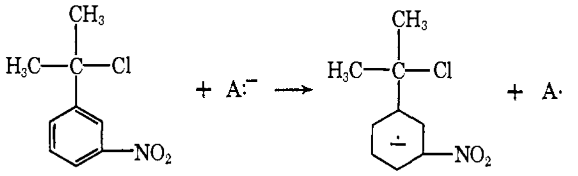
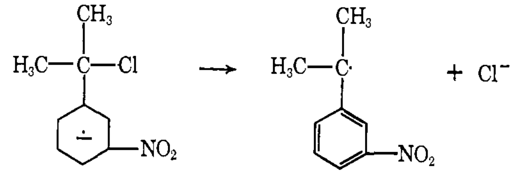
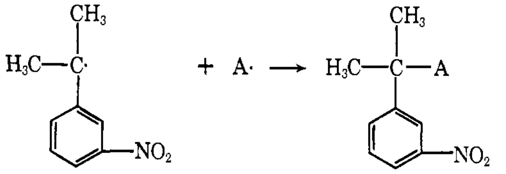
nitrocumyl series. The failure of oxygen to stop substitution and its inability to convert *m*-nitrocumyl chloride into *m*-nitrocumyl alcohol are readily intelligible on this basis. Furthermore, cage combination of two radicals (eq 11) serves to explain the lack of selectivity observed with ambident anions in the *m*-nitrocumyl series, a lack of selectivity which is to be contrasted with the high degree of selectivity exhibited in the *p*-nitrocumyl system.[8,9]


IX

(9)


(10)


(11)

Acknowledgment. We thank the Petroleum Research Fund and the Explosives Department of Du Pont for generous support.

(9) The allocation of a chain mechanism to the *p*-nitrocumyl system and a nonchain sequence to the *m*-nitrocumyl system is a matter which will be discussed in detail in the full paper.

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Received August 21, 1968

The Vibrational Frequency of the O_2^+ Cation

Sir:

A new, easy preparation method for the dioxygenyl compounds of AsF_5 and SbF_5 was recently described by two of us.[1] We now report Raman spectra of the solid powders prepared in this way. The Raman equipment, details of which will be described elsewhere, includes a Spectra-Physics 125 He–Ne laser and a Spex 1400 II double monochromator.

A photograph of the Raman spectrum recorded for $O_2^+AsF_6^-$ is presented in Figure 1 with measured frequencies and assignments marked. By means of calibrations with nearby neon lines, we determined the frequencies to a probable error of about 1 cm^{-1}. Figure 1 clearly shows the three Raman-active vibrations of the octahedral AsF_6^- anion with frequencies close to those observed earlier for $Cs^+AsF_6^-$.[2] In addition, there is one intense band at 1858 cm^{-1}, which can only be assigned to the O_2^+ vibration. This has not, to our knowledge, been observed for solid complexes before, but corresponds quite well to the frequency of 1876 cm^{-1} determined from electronic band spectra of gaseous O_2^+.[3]

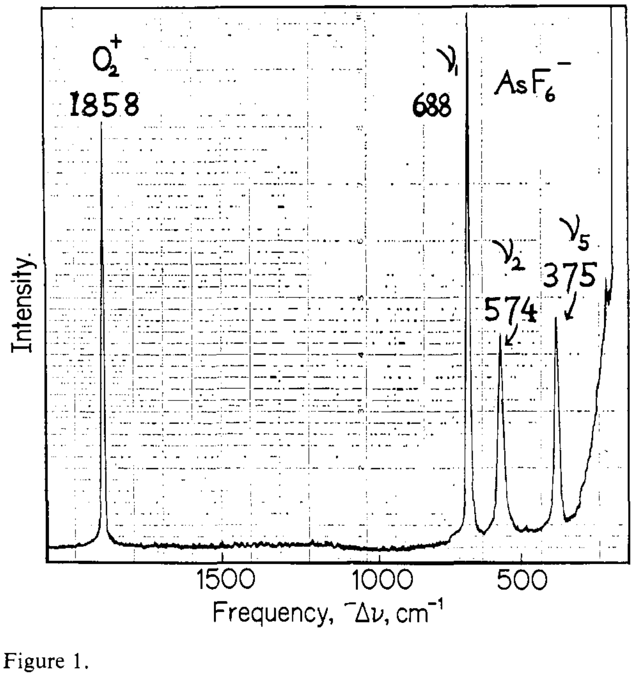

Figure 1.

Our observation of the O_2^+ vibration in the Raman spectrum is perhaps the most convincing or direct proof of the existence of the O_2^+ cation in a stable chemical compound.

We have also observed the O_2^+ vibration for solid $O_2^+SbF_6^-$, this time at 1862 cm^{-1}. It has also been possible to observe it in solution. This was done by dissolving $O_2^+SbF_6^-$ in excess liquid SbF_5. In the solution the O_2^+ vibration was observed at 1860 cm^{-1}.

Table I lists frequencies and force constants of a group of species related to O_2^+, isoelectronic species being in the same row. This table shows the marked decrease in force constant associated with increase of number of electrons.

Table I. Comparison of Frequencies and Force Constants for Related Species of Molecules or Ions

Species	Obsd frequency, cm^{-1}	Force constant, mdyn/Å	Species	Obsd frequency, cm^{-1}	Force constant, mdyn/Å
			NO^+	2387[d]	25.0
O_2^+	1860[a]	16.3	NO	1876[e]	15.5
O_2	1556[b]	11.4	NO^-	1100–1200[f]	5.52
O_2^-	1145[c]	6.18			

[a] Solid or liquid complex: this work. [b] Gas: A. Weber and E. A. McGinnis, *J. Mol. Spectry.*, **4**, 195 (1960). [c] Solid complex: J. A. Creighton and E. R. Lippincott, *J. Chem. Phys.*, **40**, 1779 (1964). [d] Solid complex: D. W. A. Sharp and J. Thorley, *J. Chem. Soc.*, 3557 (1963). [e] Gas: H. W. Thompson and B. A. Green, *Spectrochim. Acta*, **8**, 129 (1956). [f] Solid complexes, average value: W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Chem. Soc.*, 775 (1961).

For the isoelectronic pair, O_2^+ and NO, however, the force constant is nearly the same. This leads us to suggest that the frequency around 1150 cm^{-1} that

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(1) J. Shamir and J. Binenboym, *Inorg. Chim. Acta*, **2**, 37 (1968).

(2) G. M. Begun and A. C. Rutenberg, *Inorg. Chem.*, **6**, 2212 (1967).

(3) G. Herzberg, "Molecular Spectra and Molecular Structure," D. Van Nostrand Co., New York, N. Y., 1950, p 560.

has been assigned to NO^{-} [9] [4] is probably not correct. The frequency of an isolated NO^{-} ion should be nearer to the 1556 cm^{-1} of O_2.

[4] Griffith *et al.*, Table I, footnote *f*.

[5] Supported in part by the U. S. Atomic Energy Commission while on a Guggenheim Fellowship at the Hebrew University of Jerusalem.

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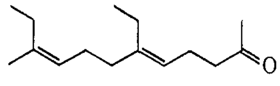
Received June 27, 1968

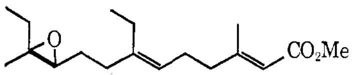
Synthetic Studies on Insect Hormones. VII.[1] An Approach to Stereospecific Synthesis of Juvenile Hormones[2]

Sir:

We wish to report a stereospecific synthesis of *trans*,-*cis*-6-ethyl-10-methyldodeca-5,9-dien-2-one (I), a key intermediate in a synthesis[3] of juvenile hormone (II).[4]



I

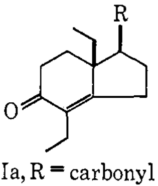


II

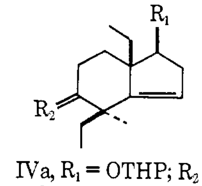
A scarcity of convenient methods for stereospecific synthesis of acyclic trisubstituted olefins led us to examine sequential fragmentation of a bicyclic precursor, VI. Control of olefin geometry is thereby transposed to control of relative stereochemistry in cyclic systems.

Consideration of the *trans* and *cis* olefin geometries in I dictates the required stereochemistry[5] at four of the asymmetric centers in the chosen precursor VI. Configuration at the fifth center, C_{3a}, does not influence the geometry of olefin formation, but markedly affects the ease of concerted internal cleavage in VIb.

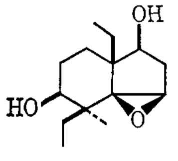
Synthesis of VI was commenced by Michael addition of 2-ethylcyclopentane-1,3-dione,[6] in refluxing methanolic potassium hydroxide solution, to propyl vinyl ketone and *p*-toluenesulfonic acid catalyzed cyclization of the adduct in boiling benzene to afford IIIa[7] [67%; bp 125–127° (0.08 mm)]. Selective reduction of the cyclopentanone carbonyl of IIIa with ethanolic sodium borohydride at 5° led stereospecifically to the required *cis*[8] relationship between hydroxyl and angular ethyl in IIIb[7] (88%; mp 61–62°).



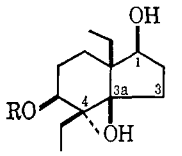
IIIa, R = carbonyl O
b, R = OH
c, R = OTHP



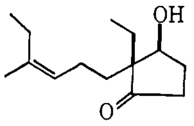
IVa, R_1 = OTHP; R_2 = O
b, R_1 = OH; R_2 = O
c, R_1 = OH; R_2 = β-OH, α-H



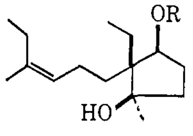
V



VIa, R = H
b, R = *p*-tosyl



VII



VIIIa, R = H
b, R = *p*-tosyl
c, R = 3,5-dinitrobenzoyl

Protection of IIIb as a tetrahydropyran-2-yl ether (THP) allowed generation from IIIc (5 equiv of 0.37 *M* potassium *t*-butoxide in refluxing *t*-butyl alcohol) of the enolate anion which was alkylated from the less hindered α face[9] by methyl iodide at 0° to afford IVa [nmr,[10] 0.81 (t, J = 7 Hz), 1.03 (t, J = 7 Hz, ethyl CH_3), and 1.15 (s, 4α-methyl); 62% from IIIa]. Stereoselectivity of alkylation was indicated to be 95% by gas chromatographic and nmr analyses of IVa and the derived acid hydrolysis product IVb [nmr, 1.14 (s, 4α-methyl)]. Lithium tri-*t*-butoxyaluminum hydride reduction of IVb in refluxing tetrahydrofuran afforded a single crystalline diol, IVc[7] [74%; mp 153–155°; nmr, 1.09 (s, 4α-methyl), 3.33 (dd, J_{aa} = 10 Hz, 5α-H)] with the necessary *cis* orientation of the new equatorial hydroxyl[11] relative to the 4β-ethyl group.

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[1] Part VI: G. Hüppi and J. B. Siddall, *Tetrahedron Letters*, 1113 (1968).

[2] Publication No. 348 from the Syntex Institute of Steroid Chemistry.

[3] K. H. Dahm, H. Röller, and B. M. Trost, *Life Sci.*, 7, 129 (1968); K. H. Dahm, B. M. Trost, and H. Röller, *J. Am. Chem. Soc.*, 89, 5292 (1967).

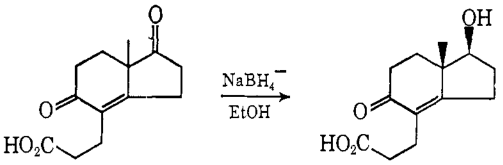
[4] H. Röller, K. H. Dahm, C. C. Sweely, and B. M. Trost, *Angew. Chem. Intern. Ed. Engl.*, 6, 179 (1967).

[5] P. S. Wharton, *J. Org. Chem.*, 26, 4781 (1961), and ref 2 therein.

[6] We are grateful to Dr. Herchel Smith for a generous gift of this compound.

[7] Satisfactory elemental analytical data were obtained for this substance.

[8] *Cf.* Z. G. Hajos, D. R. Parrish, and E. P. Oliveto, *Tetrahedron*, 24, 2039 (1968), and ref 6, 8, and 9 therein; H. Smith, *et al.*, *J. Chem. Soc.*, 4472 (1964); L. Velluz, *et al.*, *C. R. Acad. Sci., Paris, Ser. C*, 257, 3086 (1963), similarly obtained the alcohol ii of proven stereochemistry from diketone i which is closely similar to IIIa.



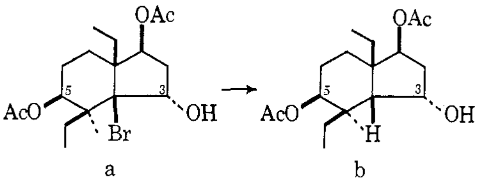
i

ii

[9] α Configuration of the 4-methyl in IVa is stated here for clarity but is assigned from the later finding that fragmentation through C-4 and C-5 in VIb gave stereospecifically a *cis* olefin which fixes[5] the relative configurations at C-4 and C-5. Establishment of configuration[11] at C-5 then allowed assignment at C-4.

[10] Nmr spectra were recorded on a Varian HA-100 spectrometer using deuteriochloroform as solvent and are quoted as δ (parts per million) downfield from tetramethylsilane as internal standard. We wish to thank Miss J. Tremble and Dr. Phyllis Kaplan for these determinations.

[11] The β configuration of hydroxyl at C_5 follows from sequential conversion of IVc to a diacetate and a bromohydrin (a)[7] (mp 144–146°) and chromous acetate–thiophenol reduction of the latter to a diacetoxy secondary alcohol (b)[7] (mp 113–114°). Nmr spectra[10] of compound



a

b