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Bridged Polycyclic Compounds. LXVI. Electrophilic Additions to Dehydrojanusene and Related Reactions[1]

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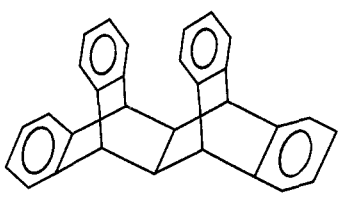
Electrophilic additions to dehydrojanusene (**2**) give mixtures of derivatives of janusenes (**10**) and of hemiisojanusenes (**11**), as do ring openings of epoxyjanusenes (**15**). Dehydrojanusene is compared in reactivity with dibenzobicyclo[2.2.2]octatriene (**9**) and its dimethyl derivative **16**.

The chemistry of the dibenzobicyclooctadiene systems has been of considerable interest to our research group for some time.[2-6] The stereochemistry of carbonium ion rearrangement attending addition or displacement reactions has commanded much attention, and recently we have been interested in reactions involving a novel polycyclic system, janusene (**1**).[7,8] We now wish to report the results of electrophilic additions to dehydrojanusene (**2**) which gives access to derivatives of janusene (**1**) and of several of its isomers (**3**, **4**, and **5**).



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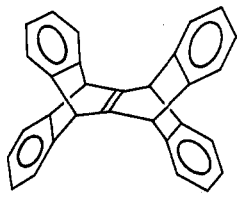

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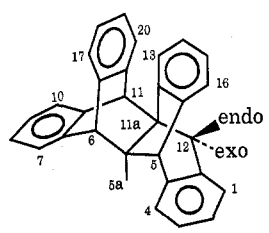
Nomenclature.—Because of the complexity of these polycyclic molecules, a trivial nomenclature has been developed. These compounds are formally described as derivatives of naphthacene, but the trivial nomenclature refers to them as relatives of janusene (**1**). For example, 5,5a,6,11,11a,12-hexahydro-5,11a:6,11-di-*o*-benzenonaphthacene (**3**) is termed hemiisojanusene. This compound can be imagined to arise from one Wagner–Meerwein rearrangement of the janusene skeleton. Compounds **4** (5,5a,6,11,11a,12-hexahydro-*cis*-5,11a:5a,11-di-*o*-benzenonaphthacene) and **5** (5,5a,6,11,11a,12-hexahydro-*trans*-5,11a:5a,11-di-*o*-benzenonaphthacene) are named *cis*-isojanusene and *trans*-isojanusene, respectively. These two compounds can be considered as arising from two Wagner–Meerwein rearrangements of the parent janusene system. The secondary benzylic positions of compounds **3**, **4**, and **5** are capable of exo



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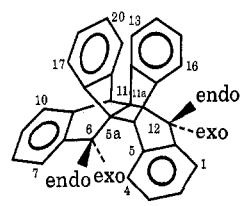

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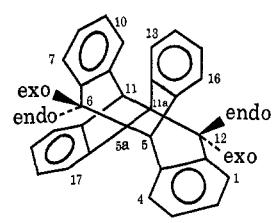

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(quasiaxial) or endo (quasiequatorial) configuration, and the tertiary position at C-5a in **3** is always syn to the C-12 carbon atom.

Synthesis.—5,6,11,12-Tetrahydro-5,12:6,11-di-*o*-benzenonaphthacene (dehydrojanusene, **2**) was synthesized in 89% yields from the zinc debromination of 5a,11a-dibromojanusene (**6**).[9]

Electrophilic Additions.—Addition of hydrogen bromide and hydrogen chloride to methylene chloride solutions of dehydrojanusene gave only **7**-Br and **7**-Cl, respectively.[9] Addition of acetic acid to olefin **2** oc-

(1) Previous paper: LXV. S. J. Cristol and J. M. Sullivan, *J. Amer. Chem. Soc.*, **93**, 1967 (1971).

(2) S. J. Cristol, R. P. Arganbright, and D. D. Tanner, *J. Org. Chem.*, **28**, 1374 (1963).

(3) S. J. Cristol, J. R. Mohrig, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *J. Amer. Chem. Soc.*, **85**, 2675 (1963).

(4) S. J. Cristol and D. D. Tanner, *ibid.*, **86**, 3122 (1964).

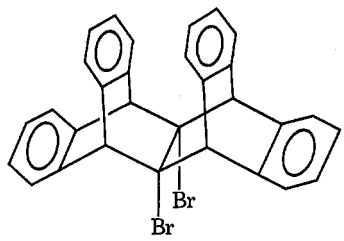
(5) S. J. Cristol, F. P. Parungo, and D. E. Plorde, *ibid.*, **87**, 2870 (1965).

(6) S. J. Cristol, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *ibid.*, **87**, 2879 (1965).

(7) S. J. Cristol and D. C. Lewis, *ibid.*, **89**, 1476 (1967).

(8) S. J. Cristol and W. Y. Lim, *J. Org. Chem.*, **34**, 1 (1969).

(9) S. J. Cristol, M. A. Imhoff, and D. C. Lewis, *ibid.*, **35**, 1722 (1970).



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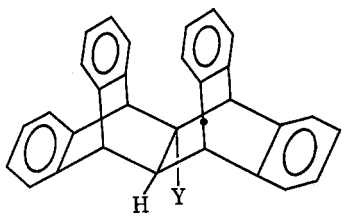
curred readily to give only 7-OAc. At this point, we did not know whether to interpret these results as cis-concerted additions,[10] as cis additions involving an intermediate carbonium ion,[11] or as additions that gave initially the hemiisojanusene derivative **8**, which in



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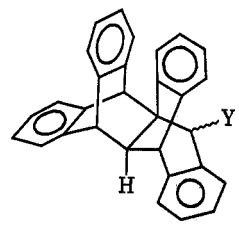

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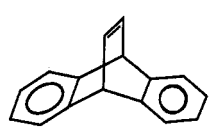
turn rearranged to **7** under the reaction conditions. This last mechanism seemed quite probable as dehydrojanusene can be viewed as a derivative of dibenzobicyclo[2.2.2]octatriene (**9**), which was known to undergo such rearrangements.[2-6]



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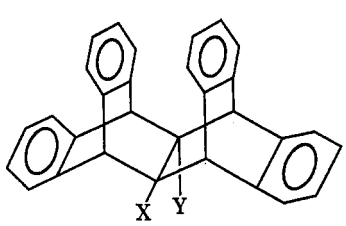
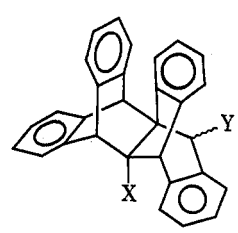
However, additions to dehydrojanusene involving electrophiles other than protonic species gave mixtures of janusene **10** and hemiisojanusene **11** derivatives (Table I). Most of the compounds of type **11** re-



10a, X = Cl; Y = Cl
b, X = Cl; Y = OAc
c, X = Cl; Y = OMe
d, X = Br; Y = OAc



11e, X = Br; Y = OMe
f, X = OH; Y = OAc
g, X = OH; Y = OMe

arranged to the janusene isomer **10** under acid catalysis[12] but were stable to the formation reaction conditions. The ratios of **10**:**11** observed were independent of the extent of reaction.

(10) R. C. Fahey in "Topics in Stereochemistry," Vol. 3, E. L. Eliel and N. L. Allinger, Ed., Interscience, New York, N. Y., 1968, pp 237-342.

(11) (a) M. J. S. Dewar and R. C. Fahey, *J. Amer. Chem. Soc.*, **85**, 2245 (1963). (b) Trans addition to dehydrojanusene was not expected, as such an addition would involve very large steric strains.

(12) Dichloride **11a** rearranged to dichloride **10a** simply upon heating in carbon tetrachloride.

TABLE I

PRODUCT MIXTURES FROM ELECTROPHILIC ADDITIONS TO DEHYDROJANUSENE (2)

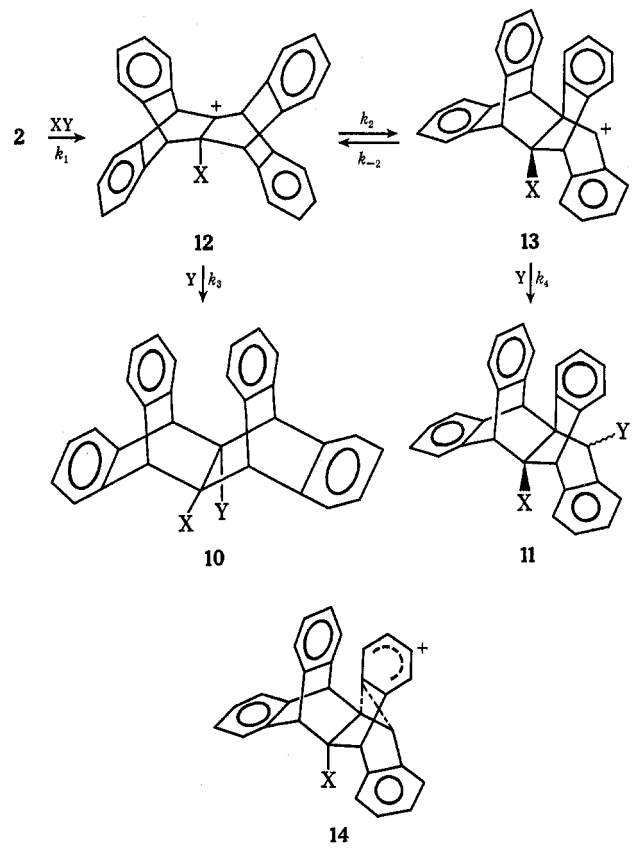
Reagents/substituents	X	Y	% 10	% 11[a]
Cl_2/CH_2Cl_2	Cl	Cl^-	20	80
tert-BuOCl/OAc^-–HOAc	Cl	HOAc	35	65
tert-BuOCl/MeOH	Cl	HOMe	60	40
NCS/MeOH	Cl	HOMe	60	40
NBS/OAc^-–HOAc	Br	HOAc	85	15
NBS/MeOH	Br	HOMe	100	0

[a] Product ratios were analyzed by pmr.

Compounds **10b** and **11b** were prepared by treatment with *tert*-butyl hypochlorite of a heterogeneous mixture of olefin **2** in a solution of sodium acetate in acetic acid. Similarly, the elements of acetyl hypobromite were added to olefin **2** to form **10d** and **11d** by using *N*-bromosuccinimide in acetic acid. Compounds **10c**, **11c**, and **10e** were formed from *tert*-butyl hypochlorite and *N*-bromosuccinimide, respectively, in methyl alcohol.

As noted in Table I, the product ratio (**10**:**11**) varied from 1:4 to 100:0 with differing electrophiles and nucleophiles. The results observed can be accommodated most simply as proceeding through the classical cations (Scheme I), **12** and **13**. Addition of an elec-

SCHEME I



trophile to dehydrojanusene (**2**) gives the tertiary cation **12**. This may rearrange to the secondary benzylic cation **13** or be trapped by a nucleophile (Y) to give the janusene derivative **10**. **13** may suffer analogous fates, that is, revert to **12** or give hemiisojanusene derivative **11**.

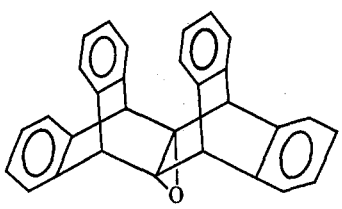
It is not possible, with the data presently available, to choose among the various alternatives for rationalizing the **10**:**11** product ratios observed. An attractive

explanation is that capture competes with rearrangement. This would explain the larger amount of **10** products in methanol as compared with acetic acid. This suggests that **12** and **13** are relatively stable compared with the transition state **14** separating them.[13] It is of interest that those cases where capture competes effectively with Wagner–Meerwein rearrangement often have tertiary classical cationic structures.[14] This explanation has the difficulty that the mixture formed by addition of chlorine is largely **11a**, while chloride ion is certainly a highly nucleophilic species[15] and is present as the gegenion in the ion pair formed directly from **2** and chlorine.

An alternative rationalization assumes that the **12** $\rightleftarrows$ **13** isomerization occurs readily and that the product mixture thus represents the result of k_3[**12**]/k_4[**13**] or the equivalent k_3k_{-2}/k_4k_2. In such a situation our predictive capabilities are minimal; we cannot estimate either k_{-2}/k_2 (except to guess that it is likely to be within a few orders of magnitude of 10°) or k_3/k_4 for a given nucleophile. Winstein[16] has suggested that bidentate carbonium ions react with nucleophiles to give mixtures of products in a ratio which depends upon the nucleophilicity of the reagent. Thus, highly nucleophilic reagents tend to capture the ion at its more electron-deficient site (the transition state reflects the cationic structure), while less strong nucleophiles capture at the site reflecting product stability. It seems to us that the same kind of argument can be brought to bear upon a set of rapidly equilibrating cations, that is, upon a ratio analogous to k_3/k_4 for our system, but we are reluctant to apply this argument over the limited range of data we have available.

The effect of X on the rates of rearrangement and/or upon the ratio of **12**:**13** and the k_3:k_4 ratio also remains to be understood.

Of some interest with regard to the electrophilic additions discussed above were the reactions of 5a,11a-epoxyjanusene (**15**) with acetic acid and methyl



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alcohol. Opening of this epoxide with acetic acid gave a 3:1 mixture of hydroxyacetates **10f** and **11f**, respectively (Table II). Reaction of **15** with methyl alcohol[17] occurred slowly to give a 1:3 mixture of hydroxy methyl ethers **10g** and **11g**, respectively. Both **11f** and **11g** rearrange to **10f** and **10g**, respectively, under acid catalysis, but the data in Table II reflect kinetic control.

TABLE II

EPOXIDE RING OPENINGS OF 5a,11a-EPOXYJANUSENE (**12**)

Reagent	X	Y	% **10**	% **11**[a]
HOAc–OAc$^-$	OH	OAc	75	25
HOAc	OH	OAc	75	25
MeOH	OH	OMe	25	75

[a] Product ratios were analyzed by pmr.

It is clear that both of these ring openings involve cationic intermediates **12**-OH and **13**-OH, and the data suggest that these are formed conjugate with an acetate ion in the acetic acid addition and with a methanol molecule in the reaction with methanol. It is not at all clear, with these assumptions, why so much **11** product is formed in the methanol case, as compared with the addition reactions to **2** in methanol, where the principal or sole products were **10** (see Table I).

Competition Reactions.—Inspection of molecular models of dehydrojanusene indicated that it might be an unreactive olefin for steric reasons. In order to obtain semiquantitative information with regard to the reactivity of **2**, we performed competitive addition reactions between **2** and 9,10-dihydro-9,10-ethenoanthracene (**9**). Olefin **9** was selected as a model which should have nearly the same characteristics of **2** with respect to bond strain but should not be sterically hindered. Also the chemistry of **9** was well understood. However, a complication was introduced in these comparisons, because **2** was tetrasubstituted but **9** was disubstituted. The results, which are summarized in Table III, indicate that dehydrojanusene (**2**) was more

TABLE III

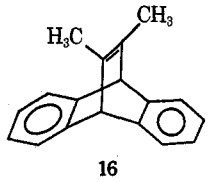
COMPETITIVE REACTIVITIES OF OLEFINS TOWARD ELECTROPHILIC REAGENTS

Substrates	Reagent	k_2/k_m[a]
2 and **9**	Br_2–CH_2Cl_2	1.5
2 and **9**	*m*-$ClC_6H_4CO_3H$	20
2 and **16**	*m*-$ClC_6H_4CO_3H$	0.05

[a] Product ratios were analyzed by pmr; k_m is the rate of the model compound.

reactive than model olefin **9**. This must be attributed to electronic effects. These results indicate only that the steric effects, if any, are not more important than the electronic effects in this system.

A competitive epoxidation between **2** and a tetrasubstituted model compound, 11,12-dimethyl-9,10-dihydro-9,10-ethenoanthracene (**16**), showed that there



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may be some steric hindrance to addition in **2**. Therefore, dehydrojanusene is a typical tetrasubstituted olefin that is only slightly deactivated due to steric hindrance.

(13) Structure **14** cannot represent the intermediate leading to products **11**, as both endo and exo epimers are formed, and we have therefore used it to represent a transition state.

(14) (a) J. D. Roberts and J. A. Yancey, *J. Amer. Chem. Soc.*, **77**, 5558 (1955); (b) H. C. Brown and C. J. Kim, *ibid.*, **90**, 2082 (1968); (c) H. L. Goering and K. Humski, *ibid.*, **90**, 6213 (1968). For examples of secondary systems, see (d) K. Takeuchi, T. Oshika, and Y. Koga, *Bull. Chem. Soc. Jap.*, **38**, 1318 (1965), and G. Fusco, Ph.D. Thesis, University of Colorado, 1965.

(15) For references, see S. J. Cristol and J. M. Sullivan, *J. Amer. Chem. Soc.*, **93**, 1967 (1971).

(16) A. Diaz, M. Brookhart, and S. Winstein, *ibid.*, **88**, 3133 (1966).

(17) Ring opening was not observed in methyl alcohol when sodium methoxide was present. It seems reasonable, therefore, to assume that the ring opening was catalyzed by adventitiously present acid.

Experimental Section

All proton magnetic resonance spectra were taken on a Varian A-60A instrument as saturated solutions in chloroform-d_1, using tetramethylsilane as an internal standard. All chemical shifts are reported in τ units (τ = 10.00 for tetramethylsilane). Infrared spectra were taken on a Beckman IR-5 spectrophotometer in either carbon tetrachloride or potassium bromide. All elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points were uncorrected. Structure assignments are given in the third paper of this group.

Preparation of Dehydrojanusene (2).—A solution of 9.9 g (18.3 mmol) of dibromide **6**[9] in 400 ml of DMSO was treated with 18 g of zinc which had been washed with 2% cupric sulfate solution until the blue color persisted. This mixture was stirred at 60° for 12 hr. It was filtered into 400 ml of water and the zinc residue was washed with 300 ml of CH_2Cl_2 and filtered. The precipitate in water was extracted with 300 ml of CH_2Cl_2 and this extract was combined with the filtrate from the zinc residue washings. The CH_2Cl_2 solution was washed seven times with 400-ml portions of water and dried ($MgSO_4$). The mixture was filtered and the solvent evaporated, yielding 6.17 g (89%) of dehydrojanusene (**2**). Recrystallization was from CH_2Cl_2–CCl_4: mp 360–361° dec; ν_{max} 1470, 1450, 1232, 1173, 1148, 1022, 926, 783, 749, 729, 637 cm^{-1} (KBr); pmr ($CDCl_3$) τ 4.84 (s, 4), 3.05 (m, 16, aromatics).

Anal. Calcd for $C_{30}H_{20}$: C, 94.70; H, 5.30. Found: C, 94.73; H, 5.21.

Addition of Acetic Acid to Dehydrojanusene (2).—To a solution of 82 mg (1.00 mmol) of sodium acetate in 40 ml of acetic acid was added 52 mg (0.14 mmol) of **2**. The heterogeneous mixture was stirred and heated at 100° for 15.5 hr, during which time **2** went into solution. The chilled mixture was poured into 100 ml of water and extracted with 150 ml of ether. The ether extract was washed five times with 150-ml portions of water and once with 100 ml of saturated NaCl solution. The ether solution was dried ($MgSO_4$) and filtered and the solvent evaporated under reduced pressure, yielding 60 mg (95%) of 5a-acetoxyjanusene (**7-OAc**): mp (after recrystallization from methanol) 236–237°; pmr ($CDCl_3$) τ 8.52 (s, 3, OAc), 7.58 (t, 1, J = 2.5 Hz), 5.74 (d, 2, J = 2.5 Hz), 4.59 (s, 2), 2.80–3.40 (m, 16, aromatics).

Anal. Calcd for $C_{32}H_{24}O_2$: C, 87.27; H, 5.45. Found: C, 87.14; H, 5.43.

Addition of Chlorine to 2.—To a solution of 312 mg (0.82 mmol) of **2** in 50 ml of CH_2Cl_2 at −78° was added 3 mmol of chlorine. The solvent was evaporated under reduced pressure at 0°, giving 348 mg (94%) of a colorless oil. The pmr spectrum of this oil identified it as a mixture of 20% 5a,11a-dichlorojanusene (**10a**) and 80% 5a,12-dichlorohemiisojanusene (**11a**). Attempts to fractionally crystallize **11a** in CCl_4 only caused it to rearrange to dichloride **10a**. Crystalline **11a** was never obtained and **11a** could not be isolated in absence of **10a**. Therefore, an elemental analysis of **11a** was not obtained. Crystallization of dichloride **10a** was from acetone–95% EtOH: mp 294–295° dec; pmr ($CDCl_3$) of **10a** τ 5.35 (s, 4), 2.90–3.30 (m, 16, aromatics).

Anal. Calcd for $C_{30}H_{20}Cl_2$: C, 79.82; H, 4.43. Found: C, 79.62; H, 4.58.

The pmr ($CDCl_3$) of **11a** showed τ 4.33 and 4.44 (s, 1), 4.89 and 5.01 (s, 1), 5.35 (s, 1), 5.58 (s, 1), 2.37–3.40 (m, 16, aromatics). Small absorptions at τ 4.44 and 4.89 were attributed to an epimer.

Reaction of *tert*-Butyl Hypochlorite in Acetic Acid with 2.—To a mixture of 1.00 g (2.63 mmol) of **2** and 390 mg (4.74 mmol) of sodium acetate in 60 ml of acetic acid was added 0.30 ml (2.7 mmol) of *tert*-butyl hypochlorite. The addition was performed over a 30-min period, and the reaction was stirred at room temperature in the dark for 2 hr. The small amount of unreacted olefin **2** which was still present was filtered, and the filtrate was dissolved in 200 ml of ether. The ether solution was washed five times with 200-ml portions of water and once with 200 ml of saturated NaCl solution. The solution was dried ($MgSO_4$) and filtered and the solvent evaporated under reduced pressure, yielding 1.17 g (94%) of acetoxy chlorides **10b** and **11b**, respectively. The two acetoxy chlorides were separated by fractional crystallization from benzene–heptane.

5a-Chloro-11a-acetoxyjanusene (**10b**) was recrystallized from benzene–heptane: mp 270–272°; pmr ($CDCl_3$) τ 8.34 (s, 3, OAc), 5.36 (s, 2), 4.49 (s, 2), 2.94–3.33 (m, 16, aromatics).

Anal. Calcd for $C_{32}H_{23}O_2Cl$: C, 80.93; H, 4.85. Found: C, 80.85; H, 4.96.

Recrystallization of 5a-chloro-12-acetoxyhemiisojanusene (**11b**) was also from benzene–heptane, mp 227–230°. This compound resolidified at about 235° and then melted with decomposition at 285°. It is believed that **11b** rearranged to another acetoxy chloride upon melting: pmr ($CDCl_3$) τ 7.96 (s, 3, OAc), 5.57 (s, 1), 5.35 (s, 1), 4.97 (s, 1), 3.48 (s, 1) 2.95 (m, 16, aromatics).

Anal. Calcd for $C_{32}H_{23}O_2Cl$: C, 80.93; H, 4.85. Found: C, 80.69; H, 4.94.

Reaction of *tert*-Butyl Hypochlorite in Methanol with 2.—To a mixture of 71 mg (0.19 mmol) of **2** in 9 ml of methanol was added 3.3 ml of 0.09 *M* *tert*-butyl hypochlorite in methyl alcohol. The mixture was stirred at gentle reflux for 13 hr in the dark and then cooled for 2 hr. The unreacted olefin **2** was filtered and the filtrate dissolved in 80 ml of ether. The ether solution was worked up as described previously and yielded 34 mg of an oil which was identified by pmr as 60% 5a-chloro-11a-methoxyjanusene (**10c**) and 40% 5a-chloro-12-methoxyhemiisojanusene (**11c**). Chloromethyl ether **11c** could not be isolated pure, but **10c** was separated *via* thin layer chromatography and was crystallized from benzene–heptane: mp 300–303° dec; pmr ($CDCl_3$) of **10c** τ 6.56 (s, 3, OMe), 5.38 (s, 2), 5.31 (s, 2), 2.97–3.33 (m, 16, aromatics).

Anal. Calcd for $C_{31}H_{23}OCl$: C, 83.31; H, 5.15. Found: C, 83.19; H, 5.23.

The pmr ($CDCl_3$) of **11c** showed τ 6.07 (s, 3, OMe), 5.64 (s, 1), 5.36 (s, 1), 5.27 (s, 1), 5.06 (s, 1), 2.95 (m, 16, aromatics).

Reaction of *N*-Chlorosuccinimide in Methanol with 2.—A mixture of 62 mg (0.16 mmol) of **2** and 30 mg (0.22 mmol) of NCS was diluted with 35 ml of methanol and stirred at gentle reflux for 5 hr. Work-up gave 60 mg (85%) of a 3:2 mixture of chloromethyl ethers **10c** and **11c**, respectively.

Reaction of *N*-Bromosuccinimide in Acetic Acid with 2.—A mixture of 326 mg (0.86 mmol) of **2**, 376 mg (4.58 mmol) of sodium acetate, and 182 mg (1.02 mmol) of NBS was partially dissolved in 45 ml of acetic acid. This mixture was stirred in the dark at room temperature for 30 hr. The reaction mixture was poured into 100 ml of ether and washed five times with 150-ml portions of water. The ether solution was dried ($MgSO_4$) and filtered, and the solvent evaporated under reduced pressure yielding 378 mg (85%) of a 85:15 mixture of 5a-bromo-11a-acetoxyjanusene (**10d**) and 5a-bromo-12-acetoxyhemiisojanusene (**11d**), respectively. Acetoxy bromide **11d** could not be isolated pure. Acetoxy bromide **10d** was crystallized from benzene–heptane: mp 259–260.5°; pmr ($CDCl_3$) τ 8.32 (s, 3, OAc), 5.13 (s, 2), 4.52 (s, 2), 2.94–3.28 (m, 16, aromatics).

Anal. Calcd for $C_{32}H_{23}O_2Br$: C, 73.99; H, 4.43. Found: C, 73.87; H, 4.43.

The pmr ($CDCl_3$) of **11d** showed τ 7.97 (s, 3, OAc), 5.45 (s, 1), 5.17 (s, 1), 4.97 (s, 1), 2.95 (m, 16, aromatics).

Reaction of *N*-Bromosuccinimide in Methanol with 2.—A mixture of 62 mg (0.16 mmol) of **2** and 40 mg (0.22 mmol) of NBS, diluted in 40 ml of methanol, was stirred at room temperature in the dark for 6.5 hr. The mixture was worked up as described previously, yielding 80 mg (100%) of 5a-bromo-11a-methoxyjanusene (**10e**) and no **11e**. Crystallization of **10e** was from benzene–heptane: mp 284–285° dec; pmr ($CDCl_3$) τ 6.53 (s, 3, OMe), 5.31 (s, 2), 5.17 (s, 2), 2.95–3.35 (m, 16, aromatics).

Anal. Calcd for $C_{31}H_{23}OBr$: C, 75.76; H, 4.68. Found: C, 75.63; H, 4.71.

Preparation of 5a,11a-Epoxyjanusene (15).—To a solution of 603 mg (1.59 mmol) of **2** in 30 ml of CH_2Cl_2 was added 341 mg (1.59 mmol) of 85% pure *m*-chloroperbenzoic acid dissolved in 25 ml of CH_2Cl_2. This mixture was stirred in the dark at room temperature for 65 hr. The reaction was worked up by washing twice with ferrous ammonium sulfate solution, twice with 10% Na_2CO_3 solution, and twice with 150-ml portions of water. The mixture was dried ($MgSO_4$) and filtered, and the solvent evaporated under reduced pressure yielding 452 mg (72%) of 5a,11a-epoxyjanusene (**15**). Crystallization of **15** was from benzene–heptane: mp 283–285° dec; pmr ($CDCl_3$) τ 5.32 (s, 4), 3.35 (m, 4, aromatics), 2.96 (m, 12, aromatics).

Anal. Calcd for $C_{30}H_{20}O$: C, 90.91; H, 5.05. Found: C, 90.82; H, 4.98.

Reaction of 5a,11a-Epoxyjanusene (15) with Sodium Acetate and Acetic Acid.—A mixture of 78 mg (0.20 mmol) of **15** and 88 mg (1.07 mmol) of sodium acetate in 15 ml of acetic acid was stirred at room temperature for 34 hr and then poured into 100

ml of water. The precipitate was extracted with 100 ml of ether which was then washed six times with 150-ml portions of water and once with 100 ml of saturated NaCl solution. The mixture was dried ($MgSO_4$) and filtered and the solvent evaporated under reduced pressure yielding 76 mg of an oil, which was identified by pmr as 15% unreacted **15**, 64% 5a-hydroxy-11a-acetoxyjanusene (**10f**), and 21% 5a-hydroxy-12-acetoxyhemiisojanusene (**11f**). The hydroxyacetates were in a ratio of 3:1, respectively.

Compound **10f** was crystallized from MeOH: mp 280–284°; pmr ($CDCl_3$) τ 8.38 (s, 3, OAc), 5.56 (s, 2), 4.53 (s, 2), 2.96–3.31 (m, 16, aromatics).

Anal. Calcd for $C_{32}H_{24}O_3$: C, 84.21; H, 5.26. Found: C, 84.09; H, 5.34.

Compound **11f** was prepared by another route which will be reported later.[18]

Reaction of 5a,11a-Epoxyjanusene (15) with Acetic Acid.—A solution of 64 mg (0.16 mmol) of **15** in 10 ml of acetic acid was stirred at room temperature for 19 hr. The mixture was then worked up as described above. The pmr spectrum of the mixture showed 22% unreacted epoxide **15**, 56% hydroxyacetate **10f** and 22% hydroxyacetate **11f**. The last two compounds were in a ratio of 3:1, respectively.

Reaction of 5a,11a-Epoxyjanusene (15) with Methanol.—A solution of 60 mg (0.15 mmol) of **15** in 15 ml of "spectro-grade" methanol was stirred at gentle reflux for 18 hr. The solvent was then evaporated under reduced pressure yielding 62 mg (100%) of a mixture of 25% 5a-hydroxy-11a-methoxyjanusene (**10g**) and 75% 5a-hydroxy-12-methoxyhemiisojanusene (**11g**). These two compounds were separated by fractional crystallization from benzene–heptane.

From benzene–heptane **10g** was crystallized: mp 325–327° dec; pmr ($CDCl_3$) τ 6.65 (s, 3, OMe), 5.57 (s, 2), 5.34 (s, 2), 2.95–3.35 (m, 16, aromatics).

Anal. Calcd for $C_{31}H_{24}O_2$: C, 86.92; H, 5.61. Found: C, 86.81; H, 5.67.

From benzene–heptane **11g** was also recrystallized: mp 257.5–259°; pmr ($CDCl_3$) τ 6.26 (s, 3, OMe), 5.76 (s, 1), 5.41 (s, 1), 5.26 (s, 1), 5.10 (s, 1), 2.9 (m, 16, aromatics).

Anal. Calcd for $C_{31}H_{24}O_2$: C, 86.92; H, 5.61. Found: C, 86.70; H, 5.79.

Reaction of 5a,11a-Epoxyjanusene (15) with Sodium Methoxide and Methanol.—A mixture of 58 mg (0.15 mmol) of **15** in 15 ml of 0.5 *M* sodium methoxide in methanol solution was stirred at reflux for 17 hr. The mixture was then poured into ether and worked up as previously described. The isolated material was identified by its pmr spectrum as 5a,11a-epoxyjanusene (**15**). This was the only product detected.

Competitive Addition of Bromine to 9,10-Dihydro-9,10-ethenoanthracene (9) and 2.—A mixture of 435 mg (2.13 mmol) of **9** and 199 mg (0.53 mmol) of **2** was dissolved in 50 ml of CH_2Cl_2. To this solution was added 3 ml of 0.18 *M* bromine–methylene chloride solution, and, although the reaction mixture became colorless immediately, it was stirred for a few hours. The solvent was then evaporated under reduced pressure and a pmr spectrum of the mixture indicated a 3:1 mixture of 4-*syn*-8-dibromodibenzobicyclo[3.2.1]octadiene[19] and 5a,11a-dibromojanusene (**6**), respectively. **6** is relatively insoluble, and the difficulty of obtaining a homogeneous pmr sample suggests that this ratio of yields of products was lower than 3.

Competitive Epoxidation of 9,10-Dihydro-9,10-ethenoanthracene (9) and Dehydrojanusene (2).—A mixture of 80 mg (0.39 mmol) of **9** and 150 mg (0.39 mmol) of **2** was dissolved in 35 ml of CH_2Cl_2. To this solution was added 44 mg (0.22 mmol) of 85% pure *m*-chloroperbenzoic acid in 10 ml of CH_2Cl_2. The reaction was stirred at room temperature in the dark for 75 hr. The reaction mixture was worked up by simply evaporating the solvent under reduced pressure. The heterogeneous pmr sample of the product mixture showed only unreacted **9**, epoxide **15**, and a trace of *m*-chlorobenzoic acid. The product from epoxidation of **9**[20] was not detected in the pmr sample. It would surely have been soluble in $CDCl_3$ and therefore detected. If it is assumed that the pmr method of analysis was good to 5%, the rate of epoxidation of **2** must be at least 20 times that of **9**.

Competitive Epoxidation of 11,12-Dimethyl-9,10-dihydro-9,10-ethenoanthracene (16)[21] and Dehydrojanusene (2).—A mixture of 120 mg (0.52 mmol) of **16**, 198 mg (0.52 mmol) of **2**, and 12 mg (0.07 mmol) of *p*-dinitrobenzene (internal standard) was dissolved in 30 ml of CH_2Cl_2. To this solution was added 53 mg (0.26 mmol) of 85% pure *m*-chloroperbenzoic acid in 10 ml of CH_2Cl_2. The reaction mixture was stirred in the dark at room temperature for 61 hr, after which it was worked up as described above. The pmr spectrum of the heterogeneous sample (dehydrojanusene was insoluble) showed unreacted olefin **16**, 11,12-epoxy-11,12-dimethyl-9,10-dihydro-9,10-ethanoanthracene, and a trace of epoxide **15**. The presence of epoxide **15** was confirmed by developing a sample of the product mixture on a thin layer plate with 5% ether–benzene. It was assumed that the trace of epoxide represented 5% of the product.

Registry No.—**2**, 29309-28-2; **7**-OAc, 29309-29-3; **10a**, 29309-30-6; **10b**, 29309-31-7; **10c**, 29308-18-7; **10d**, 29308-17-6; **10e**, 29309-34-0; **10f**, 29308-22-3; **10g**, 29308-21-2; **11a**, 29309-37-3; **11b**, 29308-24-5; **11c**, 29308-25-6; **11d**, 29308-30-3; **11g**, 29308-26-7; **15**, 29308-23-4.

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(21) The chemistry of **16** and related systems will be reported later by Hans Mueller.