_{26}\text{H}_{16}\text{BrNO}_2$	221	68.35	3.52	1 706
<i>p</i> -Br	(486.5)		68.41	3.65	1 735
<i>IIIc</i>	$\text{C}_{26}\text{H}_{17}\text{NO}_2$	236	76.66	4.18	1 709
H	(407.5)		76.92	4.38	1 740
<i>III d</i>	$\text{C}_{27}\text{H}_{19}\text{NO}_2$	235	81.72	4.51	1 710
<i>p</i> -CH <sub>3</sub>	(421.5)		81.63	4.28	1 729
<i>IIIe</i>	$\text{C}_{27}\text{H}_{19}\text{NO}_3$	225	77.63	4.35	1 708
<i>p</i> -OCH <sub>3</sub>	(437.5)		77.95	4.12	1 737

<sup>a</sup> Beginning of decomposition.

## Reaction of 2-(4-Nitro-1-naphthyl)-1,3-indanedione Anion with X-Substituted Benzyl Bromides

The reaction was carried out as described in the preceding paragraph. The yields and analytical values are given in Table IV.

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Translated by M. Tichý.