Ring-enlargement of Methoxynaphthalenes with Dichlorocarbene to Benzotropone Derivatives

Masaru SATO, Josuke TSUNETSUGU, and Seiji EBINE

Department of Chemistry, Faculty of Science and Engineering, Saitama University, Urawa, Saitama 338

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The dichlorocarbene addition to various di- and trimethoxynaphthalenes has been investigated systematically. It has been found that the carbene addition is oriented by the 1-methoxyl group to the 3,4-double bond and by the 2-methoxyl group to the 1,2-double bond of naphthalene nucleus, and that the spontaneous cyclopropane ring-opening of the intermediate carbene-adducts leads to the preferencial formation of 2,3-benzotropone over 4,5-benzotropone derivatives. The steric effects by methoxyl group seem not to be significant in either the carbene-addition or ring-opening reaction.

There are several reports on the ring-enlargement reactions of benzenoid aromatic system with dihalocarbene to seven-membered or larger ring non-benzenoid aromatic systems. For example, azulene[1] was obtained from indene, bromotropone was formed from anisole,[2] and chlorobenzotropone derivatives were prepared from methoxynaphthalenes[2,3] by ring-enlargement reactions with dihalocarbene. Recently, benzocyclooctatrienedione derivatives were synthesized by the reaction of tetramethoxynaphthalene or tetramethylpurpurogallin with dichlorocarbene.[4] A benzo[3,4]cyclobuta[1,2-*c*]tropone derivative was obtained through the ring-enlargement of methoxybiphenylene with dichlorocarbene.[5] However, scarcely no systematic investigations of dichlorocarbene addition to substituted benzenoid compounds, in contrast with that to olefinic compounds,[6] have been reported. This paper will deal with a systematic examination of the ring-enlargement of methoxynaphthalenes with dichlorocarbene and with the orientation effect of the methoxyl group on the methoxynaphthalene-dichlorocarbene addition.

Results

1,2-Dimethoxynaphthalene was treated with one equivalent amount of the dichlorocarbene source, according to Makosza's method,[7] to give three kinds of products, **1**, **2**, and **3**. The IR and NMR spectra of **1** were superimposable upon those of an authentic sample of 7-chloro-6-methoxy-2,3-benzotropone,[8] and no temperature-depression was observed on their admixture.

Compound **2** showed an NMR spectrum with two doublets at δ 6.93 and 7.51 ppm (J=12.6 Hz). The electronic spectrum of **2** was closely similar to that of 2-chloro-4,5-benzotropone.[3] These spectral data are in accordance with the structure of 2-chloro-3-methoxy-4,5-benzotropone (Fig. 1).

Compound **3** showed, in its NMR spectrum, two doublets at δ 6.62 and 7.73 ppm with a small coupling constant (J=2.0 Hz), indicating the presence of two protons in the allylic positions each other of the seven-membered ring, so suggesting that the product is identifiable as 5-chloro-7-methoxy-2,3-benzotropone. Curiously enough, **3** was not necessarily reproduced in repeated experiments. The use of a large excess of carbene source failed to improve the yield of the tropone derivatives; it resulted only in the formation of a considerable amount of an intractable substance.

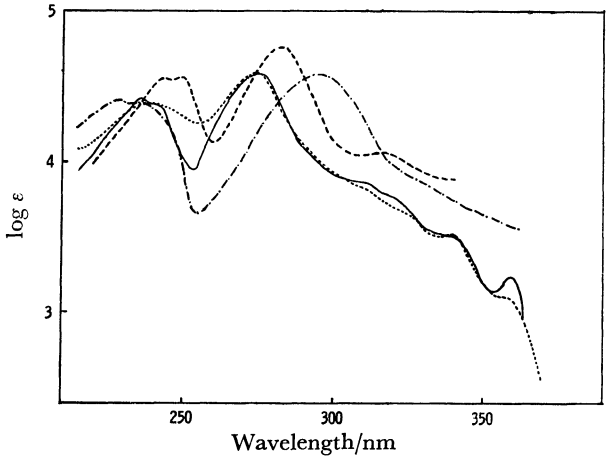
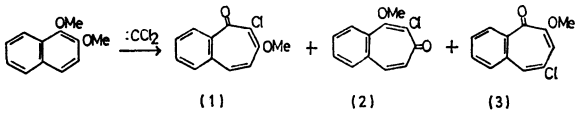


Fig. 1. The UV spectra of 4,5-benzotropones.
——: 2-Chloro-4,5-benzotropone, ·····: 2-chloro-3-methoxy-4,5-benzotropone(**2**), ----: 2-chloro-7-methoxy-4,5-benzotropone(**11**), —·—·: 2-chloro-3′-methoxy-4,5-benzotropone(**14**).

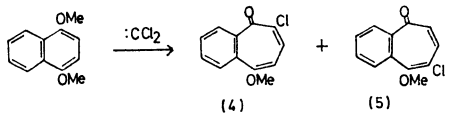


(1) (2) (3)

The reaction of 1,4-dimethoxynaphthalene with one equivalent amount of the dichlorocarbene source gave the product **4**. Its NMR spectrum showed two characteristic doublets (J=10.0 Hz), at δ 6.01 and 7.58 ppm, for H-5 and H-6, and a pair of multiplets for benzenoid 2H deshielded and benzenoid 2H not deshielded by either the carbonyl or methoxyl group. From the NMR spectra, **4** was assigned to 7-chloro-4-methoxy-2,3-benzotropone. The structure was further confirmed by conversion to the Diels-Alder adduct (**6**), whose NMR spectrum showed two olefinic doublets, at δ 6.34 and 7.08 ppm (J=9.5 Hz), indicating that **4** is unsubstituted at C-5 and C-6.

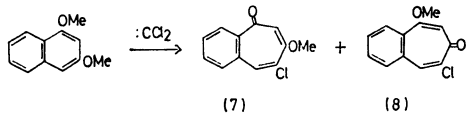
The use of three molar amounts of the dichlorocarbene source afforded an additional, thermally unstable product (**5**), which showed IR and mass spectra closely similar to those of **4**. The NMR spectrum showed two olefinic doublets (J=12.0 Hz), at δ 6.68 and 7.22 ppm. Thus, **5** was proved to be 5-chloro-4-methoxy-2,3-benzotropone.

1,3-Dimethoxynaphthalene reacted with dichloro-



(4) (5)

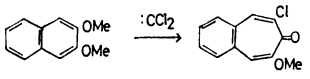
carbene to give two products, **7** in an 8.0% yield and **8** in a 2.9% yield, their UV and NMR spectra were quite similar to those of 5-bromo-6-methoxy-2,3-benzotropone and 2-bromo-6-methoxy-4,5-benzotropone respectively.[9] Therefore, **7** and **8** can be said to be 5-chloro-6-methoxy-2,3-benzotropone and 2-chloro-6-methoxy-4,5-benzotropone respectively.



(7) (8)

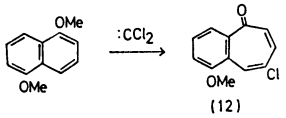
Further structural evidence was obtained by the hydrolysis of **7** and **8** with concentrated hydrochloric acid in boiling ethanol to give the same product, 5-chloro-6-hydroxy-2,3-benzotropone (**9**), whose NMR spectrum showed no methoxyl proton and two olefinic protons as two singlets at δ 6.74 and 8.31 ppm, the former disappearing on the addition of deuterated water. **7** gave the Diels-Alder adduct (**10**), but **8** gave no adduct, on heating with maleic anhydride, affording an additional proof of their structures.

The reaction of 2,3-dimethoxynaphthalene with dichlorocarbene afforded a scanty yield of 7-chloro-2-methoxy-4,5-benzotropne (**11**). The structural assignment is based on the electronic (Fig. 1) and NMR spectra : methoxyl singlet at δ 4.01 ppm, two deshielded olefinic singlets at δ 7.19 and 8.32 ppm for H-3 and H-6, and a narrow multiplet at δ 7.6—7.9 ppm for four benzenoid protons.



(11)

The reaction of 1,5-dimethoxynaphthalene with dichlorocarbene gave a product (**12**), in a poor yield, which was conclusively identified as 5-chloro-3'-methoxy-2,3-benzotropone by the following NMR spectrum: a doublet (J=2.0 Hz) at δ 8.27 ppm, deshielded by both methoxyl and chloro substituents, for H-4, a doublet (J=13 Hz) at δ 6.78 ppm for H-7, a doublet at δ 7.17 ppm for H-6, and an ABC-type three-proton system at δ 7.1—8.0 ppm for benzene-ring protons.



(12)

1,6-Dimethoxynapnthalene reacted with dichlorocarbene to give two products, **13** in a 9.9% yield and **14** in a 4.9% yield. The electronic spectrum of **13** was similar to that of 5-chloro-2,3-benzotropone (Fig. 2). The NMR spectrum of **13** showed an olefinic doublet (J=13.0 Hz) at δ 6.81 ppm, meaning that the

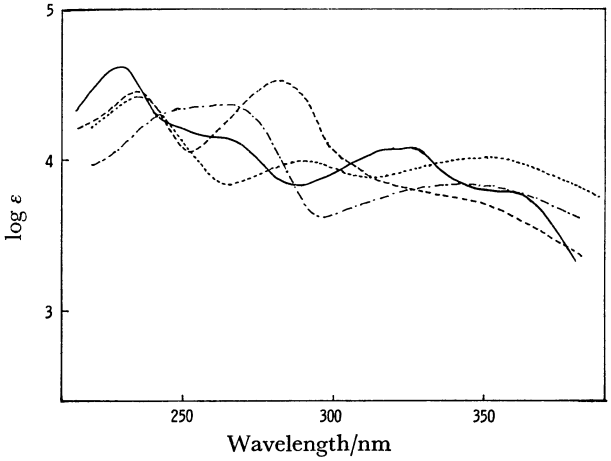
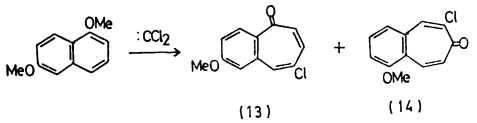


Fig. 2. The UV spectra of 2,3-benzotropones.
——: 5-Chloro-2,3-benzotropone, ·····: 5-chloro-3'-methoxy-2,3-benzotropone(**12**), ----: 5-chloro-4'-methoxy-2,3-benzotropone(**13**), —·—·: 5-chloro-6,7-dimethoxy-2,3-benzotropone(**15**).

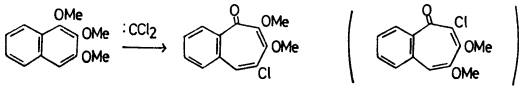
chloro substituent is at C-5 rather than at C-7, since the chemical shift of the doublet is very similar to those of 5-chloro-2,3-benzotropone (δ 6.83 ppm) and **12** (δ 6.78 ppm). Therefore, **13** is identified as 5-chloro-4'-methoxy-2,3-benzotropone. The peri-position of the benzene ring, deshielded by the carbonyl group, appeared as a doublet (J=9.0 Hz) in the lower region (δ 8.47 ppm), indicating that the methoxyl group is situated at C-4'.

The other product (**14**) showed an NMR spectral olefinic singlet (δ 8.17 ppm) and doublet (δ 8.35 ppm, J=13.5 Hz) in a remarkably lower field; they are probably due to the anisotropy of the methoxyl group and the inductive effect of the chloro substituent. The electronic spectrum showed that **14** has a chromophore of 2-chloro-4,5-benzotropone (Fig. 1). These observations can be satisfactorily explained by assigning **14** to 2-chloro-3'-methoxy-4,5-benzotropone.



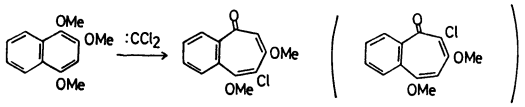
(13) (14)

1,2,3-Trimethoxynaphthalene, on treatment with dichlorocarbene, gave a sole isolable product (**15**). The electronic spectrum showed the presence of a 2,3-benzotropone structure (Fig. 2), and the NMR spectrum showed an olefinic proton signal of the seven-membered ring overlapped with benzenoid protons in a region similar to that of the H-4 of 5-chloro-2,3-benzotropone derivatives [δ 7.37 in **3** and 7.55—7.85 ppm in **7**]. Moreover, if the compound has the **16** structure, the H-4 resonance should appear in a higher field than that of 7-chloro-6-methoxy-2,3-benzotropone(**1**) (δ 7.15 ppm). This does, however, not happen. In the mass spectrum, methyl elimination preceded carbon dioxide elimination, unlike as in other benzotropone derivatives. These spectral data agree with the structure of 5-chloro-6,7-dimethoxy-2,3-benzotropone rather than with the **16** structure.



(15) (16)

1,2,4-Trimethoxynaphthalene reacted with dichlorocarbene to afford only one benzotropone derivative, in an 18% yield. The product **18** showed an NMR signal of the olefinic proton as a singlet at a fairly high field (δ 6.29 ppm) and four benzenoid protons as a pair of multiplets similar to those in 4-methoxy-2,3-benzotropones (**4** and **5**). The olefinic proton is not situated at the 6-position, since the resonance of the H-6 of 2,3-benzotropone derivatives should appear in a lower field because of the electronic effect of the carbonyl group [*e.g.*, δ 6.62 ppm in **3** and δ 7.58 ppm in **4**]. The product gave the Diels-Alder adduct (**20**) with maleic anhydride, whose NMR spectrum showed no resonance in the olefinic region, indicating that **18** has no proton at the 5- and 6-positions. Consequently, **18** proved to be 5-chloro-4,6-dimethoxy-2,3-benzotropone, excluding the **19** structure.



(18) (19)

The reaction of 1,2,3,4-tetramethoxynaphthalene with dichlorocarbene failed to give a difinite isolable product, but the NMR spectrum indicated the formation of a benzotropone derivative with no olefinic proton and three methoxyl proton signals, and the mass spectrum showed a molecular ion at *m/e* 280.

Discussion

It is known that two types of benzenoid aromatic compounds are susceptible to the attack of dichlorocarbene. One type includes fused-ring aromatic compounds, such as naphthalene,[10,11] phenanthrene,[10,11] and anthracene,[11,12] which have a small loss of resonance energy in the formation of the dihalocarbene adduct. The other type includes the aromatic compounds carrying an electron-donating substituent, such as methylnaphthalene[13] and methoxynaphthalenes,[2,3a,3b] in which the substituent not only facilitates the dichlorocarbene addition, but also might influence the orientation of the dichlorocarbene attack. The reaction of anisole with dibromocarbene affords 4-bromotropone,[2] and the reaction of 1-methoxynaphthalene gives 5-halo-2,3-benzotropone[3c-3e] exclusively, no other isomeric tropones being obtained.* 1,5- And 1,6-dimethoxynaphthalenes also reacted with dichlorocarbene to give exclusively 5-chloro-2,3-benzotropone derivatives **12** and **13** respectively. On the other hand, the reaction of 2-methoxynaphthalene with dihalocarbene afforded 2-halo-4,5-benzotropone. 2,3- And 1,6-dimethoxynaphthalenes reacted with dichlorocarbene to give 2-chloro-4,5-benzotropone derivatives, **11** and **14** respectively. These results suggest that dichlorocarbene adds regioselectively to the 3,4-double bond of 1-methoxynaphthalene derivatives and to the 1,2-double bond of 2-methoxynaphthalene derivatives. This selective carbene addition orientated by the methoxyl group was found to be consistent throughout the di- and trimethoxynaphthalenes (that is, the additivity of the effect from methoxyl groups was observed).

1,3-Dimethoxynaphthalene, in which both the methoxyl groups accelerate carbene addition to the 3,4-double bond, gave, as expected, the **7** and **8** products, which must have been derived *via* an intermediate 3,4-double bond adduct. 1,2,3- And 1,2,4-trimethoxynaphthalenes also gave a single product, **15** and **18** respectively. Carbene addition to 1,2,3-trimethoxynaphthalene occurs exclusively at the 3,4-double bond because of the orientation effect by the 1-methoxyl group, where the orientation to the 1,2-double bond by the 2-methoxyl group is cancelled by that to the 3,4-double bond by the 3-methoxyl group. Similarly, addition to 1,2,4-trimethoxynaphthalene takes place at the 1,2-double bond in terms of the 2-methoxyl group because the orientation effects by the 1- and 4-methoxyl groups cancel each other. 1,2-Dimethoxynaphthalene reacted with dichlorocarbene both at the 3,4-double bond, oriented by the 1-methoxyl group, to give **3** and at the 1,2-double bond, oriented by the 2-methoxyl group, to give **1** and **2** [although **3** was not necessarily reproduced in repeated experiments, as has been described above].

The ^{13}C-NMR spectra of methoxynaphthalenes[14] afford information about their ground-state electronic state, and may be expected to elucidate the regioselectivity of dichlorocarbene addition to the methoxynaphthalenes. In fact, a good correlation was observed between the orientation of carbene addition and the electron density deduced from the ^{13}C-NMR chemical shift of the 2-methoxynaphthalene derivatives. However, no such correlation was observed in 1-methoxynaphthalene or its derivatives. In 1-methoxy- and 1,3-dimethoxynaphthalene, for example, the electron density of C-4, as deduced from ^{13}C-NMR spectra, was lower than that of C-2, whereas the dichlorocarbene addition took place at the 3,4-double bond exclusively. The regiospecific addition observed in the dichlorocarbene addition to methoxynaphthalene derivatives might be explained in the following manner: the approach of dichlorocarbene to 1-methoxynaphthalene or its derivatives induces a dynamic polarization of electrons on the naphthalene nucleus by the methoxyl group and accumulates a negative charge at C-4 rather than at C-2, as in the electrophilic substitution of naphthalene derivatives, so that the electrophilic dichlorocarbene approaches asymmetrically to the 3,4-double bond from the direction of the electron-rich C-4 to form dihalocyclopropano-dihydronaphthalene intermediates.

The cyclopropane ring-opening of the intermediate carbene-adducts is largely facilitated by aromatization, leading to benzotropone derivatives, since the dichlorocarbene adduct of 1-ethoxy-3,4-dihydronaphthalene

* The reaction of 1-methoxynaphthalene with dichlorocarbene generated by Makosza's method gave 5-chloro-2,3-benzotropone exclusively in our experiment also.

was not affected even by silver(I) salt at room temperature.[15] The ring-enlargement of the intermediates led to the preferential formation of 2,3-benzotropone derivatives over 4,5-benzotropone derivatives. Thus, the intermediate adduct from 1,3-dimethoxynaphthalene with dichlorocarbene gave **7** more predominantly than **8**. A similar trend was observed in 1,2-dimethoxynaphthalene. 1,2,3- And 1,2,4-trimethoxynaphthalenes also gave only the 2,3-benzotropone derivatives, **15** and **18** respectively. Furthermore, it should be noted that the direction of the ring opening of the intermediate 1,2,3- and 1,2,4-trimethoxynaphthalene-carbene adducts to **15** and **18** respectively is comparable with that of an intermediate 1,4-dimethoxynaphthalene-carbene adduct to **5**.

Finally, the steric effect by the methoxyl group seems not to be significant in either the addition of dichlorocarbene to methoxynaphthalenes or the ring opening of the intermediate carbene adducts, because the carbene adds exclusively to the most hindered 1,2-double bond of 1,2,4-trimethoxynaphthalene and the ring opening of the adduct gives a more hindered product **18** rather than a less hindred **19**.

Experimental

Material. The 1- and 2-methoxynaphthalenes were commercially available. The 1,2-dimethoxynaphthalene was prepared by the reduction and methylation of commercially available 1,2-naphthoquinone. The 1,4-, 1,5-, 1,6-, and 2,3-dimethoxynaphthalenes were prepared by the methylation of the corresponding commercially available diols with dimethyl sulfate. The 1,3-,[16] 1,2,3-,[17] and 1,2,4-trimethoxynaphthalenes[18] were prepared according to the literature.

The *1,2,3,4-tetramethoxynaphthalene*[19] was prepared in the following manner. Dimethylisonaphthazalin[20] (3.7 g, 17 mmol) was stirred, portion by portion, into a mixture of ether (30 ml) and aqueous sodium dithionite (6.0 g in 30 ml of water). After 20 min, the mixture was transferred into a separable funnel and shaken vigorously. The ethereal layer was separated, and the aqueous layer was extracted with ether. The combined organic solution was dried over magnesium sulfate, filtered, and evaporated. The pale red residual oil was added to a solution of dimethyl sulfate (4.8 ml, 51 mmol) in ethanol (15 ml), and to this was added, drop by drop, 50% aqueous sodium hydroxide (5.1 ml) under an atmosphere of nitrogen. After it had then stood overnight, the solution was diluted with water, and the colorless needles which were thus precipitated were collected, washed with water, and dried. Yield: 3.6 g (86%); mp 49—53 °C, which rose to 52—53 °C upon chromatographic purification and recrystallization from hexane. Found: C, 67.75; H, 6.58%. Calcd for $C_{14}H_{16}O_4$: C, 67.72; H, 6.50%. NMR($CDCl_3$): δ 4.05 (s, 12H), 7.43 (q, 2H, J=3.2 Hz), and 8.09 (q, 2H, J=3.2 Hz).

Standard Procedure. Methoxynaphthalenes (0.03 mol), chloroform (3 ml, 0.037 mol), 50% aqueous sodium hydroxide (6 ml), and triethylbenzylammonium chloride (0.12 g) were placed in a 50-ml Erlenmeyer flask equipped with a potassium hydroxide tube, after which the mixture was stirred at room temperature for 15 to 16 h. The reaction mixture was then diluted with water and extracted with dichloromethane. The extract was washed with water and dried over anhydrous sodium sulfate. After the solvent had been removed, the residue was chromatographed on a silica gel column, with the elution of the benzene-ether mixture. Each fraction separated was purified by fractional chromatography or sublimation.

*7-Chloro-6-methoxy-2,3-benzotropone (**1**), 2-Chloro-3-methoxy-4,5-benzotropone (**2**), and 5-Chloro-7-methoxy-2,3-benzotropone (**3**).* 1,2-Dimethoxynaphthalene was submitted to the reaction with dichlorocarbene; after a standard work-up, the reaction mixture was chromatographed to give a dark red oil containing crystals. Rechromatography on a silica gel column and sublimation gave three crystalline products. One was 7-chloro-6-methoxy-2,3-benzotropone (**1**) (1.8%); yellow needles; mp 135—136 °C, which showed no depression on admixture with an authentic sample.[6] NMR($CDCl_3$): δ 4.05 (s, 3H), 6.85 (d, 1H, J=13.0 Hz), 7.45 (d, 1H, J=13.0 Hz), 7.5—7.9 (m, 3H), and 8.6 (m, 1H) ppm. The second (1.5%) is assigned to 2-chloro-3-methoxy-4,5-benzotropone (**2**); colorless needles; mp 95—96 °C. Found: C, 65.23; H, 4.16%. Calcd for $C_{12}H_9O_2Cl$: C, 65.31; H, 4.12%. UV(EtOH): 238 (log ε 4.39), 274.5 (4.59), 340 (3.52), and 357 nm (3.11). IR(KBr): 1641 (s), 1610 (sh), 1594(s), and 1572 (m) cm^{-1}. NMR($CDCl_3$): δ 3.95 (s, 3H), 6.93 (d, 1H, J=12.6 Hz), 7.51 (d, 1H, J=12.6 Hz), 7.65—7.85 (m, 3H), and 8.2—8.4 (m, 1H). The third product, 5-chloro-7-methoxy-2,3-benzotropone (**3**), which, curiously could not be reproduced, in repeated experiments, was eluted faster than the above two. After sublimation and recrystallization from cyclohexane, it formed nearly colorless needles; mp 100 °C. Found: C, 65.25; H, 4.05%. Calcd for $C_{12}H_9O_2Cl$: C, 65.31; H, 4.12%. UV(EtOH): 237 (log ε 4.38), 260sh (4.16), 330 (3.90), and 368 nm (3.14). IR(KBr): 1625 (s), 1610 (s), 1593 (s), and 1570 (m) cm^{-1}. NMR($CDCl_3$): δ 3.93 (s, 3H), 6.62 (d, 1H, J=2.0 Hz), 7.37 (d, 1H, J=2.0 Hz), 7.5—7.85 (m, 3H), and 8.5 (m, 1H).

*7-Chloro-4-methoxy-2,3-benzotropone (**4**) and 5-Chloro-4-methoxy-2,3-benzotropone (**5**).* The reaction of 1,4-dimethoxynaphthalene with dichlorocarbene was run using the standard procedure, and the product was chromatographed on silica gel to give two crystalline fractions. The yellow orange crystals obtained from the first elute (4.28 g, 76%) were the starting material. The second was a dark red oil which was then heated *in vacuo* to give 7-chloro-4-methoxy-2,3-benzotropone (**4**) as pale yellow crystals (0.68 g, 10.2%). Recrystallization from methanol gave an analytical sample; mp 133—133.5 °C. Found: C, 65.24; H, 4.04%. Calcd for $C_{12}H_9O_2Cl$: C, 65.31; H, 4.12%. UV(EtOH): 236.5 (log ε 4.36), 256.5 (4.24), 332 (3.81), and 382 nm (3.92). IR (KBr): 1612 (s), 1593 (s), and 1565 (s) cm^{-1}. NMR ($CDCl_3$): δ 3.97 (s, 3H), 6.01 (d, 1H, J=10.0 Hz), 7.58 (d, 1H, J=10.0 Hz), 7.6—7.9 (m, 2H), and 8.3—8.6 (m, 2H). Diels-Alder adduct with maleic anhydride (**7**): colorless crystals; mp 241—242 °C. Found: C, 60.09; H, 3.52%. Calcd for $C_{18}H_{11}O_5Cl$: C, 60.29; H, 3.48%. NMR(DMSO-d_6): δ 3.65 (s, 3H), 4.26 (d, 1H, J=10.8 Hz), 4.76 (d, 1H, J=10.8 Hz), 6.34 (d, 1H, J=9.5 Hz), 7.08 (d, 1H, J=9.5 Hz), 7.5—7.85 (m, 3H), and 7.95—8.2 (m, 1H).

The reaction with three molar amounts of the dichlorocarbene source was run and the crude product was chromatographed on silica gel to give an orange semi-solid besides the recovered substance (4.2 g, 75%). The semi-solid was recrystallized from ether to give (**4**) (0.88 g, 12.4%). The mother liguor gave an additional crop of crystals (**5**), which recrystallized from cyclohexane (0.19 g, 2.9%); mp 55.5—56.5 °C. Found: C, 65.29; H, 4.03%. Calcd for $C_{12}H_9O_2Cl$: C, 65.31; H, 4.12%. UV(EtOH): 231 (log ε 4.39), 312 (3.92), and 355 nm (3.83). IR(KBr): 1628 (s), 1608 (s), 1590 (s), 1570 (s), and 1530 (s) cm^{-1}. NMR-($CDCl_3$): δ 3.80 (s, 3H), 6.68 (d, 1H, J=12.0 Hz), 7.22 (d, 1H, J=12.0 Hz), 7.5—7.9 (m, 3H), and 8.1—8.5 (m, 2H).

*5-Chloro-6-methoxy-2,3-benzotropone (**7**) and 2-Chloro-6-methoxy-4,5-benzotropone (**8**).* The reaction of 1,3-dimethoxynaphthalene with dichlorocarbene was carried out by means of the standard procedure, and the reaction product was chromatographed on silica gel to give three fractions. The first fraction was the starting material (4.3 g, 76%). The second was recrystallized from ethanol to give 5-chloro-6-methoxy-2,3-benzotropone (**7**) (0.53 g, 8.0%); colorless needles; mp 149—151 °C. Found C, 65.10; H, 4.26%. Calcd for $C_{12}H_9O_2Cl$: C, 65.31; H, 4.12%. UV(EtOH): 252 (log ε 4.78), 261 (4.76), 270sh (4.60), 335 (4.00), and 368sh nm (3.26). IR(KBr): 1620(w), 1607(w), 1580(m), 1566(s), and 1560(s) cm^{-1}. NMR($CDCl_3$): δ 3.82 (s, 3H), 6.54 (s, 1H), 7.55—7.85 (m, 4H), and 8.55 (m, 1H). Diels-Alder adduct with maleic anhydride (**10**): colorless crystals, mp 251—253 °C. Found: C, 60.48; H, 3.47%. Calcd for $C_{16}H_{11}O_5Cl$: C, 60.29; H, 3.48%. NMR (DMSO-d_6): δ 3.68 (s, 3H), 4.0—4.45 (m, 4H), 7.5—7.8 (m, 3H), and 8.0—8.2 (m, 1H). The third was recrystallized from hexane-benzene to give 2-chloro-6-methoxy-4,5-benzotropone (**8**) (0.19 g, 2.9%); colorless crystals; mp 125—126.5 °C. Found: C, 65.14; H, 4.04%. Calcd for $C_{12}H_9O_2Cl$: C, 65.31; H, 4.12%. UV(EtOH): 256 (log ε 4.58), 263 (4.60), 273 (4.68), 288sh (4.22), and 312sh nm (3.92). IR (KBr): 1622(s), 1609(m), 1596(m), 1587(s), and 1522(m) cm^{-1}. NMR($CDCl_3$): δ 4.13 (s, 3H), 6.76 (s, 1H), 7.7—7.95 (m, 3H), 8.16 (s, 1H), and 8.55 (m, 1H).

*5-Chloro-6-hydroxy-2,3-benzotropone (**9**).* 5-Chloro-6-methoxy-2,3-benzotropone (**7**) (0.13 g, 0.6 mmol) and concentrated hydrochloric acid (1 ml) in ethanol (10 ml) were refluxed for 2.5 h. After evaporation, the residue was recrystallized from ethanol to give 5-chloro-6-hydroxy-2,3-benzotropone (**9**); colorless needles (0.10 g, 85%); mp 251 °C (dec). Found: C, 64.30; H, 3.66%. Calcd for $C_{11}H_7O_2Cl$: C, 63.94; H, 3.41%. IR(KBr): 3075—2300 (broad), 1620, 1590, 1557, and 1523 cm^{-1}. NMR (DMSO-d_6): δ 3.5 (broad, 1H), 6.74 (s, 1H), 7.8—8.1 (m, 3H), 8.31 (s, 1H), and 8.35—8.5 (m, 1H). UV(EtOH): 266 (log ε 4.48), 274.9 (4.60). 283.7 (4.54), 306 (3.72), 331 (3.78), and 350 nm (3.78).

*2-Chloro-6-methoxy-4,5-benzotropone (**8**)* (34 mg, 0.15 mmol) was similarly heated for 2 h with concentrated hydrochloric acid (0.3 ml) in ethanol (3 ml), giving the same product as described above (31 mg, 97%).

*2-Chloro-7-methoxy-4,5-benzotropone (**11**).* To a solution of 2,3-dimethoxynaphthalene (5.64 g, 0.03 mol) in chloroform (6 ml) and benzene (10 ml) were added triethylbenzylammonium chloride (0.12 g) and 40% aqueous potassium hydroxide (8 ml). After it had been stirred for 20 h at room temperature, the reaction mixture was worked-up as usual and the product was recrystallized from methanol to give 3.33 g of unchanged dimethoxynaphthalene. The filtrate was chromatographed on silica gel. The elute gave again 2.25 g of the starting material. The total recovery was 99%. The subsequent dichloromethane elute gave a yellow-brown crystalline product which, on sublimation (110 °C/2Torr) and recrystallization from methanol, afforded **11** as pale yellow needles (25 mg, 0.4%); mp 138—140 °C. The melting point was raised to 144—145 °C by repeated recrystallizations from methanol. Found: C, 65.10; H, 4.02%. Calcd for $C_{12}H_9O_2Cl$: C, 65.31; H, 4.12%. UV(EtOH): 244 (log ε 4.54), 250 (4.56), 286 (4.76), and 316 nm (4.06). IR(KBr): 1620(s), 1603sh, and 1538(w) cm^{-1}. NMR($CDCl_3$): δ 4.03 (s, 3H), 7.19 (s, 1H), 8.37 (s, 1H), and 7.6—7.9 (m, 4H).

*5-Chloro-3'-methoxy-2,3-benzotropone (**12**).* A mixture of 1,5-dimethoxynaphthalene, chloroform (twice the standard amount), 50% aqueous sodium hydroxide, and triethylbenzylammonium chloride was treated as usual. Benzene was added to the reaction mixture, and the crystals which precipitated were collected by filtration and extracted with ether by means of Soxhlet extractor, giving the starting material (2.85 g). The filtrate was evaporated and the brown residue was recrystallized from benzene to give a further amount of the starting substance (1.04 g). The mother liquor from recrystallization was charged on a silica gel-column chromatograph. The first fraction was the starting material (0.44 g), while the second was a yellow crystalline product which was rechromatographed and recrystallized to give 5-chloro-3'-methoxy-2,3-benzotropone (**12**) as yellow needles (93 mg, 1.4%); mp 123—124 °C. Found: C, 64.92; H, 4.05%. Calcd for $C_{12}H_9O_2Cl$: C, 65.31; H, 4.12%. UV(EtOH): 235 (log ε 4.42), 290 (3.99), and 348 nm (4.01). IR(KBr): 1630(w), 1586(s), and 1573(s) cm^{-1}. NMR($CDCl_3$): δ 3.99 (s, 3H), 6.78 (d, 1H, J= 13.0 Hz), 7.17 (dd, 1H, 13.0 and 2.0 Hz), 7.19 (dd, 1H, J=8.0 and 1.5 Hz), 7.63 (t, 1H, J=8.0 Hz), 8.01 (dd, 1H, J=8.0 and 1.5 Hz), and 8.27 (d, 1H, J=2.0 Hz).

*5-Chloro-4'-methoxy-2,3-benzotropone (**13**) and 2-Chloro-3'-methoxy-4,5-benzotropone (**14**).* The residue from the standard work-up in the reaction of 1,6-dimethoxynaphthalene was chromatographed on silica gel. The first elute was the recovered starting meterial (3.03 g, 55%). The second eluate (brown crystals) was rechromatographed on silica gel to give two crystalline fractions. One was recrystallized from benzene to give 5-chloro-4'-methoxy-2,3-benzotropone (**13**) as colorless leaflets (0.65 g, 9.9%); mp 144—144.5 °C. Found: C, 65.28; H, 4.03%. Calcd for $C_{12}H_9O_2Cl$: C, 65.31; H, 4.12%. UV(EtOH): 234.3 (log ε 4.26), 282 (4.53), and 340 sh nm (3.74). IR(KBr): 1624-(w), 1583(s), and 1573(s) cm^{-1}. NMR($CDCl_3$): δ 3.96 (s, 3H), 6.81 (d, 1H, J=13.0 Hz), 6.9—7.5 (m, 4H), and 8.47 (d, 1H, J=9.0 Hz). The other was recrystallized from ethanol to give 2-chloro-3'-methoxy-4,5-benzotropone (**14**) as pale yellow needles (0.33 g, 4.9%); mp 198—199 °C. Found: C, 65.40; H, 4.36%. Calcd for $C_{12}H_9O_2Cl$: C, 65.31; H, 4.12%. UV(EtOH): 228 (log ε 4.41), 235 (4.40), and 294.8 nm (4.59). NMR($CDCl_3$): δ 4.02 (s, 3H), 7.16 (d, 1H, J=13.5 Hz), 8.35 (d, 1H, J=13.5 Hz), 8.17 (s, 1H), and 7.2—7.8 (m, 3H).

*5-Chloro-6,7-dimethoxy-2,3-benzotropone (**15**).* The mixture of 1,2,3-trimethoxynaphthalene (1.19 g, 5.5 mmol), chloroform (2 ml, 25 mmol), 50% aqueous sodium hydroxide (2 ml), and triethylbenzylammonium chloride (60 mg) was stirred for 16 h at room temperature. After the usual work-up, the red oily product was chromatographed on silica gel to give two fractions. The first was the recovered starting material (0.13 g, 11%). The second (yellow-orange crystals) was recrystallized from cyclohexane to give 5-chloro-6,7-dimethoxy-2,3-benzortopone (**15**) as yellow needles (0.38 g, 27.5%); mp 79—84 °C. Recrystallization from cyclohexane gave an analytical sample; mp 83.5—85 °C. Found: C, 62.62; H, 4.62%. Calcd for $C_{13}H_{11}O_3Cl$: C, 62.29; H, 4.42%. UV(EtOH): 250 sh (log ε 4.95), 265 (4.38), and 340 nm (3.83). IR(KBr): 1621(s), 1593(s), 1544(w), and 1519(m) cm^{-1}. NMR($CDCl_3$): δ 3.92 (s, 3H), 3.99 (s, 3H), 7.6—7.8 (m, 4H), and 8.4—8.6 (m, 1H). Diels-Alder adduct (**17**) with maleic anhydride: colorless crystals, mp 183—184 °C. Found: C, 58.25; H, 3.64%. Calcd for $C_{17}H_{13}O_6Cl$: C, 58.55; H, 3.76%. NMR($CDCl_3$): δ 3.73 (s, 3H), 3.85 (s, 4H), 4.05 (d, 1H, J=9.6 Hz), 4.29 (d, 1H, J=2.0 Hz), 7.4—7.7 (m, 3H), and 8.1—8.3 (m, 1H).

*5-Chloro-4,6-dimethoxy-2,3-benzotropone (**18**).* A reaction mixture obtained from the standard work-up in the

reaction of 1,2,4-trimethoxynaphthalene was chromatographed on silica gel to give the starting material (4.27 g, 81.3%), as well as 5-chloro-4,6-dimethoxy-2,3-benzotropone (**18**) as straw-colored crystals (1.15 g, 17.8%), the recrystallization of which from cyclohexane gave an analytical sample, mp 98—99 °C. Found: C, 62.47; H, 4.54%. Calcd for $C_{13}H_{11}O_3Cl$: C, 62.29; H, 4.42%. IR(KBr): 1620(s), 1590(s), 1561(s), and 1540(w) cm^{-1}. NMR($CDCl_3$): δ 3.74 (s, 3H), 3.87 (s, 3H), 6.29 (s, 1H), 7.6—7.85 (m, 2H), and 8.0—8.35 (m, 2H). Diels-Alder adduct (**20**) with maleic anhydride: colorless crystals; mp 215—216 °C. Found: C, 58.60; H, 3.80%. Calcd for $C_{17}H_{13}O_6Cl$: C, 58.55; H, 3.76%. NMR($CDCl_3$): δ 3.71 (s, 3H), 2.72 (dd, 1H, J=9.6 and 1.6 Hz), 3.94 (s, 3H), 4.22 (d, 1H, J=9.6 Hz), 4.42 (d, 1H, J=1.6 Hz), 7.4—7.7 (m, 3H), and 8.1—8.4 (m, 1H).

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