# Bridged Polycyclic Compounds. LXVII. Carbonium Ion Rearrangements among Janusene, Hemiisojanusene, and Isojanusene Derivatives[1]

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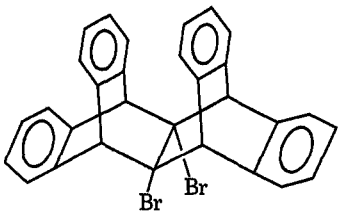
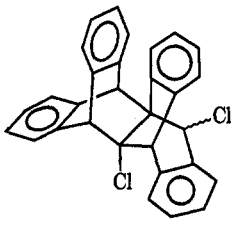
Carbonium ion rearrangements accompanying solvolysis were studied among janusene, hemiisojanusene, and *cis*- and *trans*-isojanusene compounds, using methods of kinetic and thermodynamic control. Plausible reaction schemes for these interconversions are discussed.

In the course of our work on the chemistry of janusene[2] and its derivatives and relatives,[1] we decided to look at carbonium ion rearrangements of the individual bicyclic systems. The availability of 5a,11a-dibromojanusene (**1**)[3,4] and of 5a,12-dichlorohemiisojanusene (**2**)[1,4] made entrée into this problem *via* silver-assisted solvolyses simple, even though the high reactivity of both halogen atoms in each compound made it impossible to do selective monoacetolyses.




**1**

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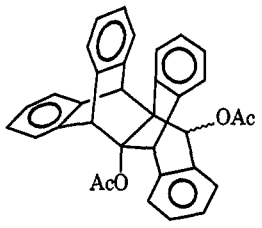
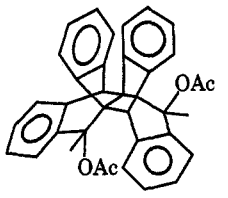


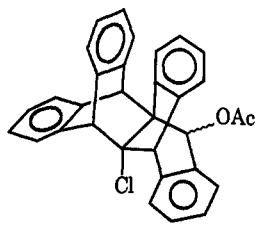

**3**



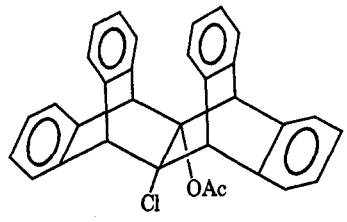

**4**

Treatment of dibromide **1** with 2 equiv of silver acetate gave an 85:15 ratio of diacetates **3** and **4**, respectively. On the other hand, dichloride **2** reacted with 2 equiv of silver acetate to give a 30:70 ratio of diacetates **3** and **4**, respectively. Although the intermediate acetoxy chlorides could not be obtained readily by treating dichloride **2** with 1 equiv of silver acetate, they were readily prepared by treating dehydrojanusene with *tert*-butyl hypochlorite in acetic acid.[1] This gave a 65:35 ratio of 5a-chloro-12-acetoxyhemiisojanusene (**5**) and 5a-chloro-11a-acetoxyjanusene (**6**), respectively. These acetoxy chlorides could be separated by fractional crystallization.

Acetoxy chloride **5**, which was a 4:1 mixture of epimers, rearranged readily in 0.1 *M* perchloric–acetic acid at room temperature in 1 hr to acetoxy chloride **6**. During the rearrangement the epimer composition of **5** did not change. Acetoxy chloride **6** was quite



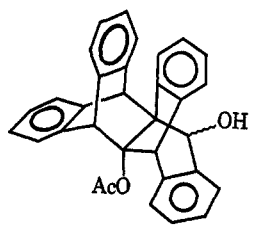

**5**



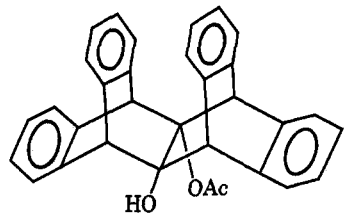

**6**

stable. Even 1.1 *M* sulfuric acid in methanol at reflux for 142 hr gave only unreacted starting material.

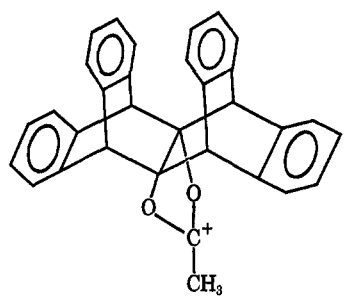
Silver-assisted acetolysis of 5a-chloro-11a-acetoxyjanusene (**6**) gave only 5a,12-diacetoxyhemiisojanusene (**3**). This same reaction in wet acetic acid gave diacetate **3** along with 5a-acetoxy-12-hydroxyhemiisojanusene (**7**). The absence of hydroxyacetate **8** from this last experiment excluded acetoxonium ion **9** as an




**7**




**8**




**9**

intermediate in this solvolysis.[5,6] Similar treatment of 5a-bromo-11a-acetoxyjanusene (**10**)[1] gave identical results.

These results are interpreted in Scheme I. Ions **11** and **12** are analogous to those observed in the electrophilic additions to dehydrojanusene.[1] A phenonium ion could be introduced into this scheme,[7] but at present we have no direct evidence for it as a product-forming intermediate. Cis-disubstituted products (re-

(1) Previous paper: LXVI. S. J. Cristol and M. A. Imhoff, *J. Org. Chem.*, **36**, 1849 (1971).

(2) S. J. Cristol and D. C. Lewis, *J. Amer. Chem. Soc.*, **89**, 1476 (1967).

(3) S. J. Cristol, M. A. Imhoff, and D. C. Lewis, *J. Org. Chem.*, **35**, 1722 (1970).

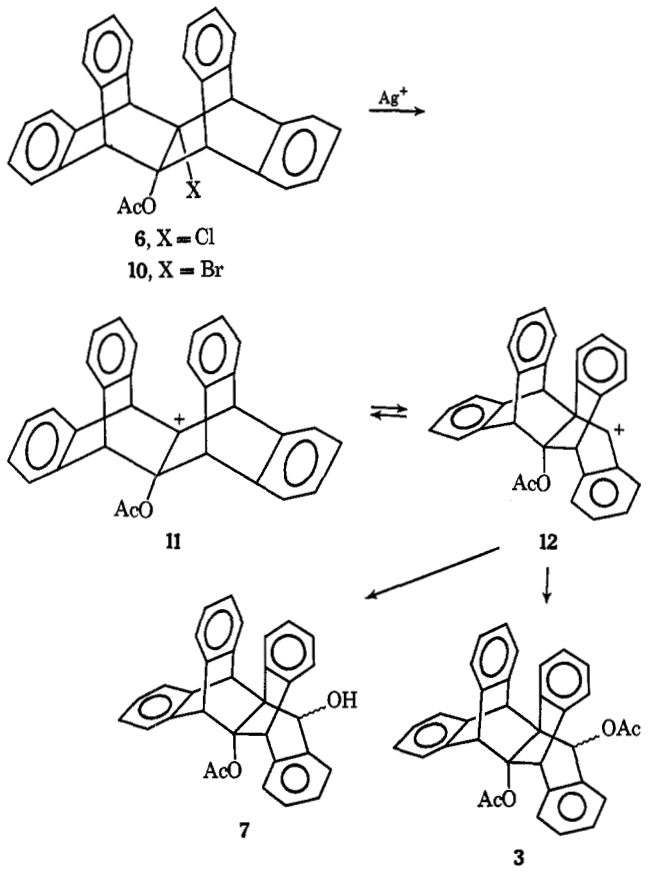
(4) The naming of compounds in this paper follows the procedure described in the previous paper (ref 1).

(5) S. J. Cristol, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *J. Amer. Chem. Soc.*, **87**, 2879 (1965).

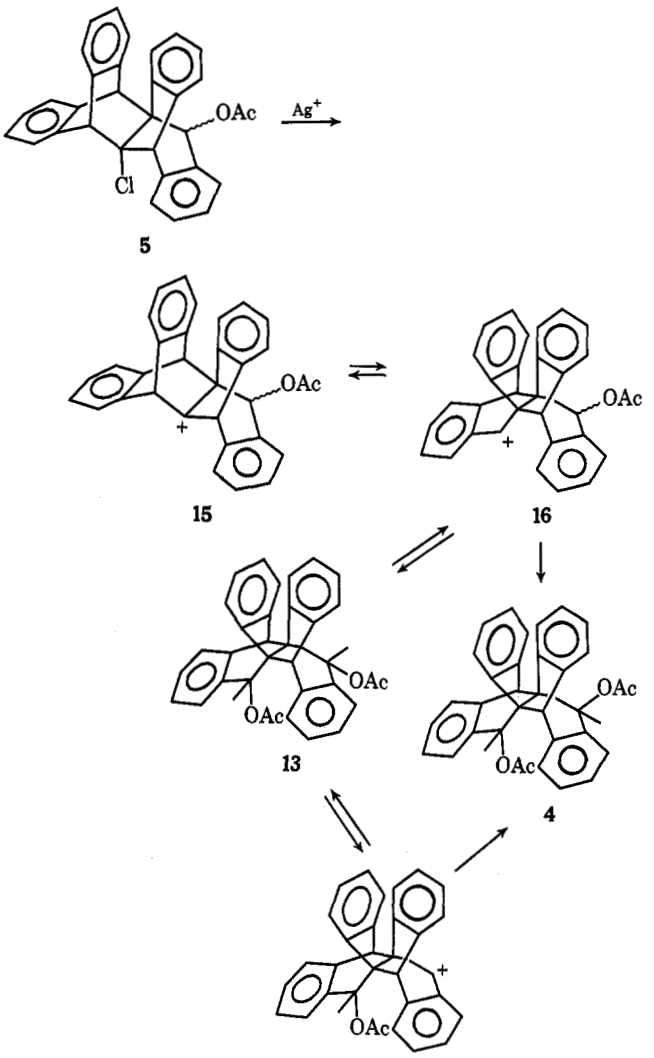
(6) R. M. Roberts, J. Corse, R. Boschan, D. Seymour, and S. Winstein, *ibid.*, **80**, 1247 (1958).

(7) Such an ion must obviously intervene in the rearrangement of **11** ⇄ **12**.

SCHEME I

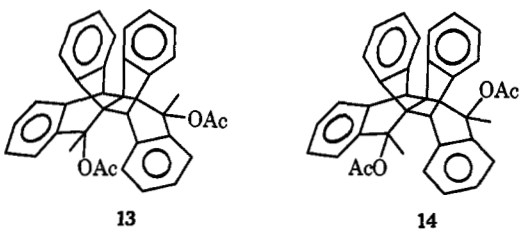



SCHEME II




sulting from intermediate **11**) were not formed (within the limits of our analysis), although such products are formed in many addition reactions. A possible explanation for the absence of products from intermediate **11** is that rotation of the acetoxy group hinders attack by nucleophiles at C-11a. In other words, the "windshield wiper" effect of this substituent sweeps away nucleophiles from the reactive site. Thus, the intermediates are trapped as diacetate **3** or hydroxyacetate **7**, which were shown to be stable to the reaction conditions. These results revealed the source of diacetate **3** in the initial solvolyses as acetoxy halides **6** and **10**.

Treatment of 5a-chloro-12-acetoxyhemiisojanusene (**5**), which was a 1:4 epimeric mixture, with silver acetate in acetic acid for 2 min (75% reaction) gave a 1:4 mixture of *exo*-6,*exo*-12-diacetoxy-*cis*-isojanusene (**13**) and *exo*-6,*endo*-12-diacetoxy-*cis*-isojanusene (**4**),




**13** **14**

respectively. After being allowed to stand in acetic acid for 30 min, **13** epimerized to **4**. Diacetate **4** was shown to be stable to the reaction conditions and did not epimerize to the corresponding "diendo" compound **14**. This latter diacetate was observed in subsequent reactions and will be discussed later. These results can be most simply explained in terms of exo attack on ion **16** (Scheme II). The dominant epimer of acetoxy chloride **5** would thus appear to be the endo one since the ratio of epimers was constant during its acid-catalyzed rearrangement to **6** and because **4** is assumed to be a kinetic product along with **13**. There is no evidence in these results for or against the existence of ion **15** since it was not trapped (diacetate **3** would have been stable to the reaction conditions), and it is conceivable that **5** ionized with simultaneous anti migration to give intermediate **16**. However, the existence of intermediate **15** will be demonstrated later under different reaction conditions. An analogous set of reactions was not performed on the corresponding acetoxy bromide, as it was not available in a pure state.

We can now interpret our initial observations from the silver-assisted acetolyses of dibromide **1** and dichloride **2** (Scheme III). These compounds ionize to give a mixture of ions **17** and **18**, which are identical with the ones formed in the electrophilic addition reactions.[1] These first-formed cations are trapped to give the intermediate acetoxy halides in a ratio identical with that of addition.[1] These intermediate compounds then react with a second equivalent of silver acetate to give either 5a,12-diacetoxyhemiisojanusene (**3**) or 6,12-diacetoxy-*cis*-isojanusenes **4** and **13**.

**Acid-Catalyzed Rearrangements.**—Treatment of 5a,-12-diacetoxyhemiisojanusene (**3**) with perchloric–acetic

SCHEME III

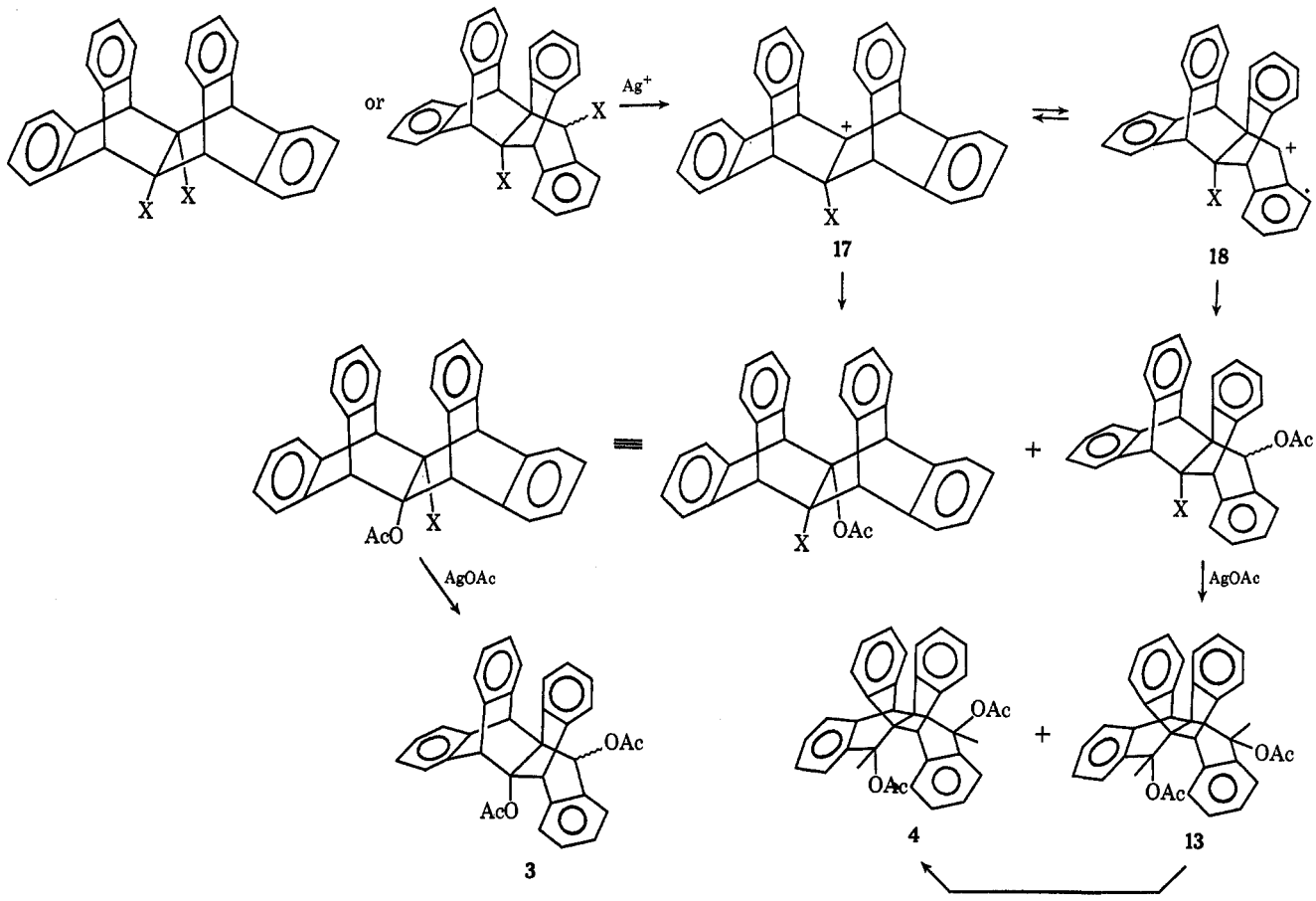


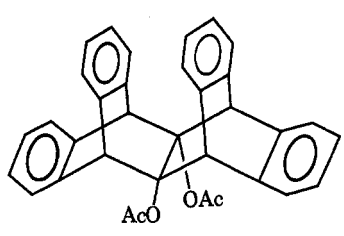

TABLE I

ACID-CATALYZED REARRANGEMENT OF 5a,12-DIACETOXYHEMIISOJANUSENE (3)[a]

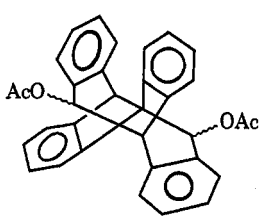
| 3, mmol | [HClO4], M | H+, mmol | Temp, °C | Time, hr | % redn | % 19 | % 20 | % 8 | 8, mmol |
|---|---|---|---|---|---|---|---|---|---|
| 0.10 | $10^{-3}$ | 0.010 | 90 | 2.5 | 100 | 80 | 14 | 6 | 0.006 |
| 0.09 | $10^{-3}$ | 0.014 | 95 | 19 | 100 | 77 | 16 | 7 | 0.006 |
| 0.10 | $10^{-3}$ | 0.017 | 95 | 144 | 100 | 57 | 29 | 14 | 0.014 |
| 0.09 | $10^{-3}$ | 0.080 | 90 | 23 | 100 | 5 | 27 | 68 | 0.061 |
| 0.13 | $10^{-2}$ | 0.12 | 25 | 33 | 50 | 78 | 22 | | |
| 0.2 | $10^{-2}$ | 0.12 | 75 | 0.25 | 100 | 80 | 20 | | |
| 0.37 | $10^{-2}$ | 0.10 | 105 | 0.25 | 100 | 51 | 23 | 26 | 0.096 |
| 0.1 | $10^{-2}$ | 0.12 | 80 | 4.0 | 100 | | 33 | 66 | 0.07 |

[a] Product analysis was by pmr.

acid solutions under various reaction conditions gave mixtures of 5a,11a-diacetoxyjanusene (**19**), 6,12-di-




**19**



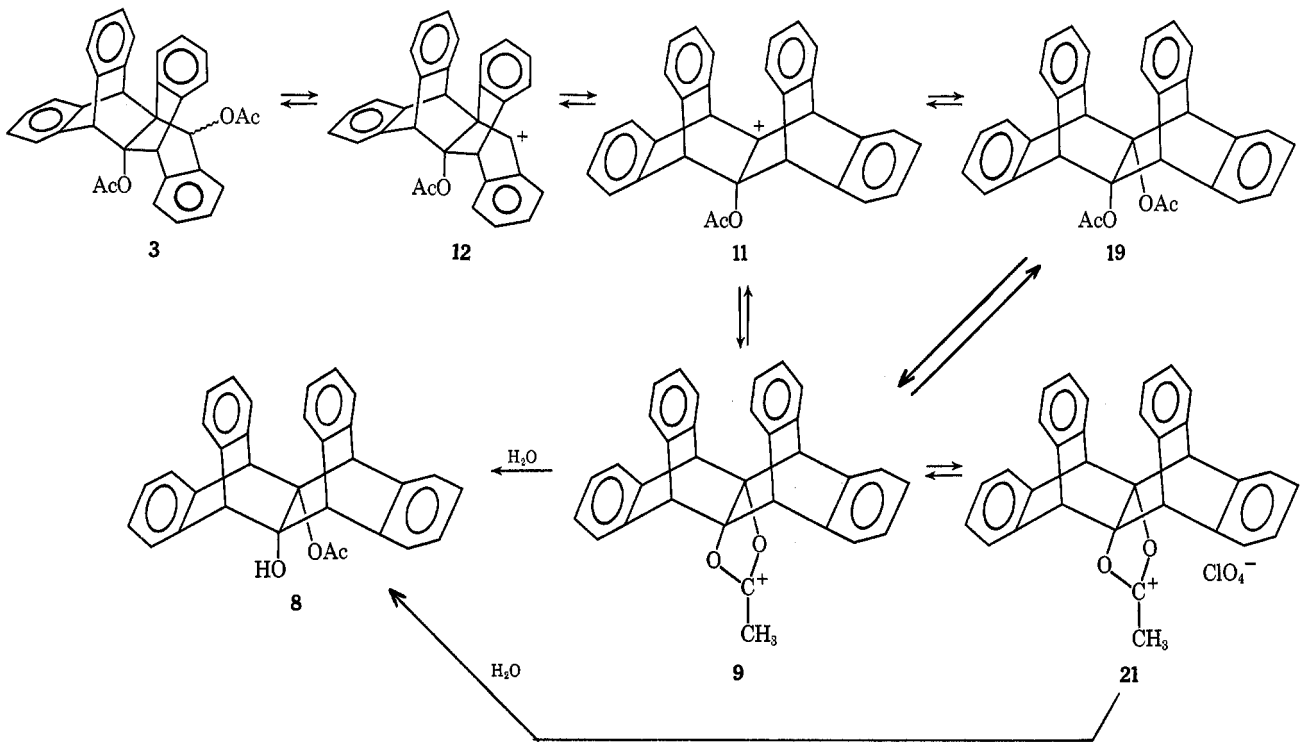

**20**

acetoxy-*trans*-isojanusene (**20**), and 5a-hydroxy-11a-acetoxyjanusene (**8**) of varying composition. The results are summarized in Table I.

Some immediate observations can be made from the data in Table I. The amount of hydroxyacetate **8** produced in these reactions never exceeded the initial amount of perchloric acid, regardless of the reaction conditions. The amount of **8** also appeared to depend upon reaction time and temperature. Under conditions in which 50% rearrangement occurred, no hydroxyacetate **8** was formed, although the amount of perchloric acid present was equal to the millimoles of starting diacetate **3**. The data also indicated that hydroxyacetate **8** was formed at the expense of diacetate **19**. Finally, when the amount of perchloric acid was about equal to the starting material, diacetate **3**, more diacetate **20** was formed than in examples of less acid, although the initial concentration of acid was the same in both cases.

A mechanistic pathway for the rearrangement of **3** to **19** is described in Scheme IV. Analogous to the solvolysis of 5a-chloro-11a-acetoxyjanusene (**5**), ionization of diacetate **3** gives a mixture of ions **11** and **12**. Cation **11** is trapped rapidly as diacetate **19** or more

SCHEME IV




slowly as acetoxonium ion **9**. This latter ion may then react with acetic acid under acidic conditions to give diacetate **19**,[8] or it can pair with perchlorate ion to form **21**. It is the formation of this salt which explains many of the observations from the data in Table I. Upon aqueous work-up, this salt gives hydroxyacetate **8**,[5] and therefore the amount of **8** cannot exceed the amount of perchloric acid. This salt also serves to tie up perchloric acid so that the effective acid concentration becomes substantially less than the initial concentration. Because of this, the amount of diacetate **20** formed also depends upon the amount rather than the concentration of perchloric acid. In other words, the rearrangement of **19** to **20** appears to stop prematurely, because the effective concentration of perchloric acid is reduced severely.

To this point the discussion has been concerned with the rearrangement of 5a,12-diacetoxyhemiisojanusene (**3**) to the janusene derivatives. The rearrangement of diacetate **3** in the other direction to give an epimeric mixture of 6,12-diacetoxy-*trans*-isojanusenes (**20**) was also examined. This latter reaction was demonstrated to proceed first through *exo*-6,*endo*-12-diacetoxy-*cis*-isojanusene (**4**).

Since diacetate **4** was a kinetic product from the silver-assisted solvolysis of acetoxy chloride **5**, one would expect that this diacetate should be first formed from the ionization of the acetoxy group at C-5a in **3**. When diacetate **4** was treated with perchloric–acetic acid, it rearranged quickly to the *trans*-isojanusene isomer **20**. However, closer examination of this rearrangement by pmr indicated that *endo*-6,*endo*-12-diacetoxy-*cis*-isojanusene (**14**) was formed as an intermediate.

Diacetate **4** was heated at 65° in 0.4 ml of 0.0025 *M* $HClO_4$–HOAc in a sealed nmr tube. From the data in Table II, the half-life for the disappearance of diacetate **4** was calculated to be about 20 min, and the half-life for the disappearance of **14** was about 325 min. Diacetate **4** rearranged to its epimer **14** and to the *trans*-isojanusene compounds **20** at about the same rate. Then diacetate **14** rearranged more slowly to diacetate **20**. The isomeric mixture of **20** consisted of three epimers as detected by pmr and thin layer chromatography (85% was believed to be the "diendo" compound), and their relative ratios remained constant over the reaction time (Scheme V).

TABLE II

ACID-CATALYZED REARRANGEMENT OF *exo*-6,*endo*-12-DIACETOXY-*cis*-ISOJANUSENE (**4**) AT 65°[a]

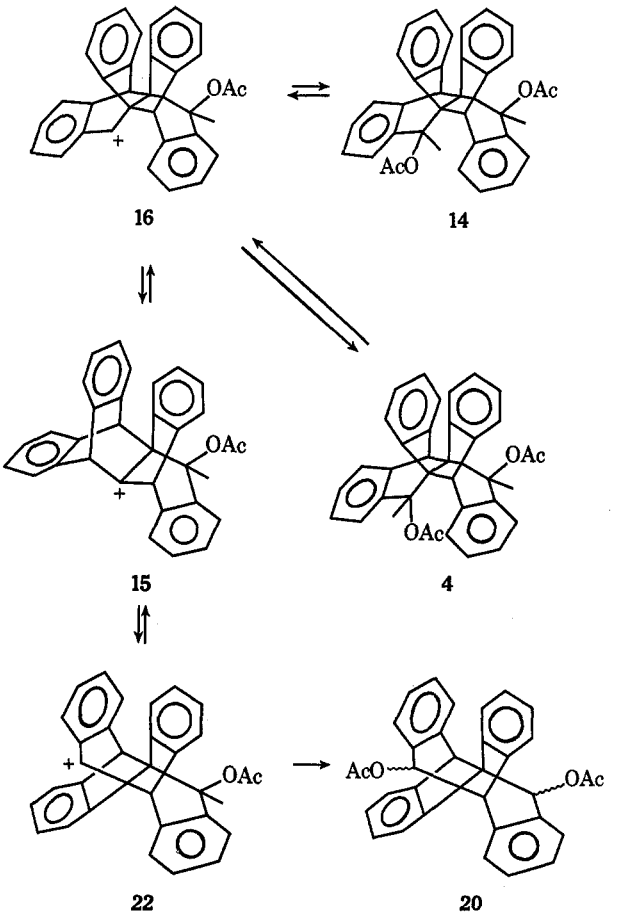
| Time, min | % 4 | % 14 | % 20 |
|---|---|---|---|
| 5 | 100 | Trace | Trace |
| 20 | 57 | 20 | 23 |
| 35 | 26 | 37 | 37 |
| 55 | 20 | 40 | 40 |
| 80 | Trace | 50 | 50 |
| 120 | | 50 | 50 |
| 195 | | 43 | 57 |
| 315 | | 33 | 67 |
| 815 | | 11 | 88 |
| 1115 | | Trace | 95 |
| 2275 | | | 100 |
| 5075 | | | 100 |

[a] Product analysis by pmr.

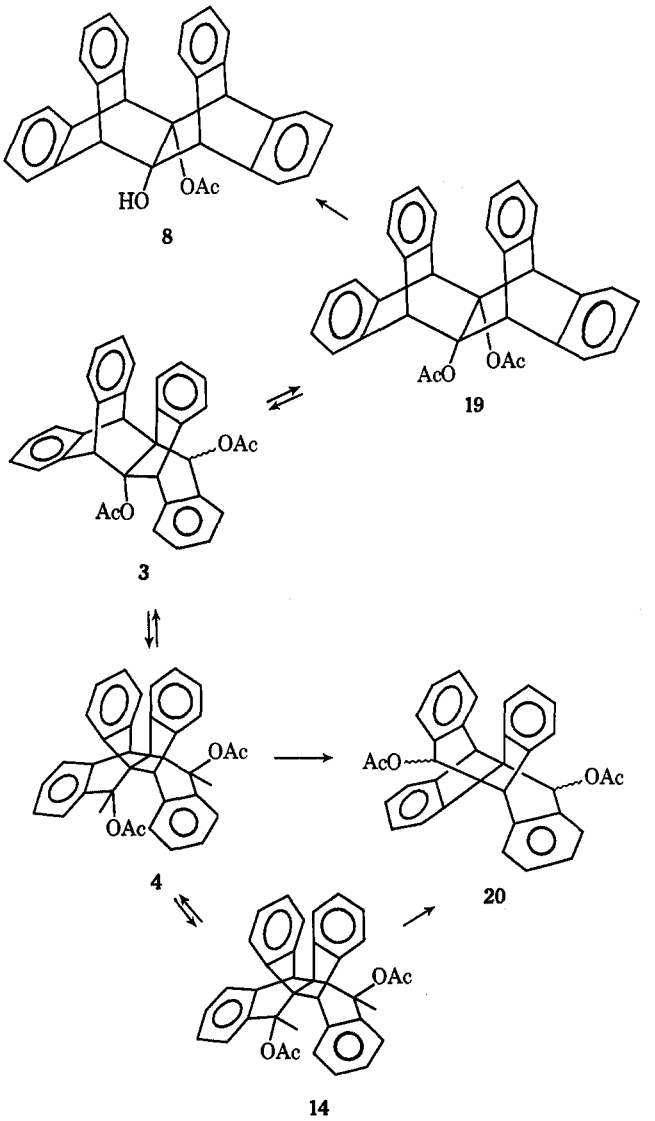
Because diacetate **4** rearranged much faster than diacetate **14**, one can conclude tentatively that the exo substituent ionized faster than the endo one. This is consistent with the preference for exo attack in the *cis*-isojanusene system as described previously. Also, the ground state energy is higher for **4** than for **14**, and therefore the former should be more reactive. Although the presence of ion **15** was uncertain in the silver-assisted solvolysis of acetoxy chloride **5**, its ex-

(8) S. Winstein and R. E. Buckles, *J. Amer. Chem. Soc.*, **65**, 613 (1943).

SCHEME V

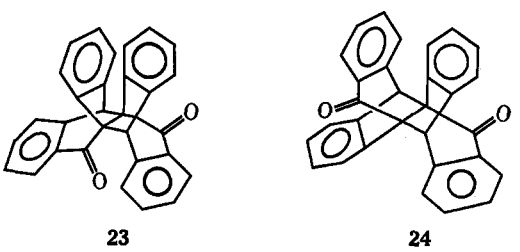



SCHEME VI




istence is necessary to explain the rearrangement of **4** to **20**.

The carbon skeletons of **4** and **20** were shown to be different when they were individually converted to different diketones **23** and **24**. One of the ketones was shown by X-ray crystallography to be a meso compound,[9] and thus had structure **24** (**23** is chiral); since



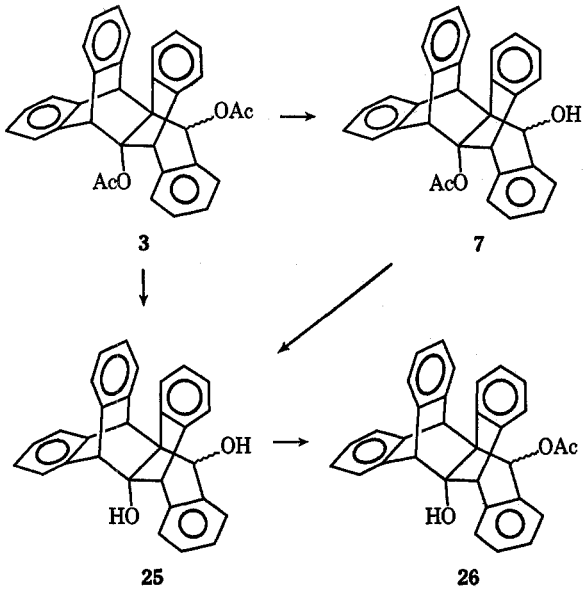

the achiral ketone was formed from the thermodynamically stable diacetate, diacetate **20** was assigned the *trans*-isojanusene structure. Diacetates **14** and **4** were shown to be epimers, because both gave the same diketone **23**.

The rearrangement of 5a,12-diacetoxyhemiisojanusene (**3**) is summarized in Scheme VI. Diacetate **3** rearranges to 5a,11a-diacetoxyjanusene (**19**) and *exo*-6,-*endo*-12-diacetoxy-*cis*-isojanusene (**4**) at a relative rate of 3:1, respectively. Diacetate **4** then quickly epimerizes to the endo,endo diacetate **14** or rearranges to 6,12-diacetoxy-*trans*-isojanusene (**20**). At a slightly slower rate diacetate **14** also rearranges to **20**. At the other end, diacetate **19** slowly rearranges back through diacetate **3** to the isojanusene systems and also is trapped as perchlorate salt **21**, which reacts with water to give hydroxyacetate **8**.

**Preparation of Derivatives.**—During the course of this work several of the compounds observed were prepared by other routes along with derivatives of some of these compounds. These reactions also revealed some of the structural features of janusene and its skeletal isomers. Diacetate **3** was converted into the corresponding diol **25** with lithium aluminum hydride or upon refluxing in a sodium hydroxide–ethanol mixture. However, treatment of acetate **3** with sodium methoxide–methanol for a shorter time and cooler temperature gave hydroxyacetate **7** which was identical with the hydroxyacetate formed in the silver-assisted solvolysis of acetoxy chloride **6** in wet acetic acid (Scheme VII). Compound **7** could be converted into diol **25** with longer reaction times. This result reflects the steric environment of the two acetoxy groups. The group at the secondary benzylic position is apparently less hindered than the one at the tertiary position. Treatment of diol **25** with acetic anhydride and pyridine yielded hydroxyacetate **26**, which was identical with

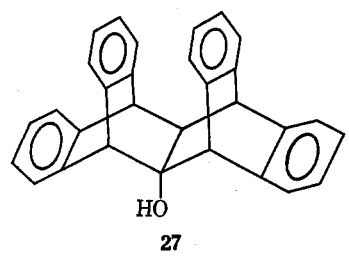
(9) W. M. Macintyre, M. A. Imhoff, and S. J. Cristol, *J. Org. Chem.*, **36**, 1865 (1971).

SCHEME VII

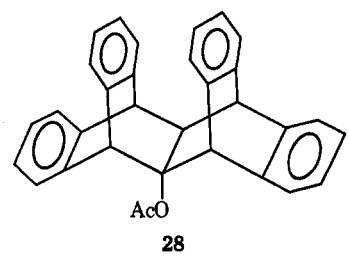



the one formed in the addition of acetic acid to 5a,11a-epoxyjanusene.[1]

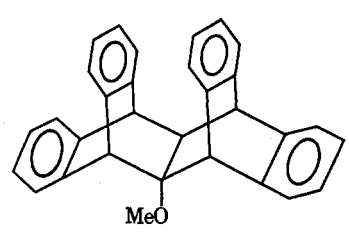
Another indication of the steric hindrance in these systems was observed in an attempt to prepare 5a-hydroxyjanusene (**27**). Attempted transesterification of




**27**




**28**




**29**

acetate **28** in hydrochloric acid–methanol solution gave mostly starting material **28** and a small amount of **27** and **29**. Alcohol **27** was prepared by prolonged treatment of **28** with sodium hydroxide in ethanol.

Finally, hydroxyacetate **8** could be converted into the corresponding diol upon treatment of it with hydroxide in ethanol, or it could be converted into diacetate **19** upon treatment with sulfuric acid and acetic anhydride.

## Experimental Section

All nuclear 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 $\tau$ units ($\tau$ = 10.00 for tetramethylsilane). Infrared spectra were taken on a Beckman IR-5 spectrophotometer in KBr or $CCl_4$. All elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points were uncorrected.

"Work up" involved partitioning the reaction mixture between water and ether, washing the ether layer, drying it over magnesium sulfate, filtering, and evaporating the solvent under reduced pressure.

**Reaction of 5a,11a-Dibromojanusene (1) with Silver Acetate in Acetic Acid.**—A mixture of 973 mg (1.80 mmol) of **1** and 605 mg (3.61 mmol) of silver acetate was stirred at reflux in 50 ml of acetic acid for 10 hr to yield 764 mg (85%) of crude product. The pmr spectrum of the product mixture showed 85% 5a,12-diacetoxyhemiisojanusene (**3**) along with 15% *exo*-6,*endo*-12-diacetoxy-*cis*-isojanusene (**4**). These compounds were obtained pure by fractional crystallization from methanol (compound **4** was less soluble).

Diacetate **3** was recrystallized from methanol: mp 204–207°; pmr ($CDCl_3$) $\tau$ 8.87 (s, 3, OAc at C-5a), 7.98 (s, 3, OAc at C-12), 4.99 (s, 2), 4.67 (s, 1), 3.48 (s, 1), 3.0 (m, 16, aromatics).

*Anal.* Calcd for $C_{34}H_{26}O_4$: C, 81.93; H, 5.22. Found: C, 81.71; H, 5.19.

Diacetate **4** was recrystallized from acetone–95% EtOH: mp 293–296°; pmr ($CDCl_3$) $\tau$ 8.80 (s, 3, OAc at C-6), 7.89 (s, 3, OAc at C-12), 5.51 (s, 2), 3.92 (s, 1), 3.63 (s, 1), 2.90 (m, 16, aromatics).

*Anal.* Calcd for $C_{34}H_{26}O_4$: C, 81.93; H, 5.22. Found: C, 82.06; H, 5.23.

**Reaction of 5a,12-Dichlorohemiisojanusene (2) with Silver Acetate in Acetic Acid.**—A mixture of 1.20 g (2.63 mmol) of **2** and 670 mg (4.0 mmol) of silver acetate in 60 ml of acetic acid was stirred at reflux for 8 hr. The isolated crude oil, 1.3 g, gave a complicated pmr spectrum. Identified in this spectrum were diacetates **3** and **4** in a ratio of 3:7, respectively. Also present were 5a,11a-dichlorojanusene[1] and a small amount of 5a-chloro-11a-acetoxyjanusene (**6**).[1]

**Reaction of 5a-Chloro-12-acetoxyhemiisojanusene (5) with Perchloric Acid—Acetic Acid Solution.**—A solution of 250 mg (0.53 mmol) of a 1:1 mixture of 5a-chloro-11a-acetoxyjanusene (**6**) and 5a-chloro-12-acetoxyhemiisojanusene (**5**) in 16 ml of 0.11 *M* perchloric–acetic acid was stirred at room temperature. At 15 min, 1 hr, 2 hr, and 5 hr, a 4-ml aliquot was taken and the product mixture analyzed by its pmr spectrum. The 15-min aliquot showed a mixture of **5** and **6** with the epimeric composition of **5** the same as initially. The other aliquots contained only acetoxy chloride **6**.

**Reaction of 5a-Chloro-11a-acetoxyjanusene (6) with Sulfuric Acid and Methanol.**—A solution of 73 mg (0.15 mmol) of **6** in 1.1 *M* sulfuric acid–methanol was stirred at reflux for 142 hr. The colorless oil, 70 mg, was identified by its pmr spectrum as starting material **6**.

**Reaction of 5a-Chloro-11a-acetoxyjanusene (6) with Silver Acetate and Acetic Acid.**—A mixture of 494 mg (1.04 mmol) of **6** and 174 mg (1.04 mmol) of silver acetate in 35 ml of acetic acid was stirred at reflux for 24 hr. The pmr spectrum of the crude product showed only 5a,12-diacetoxyhemiisojanusene (**3**). Crystallization from methanol yielded 350 mg (68%) of diacetate **3**, mp 204–207°.

**Reaction of 5a-Chloro-11a-acetoxyjanusene (6) with Silver Acetate in Wet Acetic Acid.**—A mixture of 73 mg (0.15 mmol) of **6**, 26 mg (0.15 mmol) of silver acetate, and 26 mg (0.31 mmol) of sodium acetate was dissolved in 10 ml of wet acetic acid (3 ml of water/100 ml of solution). This amounted to 300 mg (16.6 mmol) of water. The mixture was stirred at gentle reflux for 2.5 hr. The pmr spectrum of the product mixture showed that 50% of the starting material remained. Also present were diacetate **3** and hydroxyacetate **7** in a ratio of 3:1, respectively. No 5a-hydroxy-11a-acetoxyjanusene (**8**)[1] could be detected. Hydroxyacetate **7** was not separated from the reaction mixture, but its properties will be reported later.

**Reaction of 5a-Bromo-11a-acetoxyjanusene (10) with Silver Acetate and Acetic Acid.**—A mixture of 90 mg (0.17 mmol) of **10** and 33 mg (0.20 mmol) of silver acetate in 12 ml of acetic

acid was stirred for 6 hr at 55°. The crude product, 82 mg (90%), was identified as 5a,12-diacetoxyhemiisojanusene (**3**).

**Reaction of 5a-Bromo-11a-acetoxyjanusene (10) with Silver Acetate in Wet Acetic Acid.**—A mixture of 135 mg (0.26 mmol) of **10**, 44 mg (0.26 mmol) of silver acetate, and 22 mg (0.27 mmol) of sodium acetate was dissolved in 11.7 ml of wet acetic acid (5 ml of water/100 ml solution). This corresponded to 32.5 mmol of water. The mixture was stirred at 60° for 18 hr. The pmr spectrum of the crude product indicated a 3:2 ratio of diacetate **3** and hydroxyacetate **7**, respectively. No 5a-hydroxy-11a-acetoxyjanusene (**8**)[1] could be detected.

**Reaction of 5a-Chloro-12-acetoxyhemiisojanusene (5) with Silver Acetate and Acetic Acid (2 Min).**—To a warm solution of 51 mg (0.11 mmol) of **5** in 10 ml of acetic acid was added 18 mg (0.11 mmol) of silver acetate. Two minutes later a white precipitate appeared and the reaction was worked up. The pmr spectrum showed a complex mixture of products which were identified as 25% starting material, 40% *exo*-6,*endo*-12-diacetoxy-*cis*-isojanusene (**4**), 10% *exo*-6,*exo*-12-diacetoxy-*cis*-isojanusene (**13**), and 25% of an unknown alcohol. The presence of an alcohol was based upon anomolous peaks in the pmr spectrum of the product mixture and a weak absorption at 3600 $cm^{-1}$ in the infrared spectrum.

Compound **13** could not be separated and characterized: pmr ($CDCl_3$) $\tau$ 8.78 (s, 6, OAc), 5.50 (s, 2), 3.89 (s, 2), 2.9 (m, 16, aromatics).

**Reaction of 5a-Chloro-12-acetoxyhemiisojanusene (5) with Silver Acetate and Acetic Acid.**—A mixture of 64 mg (0.14 mmol) of **5** and 22 mg (0.13 mmol) of silver acetate in 10 ml of acetic acid was stirred at 60° for 45 min. The crude product, 60 mg (85%), was identified by its pmr spectrum as exclusively diacetate **4**.

**Reaction of 5a,12-Diacetoxyhemiisojanusene (3) in Perchloric Acid–Acetic Acid Solution.**—This reaction was performed under a variety of conditions with respect to time, acid concentration, substrate concentration, and temperature. This is one example. A solution of 60 mg (0.12 mmol) of diacetate **3** in 14 ml of 0.001 *M* $HClO_4$–HOAc was stirred at 90° for 19 hr. The crude product mixture (80% yield) was analyzed by its pmr spectrum (Table I). None of the products were separated and characterized but instead were prepared independently and shown to give identical pmr spectra.

**Reaction of *exo*-6,*endo*-12-Diacetoxy-*cis*-isojanusene (4) in Perchloric Acid–Acetic Acid Solution.**—A solution of 166 mg (0.34 mmol) of diacetate **4** in 11 ml of 0.02 *M* $HClO_4$–HOAc was stirred at 100° for 37 min. The yellow solution was then allowed to cool for 2 hr. The crude product, 141 mg (85%), was identified by its pmr spectrum as an epimeric mixture of 6,12-diacetoxy-*trans*-isojanusene (**20**). This compound was identical with one of the products from the acid-catalyzed rearrangement of diacetate **3**.

One of the epimers of **20** represented about 85% of the mixture and was believed to be the diendo isomer. It was fractionally crystallized from acetone–95% EtOH: mp 267.5–269°; pmr ($CDCl_3$) $\tau$ 8.20 (s, 6, OAc), 5.24 (s, 2), 3.85 (s, 2), 2.9 (m, 16, aromatics).

*Anal.* Calcd for $C_{34}H_{26}O_4$: C, 81.93; H, 5.22. Found: C, 81.71; H, 5.09.

Although the other epimer(s) was not isolated, its pmr spectrum was recorded: pmr ($CDCl_3$) $\tau$ 8.27 (s, 3, OAc), 7.72 (s, 3, OAc), 5.44 (s, 1), 5.16 (s, 1), 3.80 (s, 1), 3.60 (s, 1).

**Reaction of *exo*-6,*endo*-12-Diacetoxy-*cis*-isojanusene (4) in Perchloric Acid–Acetic Acid Solution (Nmr).**—A mixture of 51 mg (0.10 mmol) of diacetate **4** and 9.5 mg of *p*-dinitrobenzene (internal standard) was placed in an nmr tube and partially dissolved in 0.4 ml of 0.0025 *M* $HClO_4$–HOAc. The tube was heated in an oil bath at 65° and removed periodically in order to take a pmr spectrum of the sample. The starting material did not completely dissolve until about 80 min into the reaction.

The intermediate diacetate **14** could not be isolated and characterized. Also attempts to prepare it independently were unsuccessful. Its pmr spectrum was recorded: pmr ($CDCl_3$) $\tau$ 8.00 (s, 6, OAc), 5.56 (s, 2), 3.92 (s, 2), 2.9 (m, 16, aromatics).

**Preparation of *exo*-6,*endo*-12-Dihydroxy-*cis*-isojanusene.**—A solution of 525 mg (1.05 mmol) of diacetate **4** in 50 ml of anhydrous ether was added slowly to a slurry of 435 mg (11.4 mmol) of lithium aluminum hydride in 20 ml of dry ether. The reaction was stirred at room temperature for 17.5 hr and then the excess $LiAlH_4$ destroyed. Work-up was as usual and the product was identified as *exo*-6,*endo*-12-dihydroxy-*cis*-isojanusene by its pmr spectrum. The diol was crystallized from benzene–heptane, yielding 280 mg (68%) of white crystals: mp 260–261.5°; pmr ($CDCl_3$) $\tau$ 5.43 (s, 1), 5.34 (s, 1), 5.02 (s, 1), 4.97 (s, 1), 2.9 (m, 16, aromatics).

*Anal.* Calcd for $C_{30}H_{22}O_2$: C, 86.96; H, 5.31. Found: C, 87.26; H, 5.45.

**Preparation of 6,12-Dihydroxy-*trans*-isojanusene.**—A solution of 323 mg (0.65 mmol) of diacetate **20** in 30 ml of dry ether was added slowly to a slurry of 270 mg (7.1 mmol) of $LiAlH_4$ in 5 ml of anhydrous ether. The mixture was stirred at room temperature for 22 hr and the excess $LiAlH_4$ was destroyed in the usual manner. The product mixture, 207 mg (77%), was identified by its pmr spectrum as 6,12-dihydroxy-*trans*-isojanusene. The diol was crystallized from $CH_2Cl_2$–benzene: mp 304–306° dec; pmr ($CDCl_3$) $\tau$ 5.50 (s, 2), 5.16 (s, 2), 2.9 (m, 16, aromatics).

*Anal.* Calcd for $C_{30}H_{22}O_2$: C, 86.96; H, 5.31. Found: C, 83.79; H, 5.37.

**Preparation of 5a,12-Dihydroxyhemiisojanusene (25).**—A solution of 420 mg (0.84 mmol) of diacetate **3** in 20 ml of anhydrous ether was added slowly to a slurry of 335 mg (8.8 mmol) of $LiAlH_4$ in 10 ml of dry ether. The reaction was stirred at room temperature for 21 hr, after which time the excess $LiAlH_4$ was destroyed. The isolated oil, 306 mg (88%), was identified by its pmr spectrum as 5a,12-dihydroxyhemiisojanusene (**25**). Recrystallization was from benzene–heptane: mp 248–249°; pmr ($CDCl_3$) $\tau$ 7.65 (s, 1, OH at C-5a), 6.8 (m, 1, OH at C-12), 5.87 (s, 1), 5.50 (s, 1), 5.03 (m, 1), 2.9 (m, 16, aromatics).

*Anal.* Calcd for $C_{30}H_{22}O_2$: C, 86.96; H, 5.31. Found: C, 87.15; H, 5.48.

**Preparation of 5a-Acetoxy-12-hydroxyhemiisojanusene (7).**—A solution of 328 mg (0.66 mmol) of diacetate **3** in 50 ml of sodium methoxide in methanol (prepared by treating 125 ml of methanol with 0.3 g of sodium) was stirred at 50° for 3.5 hr. The pmr spectrum of the crude product, 300 mg (100%), identified it as hydroxyacetate **7**. Crystallization of the hydroxyacetate **7** was from benzene–heptane: mp 228–230°; pmr ($CDCl_3$) $\tau$ 8.89 (s, 3, OAc), 7.61 (s, 1, OH), 5.04 (s, 1), 4.92 (s, 1), 4.91 (s, 1), 4.67 (s, 1), 2.9 (m, 16, aromatics).

*Anal.* Calcd for $C_{32}H_{24}O_3$: C, 84.21; H, 5.26. Found: C, 84.05; H, 5.28.

**Preparation of 5a-Hydroxy-12-acetoxyhemiisojanusene (26).**—A solution of 149 mg (0.36 mmol) of diol **25** in a mixture of 7 ml of acetic anhydride and 7 ml of pyridine was stirred at 80° for 45 min and then poured into ice. The isolated oil, 166 mg (100%), was identified by its pmr spectrum as 5a-hydroxy-12-acetoxyhemiisojanusene (**26**). Crystallization of **26** was from methanol: mp 234–235.5°; pmr ($CDCl_3$) $\tau$ 8.06 (s, 3, OAc), 5.73 (s, 1), 5.37 (s, 1), 5.02 (s, 1), 3.42 (s, 1), 2.9 (m, 16, aromatics). The spectrum of this compound was identical with the one prepared from the ring opening of 5a,11a-epoxyjanusene in acetic acid.[1]

*Anal.* Calcd for $C_{32}H_{24}O_3$: C, 84.21; H, 5.26. Found: C, 84.41; H, 5.38.

**Preparation of 5a-Hydroxyjanusene (27).**—A sodium hydroxide–ethanol solution was prepared by treating 125 ml of 95% EtOH with 0.5 g of sodium. To 75 ml of this solution was added 400 mg (0.91 mmol) of 5a-acetoxyjanusene (**28**) and the mixture stirred at gentle reflux for 50 hr. The pmr spectrum of the product oil, 313 mg (86%), indicated 5a-hydroxyjanusene as the sole product. Alcohol **27** was crystallized from benzene–heptane: mp 268–270.5°; pmr ($CDCl_3$) $\tau$ 8.48 (s, 1, OH), 7.87 (t, 1, $J$ = 2.5 Hz), 5.82 (d, 2, $J$ = 2.5 Hz), 5.72 (s, 2), 2.85–3.40 (m, 16, aromatics).

*Anal.* Calcd for $C_{30}H_{22}O$: C, 90.45; H, 5.53. Found: C, 90.16; H, 5.39.

**Preparation of 5a-Methoxyjanusene (29).**—A solution of 203 mg (0.46 mmol) of 5a-acetoxyjanusene (**28**) in 25 ml of 0.97 *M* $H_2SO_4$–MeOH was stirred at gentle reflux for 2 days. The crude oil was identified as 5a-methoxyjanusene (**29**) and was crystallized from benzene–heptane, yielding 142 mg (75%) of white crystals: mp 274–275.5°; pmr ($CDCl_3$) $\tau$ 6.80 (s, 3, OMe), 7.70 (t, 1, $J$ = 2.5 Hz), 5.75 (d, 2, $J$ = 2.5 Hz), 5.35 (s, 2), 2.8–3.4 (m, 16, aromatics).

*Anal.* Calcd for $C_{31}H_{24}O$: C, 90.29; H, 5.83. Found: C, 90.17; H, 5.98.

**Reaction of 5a-Acetoxyjanusene (28) with Hydrochloric Acid in Methanol.**—A solution of 100 mg (0.23 mmol) of acetate **28** in a mixture of 1 ml of concentrated hydrochloric acid and 15 ml of methanol was stirred at reflux for 8 hr. The reaction mixture was worked up as usual and the pmr spectrum of the

mixture indicated 62% acetate **28**, 19% alcohol **27** (transesterification product), and 19% methyl ether **29** (solvolysis product).

**Preparation of 5a,11a-Diacetoxyjanusene (19).**—To a solution of 218 mg (0.48 mmol) of 5a-hydroxy-11a-acetoxyjanusene (**8**) in 15 ml of acetic anhydride was added 6 drops of concentrated sulfuric acid. The mixture was stirred at 80° for 15 min and then worked up. The crude product, 265 mg (110%), was identified by its pmr spectrum as 5a,11a-diacetoxyjanusene (**19**). Diacetate **19** was crystallized from methanol: mp 270.5–272°; pmr ($CDCl_3$) $\tau$ 8.40 (s, 6, OAc), 4.48 (s, 4), 2.85–3.40 (m, 16, aromatics).

*Anal.* Calcd for $C_{34}H_{26}O_4$: C, 81.93; H, 5.22. Found: C, 81.77; H, 5.22.

**Preparation of 5a,11a-Dihydroxyjanusene.**—A solution of 199 mg (0.44 mmol) of hydroxyacetate **8** in 25 ml of sodium methoxide–methanol solution (prepared by treating 100 ml of methanol with 0.25 g of sodium) was stirred at reflux for 2 days. The crude product, 155 mg (85%), was identified by its pmr spectrum as 5a,11a-dihydroxyjanusene and it was crystallized from acetone–95% EtOH: mp >340°; pmr ($CDCl_3$) $\tau$ 8.02 (s, 2, OH), 5.57 (s, 4), 2.87–3.27 (m, 16, aromatics).

*Anal.* Calcd for $C_{30}H_{22}O_2$: C, 86.96; H, 5.31. Found: C, 87.17; H, 5.36.

**Registry No.**—**3**, 29246-46-6; **4**, 29246-47-7; **7**, 29246-48-8; **19**, 29320-07-8; **20**, 29435-62-9; **25**, 29179-05-3; **26**, 29246-49-9; **27**, 29179-06-4; **29**, 29179-07-5; *exo*-6,*endo*-12-dihydroxy-*cis*-isojanusene, 29179-08-6; 6,12-dihydroxy-*trans*-isojanusene, 29179-09-7; 5a,11a-dihydroxyjanusene, 29246-50-2.

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# Bridged Polycyclic Compounds. LXVIII. The Proton Magnetic Resonance Spectra of Some Derivatives of Janusene, Hemiisojanusene, and Isojanusene[1]

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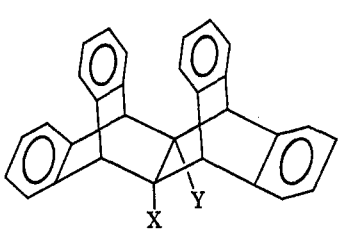
Proton magnetic resonance spectra are given for 41 compounds of various polyhydrodi-o-benzenonaphthacene types. Based upon correlations, it is possible to assign structures to many derivatives of janusene, hemiisojanusene, *cis*-isojanusene, and *trans*-isojanusene.

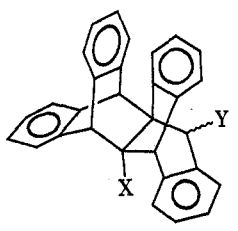
The examination of the carbonium ion reactions of janusene, hemiisojanusene, and isojanusene derivatives[1-4] was made possible by interpretation of pmr spectra. Independent syntheses of most of these compounds was not practicable. However, these spectra, when coupled with certain specific reactions and consideration of possible isomeric structures, appear quite conclusive in making structure assignments.

All spectra were obtained using a Varian A-60A nuclear magnetic resonance instrument. The spectra were taken in deuteriochloroform, usually as saturated solutions, and were scanned over $\tau$ 1.7–10.0 using tetramethylsilane ($\tau$ 10.00) as an internal standard.

Generally, the pmr spectra of disubstituted janusenes (**1**), hemiisojanusenes (**2**), *cis*-isojanusenes (**3**), and *trans*-isojanusenes (**4**) consist of a complex multiplet centered approximately at $\tau$ 3.0, which corresponds to the aromatic hydrogens, and a series of singlets, which arise from the aliphatic hydrogens.[5] Although the general patterns of the singlets are such that skeletal isomers can be easily distinguished, individual proton assignments are difficult and have to be made strictly on the basis of chemical shift data. A number of monosubstituted janusenes (Figure 1), whose structures were derived from chemical knowledge, were prepared as model compounds. In these cases individual proton assignments can be made with certainty, based upon the splitting patterns and expected chemical shifts. The spectral data are listed in Table I.




1

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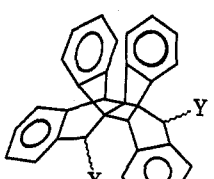


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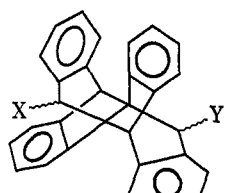
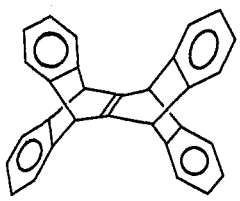



4



11

5a-Bromojanusene (**6**), which was prepared by the addition of hydrogen bromide to dehydrojanusene (**11**),[3] could be converted back to starting olefin upon treatment with potassium *tert*-butoxide. This same monobromide was also prepared from the radical bromination of janusene (**5**).[3] Also, 5a-chlorojanusene (**7**) was prepared by either addition of hydrogen chloride to olefin **11**[3] or as a Diels–Alder adduct from the reaction of

(1) Previous paper: LXVII. S. J. Cristol and M. A. Imhoff, *J. Org. Chem.*, **36**, 1854 (1971).

(2) S. J. Cristol and M. A. Imhoff, *ibid.*, **36**, 1849 (1971). Methods for trivial nomenclature are given in this paper.

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

(4) W. M. Macintyre, M. A. Imhoff, and S. J. Cristol, *ibid.*, **36**, 1865 (1971).

(5) The secondary benzylic protons in **2**, **3**, and **4** were split when the substituent was hydroxyl.