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Acetolyses of 1-Substituted trans-7,8-Dichlorodibenzobicyclo [2.2.2] octadienes.

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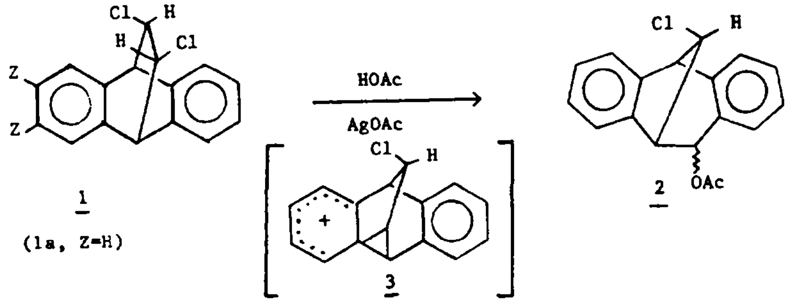
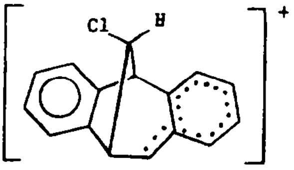
Abstract: The preparations and silver-assisted acetolyses of the 1-methoxy (5), 1-methyl (6), 1-carbomethoxy (7), and 1-nitro (8) derivatives of trans-7,8-dichlorodibenzobicyclo [2.2.2] octa-2,5-dienes are described. Rearranged products possessing the dibenzobicyclo [3.2.1] octadiene skeleton were identified. With compound 5, the P_8:P_7 ratio (ratio of products derived from ionizations of C_8-Cl and C_7-Cl bonds) was 1.3. For 6 and 7, the corresponding P_8:P_7 ratios were 0.4 and 33 respectively. Acetolysis of 8 led to products in detectable quantities from ionization of the C_8-Cl bond only. The data support the proposal by Cristol that the transition states for these solvolytic rearrangements more closely resemble phenonium ion-like intermediates than benzyl cations.

Investigations by Cristol and coworkers[1] suggested that the transition state for the silver ion-assisted acetolysis of trans-7,8-dichlorodibenzobicyclo [2.2.2] octadiene (1a) to form the corresponding [3.2.1] acetates 2 resembles the phenonium ion intermediate 3. Migratory preferences of the aryl rings for substrates possessing methyls (1b, Z=CH_3) or chlorine (1c, Z=Cl) although only modest in magnitude support a phenonium ion-like transition state and are not in accord with expectations based upon substantial benzylic cation character such as 4. As part of





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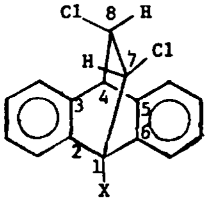
a continuing study of charge distributions in elimination transition states for substrates related to 1[2,3] we had occasion to prepare a number of derivatives of 1a bearing a dipolar substituent at the bridgehead (C-1) position. It appeared to us that an investigation of the product distributions from the acetolyses of these compounds might provide additional evidence regarding the nature of these rearrangements. The compounds selected for this study were 5-8.



5 (X = OCH_3)

6 (X = CH_3)

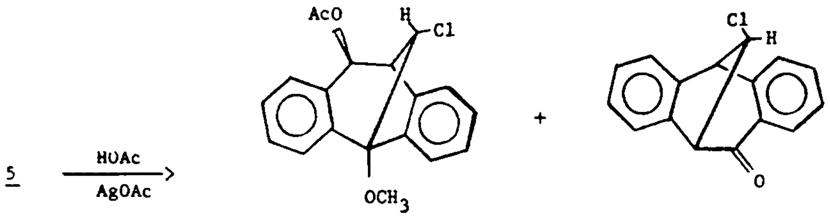
7 (X = CO_2CH_3)

8 (X = NO_2)

Results

The requisite starting dichlorides were prepared by the cycloadditions of the appropriate 9-substituted anthracenes with trans-dichloroethene. Yields of the purified adducts ranged from 25-67%.

The solvolyses were performed in boiling glacial acetic acid containing silver acetate. Reaction times ranged from 50 to 147 h. From 5 an 87% (gc) yield of a mixture of 9 and 10 was obtained. The acetate 9 and ketone 10 were formed in a ratio of 1.3/1. Pure samples of 9 and 10 were isolated by fractional crystallization and characterized as follows. Product 9 was shown to be a methoxy-containing monochloroacetate (with a molecular weight expected for 9) by a combination mass, ir, and ^1H NMR spectroscopy. A closer examination of the proton NMR spectrum of 9 establishes the specific geometric assignments. This is possible by making use of the extensive data for chemical shifts and coupling constants involving protons at C-1, C-4, C-5, and C-8 in disubstituted (C-4 and C-8) dibenzobicyclo [3.2.1] octadienes (11) compiled by Cristol, Mohrig, and Plorde[4] (see discussion). In Table I the chemical shifts (and coupling



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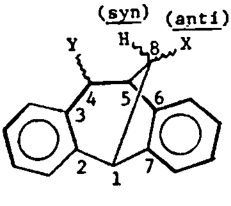
10



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constants where doublets appear) for 9 are compared with those for the analogs 11a (X=Cl, anti; Y=AcO, exo) and 11b (X=Cl, anti; Y=AcO, endo) devoid of the bridgehead methoxyl.

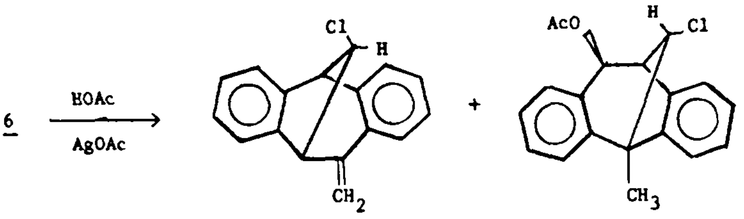
Table I.
Chemical Shift and Coupling Constant Comparisons of 11a and 11b with Products from Acetolysis of 5, 6, 7, and 8.

Compd	endo C-4H	syn C-8H	C-5H	OCOCH3
11a	δ 5.93($J_{4,5}$=2.4)	δ 4.90	δ 3.64($J_{5,4}$=2.4)	δ 2.03
9[a]	δ 5.80($J_{4,5}$=2.5)	δ 5.00	δ 3.70($J_{5,4}$=2.5)	δ 2.13
13[b]	δ 6.00($J_{4,5}$=2.5)	δ 4.95	δ 3.76($J_{5,4}$=2.5)	δ 2.17
14[c]	δ 6.00($J_{4,5}$=2.4)	δ 5.23	δ 3.80($J_{5,4}$=2.4)	δ 2.20
17	δ 5.83($J_{4,5}$=2.5)	δ 5.33	δ 3.80($J_{5,4}$=2.5)	δ 2.17
18	δ 6.18($J_{4,5}$=6.0)[d]	δ 4.98	δ 4.16($J_{5,4}$=6.0)	δ 2.10
11b	δ 6.16($J_{4,5}$=5.5)[d]	δ 4.56	δ 3.98($J_{5,4}$=5.5)	δ 2.03

(a) OCH_3, δ 3.56; (b) CH_3, δ 1.90; (c) OCH_3, δ 3.88; (d) This entry represents δ and J for exo C-4H.

The structure for 10 was confirmed by comparison of its IR and pmr spectra with those of an authentic sample.[5]

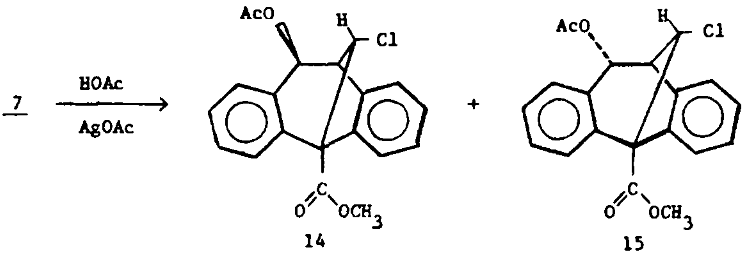
The acetolysis of 6 leads to 12 and 13 in a ratio of 2.5/1. These two products constituted 95% of the product mixture.



12 13

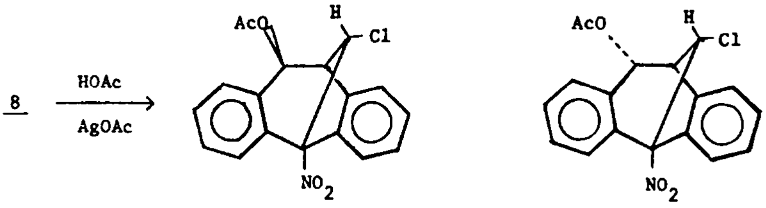
Products 12 and 13 were separated by a combination of chromatography and crystallization. Some epimerization of 13 appears to occur on the silica gel column. Spectroscopic and elemental analysis facilitated structural assignments (see Table I). Further confirmation of the structure for 12 was obtained by its oxidation to the known chloroketone.[5]

The acetolysis of 1-carbomethoxy-trans-7,8-dichloro-dibenzobicyclo [2.2.2] octadiene (7) was conducted for a 70 h period. Three components were found to comprise 96% of the reaction mixture. In addition to 15% unreacted starting material, 14 and 15 were formed in a ratio of 10/1. Isomer 14 was isolated and fully characterized. The structural assignment for 15 rests upon a similar retention time (capillary gc) and upon its mass spectrum which is essentially identical to that for 14. A third isomer, 16, with 1/3 the gc trace area of 15 is also formed (see Discussion).



14 15

When 1-nitro-trans-7,8-dichlorodibenzobicyclo [2.2.2] octadiene (8) was subjected to the acetolysis, approximately 90% of 8 remained unreacted even after boiling for 147 h. Two products were formed in a ratio of 5.5/1 with assigned structures 17 and 18. Structural

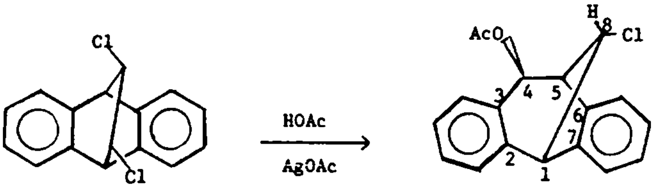


17 18

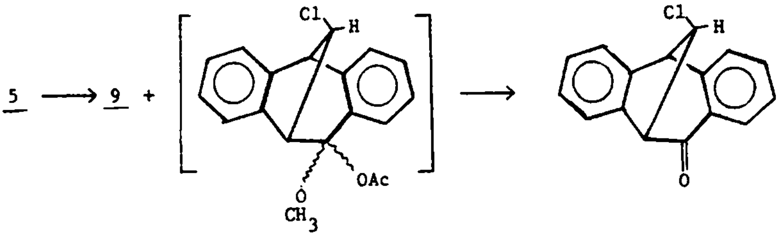
assignments for 17 and 18 were again made on the basis of mass spectra, proton nmr spectra (see Table I) and elemental analyses.

Discussion

The *trans*-dichloroderivatives, 5–8, were chosen for the solvolysis study because the parent *trans* substrate (unsubstituted at the bridgehead position) reportedly undergoes acetolysis to the single *anti-exo* chloroacetate in nearly quantitative yield.[6] Stereochemical assignments for the dibenzobicyclo [3.2.1] octadiene products can be made with reasonable certainty based upon the coupling constants for protons at C-4, C-5, and C-8 and comparisons of these values with those for related derivatives of 11 published by Cristol and coworkers[4].



In the acetolysis of 5, in addition to 9, the major product, the chloroketone 10 is also formed. The ratio 9:10 is 1.3. The acetate 9 results from ionization of the C_8-Cl bond (the chlorine remote from the bridgehead methoxyl). The ketone must be derived from loss of the C_7-chloride presumably *via* work-up hydrolysis of the α-acetoxy ether.[7]



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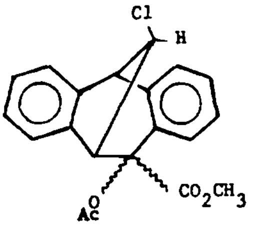
The *exo* and *endo* acetates 14 and 15 (10:1 ratio) formed in the acetolysis of 7 have as their origin the ionization of the C_8-Cl bond. A third isomer with 1/3 the gc trace area of 15 although not isolated, is presumably 16. It, like 14 and 15 shows a molecular ion, m/z of 356. However, unlike the mass spectra for 14 and 15 which are essentially identical in all mass regions, the mass spectrum of 16



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(gc/ms analysis) shows significant differences including the identity of the base peak.

The final acetolysis studied (with the nitro derivative 8) proceeds very slowly (90% unreacted 8 after 147 h) and yields detectable quantities only of products 17 and 18 (in a ratio of 5.5:1) involving ionization only of the C_8-Cl bond. That the minor component 18 possesses the anti-8-Cl, endo-4-acetate structure can be deduced from the pmr spectrum of 18 (as a mixture with 17). The C-8 proton is an apparent singlet (no appreciable coupling to C-5H). And the coupling constant for protons at C-4 and C-5 is 6.0 Hz, comparable with that in 11b (Table I).

The regioselectivity of the solvolytic rearrangements can best be summarized in terms of product distribution based upon relative amounts of C_7-Cl and C_8-Cl ionization. This is shown in Table II.

Table II.
Regioselectivities in the Acetolytic[a] Rearrangements of Dichlorodibenzobicyclo [2.2.2] Octadienes 5-8

Compd	Ratio of Products P_8:P_7[b,c]
5	1.3
6	0.4
7	33
8	only P_8 detected[d]

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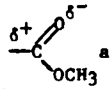
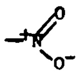
[a] Boiling acetic acid in presence of silver acetate.

[b] P_7 and P_8 represent products derived from the ionization of C_7-Cl and C_8-Cl respectively.

[c] Standard addition techniques employed in gc analyses of P_8:P_7 ratios from acetolyses of 5 and 6.

[d] The ratio of major (17) to minor (18) P_8 products was estimated from gc areas only.

Large regioselectivities are observed only for the acetolyses of 7 and 8. In both cases it is C_8-Cl (remote from the dipolar groups 

and 

) which undergoes heterolysis almost exclusively. This is qualitatively consistent with a transition state resembling 3 (probably possessing some cation character at C-8, in preference to the competitive transition state with cation character at C-7) or resembling 4. However, the minimal regioselectivity attending the solvolytic rearrangements of 5 and 6 appears to be best explained in terms of a transition state approximated by 3. Were substantial benzyl-ion character developing, one would expect considerable selectivity in the product distribution from 5 (and modest selectivity from 6). Such selectivity would favor the formation of 10(C_7-Cl ionization) which is not experimentally observed. The modest preference for C_8-Cl ionization in the acetolysis of 5 is somewhat surprising. This may reflect the fact that ionization of the C_7-Cl bond would lead to a highly strained "phenyl-bridged" ion (as in C_8-Cl ionization) with enhanced s-character in the exocyclic C-1 bond[8] opposing the electron withdrawing oxygen of the methoxyl. A "phenyl-bridged" ion such as 3 can be viewed as a cyclopropylcarbinyl-like cation. As such, a methyl group at the bridgehead position would be expected to provide a small stabilizing effect[9] in agreement with the small regioselectivity effect observed in the present study.

Thus the data obtained in the present study combined with evidence from earlier work[1] support the proposal that the transition states for these solvolytic rearrangements more closely resemble phenonium ion-like intermediates, 3 than benzyl cations, 4.

Experimental Section

Melting points are uncorrected and were determined in open capillary tubes with a Thomas-Hoover melting point apparatus. Infrared spectra were obtained on a Perkin-Elmer Model 621 spectrophotometer. ^{1}H NMR spectra were determined on a Varian EM-390 spectrometer or in several cases with a Varian modified 360 MHz spectrometer. Mass spectra were obtained on a Hitachi Perkin-Elmer model RMU mass spectrometer or in conjunction with GC analyses using a Finnigan Model 4021 GC/Mass Spectrometer. A Carlo Erba Series 4160 chromatograph equipped with SE-52 and SE-54 fused silica capillary columns was also employed. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

1-Methoxy-*trans*-7,8-dichloro-2,3,5,6-dibenzobicyclo [2.2.2] octa-2,5-diene (5).

A 1.14 g (5.48 mmol) sample of 9-methoxyanthracene (prepared by the method of Meek et.al.[10]), 3.8 g (39 mmol) of *trans*-dichloroethene, 0.05 g of 2,6-di-*t*-butylphenol, and 5 mL of benzene was placed in a heavy-walled glass tube and degassed. The tube was sealed and then heated in a steel bomb at 200°C for 24 h. The mixture was concentrated and chromatographed over alumina. The product eluted with hexane and was then recrystallized from ethanol affording 0.84 g (50%) of colorless crystals, mp 120-121°C (lit.[10] mp 134-136°C)[11]; ^{1}H NMR δ 6.90-7.50 (8H, m, 8x ArH), 4.13-4.26 (3H, m), 4.79 (3H, s, -CH$_3$); mass spectrum, m/z 304 [M$^+$ (M$^+$ + 2 = 0.67 M$^+$, 2 Cl)].

1-Methyl-7,8-*trans*-dichloro-2,3,5,6-dibenzobicyclo [2.2.2] octa-2,5-diene (6).

The procedure was essentially identical to that for the methoxy derivative and afforded 6 in a 67% yield, mp 99.5-101°C (lit.[10] mp 104-105°C); ^{1}H NMR (CDCl$_3$) δ 6.96-7.29 (8H, m, 8x ArH), 4.25 (1H, d), 4.16 (1H, m), 3.84 (1H, d), 1.98 (3H, s, -CH$_3$), mass spectrum, m/z 290 [M$^+$ (M$^+$ + 2 = 0.67 M$^+$, 2 Cl)].

1-Carbomethoxy-*trans*-7,8-dichloro-2,3,5,6-dibenzobicyclo [2.2.2] octa-2,5-diene (7).

The cycloaddition was conducted as described for 5 and 6. The reaction time was 48 h in this case. The product mixture was chromatographed over Florisil. The dichloro ester eluted with 4:1 hexane: dichloromethane. The product was crystallized from a 9:1 mixture of hexane/dichloromethane affording a 50% yield of 7 as colorless crystals, mp 126-127°C. In several reactions using these reagents, product yields ranged from 31 to 50%. The ^{1}H NMR spectrum of 7 (CCl$_4$) exhibits the following features: δ 6.65-7.83 (8H, m, 8x ArH), δ 4.35 (1H, d, C$_4$-H) 4.15 and 4.10 (2H, m, C$_7$ and C$_8$-H), 4.0 (3H, s, OCH$_3$); IR (cm^{-1}, KBr) 1740. Anal. Calcd for $C_{18}H_{14}O_2Cl_2$: C, 64.88; H, 4.23; Cl, 21.28. Found: C, 64.80; H, 4.20; Cl, 21.50.

1-Nitro-*trans*-7,8-dichloro-2,3,5,6-dibenzobicyclo [2.2.2] octa-2,5-diene (8).

The nitro derivative was similarly prepared employing a 48 h reaction time. The crude product which had separated in the reaction tube was collected on a filter and washed with cold hexane. It was recrystallized from a mixture of dichloromethane and hexane affording a 25% yield of 8 as colorless crystals mp 137.5-138.5°C; IR (cm^{-1}, KBr) 1360 and 1555 (NO$_2$); ^{1}H NMR (CDCl$_3$) δ 6.7-7.7 (8H, m, 8x ArH), 4.73 (1H, d), 4.40 (1H, d), 4.20 (1H, t). Anal. Calcd for $C_{16}H_{11}Cl_2NO_2$: C, 60.02; H, 3.46; N, 4.38. Found: C, 60.27; H, 3.49; N, 4.36.

Acetolysis of 5.

A mixture of 0.49 g (1.6 mmol) of 5, 0.28 g (1.7 mmol) of silver acetate and 30 mL of acetic acid was boiled under reflux for 72 h. The cooled mixture was filtered. The filtrate was concentrated under reduced pressure. The residue was then dissolved in 40 mL of hot benzene and filtered. The cooled benzene solution was washed twice with 50 mL of 5% aqueous NaHCO$_3$, then with water, and finally dried over magnesium sulfate. The benzene was removed under reduced pressure leaving 0.49 g of a brown crystalline mixture, mp 87-148°C. GC analysis (SE 54 capillary column) showed in addition to several minor components, two major products constituting 87% of the mixture. Data subsequently obtained (see below) showed the two products to be 9 and 10. GC analysis showed them to be formed in a ratio of 1.3:1. A 0.34 g sample of the crude mixture was recrystallized from ethanol affording 0.096 g of 9 as a tan solid, mp 165-166.5°C (Analytical sample, mp 169-170°C). The filtrate from this crystallization was concentrated yielding 0.063 g of crude 10, mp 132.5-136. Recrystallization from hexane raises the melting point to 136.5-138°C. The spectral data for 9 are as follows: IR (KBr, cm^{-1}) 1740 (ester C=O); ^{1}H NMR (CDCl$_3$) δ 6.9-7.5 (8H, m, 8x ArH), 5.80 (1H, d, J = 2.5 Hz, C$_4$-H), 5.00 (1H, s, C$_8$-H), 3.70 (1H, d, J = 2.5 Hz, C$_5$-H), 3.56 (3H, s, OCH$_3$), and 2.13 (3H, s, CH$_3$CO); mass spectrum, m/z 328 [M+ (M+ + 2 = 0.3 M+, one Cl)]. Anal. Calcd for $C_{19}H_{17}O_3Cl$: C, 69.40; H, 5.21; Cl, 10.78. Found: C, 69.24; H, 5.42; Cl, 11.08.

The infrared spectrum of 10 was identical with that of an authentic sample[5]; ^{1}H NMR (CDCl$_3$) δ 6.9-7.8 (8H, m, 8x ArH), 4.86 (1H, s), 4.29 (1H, s), and 4.15 (1H, s); mass spectrum, m/z 254 [M$^+$(M$^+$ + 2 = 0.33 M$^+$, one Cl)].

Acetolysis of 6.

A solution prepared from 1.9 g (6.4 mmol) of 6, 1.2 g (6.8 (mmol) of silver acetate, and 120 mL of glacial acetic acid was boiled under reflux for 72 h. The reaction mixture was worked up as described for 5. GC analysis (SE 54 capillary column) revealed two major products, 12 and 13, in a ratio of 2.5:1. Several minor components present in a combined total of less than 5% accompanied the two major products. The crude product mixture (2.0 g of an orange oil) slowly crystallized. This mixture was chromatographed in two portions using 22 x 240 mm columns of 60-200 mesh silica gel packed in CCl_4. Elution with carbon tetrachloride removed an orange-colored band which afforded 900 mg of an orange crystalline solid when concentrated. This was recrystallized from hexane affording 620 mg of 12 as colorless crystals, mp 128-130°C; IR (cm^{-1}, KBr) 2970 (C-H), 1640 (C=C), and 910 ($R_2C{=}CH_2$); ^1H NMR ($CDCl_3$) δ 7.55 (1H, m, ArH), 7.37 (1H, m, ArH), 7.14-7.30 (6H, m, 6x ArH), 5.50 (1H, s, vinyl), 5.21 (1H, s, vinyl), 4.76 (1H, s, C_8-H), and 4.18 (2H, 2 partially resolved singlets, bridgehead); mass spectrum, m/z 252 [M^+ (M^+ + 2 = 0.33 M^+, one Cl)]. Anal. Calcd for $C_{17}H_{13}Cl$: C, 80.79; H, 5.18; Cl, 14.03. Found: C, 80.90; H, 5.23; Cl, 14.09.

A second orange-colored band was eluted with 10% $CHCl_3$ in CCl_4. This was concentrated to a viscous oil, dissolved in hexane and the hexane solution concentrated until the crude product (246 mg) crystallized. The crude product was recrystallized from 1:1 low boiling petroleum ether/hexane affording 115 mg of 13 as a nearly colorless (cream-white) crystalline solid, mp 155-156.5°C; IR (cm^{-1}, KBr) 1735 (ester C=O); ^1H NMR ($CDCl_3$) δ 6.8-7.5 (8H, m, 8x ArH), 6.00 (1H, d, J = 2.5 Hz, C_4-H), 4.95 (1H, s, C_8-H), 3.76 (1H, d, J = 2.5 Hz, C_5-H), 2.17 (3H, s, $COCH_3$), and 1.90 (3H, s, C_1-CH_3); mass spectrum, m/z 312 [M^+ (M^+ + 2 = 0.35 M^+, one Cl)]. Anal. Calcd for $C_{19}H_{17}ClO_2$: C, 72.96; H, 5.48; Cl, 11.33. Found: C, 73.06; H, 5.46; Cl, 11.03.

Further elution with 25:75 ether: CCl_4 provided a third band (59 mg) the ^1H NMR of which suggests a mixture of 13 and the corresponding endo acetate. In addition to chemical shift differences, between 13 and the presumed endo isomer, the doublet in the 6 ppm region (6.27 for the exo C_4-H of this endo acetate) shows a coupling constant (with C_5-H at 4.12) of 5.7 Hz.

Oxidation of 12 to anti-8-chlorodibenzobicyclo [3.2.1] octa-3,6-dien-2-one (10).

A mixture of 0.100 g (0.40 mmol) of 12, 10 mg of osmium tetroxide, and 2.0 mL of dioxane was stirred while 0.180 g (0.84 mmol) of sodium periodate in 1.0 mL of water was added. The resulting tan-colored mixture was stirred for 6 h at room temperature. Dichloromethane (5.0 mL) was added and the mixture washed with water. The organic layer was dried over magnesium sulfate and then concentrated under vacuum giving 0.111 g of a pale-brown, viscous oil. The oil was dissolved in 1:1 ether: ethanol and cooled affording 0.016 g (16%) of 10, mp, 138.5-139.5°C [lit.[6] mp, 138-139°C.] The infrared spectrum of 10 was identical to that of an authentic sample[5]. A mixture melting point showed no depression.

Acetolysis of 7.

In an initial experiment 1.00 g (3.01 mmol) of 7 was added to 0.551 g (3.30 mmol) of silver acetate in 100 mL of glacial acetic acid. The mixture was boiled under reflux for 50 h. The hot reaction mixture was filtered and the filtrate concentrated under reduced pressure. This residue was taken up in 100 mL of hot benzene and filtered again. The filtrate was washed with 250 mL of 0.1 M $NaHCO_3$ in several portions, washed with water, dried over magnesium sulfate and concentrated. The oily residue was dissolved in 10 mL of 95% aqueous ethanol and allowed to crystallize affording 0.645 g of a colorless solid, mp 113-117°C. This was recrystallized from hexane affording 0.230 g of 14, mp 124-125°C. A second crop (0.217 g, mp 119-121°C) was also obtained; IR (cm^{-1}, KBr) 1742 (two overlapping C=O bands), 1205 and 1225 (C-O); ^1H NMR ($CDCl_3$) δ 7-7.82 (8H, m, 8x ArH), 6.0 (1H, d, J = 2.4 Hz, C_4-H), 5.23 (1H, d, J = 0.6 Hz, C_8-H), 3.88 (3H, s, OCH_3), 3.80 (1H, d, J = 2.4 Hz, C_5-H), 2.2 (3H, s, CH_3CO); mass spectrum, m/z 357 M^+, 314 (M^+ -$COCH_3$). Anal. Calcd for $C_{20}H_{18}ClO_4$: C, 67.52; H, 4.53; Cl, 9.96. Found: C, 67.43; H, 4.67; Cl, 9.86.

In a similar experiment, 0.200 g (0.602 mmol) of 7, 0.132 g of silver acetate, and 25 mL of glacial acetic acid were boiled under reflux for 70 h. The reaction mixture was filtered and the filtrate concentrated to constant weight under reduced pressure. This crude product mixture (0.201 g) was investigated using capillary gc/mass spectrometry. Three major peaks accounted for approximately 96% of the mixture. The elution order on either an SE 52 or SE 54 capillary column was (a) unreacted starting compound (15%), (b) the main acetolysis product 14 (74%) and (c) a second product, the mass spectrum of which shows it to be an isomer of 14 (7%).

Acetolysis of 8.

A mixture of 0.300 g (0.937 mmol) of 8, 0.240 g (1.46 mmol) of silver acetate and 30 mL of acetic acid was boiled under reflux for 147 h. The cooled reaction mixture was filtered and the filtrate concentrated to a tan semisolid. This was taken up with a mixture of 15 mL of benzene and 5 mL of ether. An insoluble inorganic residue was filtered and the filtrate (now containing 296 mg of crude reaction product) washed successively with water, 5% aqueous sodium bicarbonate, water, saturated aqueous sodium chloride, and finally with water. The benzene-ether layer was dried over magnesium sulfate, filtered, and concentrated to 282 mg of nearly colorless oil which slowly crystallized to a cream colored solid, mp 117-133°C. Capillary gc analysis of the mixture shows two principal products in a ratio of 5.5/1 in addition to approximately 90% of unreacted starting material. The two products were assigned structures 17 and 18 respectively on the basis of the spectroscopic data below. In a second acetolysis which gave similar results, the product mixture was subjected to gc/ms analysis (using a 30 meter x 0.25 mm SE54 capillary column). In addition to starting material and two products in trace quantities, the two major products were observed. Their mass spectra were nearly identical and showed the following features: m/z 343 (M^+), 301 (M^+ $-CH_2CO$), 297 (M^+ $-NO_2$). The two major products were separated from starting material by crystallization from a mixture of methylene chloride and hexane (1:3). The ^1H NMR ($DCCl_3$) of a mixture of the two products showed the following: for 17 δ 2.17 (3H, s, $OCCH_3$), 3.80 (1H, d, J = 2.5 Hz, C_5-H), 5.33 (1H, s, C_8-H), 5.83 (1H, d, J = 2.5 Hz, C_4-H), 6.8-7.9 (8H, m, 8x ArH)[12]; for 18 δ 2.10 (3H, s, $OCCH_3$), 4.16 (1H, d, J = 6.0 Hz, C_5-H), 4.98 (1H, s, C_8-H), 6.18 (1H, d, J = 6.0 Hz, C_4-H), 6.8-7.9 (8H, m, 8x ArH). A chromatographically purified mixture of 17 and 18 was subjected to elemental analysis. Anal. Calcd for $C_{18}H_{14}ClNO_4$: C, 62.89; H, 4.10; Cl, 10.31; N, 4.08. Found: C, 62.79; H, 4.26; Cl, 10.59; N, 3.97.

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References and Notes

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12. Represents the entire region for the aromatic protons of both 17 and 18.