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Transformations in bromo- and alkoxybenzotropones

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Abstract

The *ipso*/*cine* ratios in the displacement of bromine by methoxide changes from 9:1 in the case of 5-bromo-2,3-benzotropone **1** to 2:7 in that of 2-bromo-4, 5-benzotropone 2. Under a possibility that an aryne-type mechanism operates, these regioselectivities show a considerable steric influence on the part of the *peri* hydrogen, implying a lateral or in-plane approach of methoxide towards the benzylic position of benzodehydrotropone intermediates.

None of the four derived alkoxybenzotropones furnished an oxonium salt on treatment with dimethyl sulphate but an unexpected transformation was mediated in the case of 3-methoxy-4,5-benzotropone **4b**, the *cine* product from **2**, into its carbonyl–ether transposition product, 6-methoxy-2,3-benzotropone **9a**. While a similar transformation cannot be apparent, for symmetry reasons, in the case of 4-methoxy-2,3-benzotropone **3b**, the mechanism proposed suggests why the transformation does not take place in the case of the two remaining methoxybenzotropones **3a** and **4a**.

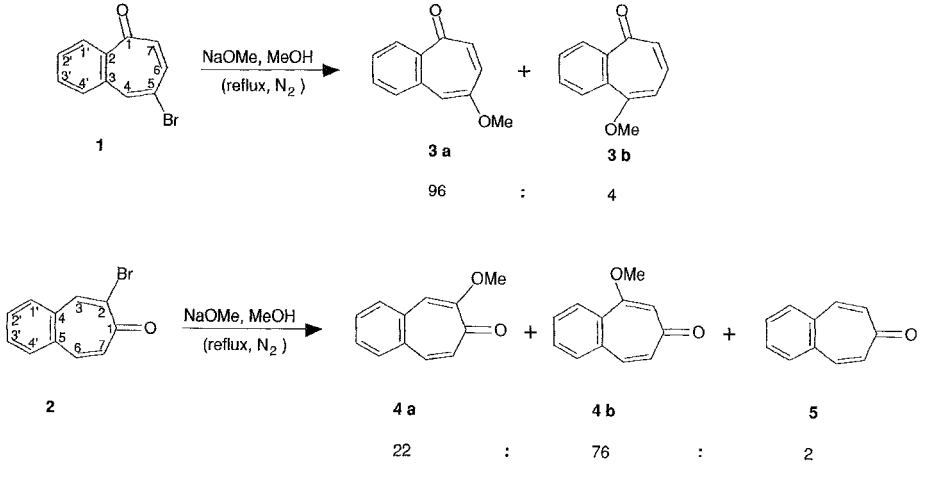
Key words : Regioselectivity, aryne mechanism, carbonyl transposition, bromo-, alkoxy- and dehydrobenzotropones.

1. Introduction

The formation of mixtures of *ipso* and *cine* substitution products[1] has been noticed in most of the not too many attempts to replace the halogen by an alkoxy group in substituted halotropones[2]. Bromobenzotropones **1** and **2** are no exception and mixtures of *ipso* and *cine* products are formed, in good total yield, when each is heated under reflux with sodium methoxide in methanol. But, while the *ipso* product **3a** is dramatically favoured over the *cine* product **3b** (96:4) in the case of bromoketone **1**, there is a near reversal in the *ipso*/*cine* ratio **4a**/**4b** (22:76) in the case of bromoketone **2** (Scheme 1)[3]. No temperature dependence of the isomer ratio is apparent (in contrast with the case of direct amination of bromobenzotropones)[4] but the reaction either does not take place or is very sluggish at room temperature.

Results from trapping experiments (employing either a strong nucleophile or a reactive diene)[2c,5] and from regioselectivities observed in unsymmetrically substituted cases[6] have indicated that dehydrotropone (aryne-like) intermediates are readily formed from tropone precursors, apparently more so than dehydrobenzenes from their precursors, because of lower strain in a 7-membered ring[2a,2c,5a]. That benzodehydrotropones (**6** and **7**, respectively) are

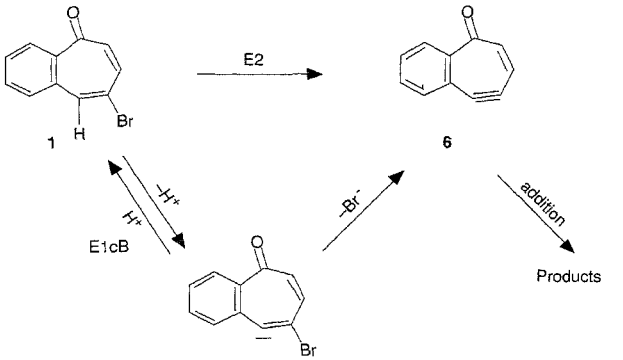
* For correspondence.



SCHEME 1.

formed when bromobenzotropones **1** and **2** are exposed to alkoxide was confirmed through adduction employing 1,4-diphenylisobenzofuran (see Experimental).

The dehydrohalogenations of halobenzenes can, apparently, occupy different positions in the spectrum between wholly concerted (E2; Scheme 2, taking system **1** as example) and wholly nonconcerted (ElcB; Scheme 2) since regioselectivities found with unsymmetrical



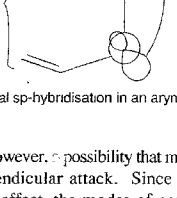
SCHEME 2.

arynes have been attributed to different factors in different cases: the relative rates of dehalogenation, the reversibility of the deprotonation[7] step, the reactivity of the nucleophile[8], the structure and stability of the aryne[9] or the nature of the substituent(s) on the aryne[10]. The formation of benzodehydrotropones **6** and **7** from systems **1** and **2** is likely to be concerted (in spite of the necessity of *cis*-elimination) in view of the presence of the electron-withdrawing oxo group, the use of the strongly basic methoxide, the ability of bromine to behave as a good leaving group as well as the inability of the conjugate base to stabilise itself through delocalisation.

Marked electrophilicity has been associated with arynes and it may be enhanced in the cases of dehydrotropones due to the presence of the electron-withdrawing oxo group. Neither the enhanced electrophilicity nor the use of the strongly nucleophilic methoxide can be expected to contribute to high regioselectivity in the addition reaction[8,9,11]. The regioselectivities observed[11,12], high in the case of bromobenzotropone **1**, can only imply that the intermediate benzodehydrotropones have appreciable lifetimes[12], comparable to those of naphthalynes[7,10], said to be stabler than benzynes due to a more effective overlap across a shorter dehydro bond. An effectively long lifetime affords an opportunity to the substituent(s) on the aryne to exert such influences as orienting the incoming nucleophile through electronic or steric means[10,13].

A recent *ab initio* study[14], which took account of electron correlation, has indicated the presence of cumulene-like features in benzyne. It is usual, however, to picture the arynes as having a 'triple bond' with a weak 'third' bond because of the possibility of only a small

overlap of the in-plane (lateral) π-orbitals (Fig. 1)[10,15]. These orbitals may be considered as the more reactive of the two sets of orthogonal π-orbitals constituting the dehydro bond and lateral approach by a nucleophile may afford a pathway of low energy change for bond formation ('faster' bond formation than when the approach is orthogonal to the ring). Such effectiveness of lateral (periplanar) approach raises the possibility that any steric demand that an *ortho* substituent may place will have a prominent role in determining the regioselectivity of addition: the addition of nucleophiles to 1,2-naphthalynes is known to take place preferentially at C-2 in spite of the higher reactivity of C-1 and this has been attributed to the steric hindrance offered by the *peri*-hydrogen (at C-8) when the approach is towards C-1[16]. The *peri* effect could be actually stronger in benzodehydrotopones **6** and **7** than in 1,2-naphthalynes because the trajectory of periplanar approach of maximum overlap would be inclined towards the *peri*-hydrogen when the junction is between 6- and 7-membered rings.



Partial sp-hybridisation in an aryne

FIG. 1.

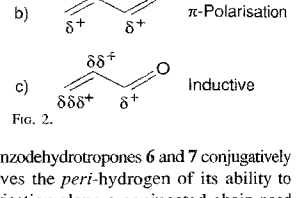


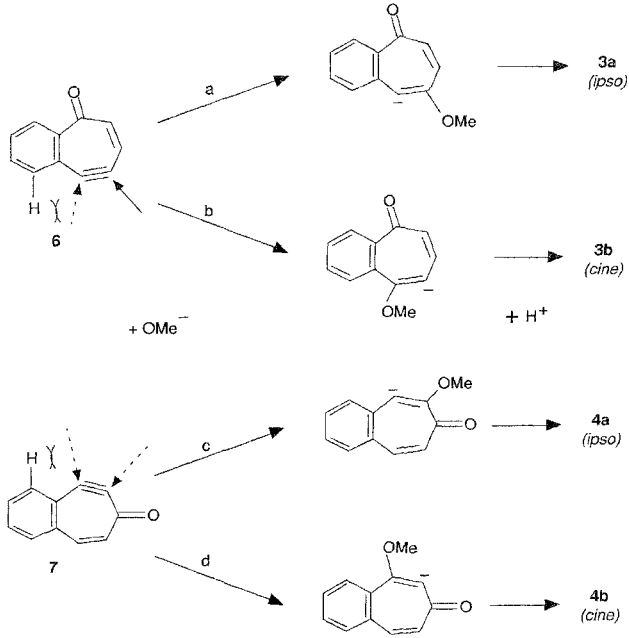
FIG. 2.

There is, however, a possibility that methoxide adds to benzodehydrotropones **6** and **7** conjugatively through perpendicular attack. Since such attack deprives the *peri*-hydrogen of its ability to exert a steric effect, the modes of conveyance of polarisation along a conjugated chain need to be examined in attempting to explain the regioselectivities. Among the possible modes, mesomerism which draws away negative charge from the γ-carbon and localises it on the carbonyl oxygen, and π-polarisation which produces an alternating charge distribution, leading to some concentration of negative charge at the α-carbon (Fig. 2 a and b; illustrated for an enone), could be most relevant to the present context.

2. Discussion of mechanisms

It appears, however, that neither of these modes can be very effective in polarising the triple bond in benzodehydrotropone **6** because, were one to consider the 'ethylenic pathway' as not very different from the 'benzo pathway', the triple bond will be seen to be symmetrically disposed with respect to the carbonyl. The remanent effect, then, is only inductive polarisation, operating through the σ-framework and falling off with the distance from the carbonyl (Fig. 2c). The electron-withdrawing (-I) effect of the benzo group can combine with that of the carbonyl and can polarise the dehydro bond in the manner that facilitates *ipso* attack (at C-5). While the effect can influence selectivity irrespective of the direction of approach of the nucleophile (perpendicular or periplanar), the steric demand of the *peri*-hydrogen can make its effect felt only if bond formation were through periplanar approach of the nucleophile assuming, of course, that the transition state is reached at the requisite (late)

stage. It appears that this is the case with system **6**, the inductive effect assisting in depositing the methoxide at the *ipso* centre (Scheme 3, path a).



	Inductive	*Mesomeric*	*π-Polarisation*	*Steric*
a.	Favourable	Neutral	Neutral	Favourable
b.	Not favourable	Neutral	Neutral	Not favourable
c.	Neutral	Not favourable	Not favourable	Favourable
d.	Neutral	Favourable	Favourable	Not favourable

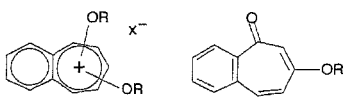
SCHEME 3.

In contrast with the possible neutralisation of the mesomeric and π-polarisation effects in benzodehydrotropone **6**, the two can reinforce each other to favour an approach of the nucleophile towards the *cine* centre (C-3) in benzodehydrotropone **7**. The -I effects of the benzo and carbonyl groups, however, oppose each other across the dehydrobond. At the same time, the approach of the nucleophile towards the α-carbon (C-2, the *ipso* centre) would be disfavoured by the electrostatic effect of a build up of negative charge at that centre as

well as the space effect of the carbonyl oxygen. One may then expect the predominance of the *cine* product in system **7** (Scheme 3, path c) to resemble that of the *ipso* product in system **6**. But the predominance is only moderate (Scheme 1) and it could mean that the approach of the nucleophile is periplanar here also and the *peri*-hydrogen is able to make its steric effect felt.

In attempts made to obtain alkoxonium salts **8**, keto-ethers **3a,b** and **4a,b** were independently treated with dimethyl sulphate in methanol[17]. While keto-ethers **3a, 3b** and **4a** were recovered unchanged, **4b** was found to have been converted, to the extent of about 50%, into the keto-ether 6-methoxy-2,3-benzotropone **9a**, the product of transposition of the carbonyl and alkyl ether groups (TLC and NMR evidence). No transformation was observed when keto-ether **4b** was heated under reflux in methanol in the absence of dimethyl sulphate, establishing that the alkyl sulphate was necessary to mediate the transposition. An influence on the part of the solvent was also ruled out since a change of solvent from the polar protic methanol to the aprotic benzene did not suppress the transposition reaction[18].

That only about 50% of keto-ether **4b** had been transformed appeared to indicate that the system was attaining a dimethyl sulphate-mediated thermodynamic equilibrium (Scheme 4a)[19]. As a partial test of the possibility of equilibrium, the 'rearranged' product **11a** was treated with dimethyl sulphate and a 20% conversion to the starting keto-ether **4b** was observed. A reason for the inequality in the two conversions could be a difference in the reactivities of the starting keto-ether **4b** and its 'rearranged' product, keto-ether **9a** whereby the latter is converted slowly.

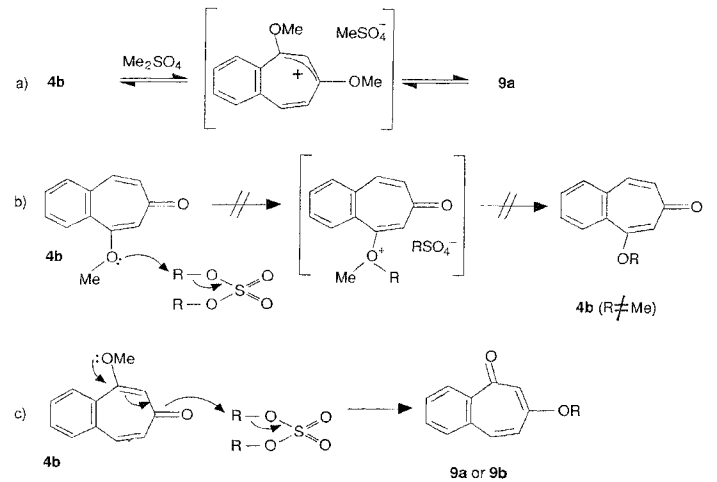


8 **9a:** R = Me
9b: R = Et

This last received a measure of support from a further experiment. On treating the keto-ether **4b** with diethyl sulphate it was found that an ethyl group had been introduced only into the rearranged product (**9b**), the methyl ether group remaining intact in the unrearranged material (**4b**). This result really does not negative the proposition that the 'rearrangement' is concomitant to a process of attainment of dynamic equilibrium between the two isomeric keto-ethers under the influence of alkyl sulphate because the factor behind the result could be the lower reactivity of the 'rearranged' keto-ether **9b** with dialkyl sulphate compared with the starting keto-ether **4b**. More important, however, is that the result demonstrates that the direct replacement of one alkyl group by another (Scheme 4b)[20] is not the primary process but an attack on dialkyl sulphate by the carbonyl oxygen of keto-ether **4b** (Scheme 4c; the carbonyl oxygen could be more reactive than the vinyl alkyl ether oxygen).

Finally, the reason for keto-ether **3b** not appearing to have undergone any 'reaction' is simply because no substituent is present to distinguish the starting material from the rearranged 'product'. The reason for the inertness of keto-ethers **3a** and **4a** under the rearranging

conditions appears quite clear: the establishment of mesomeric communication between the two oxygens for attainment of equilibrium (see Scheme 4c) cannot be facile in these cases since the canonical forms involved are without the 6π cyclic stabilisation and would, therefore, be highlyl endoenergetic.



Scheme 4

3. Experimental

Melting points, determined for samples taken in open capillaries using a standardised thermometer, are reported as observed. Infrared and ultraviolet spectra were recorded, respectively, with a Perkin–Elmer model 721 IR and a Shimadzu model UV-190 UV spectrophotometers. ^1H and ^{13}C NMR spectra were obtained with a JEOL FX90-Q (90 and 22.5 MHz) NMR spectrometer for solutions in $CDCl_3$ with TMS as the internal standard and the solvent providing the internal lock. Mass spectra (LR and HR) were taken under 70 eV EI conditions employing a JEOL JMX-DX 303 mass spectrometer equipped with a D-3000 data processor. While TLC tests on silica-gel (Acme Synthetic) were by standard procedures, separation, isolation and purifications were carried out using a Harrison Research Chromatotron centrifugal TLC system in conjunction with an ISCO Retriever IV precision fraction collector. Solvents were repurified and dried just prior to use employing recommended methods[21]. Commercial samples of α- and β-methoxynaphthalenes were recrystallised prior to use. Bromoform and diphenylisobenzofuran were reagent grade materials.

3.1 Bromobenzotropones

The respective dibromocarbene adducts of α- and β-methoxynapthalenes rearrange spontaneously to yield bromobenzotropones **1** and **2**[22]. Products obtained by following the published procedures satisfied all the characterisation data reported[4,22] for the two bromobenzotropones.

3.2. Methoxylation of bromobenzotropones

A solution of the benzotropone (**1** or **2**; 950 mg, 4 mmol) in absolute methanol (10 ml) containing sodium methoxide (220 mg; 4 mmol) was heated under reflux in an atmosphere of nitrogen during 3.5 h. The product mixture was poured on to cold water and extracted with ether (15 ml × 4). The combined ether extracts of the organics were dried over anhyd. sodium sulphate and the ether removed.

The residue from each reaction was tested by TLC, subjected to separation by centrifugal TLC over silica gel and the components taken to the identification procedures. That from the reaction of bromoketone **1** (498 mg; 67%) was a mixture of two components. The more mobile one was identified as the *cine*-product, 4-methoxy-2,3-benzotropone (**3b**; 20 mg; 4%) and the less mobile one as the *ipso*-product, 5-methoxy-2,3-benzotropone (**3a**; 478 mg; 96%).

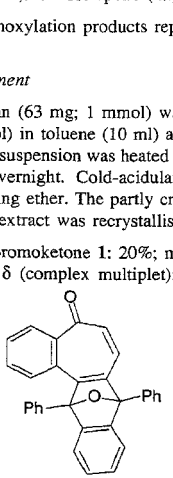
The residue from bromoketone **2** (580 mg; 78%) consisted of three components. They were in the order of decreasing mobility: 4,5-benzotropone (**5**; 12 mg; 2%), a product of reductive dehalogenation, 3-methoxy-4,5-benzotropone (**4b**), the *cine*-product (440 mg; 76%), and 2-methoxy-4,5-benzotropone (**4a**), the *ipso* product (130 mg; 22%).

The ratios of methoxylation products reported above were reconfirmed by repeating the alkoxylations.

3.3. Trapping experiment

Diphenylisobenzofuran (63 mg; 1 mmol) was stirred into a solution of the bromoketone (**1** or **2**; 240 mg; 1 mmol) in toluene (10 ml) and potassium *t*-butoxide (120 mg; 1 mmol) was added. The resulting suspension was heated under reflux in an atmosphere of nitrogen during 24 h and let to cool overnight. Cold-acidulated (HCl) water was added and the organic layer was shaken after adding ether. The partly crystalline residue which separated on removal of ether from the dried extract was recrystallised from ether.

Adduct **10** from bromoketone **1**: 20%; mp 130–132°; IR: 1653, 1596, 1446, 1272 cm^{-1}; ^1H NMR: 7.94–6.32 δ (complex multiplet); LRMS (m/e): 424 (M^+), 286, 209, 172 (base



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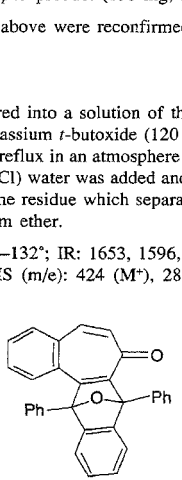

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Table I

Physical data on the benzotropones

Compound	*Physical*	*Mol. wt (by HRMS)*	*MS (m/z)*	*IR (cm^{-1})* (film)*	*UV nm# (log ε)*
3a	Yellow oil	186.0673@	186 (M^+) 157, 128 115&	1620 1593 1575 1539	222 (4.08) 250 (4.04) 272 (4.12) 282 (4.04)
3b	Yellow crystals mp 69–70°	186.0679@	186 (M^+) 158, 143 128, 115&	1644 1611 1584 1479	227 (4.17) 267 (3.54) 327 (3.44)
4a	Yellow crystals mp 88°^	186.0667@	186 (M^+)& 157, 128 115	1626 1602 1542	238 (4.25) 245 (4.22) 275 (4.37)
4b	Yellow crystals mp 72–73°	186.0680@	186 (M^+) 158&, 143 115	1638 1605 1593 1575	227 (4.12) 266 (4.48) 285 (4.03)
5	Yellow crystals mp 68°$	—	—	1620 1580 1540	—
9a	Yellow oil	186.0679@	186 (M^+) 15&, 115	1647 1587	249 (4.63) 255 (4.60) 263 (4.47)
9b	Light Yellow needles mp 56°	200.0824+	200 (M^+) 172, 144&	1650 1590	—

* Smears for liquids and mineral oil mulls for crystalline materials. # Ca. 10^{-4} molar solutions in spectra-grade ethanol. @ MW calc. 186.0681 for MF $C_{12}H_{10}O_2$. & Base peak. ^ Lit. mp: 89.5–90°, D.S. Tarbel and J.C. Bill, *J. Am. Chem. Soc.*, 1952, **74**, 1234–1238. $ Lit. mp: 66–67°, ref. 23; + MW Calc. 200.0837 for MF $C_{13}H_{12}O_2$.

peak); HRMS: MW (Found) 424.1469; MW (Calc.) 424.1463 for MF $C_{31}H_{20}O_2$.

Adduct **11** from bromoketone **2**: 75%; mp 144–146°; IR: 1656, 1596, 1446, 1272 cm^{-1}; ^1H NMR: 7.24–7.72 δ (complex multiplet); LRMS (m/e): 424 (M^+), 286, 209 (base peak); HRMS: MW (Found) 424.1515; MW (Calc.) 424.1463 for MF $C_{31}H_{20}O_2$.

3.4. Treatment of methoxybenzotropones with dialkyl sulphate

A solution of a mixture of each of the methoxyketones (**3a, 3b, 4a** or **4b**; ca. 190 mg; 1 mmol) and dimethyl sulphate (2 mmol) in dry methanol (10 ml) was heated under reflux for 12 h. The residue obtained on removal of the solvent under vacuum was TLC tested and taken to centrifugal chromatography employing EtOAc:light petroleum as the eluant. The products from methoxyketones **3a, 3b** and **4a** were found to consist only of single materials identified as the unchanged starting methoxyketones.

Table IIa

Correlation of ^{1}H NMR shifts in the 2,3-benzotropone series

Compound	*4*	*5*	*6*	*7*	*1'*	*2', 3' & 4'*	*Others*
3a	7.16 (d,1H,2.6*)	—	6.65 (dd, 1H, 10.8 & 2.6)	6.60 (d, 1H, 10.8)	8.50–8 66 (m, 1H)	7.50–7 70 (m, 3H)	3 88 (s, 3H, OMe)
3b	—	6 92 (br s, 1H)	7.24 (s, 1H)	6.52 (br s, 1H)	8.30–8.50 (m, 1H)	7.40–7.70 (m, 3H)	3.82 (s, 3H, OMe)
9a	7.16 (d, 1H, 12.6)	6.44 (dd, 1H, 12.6 & 3.6)	—	6.60 (d, 1H, 3 6)	8.44–8.60 (m, 1H)	7.52–7.70 (m, 3H)	3 80 (s, 3H, OMe)
9b	7.18 (d, 1H, 12.6)	6.44 (dd, 1H, 12.6 & 3.6)	—	6.62 (d, 1H, 3 6)	8.44–8.60 (m, 1H)	7.52–7.70 (m, 1H)	1.46 (t, 3H, Me) 4.00 (q, 2H, OCH_2)
Correlated with:							
2, 3-benzotropone **(A)**	7.35 (d, 1H, 13.5)	6.70 (dd, 1H, 13.5 & 8.5)	7.15 (dd, 1H, 8.5 & 13.5)	6.95 (d, 1H, 12.0)	8.45–8.50 (m, 3H)	7 60–7.75 (m, 3H)	—
1	7.74 (d, 1H, 2.0)	—	7.28 (dd, 1H, 13.0 & 2.0)	6.74 (d, 1H, 13.0)	8.36–8.50 (m, 1H)	7 50–7 70 (m, 3H)	—
4-Dimethylamino-2, 3-benzotropone@ **(B)**	—	6.88 (d, 1H, 12.6)	7.15 (dd, 1H, 12.6 & 2.2)	6.38 (d, 1H, 2.2)	8.12–8 38 (m, 1H)	7 20–7 62 (m, 3H)	2.97 (s, 6H, NMe_2)
5-Dimethylamino-2, 3-benzotropone@ **(C)**	6.78 (d, 1H, 2.7)	—	6 72 (dd, 1H, 10.8 & 2.7)	6.14 (d, 1H, 10.8)	8.00–8 12 (m, 1H)	7.24–7 66 (m, 3H)	2.90 (s, 6H, NMe_2)

* *J* (in Hz) placed at this and where necessary at corresponding locations in this table and in Table IIb. # This compound has been described (M. Sato, T. Tanaka, J. Tsunetsugu and S. Ebine, *Bull Chem Soc Jap.*, 1975, **48**, 2395–2396) but its ^{1}H NMR spectrum has not been reported @ See ref. 4.

Table IIb

Correlation of ^1H NMR shifts in the 2,3-benzotropone series

Compound	*2*	*3*	*6*	*7*	*1'*	*2', 3' & 4'*	*Others*
4a	—	7.04 (s, 1H)	7.27 (AB-q, 2H, 12.6)		7.54–7.72 (m, 4H)		3.96 (s, 3H, OMe)
4b	6.40 (d, 1H, 3.6)	—	7.32 (d, 1H, 14.4)	6.72 (dd, 1H, 14.4 & 3.6)	8.32–8.43 (br s, 1H)	7.59–7.66 (m, 3H)	3.84 (s, 3H, Me)
Correlated with:							
5*	7.06 (AB-q X 2, 4H, 13.5)				7.50-7.76 (m 4H)		—
2#	—	8.44 (s, 1H)	7.24 (AB-q, 2H, 12.6)		7.60–7.80 (m, 4H)		—
2-(Dimethyl) amino-4, 5-benzotropone@ **(D)**	—	6.90 (s, 1H)	7.08 (AB-q, 2H, 13.5)		7.25–7.88 (m, 4H)		2.86 (s, 6H, NMe_2)
3- (Dimethyl) amino-4, 5-benzotropone@ **(E)**	6.31 (d, 1H, 2.7)	—	7.20 (d, 1H, 11.7)	6.66 (dd, 1H, 11.7 & 2.7)	7.88-8.08 (m, 1H)	7.14-7.64 (m, 3H)	2.82 (s, 6H, NMe_2)

* See ref. 23; the specific assignments of H-2, 7 and H-3, 6 given in this reference may have to be interchanged. # See ref. 22c. @ See ref. 4.

Table IIIa

Correlation of ^{13}C NMR data in the 2, 3-benzotropone series

Compound	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*1'*	*2'*	*3'*	*4'*	*Others*
3a	182.56	135.69	136.02	110.26	158.68	132.15	130.82	131.71[&]	123.86	131.71[*]	128.61	55.75 (OMe)
3b	187.28	135.82*	135.82*	156.08	111.98	134.52[#]	127.80	134.52[#]	130.51	132.46[$]	132.46[$]	55.21 (OMe)
9a	186.00	134.40	138.00	131.92	125.96	165.07	111.76	137.33	130.51	133.87	130.94	55.64 (OMe)
Correlated with:												
A[@]	188.37	139.00	141.99	139.60	126.72	135.49	130.50	136.36	132.35	130.94	133.97	—
1	186.58	121.16	134.40	130.52*	137.68	140.28	138.59	134.56	132.47	133.12	130.52*	—
B	187.99	137.64	139.47	148.76	114.49	133.28	126.46	134.25	130.04	132.60	132.22	41.89 (NMe_2)
C	188.27	135.33	136.77	109.45	152.37	130.27	127.01	129.48[&]	125.84[#]	129.48*	125.84[#]	40.92 (NMe_2)

[*#$] Accidentally isochronous. [@] Letters **A**–**C** refer to compounds named in Table IIa.

Table IIIb

Correlation of ^{13}C NMR data on the 4, 5-benzotropone series

Compound	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*1'*	*2'*	*3'*	*4'*	*Others*
4a	181.32	156.84	116.64	133.76	139.93	141.02	131.26	130.40	132.24	127.78	133.32	55.64 (OMe)
4b	185.34	112.10	161.50	131.81	133.44*	139.29	130.30	134.31	127.15	129.75	133.44*	55.75 (OMe)
Correlated with:												
2	180.21	134.43	140.28	133.25*	133.25*	143.79	133.90	130.78[#]	133.50[$]	130.78[#]	133.50[$]	—
D[@]	184.55	152.71	121.31	139.44*	135.46	139.44*	131.37	129.72	132.37	126.62	132.59	41.71 (NMe_2)
E	186.99	118.66	159.57	133.92	135.13	137.90	130.50	135.46	128.72	129.16	132.59	43.26 (NMe_2)

[*#$] Accidentally isochronous. [@] Letters **D** and **E** refer to compounds named in Table II b.

The product obtained from the reaction of methoxyketone **4b** consisted of two components. The more mobile one (90 mg; 50%) was identified as 6-methoxy-2,3-benzotropone (**9a**) and the less mobile one (90 mg; 50%) as the starting methoxyketone **4b**.

A 'reaction in reverse', carried out with 6-methoxy-2,3-benzotropone (**9a**) isolated from the previous experiment, under the conditions described above, provided a mixture of two components, identified as the starting material, the methoxyketone **9a** (80%), and the 'rearranged' product, 3-methoxy-4,5-benzotropone **4b** (20%).

The product from the reaction of methoxyketone **4b** with diethyl sulphate was found to be a mixture of two components. The more mobile one was 6-ethoxy-2,3-benzotropone (**9b**; 50%), the ethoxylated 'rearranged' product, and the less-mobile one was the starting material, methoxyketone **4b** (50%).

3.5. Structural assignments

Data on compounds characterised are assembled in Tables I–III. Structural assignments of the alkoxybenzotropones isolated are based on correlation of their ^1H and ^{13}C NMR chemical shifts in related systems[4,22c,23], as shown in Tables IIa–IIIb. The bases of assignments in the latter systems have been fully discussed[4].

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