Bridged Polycyclic Compounds. XLV. Synthesis and Some Properties of 5,5a,6,11,11a,12-Hexahydro-5,12:6,11-di-*o*-benzenonaphthacene (Janusene)[1]

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Abstract: A Dreiding model of the title compound (I, for which the trivial name "janusene" is proposed) has two of its four benzene rings parallel and about 2.5 A apart, while each of the other two rings is remote from the other benzene rings. Consideration of the model encouraged spectral and chemical studies of the effects of π-cloud interaction between the "parallel" or "face" rings. Janusene and its bridge chloro derivative were synthesized by Diels–Alder reactions between anthracene and dibenzobicyclo[2.2.2]octatriene and its chloro derivative. The pmr spectrum of janusene and its derivatives show that the "face" ring (F ring) protons are shielded and absorb about 0.4 ppm higher than those of the lateral rings (L rings). The ultraviolet spectra also show significant differences from those of the analogous dibenzobicyclooctadienes, II. Electrophilic nitration and bromination show that the F rings are considerably more reactive than the L rings, the principal products being the F_β derivatives. Results on nitration of F_β-nitrojanusene suggest that the interaction between F rings is a general polarization phenomenon rather than a resonance phenomenon involving specific bond formation between rings in the transition state.

The consequences of bringing aromatic rings into close range and approximately parallel to each other upon physical and chemical properties have been of considerable interest for some time. A large share of the work done on such compounds has been carried out with the [*m.n*]paracyclophanes.[2–4] In addition, some study of effects upon spectral properties has been conducted with compounds in which aromatic rings might be constrained to approximately parallel positions within distances close to or less than the sum of the van der Waals radii by being placed *cis* and vicinal on five-[5,6] or three-membered[6,7] rings, on the 9,10 positions of phenanthrene,[8] or on *peri* positions in naphthalene,[9] anthracene,[10] and naphthacene.[11,12] When aromatic rings are held face-to-face and are not constrained, the normal van der Waals distance is about 3.40 A[13] and, if aromatic rings are forced to approach each other within these distances, one may anticipate effects on physical and chemical properties caused by π-cloud interaction. Effects on ultraviolet and proton magnetic resonance (pmr) spectra have been noted in many of the polyphenylated fused aromatic systems, but chemical effects are not readily studied as reactions tend to occur in the fused aromatic system rather than in the phenyl substituents. Both spectral and chemical properties have been amenable to study with the paracyclophanes, and in particular have been studied in detail with [2.2]paracyclophane.[4,5,14] However, with the latter compound, the extremely close approach of the benzene rings causes them to be distorted significantly from planarity,[2] so that it is difficult to decide which properties of the aromatic rings result directly from π-cloud interaction and which from ring distortion, although Cram and his co-workers have given arguments regarding the assignment of the perturbations in the ultraviolet spectrum produced by these two causes.

It occurred to us that a 1,4,4a,5,8,8a-hexahydro-1,4:5,8-di-*o*-benzenonaphthalene might be rigid enough to constrain the *o*-benzeno bridges within the van der Waals distance limits. For the purpose of synthetic ease and for the other reasons described below, we undertook a study of the synthesis of the title compound (5,5a,6,11,11a,12-hexahydro-5,12:6,11-di-*o*-benzenonaphthacene, I). A Dreiding model of this compound, which we call by the trivial name janusene,[15] shows that if there were no distortions by π-cloud or other repulsion, the bridge benzene rings would be parallel and about 2.5 A apart, while the lateral rings are far apart, similar to the rings in 9,10-dihydro-9-10-ethanoanthracene (dibenzobicyclo[2.2.2]octadiene, II).[17] The mutual repulsion of the π-electron clouds would be expected to push the "parallel" rings some-

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[1] Previous paper in this series: S. J. Cristol and B. B. Jarvis, *J. Am. Chem. Soc.*, 89, 401 (1967).

[2] (a) C. J. Brown and A. C. Farthing, *Nature*, 164, 915 (1949); (b) A. J. Farthing, *J. Chem. Soc.*, 3261 (1953); (c) C. J. Brown, *ibid.*, 3265 (1953).

[3] D. J. Cram and H. Steinberg, *J. Am. Chem. Soc.*, 73, 5691 (1951).

[4] For summaries of work on these compounds and extensive references, see (a) D. J. Cram, *Record Chem. Progr.*, 20, 71 (1959); (b) B. H. Smith, "Bridged Aromatic Compounds," Academic Press Inc., New York, N. Y., 1964.

[5] D. J. Cram, N. L. Allinger, and H. Steinberg, *J. Am. Chem. Soc.*, 76, 6132 (1954).

[6] D. Y. Curtin, H. Gruen, Y. G. Hendrickson, and H. E. Knipmeyer, *ibid.*, 83, 4838 (1961); 84, 863 (1962).

[7] M. H. Gianni, E. L. Stogryn, and C. M. Orlando, Jr., *J. Phys. Chem.*, 67, 1385 (1963).

[8] R. C. Fuson and P. Tomboulian, *J. Am. Chem. Soc.*, 79, 956 (1957).

[9] H. O. House, R. W. Magin, and H. W. Thompson, *J. Org. Chem.*, 28, 2403 (1963).

[10] S. C. Dickerman, D. de Souza, and P. Wolf, *ibid.*, 30, 1981 (1965).

[11] C. Moureu, C. Dufraisse, and P. M. Dean, *Compt. Rend.*, 182, 1440 (1926).

[12] H. Jaffé and O. Chalvet, *J. Am. Chem. Soc.*, 85, 1561 (1963).

[13] J. M. Robertson, "Organic Crystals and Molecules," Cornell University Press, Ithaca, N. Y., 1953, pp 157, 174, 206, 270.

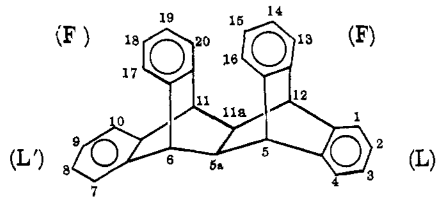
[14] R. C. Hegelson and D. J. Cram, *J. Am. Chem. Soc.*, 88, 509 (1966), and references cited therein.

[15] Although we originally thought of the bridge rings as face-to-face, names based upon the legend of Narcissus seem awkward because of the family of alkaloids with the same root. We have therefore chosen the trivial name "janusene," which was suggested to us[16] because of the resemblance of the model to the two-faced Roman god Janus. This revises the viewpoint of the bridge rings as looking outward toward their environment rather than at each other.

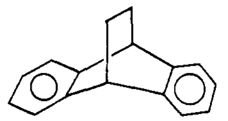
[16] We are indebted to Dr. Walter M. Macintyre for this suggestion.

[17] (a) C. L. Thomas, U. S. Patent 2,406,245 (1946); (b) S. J. Cristol and N. L. Hause, *J. Am. Chem. Soc.*, 74, 2193 (1952).

what farther apart than the model shows and also to increase the angle between them, and there may be further deviation from the model by twisting (scissoring) of the bicyclooctadiene rings. There would appear to be little advantage gained by the molecule by distortion (nonplanarity) of the benzene rings. Details of the structure must await the X-ray study of a janusene derivative now being conducted by Professor Walter M. Macintyre of this department.



I



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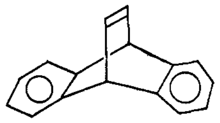


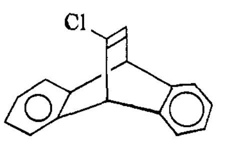
III

In spite of the lack of information regarding the precise structure of janusene, it does not seem inappropriate to report its synthesis and some of its physical properties and chemistry at this time. The molecule has a system of four aromatic rings which are identical except for the positioning described in the previous paragraph, and the consequences of having the two face rings close enough to interact can be directly measured by comparison internally with the other two rings or externally with the rings in II.

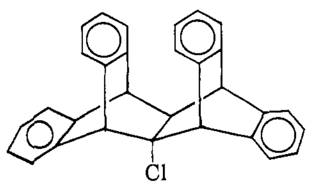
Synthesis. Janusene was synthesized in excellent yield[18] by a Diels–Alder reaction between anthracene and dibenzobicyclo[2.2.2]octatriene (III). The structure proof of janusene is based upon various types of evidence. Elemental analysis gives a carbon–hydrogen ratio of 15:11, and the parent peak in the mass spectrum at m/e 382 ± 1 confirms the analysis as $C_{30}H_{22}$. As Diels–Alder reactions with anthracene occur at the 9,10 positions,[19–21] the synthesis itself suggests structure I. The pmr spectrum (discussed in detail below) is also consistent with structure I, which has two sets of eight aromatic protons each, four benzohydrylic protons, and two nondescript aliphatic protons. Furthermore, the number and variety of derivatives (see below) are also consistent with structure I.

Use of chlorodibenzobicyclo[2.2.2]octatriene (IV)[17b] with anthracene gave 5a-chlorojanusene (V), although in very poor yield. Attempted synthesis of the corresponding bromide *via* the Diels–Alder reaction was unsuccessful.

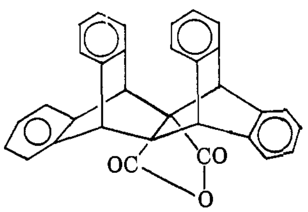
A review of the literature discloses that one compound with the janusene skeleton has been described. It is 5a,11a-janusenedicarboxylic anhydride (VI) prepared fortuitously[22] when the anhydride VII was heated in nitrobenzene. VI is readily prepared by the reaction of anthracene with VII.[23]



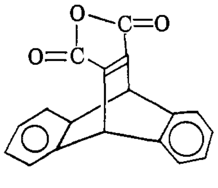
IV



V



VI



VII

Spectra. The pmr spectrum of janusene dissolved in carbon tetrachloride is displayed in Figure 1. The peak at τ 7.49 has an intensity equivalent to two protons and may be assigned with confidence[24] to the 5a and 11a protons. Better resolution splits this peak into an apparent triplet with apparent J = 1.1 cps. The peak at τ 5.96 may be assigned[24] to the four benzohydrylic protons at C-5, C-6, C-11, and C-12. Again higher resolution shows an apparent triplet with apparent J = 1.1 cps. As this is an A_2X_4 system, the actual coupling constants differ from the observed ones, but the low value of the apparent J is consistent with the dihedral angle between the aliphatic protons in the model of janusene.[24,25] The values are quite similar to those for dibenzobicyclo[2.2.2]octadiene (II)[24] except that the nonbenzohydrylic protons are shifted downfield in janusene by about 0.8 ppm.

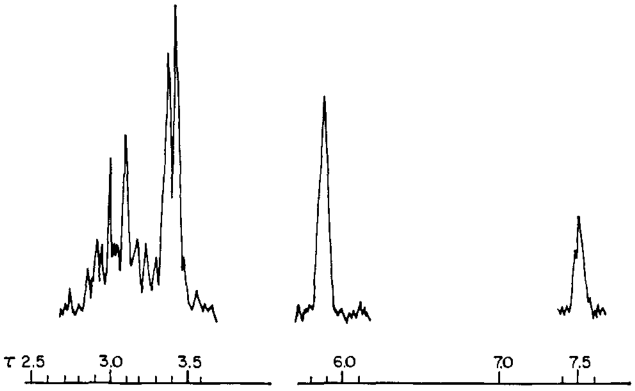


Figure 1. The pmr spectrum of janusene.

Of somewhat more interest are the peaks assignable to the aromatic protons. These may readily be separated into two complex multiplets, one centering at about τ 3.05 and the other at about τ 3.40, with each multiplet integrating for eight protons. The higher field multiplet, which is narrower and less complex than the other, is undoubtedly assignable[26] to the protons of the face rings, each of which is shielded by the opposed ring. The assignment is supported

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[18] We are indebted to Mr. Michael A. Imhoff for improvements in this synthesis.

[19] M. C. Kloetzel, *Org. Reactions*, 4, 1 (1948).

[20] H. L. Holmes, *ibid.*, 4, 60 (1948).

[21] L. W. Butz and A. W. Rytina, *ibid.*, 5, 136 (1949).

[22] O. Diels and W. Friedrichsen, *Ann.*, 513, 145 (1934).

[23] Dr. D. W. Wiley, private communication.

[24] S. J. Cristol, T. W. Russell, J. R. Mohrig, and D. E. Plorde, *J. Org. Chem.*, 31, 581 (1966).

[25] M. Karplus, *J. Chem. Phys.*, 30, 11 (1959).

[26] L. M. Jackman, "Applications of Nuclear Magnetic Resonance to Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, pp 125–129.

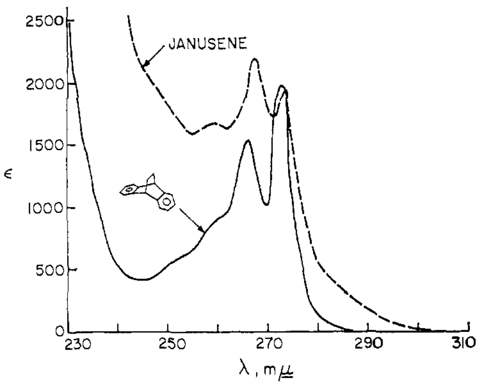

Figure 2. Ultraviolet spectra of janusene and dihydroethanoanthracene in cyclohexane.

by the fact that the lower field multiplet bears great resemblance to the aromatic pmr multiplet for II, except that the latter centers at *ca.* τ 2.95. Relative to the aromatic hydrogens of *o*-xylene (at τ 2.90[27]), the face ring protons of janusene are shifted upfield by 0.5 ppm. In comparison, [2.2]paracyclophane has its aromatic protons at τ 3.63,[28] 0.68 ppm higher than *p*-xylene.[29] Shifts of 0.5–0.6 ppm have also been noted with the phenylated naphthalenes[9,30] and anthracenes.[10] The chloro derivative V also had two aromatic multiplets (centering at τ 2.90 and 3.30), a singlet at τ 5.42 assignable to the benzohydrylic protons vicinal to the carbon nearest the chlorine atom, a doublet at τ 5.73 (J = 2.8 cps) assignable to the other benzohydrylic protons, and a triplet at τ 7.03 assignable to the 11a proton.

The ultraviolet spectra of solutions of janusene and of dibenzobicyclo[2.2.2]octadiene (II) in cyclohexane solvent are shown in Figure 2. It should of course be noted that janusene has four aromatic rings while II has only two, so that the spectrum for II perhaps should have been doubled in intensity to be somewhat more comparable. The spectrum of janusene has several differences from that of II. Although the two maxima in the 270-mμ region lie at substantially the same location, the tail for janusene extends about 15 mμ further toward the visible than does that for II. In addition, the short wavelength band (which, although not shown in Figure 2, has a λ_{max} at 208 mμ (ϵ 50,000)) for janusene also begins at longer wavelength than that for II (λ_{max} 206 mμ (ϵ 38,000)). This is noted in the minima at 255 and 245 mμ for I and II, respectively. Thus both the long and short wavelength bands are broader for janusene than for II. Cram and his colleagues,[5,31] in their discussion of the ultraviolet spectra of paracyclophanes, have suggested that the spectral differences between the smaller paracyclophanes and model compounds are caused in part by warping of the rings and in part by transannular electronic interactions. If our assumption that the face rings in janusene are planar is correct, it is necessary to assume that the differences we have noted are due largely to transannular interactions.

Electrophilic Substitution Reactions. We have decided to look at nitration in acetic anhydride–nitromethane (acetyl nitrate) and at iron-catalyzed bromination in carbon tetrachloride as typical aromatic electrophilic substitution reactions for janusene. Most of our work was done with mono- and dinitration, and we are therefore in a position to discuss these reactions in some detail.

Mononitration. Although tetralin and hydrindene are nitrated at approximately equal rates at α and β positions,[32] dibenzobicyclo[2.2.2]octadiene (II) is nitrated by acetyl nitrate in nitromethane largely in the β position.[33] This is also true for dibenzobicyclo[2.2.2]octatriene where β nitration is observed as a corollary of addition of acetyl nitrate.[34] It might therefore be anticipated that janusene would be nitrated at one of its β positions. Of much more interest, however, is the question of whether the face rings (F rings) or lateral rings (L rings) would be nitrated more rapidly. If there were no electronic factors involved, one might anticipate that the lateral rings would be more reactive. Thus, it would appear from models that nitronium ion or protonated acetyl nitrate could attack each of the L rings from either side, while the F rings can only suffer attack form the outside, as it seems impossible to have the reagent form a π complex[35] from the inside positions and as a σ complex[35] with a nitro group inside also has severe steric interactions. On the other hand, it might be anticipated that transannular electron interaction between F rings would be greater in the transition state for electrophilic substitution than in the ground state, and that these rings would show reactivity greater than that of the L rings.

Nitration was carried out with nitric acid dissolved in acetic anhydride–nitromethane at 0–3° essentially as described by Tanida and Ishitobi[33] for II. As polynitration occurred readily, it was necessary to use an excess of janusene to avoid the formation of significant amounts of dinitro and polynitro derivatives. Fortunately, chromatography on alumina with elution by petroleum ether, bp 60–70°, containing increasing amounts of benzene, allowed the separation into janusene, mononitrojanusene mixtures, dinitrojanusene mixtures, etc. The mononitro and dinitro isomers which were formed could be isolated and purified by further chromatography and/or recrystallization from acetone–ethanol.

We were fortunate in that we were able to distinguish the mono- and dinitrojanusenes which were formed by using pmr techniques. The mononitro isomers which were formed in observable amounts were the F_α (VIII), F_β (IX), and L_β (X) isomers. The pmr spectra of these materials are summarized in Table I.

Ordinarily a nitro group on a benzene ring shifts *o*-hydrogens downfield by about 1.0 ppm and *m*-hydrogens about 0.3 ppm in the pmr spectrum.[36] Such shifts then enable us to identify the mononitro isomers. In the case of the F_α isomer VIII, there is no distinct band

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[27] N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectroscopy," Varian Associates, Palo Alto, Calif., 1962, Spectrum No. 201.

[28] D. J. Cram, C. K. Dalton, and G. R. Knox, *J. Am. Chem. Soc.*, **85**, 1088 (1963).

[29] Reference 27, Spectrum No. 203.

[30] M. Rabinowitz, I. Agranat, and E. D. Bergman, *Tetrahedron Letters*, 4133 (1965).

[31] D. J. Cram, R. H. Bauer, N. L. Allinger, R. A. Reeves, W. J. Wechter, and E. Heilbronner, *J. Am. Chem. Soc.*, **81**, 5977 (1959).

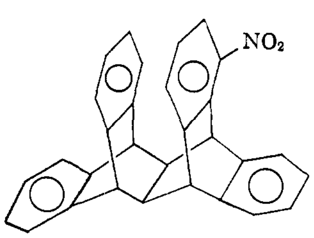
[32] H. Tanida and R. Muneyuki, *ibid.*, **87**, 4794 (1965).

[33] H. Tanida and H. Ishitobi, *Tetrahedron Letters*, 807 (1964).

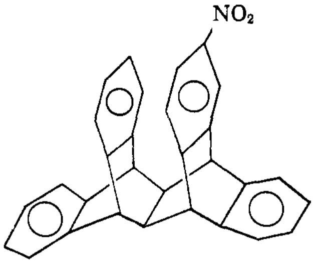
[34] J. R. Mohrig, Ph.D. Dissertation, University of Colorado, 1963.

[35] P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution: Nitration and Halogenation," Butterworth & Co. (Publishers), Ltd., London, 1959, pp 40–46, 71–73.

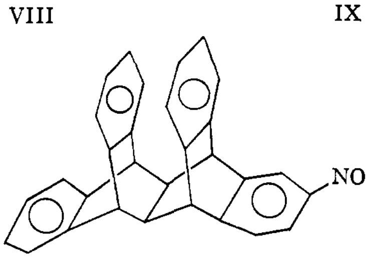
[36] Reference 26, p 63.



VIII



IX



X

for the *ortho* proton in the nitrated ring, but compared with the spectrum of janusene, that for F_α has its upfield aromatic multiplet cut substantially and the downfield multiplet increased in intensity, approximately consistent with a ratio of 6:9 protons. The benzohydrylic hydrogen absorptions support the assignment with one proton at τ 4.62 (bridgehead C-5), one at τ 5.57 (presumably the C-12 proton), and two at τ 5.70 (presumably at C-6 and C-11).

Table I. Chemical Shifts in the Pmr Spectra of Janusenes and Some Nitrojanusenes[a]

Compd	Aromatic protons	Benzohydrylic protons	Bridge protons
Janusene (I)	2.8–3.65	5.96	7.49
Mononitro			
F_α (VIII)	2.7–3.5	4.62 (1 H) 5.57 (1 H) 5.70 (2 H)	7.41
F_β (IX)	2.50 (2 H) 2.75–3.6 (13 H)	5.71 (2 H) 5.80 (2 H)	7.48
L_β (X)	2.09 (2 H) 2.65–3.55 (13 H)	5.66 (2 H) 5.78 (2 H)	7.52
Dinitro			
$(F_\alpha F_\beta')$[b]	2.4 2.5–3.3	4.71 (1 H) 5.5 (3 H)	7.40
$(F_\beta L_\beta)$[b]		5.4 5.8	
$F_\beta L_\beta'$	2.06 (2 H) 2.44 (2 H) 2.6–3.45	5.63	7.47
$F_\beta F_\beta'$ (XI)	2.40 2.65–3.2	5.62	7.33
$F_\beta F_\beta'$ (XII)	2.40 2.65–3.2	5.66	7.32

[a] The spectrum of janusene was taken in carbon tetrachloride solution, and that of the mononitro and dinitro compounds except $F_\beta L_\beta$ in deuteriochloroform solution. That of $F_\beta L_\beta$ was taken in acetone. Values are given in τ units. [b] The mixtures whose notations are given in parentheses were not isolated completely free of other materials, so that spectral data given herein were obtained from pmr data on mixtures.

The isomer assigned the F_β structure IX has a spectrum with a multiplet which appears to be a singlet overlapping with a doublet ($J \sim 10$ cps) centering at about τ 2.50 and representing the two protons *ortho* to the nitro group. The remaining 13 aromatic protons lie in the τ 2.75–3.6 region. Integration of protons of this region makes it clear that areas assignable to the upfield F protons have been diminished compared with janusene while those of the downfield protons are undiminished. The peak at τ 5.71 is assigned to the two benzohydrylic protons closer to the nitro groups while that at τ 5.80 is assigned to the more remote benzohydrylic protons.

The spectrum of the L_β isomer X has a multiplet (again an apparent broad singlet overlapping with a broad doublet, $J \sim 10$ cps) centering at about τ 2.10 representing the two protons *ortho* to the nitro group. The remaining portion of the aromatic protons lies in the τ 2.55–3.55 envelope, but here the 13 protons have their major intensity in the upfield portion (*i.e.*, are principally in the F ring rather than in the L ring). The peak at τ 5.66 is assigned to the two benzohydrylic protons close to the nitro groups, while that at τ 5.78 is assigned to the more remote areas.

The pmr spectral assignments are consistent with those made for the corresponding β-nitro derivative of II.[33]

When janusene was nitrated with ~0.5 equiv of acetyl nitrate at about 0°, 55% of the starting material was recovered and 34% of a mononitrojanusene mixture was obtained. There appeared to be no dinitro or polynitro compounds. A combination of chromatographic fractionation and pmr analysis of the mononitro fractions indicated that the mixture contained 80% F_β, 6% F_α, 13% L_β, and perhaps 1% L_α isomer.[37] The F_β/F_α ratio of 13 is consistent with the principal nitration of dibenzobicyclo[2.2.2]octadiene at the β position referred to above.

The ratio of face-ring to lateral-ring nitration was ~6:1. In order to show that this is the result of activation of the F rings, rather than deactivation of the L rings, we ran a competition between janusene and II. We observed that janusene was nitrated eight times faster than was II, a result consistent with the F:L ring-nitration ratio. This confirms the fact that the F rings are activated ones.[38]

One may consider three factors as contributing to the higher activity of the F rings. These are: (a) destabilization of the F rings by transannular electronic repulsion, (b) stabilization of the transition state for F-ring substitution by transannular electronic stabilization, and (c) steric effects. Of these, the last would appear to decrease F-ring reactivity.[38] It does not appear possible at this time to sort out the first two effects. Thus the increase in rate may be largely due to the possibility of increased π-electron density on the outside of the F rings due to repulsion in the ground state, or may be largely due to stabilization of the electron-deficient transition state involved in the attack of electrophile

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(37) Certain of the chromatography fractions rich in the F_α isomer contained an impurity with pmr absorption at about τ 2.0. If this is assumed to be the L_α isomer, it represents about 1% of the mononitro product. This amount is consistent with the β/α ratio observed in the F-ring nitration.

(38) As the L rings have two nearly equivalent sides available for attack, while the F rings have only one side available, the reactivity ratio may possibly be considered as close to 12 rather than 6. For comparison, it may be noted that introduction of a phenyl group into benzene increases the rate of nitration at the *p*-carbon atom by a factor of 38.[39] Thus the interaction of the two rings in janusene causes almost as dramatic a rate increase as is caused by a ring in direct conjugation with the reaction site.

(39) O. Simamura and Y. Mizuno, *Bull. Chem. Soc. Japan*, 30, 196 (1957).

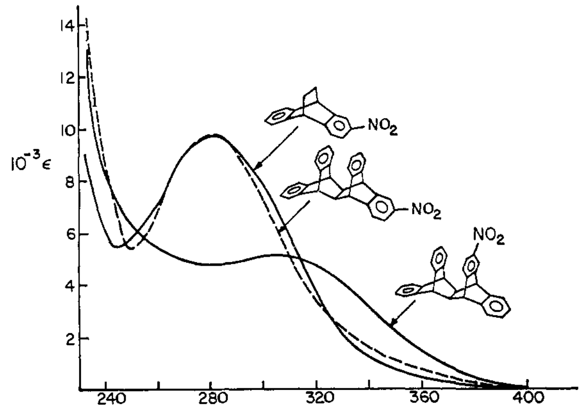


Figure 3. Ultraviolet spectra (in 95% C_2H_5OH).

on one F ring by the π electrons of the second F ring. This latter effect can be imagined to occur by a generalized polarization of the π cloud or by transannular resonance stabilization involving specific bond formation. This will be considered further in the section on dinitration.

The ultraviolet spectra of F_β-nitrojanusene, L_β-nitrojanusene, and β-nitrodibenzobicyclo[2.2.2]octadiene are given in Figure 3. Inspection of the spectra shows the strong similarity of the L_β isomer and the β-nitro-II compound. On the other hand, the F_β isomer has a spectrum quite dissimilar from those of the others. The spectral changes may presumably be attributed to electronic interaction of the unsubstituted F ring with the nitrated ring. The bathochromic shift in the long wavelength band of λ_{max} from 282 to 307 mμ is comparable in magnitude with that (35 mμ) observed in the change from nitrobenzene (269 mμ) to nitro[2.2]paracyclophane (304 mμ).[31]

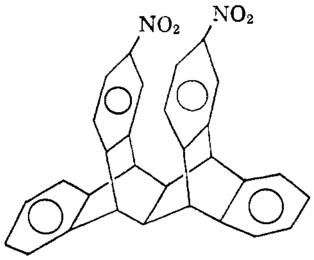
Monobromination. Janusene was brominated heterolytically by treatment with a small excess of bromine in carbon tetrachloride using iodine and iron as catalysts, as in a procedure described for bromination of *o*-xylene.[40] Chromatography was carried out on basic alumina, using benzene–petroleum ether (bp 60–70°) mixtures as eluents. The product with substitution in one of the *F* rings was by far the most abundant, with almost 50% yield being recovered pure by recrystallization from acetone–alcohol after the first chromatography. Further chromatography allowed the following over-all yield estimations for the reaction: recovered janusene, 4–8%; F_β-bromojanusene, 57–61%; F_α- + L_β-bromojanusene, 2–5%. A moderate amount of more slowly eluting material (presumably dibromides) was also found.

The pmr spectrum of F_β-bromojanusene in carbon tetrachloride (aromatic protons centered at τ 3.17, benzohydrylic protons at τ 5.87, and bridge protons at τ 7.47) showed a cutting down of some of the high-field aromatic intensity; this, together with the pattern of electrophilic attack for nitration, suggests the structure assigned. The presence of L_β and/or F_α was implied at first only by certain bands in the infrared spectra of chromatography fractions in making the transition from janusene to F_α in elution; the only other isomer (other than F_β) isolated (in moderately impure form in less than 1% yield) after several successive chromatographies and recrystallizations was F_α. It was distinguished from the L_β isomer by the pmr spectrum in carbon tetrachloride. Aromatic protons were centered at τ 3.11, benzohydrylic protons at τ 5.31 (1 H) and 5.86 (3 H), and bridge protons at τ 7.47; the high-field aromatic protons were reduced in intensity somewhat.

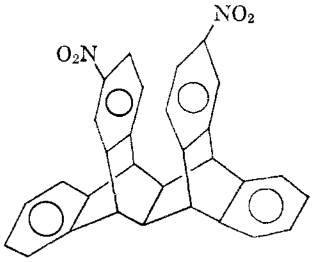
Thus, bromination, like nitration, shows a significant preference for F- *vs.* L-ring attack, and it seems safe to assume that this will be a general preference in electrophilic substitution reactions of janusene.

Dinitration. We next wish to inquire into the nitration of F_β-nitrojanusene (IX). Two questions raised themselves in considering this problem. We were concerned with the question of whether the nitrobenzene F ring would deactivate the other F ring relative to the L rings and to janusene. Furthermore, we were concerned with the question of specificity of nitration of the second F ring at one of the β positions or the other, as we felt that this might teach us whether the ring interactions were generalized polarizations or resonance interactions involving specific bond formation.

The proof of structure of the various dinitrojanusenes represents a formidable problem, and it is fortunate that the answer to the questions mentioned above do not require complete structure proofs. For example, while there are two $F_\beta L_\beta$-dinitro racemates (*i.e.*, one nitro substituent at 14 and another at either 2 or 3 in formula I) and two similar racemates of $F_\beta L_\beta'$ isomers, it is not necessary to distinguish the members of each of these sets to determine the relative reactivities of the L and L′ rings of F_β-nitrojanusene. It would be useful to know the structures of each of the $F_\beta F_\beta'$ isomers, but we have not carried out the necessary work. One of the isomers is *meso*, with eclipsed nitro groups (XI), and one is a racemate (XII), so that resolution experiments could be attempted. We have tentatively assigned structure XI to the less soluble $F_\beta F_\beta'$ isomer and XII to the more soluble isomer, but these assignments are without other bases.[41]



XI



XII

Before carrying out the nitration of F_β-nitrojanusene, we conducted a number of nitrations of janusene to produce substantial amounts of dinitrojanusenes for separation, partial identification, and characterization. When 0.01 mole of janusene was treated with 0.04 mole of acetyl nitrate, polynitration occurred almost exclusively and no janusene was recovered unchanged. The

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[40] W. A. Wisansky and S. Ansbacher in "Organic Syntheses," Coll. Vol. III, E. C. Horning, Ed., John Wiley and Sons, Inc., New York, N. Y., 1955, p 138.

[41] As will be seen below, the isomers XI and XII are formed upon nitration of F_β-nitrojanusene in almost equal amounts, so that the lack of complete structure proof is not as serious as would be the case if there were a large preference for the formation of one isomer over the other.

apparent yields after chromatographic separation included 1% mononitrojanusene, 45% dinitrojanusene isomers, and 29% trinitrojanusene isomers. We were able to separate the dinitrojanusene mixture into what appeared to us on the basis of pmr spectral data to be relatively pure $F_\beta L_\beta'$ isomers (admixed with each other), pure XI and pure XII, and to get pmr evidence for what we have assumed to be $F_\alpha F_\beta'$, $F_\alpha L_\beta'$, and $F_\beta L_\beta$ isomeric mixtures. The pmr assignments to the various isomers or mixtures of isomers are given in Table I and are consistent with the arguments given above for the mononitrojanusenes. Of the dinitro products a combination of chromatographic separation and pmr analysis suggests that the composition was 2–5% $F_\alpha F_\beta' + F_\alpha L_\beta$, 30–40% $F_\beta L_\beta'$, 3–6% $F_\beta L_\beta$, 22–27% XI, and 35–40% XII.

When F_β-nitrojanusene was nitrated (excess F_β-nitrojanusene), 84% starting material was recovered, along with 13% dinitrojanusene isomers. No trinitrojanusenes were formed in this experiment. Analysis indicated that the sum of the $F_\beta L_\beta$ and $F_\beta L_\beta'$ isomers was 35–41% of the product, while the remaining $F_\beta F_\beta'$, $F_\alpha F_\beta'$, and $F_\beta F_\alpha'$ sum represented 59–65% of the product. Thus the single F′ ring was about 1.6 times as reactive as both of the L rings combined. A competitive experiment showed that janusene was nitrated about 11 times as fast as F_β-nitrojanusene.

Although these experiments were not as clear as we would wish, they do answer the questions we have raised. First, it is clear that the presence of a nitro group in the F ring does in fact lower the reactivity of the janusene molecule substantially. It would appear that the lowered reactivity is especially felt in the L (rather than L′) ring and in the other face ring, and this suggests that the interaction is transannular in nature. Second, the fact that both XI and XII are formed in substantial amounts, even though the formation of XI involves more serious steric compressions, suggests that interaction between F rings is a general polarization phenomenon rather than a resonance phenomenon involving specific bond formation between rings in the transition state.[42] If the latter were important and resulted in the expected directive effect, the formation of XII should be greatly favored, assuming resonance interaction such as proposed in the dinitration of [2.2]paracyclophane.

Experimental Section

Spectra. All pmr data were measured on a Varian A-60 spectrometer and are reported in τ units, where $\tau = 10.00$ for the internal standard of tetramethylsilane. Side-band calibration of spectra was made with a Hewlett-Packard Model 202A low frequency function generator and Model 521C electronic counter. The ultraviolet spectra were determined on a Cary Model 14 spectrophotometer. Infrared spectra determined in carbon tetrachloride were taken on a Perkin-Elmer Model 21 instrument; those determined in potassium bromide pellets were taken on a Beckman IR-5 instrument. Mass spectra were taken on a CEC 21-103C mass spectrometer with an inlet heated to about 300°; they were determined by Mr. David C. Scheesley of this department.

Preparation of Janusene (I).[18] A mixture of 18.9 g (0.0925 mole) of dibenzobicyclo[2.2.2]octatriene (III),[43] 16.5 g (0.0925 mole) of anthracene, and 1 g of hydroquinone was heated in a sealed tube under nitrogen at 220 ± 5° for 3 days. The resulting brownish solid was dissolved in benzene–petroleum ether (bp 60–70°), given liberal charcoal treatment, and recrystallized several times from this solvent mixture to give 5.16 g, mp 236–237°, of pure janusene. The remaining material was treated with 10 g of maleic anhydride in 250 ml of refluxing xylenes for 2 hr to remove anthracene; the maleic anhydride adduct was converted to the water-soluble diacid salt by refluxing the xylene solution with 20 g of sodium carbonate and several hundred milliliters of water, after which the xylenes were removed by steam distillation. Recrystallization of the recovered solids gave 7.09 g of pure I, thus giving a total yield of 13.1 g (37%). About 10 g of a yellow oil remaining was chromatographed on Merck 71707 basic alumina; only 0.67 g (4%) of nearly pure III and 1.12 g of I contaminated with bianthryl were recovered. The infrared spectrum of I determined in carbon tetrachloride revealed C–H stretching absorptions at 2905, 2980, and 3010 cm^{-1}, with other strong bands at 1022, 1169, 1458, and 1503 cm^{-1}; the spectrum taken in a potassium bromide pellet also revealed very strong absorptions at 741–735 and 757 cm^{-1}. *Anal.* Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.23; H, 6.05.

Preparation of Chlorodibenzobicyclo[2.2.2]octatriene (IV).[17b] This intermediate was prepared from either *cis*- or *trans*-11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene[17b] according to a procedure typified as follows: 20.4 g (0.074 mole) of the *cis*-dichloride was dissolved in about 200 ml of dimethyl sulfoxide (distilled under reduced pressure and nitrogen from Linde Type 4A Molecular Sieves) by warming to about 60° on a steam bath. The solution was allowed to cool to about 40°; then 12.1 g (0.108 mole) of potassium *t*-butoxide was added rapidly, followed by occasional swirling for about 5 min, with cooling under the water tap. Several volumes of water were then added; the white precipitate was filtered and recrystallized from isopropyl ether–isopropyl alcohol to give 17.8 g (92%) of IV, mp 128.8–129.3°.

Preparation of 5a-Chlorojanusene (V). A mixture of 16.3 g (0.068 mole) of chlorodibenzobicyclo[2.2.2]octatriene (IV), 25.5 g (0.143 mole) of anthracene, and a few tenths of a gram of hydroquinone was heated at 240 ± 10° for 3 days in a sealed tube. The resulting black solid was dissolved in 200–300 ml of benzene, from which some of the unreacted anthracene crystallized and was filtered off. Evaporation of the filtrate gave 27 g of black solid (not dried thoroughly) which was treated with maleic anhydride, as in the preparation of janusene above, and chromatographed twice on 300–500-g portions of Merck 71707 basic alumina with 5–25% benzene in petroleum ether (bp 60–70°). This gave 0.35 g (1.3%) of I (recrystallized to purity from benzene–petroleum ether), 0.3 g (1%) of V, mp 260–262° dec (recrystallized to purity from acetone–alcohol), 0.8 g (6%) of a not fully characterized substance XIII[45] (0.1 g, mp 253–254° after further purification by several recrystallizations from acetone–alcohol), 2 g (10%) of impure unreacted IIb, and traces of bianthryl and the olefin[46] formed by elimination of hydrogen chloride from the bridge positions of V. *Anal.* Calcd for $C_{30}H_{21}Cl$: C, 86.42; H, 5.08. Found: C, 86.15; H, 4.87.

Mononitration of Janusene. Several experiments with moderate variations in conditions were made to prepare the mononitrojanusene isomers. The experiment giving the highest yield of mononitro isomers with less than 1% dinitration is here given in detail. Into a 500-ml erlenmeyer flask with a magnetic stirrer was placed 5.00 g (0.0131 mole) of janusene (I). To this was added most of a portion of 160 ml of nitromethane and 160 ml of acetic anhydride; the janusene was then dissolved and the solution cooled in an ice bath to 2–3°. To this was added the remainder of the solvent portion (10–20 ml, also chilled) containing 0.45 ml (0.0078 mole) of concentrated nitric acid. A cotton plug was placed in the mouth of the flask. The reaction mixture was maintained for 6.2 hr at 1°. Work-up involved addition of several volumes of water and enough concentrated hydrochloric acid to make the solution 2–5% in this acid; warming on the steam bath caused the organic solvents to dissolve, leaving a light yellow precipitate which was filtered, washed, and dried for 1–3 hr at 150° giving about 4.5 g of

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(42) Cram and his co-workers[31] have come to the opposite conclusion for [2.2]paracyclophane, but their results are based upon rather low yields and recoveries.

(43) The olefin III[17] has been prepared in yields of over 90% by treating *cis*- or *trans*-11,12-dichloro-9,10-dihydro-9,10-ethanolanthracene[17b] with zinc (activated by 2–3% copper sulfate) in refluxing 95% ethanol.[44]

(44) S. J. Cristol and W. Y. Lim, unpublished results.

(45) The substance XIII gave a mass spectrum parent peak at *m/e* 442 ± 2. Multiplets in the pmr spectrum occurred at τ 2.96 (15–16 H), 5.9 (4 H), and 7.3 (3 H). These data and the analysis suggest a dimer of IV (which could eliminate hydrogen chloride in the heated inlet of the mass spectrometer to give the observed parent peak). *Anal.* Calcd for $C_{32}H_{22}Cl_2$: C, 80.50; H, 4.65; Cl, 14.85. Found: C, 79.80; H, 4.70; Cl, 15.11.

(46) The synthesis, characterization, and chemistry of this olefin will be published later.

product. The solid was dissolved in warm benzene, with as much petroleum ether (bp 60–70°) added as would not cause precipitation, and chromatographed on about 500 g of Merck 71707 basic alumina. Increasing percentages of benzene in petroleum ether were used in elution; solvent was removed from fractions by evaporation under heat and reduced pressure. Complete separation of unreacted I from mononitrojanusenes and about 90–95% separation of F_α from the other two major mononitro isomers were obtained in this one chromatography; the mixture of F_β and L_β, which came off the column last, was not resolved into its components in this experiment. Petroleum ether and reagent grade benzene used in elution were distilled prior to use to ensure the absence of water and high-boiling impurities. Chromatography fractions were carefully dried at 150° and examined by pmr for purity and to determine the isomer ratio of F_β to L_β. Thus 2.75 g (55%) of I (pure to pmr observation), 0.13 g (2%) of F_α (slightly impure contaminated with 10–20% L_α and/or L_β), and 1.77 g (32%) of the F_β–L_β mixture were obtained. Whereas this experiment gave rise to the isomer percentages reported above in the text, isolation of the pure isomers was pursued further in two other experiments done on the same scale as discussed below.

When 4.94 g (0.0129 mole) of I was treated with 0.0155 mole of concentrated nitric acid at 0–1° for 4.5 hr in a mixture of 150 ml of nitromethane and 150 ml of acetic anhydride, with work-up involving chromatography as above, yields were as follows: recovered I, 16%; mononitrojanusenes, 65%; and dinitrojanusenes, 13%. The F_α mononitro isomer was separated from the other mononitro isomers in the chromatography; after several recrystallizations from acetone–alcohol there was obtained 91 mg (1.3%) of F_α, mp 261–263°. *Anal.* Calcd for $C_{30}H_{21}NO_2$: C, 84.28; H, 4.95. Found: C, 84.46; H, 5.09.

The isomer L_β, being by far the hardest of the three major mononitro isomers to isolate, required several chromatographies interspersed with recrystallization from acetone–alcohol done on material combined from the above two experiments. Use of Woelm Grade I neutral alumina instead of the Merck basic alumina gave moderate improvement in separation of the L_β from F_β. Recrystallization was carried out until 27 mg (0.25% yield from the combined experiments) of L_β (mp 242–244°, isomer purity $\geq 95\%$ by pmr) was isolated. *Anal.* Calcd for $C_{30}H_{21}NO_2$: C, 84.28; H, 4.95. Found: C, 84.12; H, 5.06.

The isomer F_β was the slowest of the three isomers to elute and by far the most abundant, although requiring successive chromatographies and recrystallization from acetone–alcohol to purify it from L_β. Isolation of pure F_β was pursued furthest in a third experiment: 5.02 g (0.0131 mole) of janusene (I) was treated with 0.0157 mole of concentrated nitric acid in 200 ml of nitromethane and 210 ml of acetic anhydride at 1° for 4.0 hr; a yield estimation of 20% I, 54% mononitrojanusenes, and $\leq 8\%$ dinitrojanusenes was made by isolating I and most of the F_β by the above techniques of chromatography and recrystallization, with pmr examination of the remaining mother liquors. A total of 1.77 g (31%) of F_β, mp 288–290°, was obtained. *Anal.* Calcd for $C_{30}H_{21}NO_2$: C, 84.28; H, 4.95; N, 3.28. Found: C, 84.27; H, 4.89; N, 3.26.

Dinitration of Janusene. Direct nitration of janusene (I) with the objective of producing dinitrojanusene isomers was carried out as follows: 4.01 g (0.0105 mole) of I was treated with 0.042 mole of concentrated nitric acid in 170 ml of nitromethane and 170 ml of acetic anhydride at 1° for 4.3 hr; work-up was done as in the mononitration experiments above. Yield estimations of 0% I, 1% mononitrojanusenes, 45% dinitrojanusenes, and 29% trinitrojanusenes were made. Chromatography fractions rich in the isomer $F_\beta L_\beta'$, $F_\beta F_\beta'$ (XI), and $F_\beta F_\beta'$ (XII) were recrystallized from acetone–alcohol to obtain pure isomers (or a pure mixture of isomers having indistinguishable pmr spectra in the case of $F_\beta L_\beta'$).

The $F_\beta L_\beta'$ fractions were contaminated with several other dinitro isomers, but the amount of the latter could be readily reduced by the recrystallization. Two recrystallizations of the combined $F_\beta L_\beta'$ fractions gave 385 mg (7.7%) of $F_\beta L_\beta'$ (mp 234–243°, $\geq 90\%$ isomeric purity by pmr) for which the carbon–hydrogen analysis following was made. *Anal.* Calcd for $C_{30}H_{20}N_2O_4$: C, 76.26; H, 4.27. Found: C, 75.91; H, 4.65. Several fractions of $F_\beta F_\beta'$ (XII) gave no noticeable change in infrared or pmr spectrum when recrystallized once to give 531 mg (11%) of material (decomposes >320°). One of the middle of these fractions was recrystallized a second time to give 25 mg for the analysis following. *Anal.* Calcd for $C_{30}H_{20}N_2O_4$: C, 76.26; H, 4.27. Found: C, 75.92; H, 4.22.

An amount of 0.38 g of material containing $F_\beta F_\beta'$ (XI) and some trinitrojanusenes was rechromatographed on 40 g of Woelm Grade I neutral alumina with benzene, giving 0.22 g of XI pure as to pmr and infrared spectra; the latter spectrum was especially useful in distinguishing XI from XII (see tabulation below). Further recrystallization gave 170 mg (4%) of XI (decomposed above 330°). *Anal.* Calcd for $C_{30}H_{20}N_2O_4$: C, 76.26; H, 4.27. Found: C, 76.32; H, 4.30.

It was also noted that XII was more soluble than XI in benzene, carbon disulfide, chloroform, and acetone; XI was barely soluble enough in acetone and deuteriochloroform to obtain the pmr spectrum. Both isomers decomposed without melting when inserted at 350°, but a mixture of the two gave mp 322–324° dec.

Infrared spectral bands in regions where XI may be distinguished from XII (in potassium bromide pellets) and the ultraviolet spectra for the major dinitrojanusene isomers (in 95% ethanol) are given in Table II.

Table II

XI		XII	
Band, cm^{-1}	Intensity[a]	Band, cm^{-1}	Intensity[a]
760	vs	750	vs
791	m	761	w
826	w	790	w
833	w	828	s
849	m	852	w
1140	m	1154	m

Isomer (s)	λ_{max}, mμ	$10^4\epsilon$
$F_\beta L_\beta'$	305 sh	1.1
	278	1.28
	225 sh	3
XI	306 sh	1.01
	283	1.50
	228 sh	2.2
XII	301	1.09
	272 sh	0.94
	266 sh	0.95
	240 sh	1.6

[a] w = weak, m = medium, s = strong, and vs = very strong.

Nitration of F_β-Nitrojanusene (IX). To 0.935 g (0.00219 mole, $\geq 97\%$ isomeric purity) of IX in 50 ml of nitromethane and 50 ml of acetic anhydride was added 0.00175 mole of concentrated nitric acid; the reaction was maintained for 44 hr at 1°. Work-up, chromatographic separation, and pmr analysis of chromatography fractions was done as in the above mono- and dinitration experiments carried out on janusene, giving rise to the yields and dinitrojanusene isomer ratios reported in the section on results.

Competitive Nitrations. A mixture of 500 mg (1.31 mmoles) of janusene (I) and 404 mg (1.91 mmoles) of dibenzobicyclo[2.2.2]-octadiene (II) in 11 ml of nitromethane and 11 ml of acetic anhydride containing 0.79 mmole of nitric acid was allowed to react for 4.0 hr at 1°. Yield estimations of unreacted I and II were made by chromatography of the solid precipitated from the reaction mixture by water, with pmr analysis of chromatography fractions. As losses of 20–30% of the solid product (assumed to be homogeneous) occurred in the work-up prior to chromatography, the yield estimations are corrected for this to give the amounts of I and II expected to be present in the 22 ml of solution at the end of the reaction: 0.69 mmole of I and 1.74 mmoles of II. Using the expression, $\log [(A)/(A_0)]/\log [(B)/(B_0)] = k_A/k_B$, where (A) and (B) refer to final concentrations of the substrates A and B, and where (A_0) and (B_0) refer to the initial concentrations of A and B, respectively, $k_I/k_{II} \cong 8$.

A second competitive experiment was done with dibenzobicyclo-[2.2.2]octadiene (II) and F-nitrojanusene (IX). A mixture of 241 mg (1.17 mmoles) of II and 500 mg (1.17 mmoles) of IX in 11 ml of nitromethane and 11 ml of acetic anhydride containing 1.17 mmoles of nitric acid was allowed to react for 5.0 hr at 1°. Work-up and analysis were done as in the above experiment, with correction made for 20–30% losses of solids prior to chromatography to give the amounts of II and IX expected to be present in the solution at the end of the reaction: 0.47 mmole of II and 0.63 mmole of IX in 22 ml of solution. Use of the above method of calculation gave $k_{II}/k_{IX} \cong 1.4$. Combining the results of these two experiments gives $k_I/k_{IX} \cong 11$.

Electrophilic Bromination. A quantity of 3.00 g (0.00785 mole) of janusene (I) in 75 ml of carbon tetrachloride was treated with

0.43 ml (0.0080 mole) of bromine in 25 ml of carbon tetrachloride added in portions over a period of 2 hr, with magnetic stirring. A few crystals of iodine were added at first, but very little hydrogen bromide evolution was observed. About 1 g of iron powder was then added in portions so that the evolution went at a good rate at 25°. After 4 hr the brown color gave way to the purple of iodine; the reaction was continued for 1 hr, giving a total time of 5 hr since the start of bromine addition. The solution was washed once with water, twice with aqueous potassium hydroxide, and twice more with water; evaporation gave 3.27 g of nearly colorless solids. Chromatography on 130 g of Merck 71707 basic alumina with 15% benzene in petroleum ether gave 3.20 g of a solid (not thoroughly dried) containing I and monobromojanusenes; elution with 40–95% benzene gave another 0.20 g of material, probably containing dibromojanusenes, as indicated by the infrared spectrum. Recrystallization of the former material from acetone–alcohol gave 1.55 g of the pure F_β isomer, mp 271–273°, and 1.03 g of solid. The latter was chromatographed on 150 g of Woelm Grade I neutral alumina using 5–10% benzene in petroleum ether; partial separation of I from monobromojanusenes was obtained, allowing most of the I and another 0.3 g of pure F_β-bromojanusene to be harvested after recrystallization, giving a total of 1.88 g (52%) of the F_β isomer, mp 271–273°. The infrared spectrum of the F_β isomer (potassium bromide pellet) had a sharp band at 1408 cm^{-1} (m), an unsymmetrical doublet at 1058–1069 cm^{-1} (m), and a broad band at 800 cm^{-1} (m); these absorptions were the most useful in detecting this monobromo isomer in the presence of I or other monobromides in chromatography fractions. *Anal.* Calcd for $C_{30}H_{21}Br$: C, 78.09; H, 4.59. Found: C, 77.75; H, 4.37.

Further chromatography and recrystallization from acetone–alcohol allowed isolation of 10 mg of impure F_α-bromojanusene, mp 244–245°. The analysis below indicates that this isomer was probably contaminated with I. *Anal.* Calcd for $C_{30}H_{21}Br$: C, 78.09; H, 4.59. Found: C, 80.33; H, 5.07.

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Total Synthesis of *dl*-Atisine[1,2]

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Abstract: The first total synthesis of atisine in a racemic form is described. The synthesis of the pentacyclic compound **42c** having the fundamental skeleton of the alkaloid was achieved in a stereochemically unequivocal and highly selective manner starting from the tricyclic conjugated ketone **2**, implying that the suggested configuration of the atisine skeleton is substantiated synthetically. The new hydrocyanation reaction using alkylaluminum and hydrogen cyanide was successfully applied for building up both the A–E and C–D bridged ring system. The pentacyclic compound was further transformed by a three-step reaction sequence to the final compound **46**, which is connected with the six-step, partial synthesis of Pelletier in the natural series to complete the total synthesis of atisine.

The diterpene alkaloids widely distributed throughout the plant world have long been noted for their high toxic properties. In the past decade, the chemistry in this field has been markedly advanced despite the limited availability of the materials in quantity and complexity of the structures.[3] Abundant evidence[3] has been accumulated by the extensive degradative and synthetic work in support of the structure **1**[4] suggested for the first representative aconite alkaloid, atisine. The stereochemistry[3,5–9] of this alkaloid, including the absolute configuration, has also been elucidated as depicted in the formula by interrelating the degradation products with those of the related diterpene alkaloids and diterpenes with some ambiguities remaining in points of the configuration[3c,5,10,11] of the hydroxyl group at C-19 and of the conformation[3c,d,5,10,12] of the E ring.[13]

Since the structure and configuration had been defined, total synthesis of atisine, because of its relative simplicity, has become a target of many synthetic organic chemists. The success is of importance also as a means of providing a definitive proof of the suggested formula **1**. The main difficulty for the synthesis was presumed to be in constructing two bridged ring systems, A–E and C–D, one of the bridge

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[1] Studies on Total Syntheses of Diterpenes and Diterpene Alkaloids I.

[2] For a preliminary communication on this work see W. Nagata, T. Sugasawa, M. Narisada, T. Wakabayashi, and Y. Hayase, *J. Am. Chem. Soc.*, **85**, 2342 (1963). An outline of this work was also presented at the 3rd International Symposium on the Chemistry of Natural Products, Kyoto, Japan, April 1964.

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[11] Pelletier[3c] and Whalley[10] have proposed the 19β configuration of the hydroxyl group on the basis of the fact that atisine is less strongly adsorbed on alumina than its 19 epimer. However, Dvornik and Edwards[5] have considered this basis to be tenuous, although they showed other evidence which might lead to the same conclusion. We adopt this tentative assignment of the allylic hydroxyl group in the present paper.

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[13] Argument on this point has been advanced. See ref 3c,d, 5, and 10. Our work, however, has no concern with this problem.

Nagata, et al. / Synthesis of dl-Atisine