

plex III was formed in high yield. However, in the absence of such a nucleophile using several acid azides, the nitrogen complex was not obtained, but instead a series of new complexes formulated as VI was isolated and characterized through elemental analyses and infrared and nmr spectra.

The mechanism was further clarified by examining the infrared spectrum during the course of the reaction.⁵ Strong, sharp absorption bands were observed at the frequencies illustrated on Figure 1 for the starting carbonyl I, the nitrogen product III, the intermediate acyl isocyanate IV, the carbamate V, and the isocyanate complex VI, depending on the conditions under which the reaction was carried out. These assigned frequencies were independently confirmed by measuring the spectrum of each individual component.

A spectral study of the reaction between furoyl azide and Vaska's complex I in CHCl_3 containing ethanol revealed complete disappearance of the CO peak at 1970 cm^{-1} within 2 to 3 min and simultaneous reduction of the azide band at 2145 cm^{-1} (the azide was present in excess). Synchronous with the diminution of these two bands was the appearance of the nitrogen peak at 2105 cm^{-1} and the carbamate at 1780 and 1710 cm^{-1} . Repeated scans over the lifetime of the reaction revealed no other intermediate peaks in the range $1600\text{--}2400\text{ cm}^{-1}$.

Examination of the same reaction in pure, dry CHCl_3 revealed the appearance of the acyl isocyanate peak at 2250 cm^{-1} along with that of the nitrogen peak at 2105 cm^{-1} . The rapid disappearance of the peak at 2250 cm^{-1} and enhancement of peaks at 1720 and 1690 cm^{-1} , characteristic of the acyl isocyanate complex VI, were observed. Intermediate peaks at 2065 and 1820 cm^{-1} were also observed and are considered to represent an intermediate in the formation of VI.

Further support for this scheme was obtained by examining the infrared spectrum during the course of the reaction between I and phenyl azide. Using CHCl_3 containing alcohol, a doublet at 2260 and 2280 cm^{-1} , characteristic of phenyl isocyanate, appeared at a rate commensurate with the appearance of the nitrogen complex (2105 cm^{-1}) and the disappearance of the carbonyl (1970 cm^{-1}) and the azide (2130 cm^{-1}). In this case the formation of nitrogen complex is slower than the reaction with the more electrophilic acyl azides. Further reaction between phenyl isocyanate and the nitrogen complex is very slow.

Finally, we have independently carried out the reaction between benzoyl isocyanate and the nitrogen complex III, observing the same spectral changes described above for the "dry" reaction and isolating the isocyanate complex VIc.

From these data we propose an initial attack on the acyl azide by the nucleophilic complex I (probably bimolecular) to form a presumed intermediate II (kinetically undetectable) which collapses to the nitrogen complex III and an acyl isocyanate IV. If an alcohol is present, IV is irreversibly intercepted; otherwise, it reacts with the nitrogen complex III to yield VI.

(5) A solution of azide (0.05 M) was slowly added and frozen on a solution (0.05 M) of Vaska's compound previously frozen. The mixture was allowed to partially melt, and samples removed by inverse filtration were rapidly introduced into a 1-mm calcium fluoride cell of special construction such that the solution is not in contact with any metal.

Our tentative formulation of VI as a π -bonded isocyanate is based on its infrared spectrum⁶ (no absorption from 1720 to 2800 cm^{-1}) and its similarity to analogous acetylene complexes prepared from III.⁷ The isocyanate group in VIa has been replaced by disubstituted acetylenes. Two of the isocyanate complexes have been shown to absorb 1 equiv of CO to form stable six-coordinate complexes.⁸ The formulation of the complexes as depicted for VI is of interest inasmuch as heteronuclear multiple bonds transversely π bonded to metals are very unusual.^{9a,b}

This mechanism suggests that other metal carbonyls can be converted to nitrogen complexes by reaction with organic azides. It may be anticipated that a bimolecular pathway involving a low activation energy will be required if the nitrogen complex is to be isolated. Kinetically labile but thermodynamically stable metal carbonyl complexes would be the most appropriate substrates. However, under more vigorous conditions the coordinated nitrogen could act as a reactive intermediate to trap other π -bonding ligands. This could be utilized as a method for preparing new catalyst systems. It is further anticipated that other ligands (such as tertiary phosphines) which react with organic azides can be replaced by nitrogen in this manner. Finally, systems electronically resembling azides, such as nitrous oxide, diazoalkanes, and carbodiimides, may be found to react by analogous pathways. Experiments in progress are testing these hypotheses.

(6) A coordinated isocyanate anion can be excluded since these absorb at $2180\text{--}2200\text{ cm}^{-1}$: D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 1286 (1965).

(7) J. P. Collman and J. W. Kang, *J. Am. Chem. Soc.*, in press.

(8) Acceptable elemental analyses have been obtained on these and all new compounds prepared in this work.

(9) (a) D. P. Tate, A. A. Buss, J. M. Augl, B. L. Ross, J. G. Grasselli, W. M. Ritchey, and F. J. Knoll, *Inorg. Chem.*, 4, 1323 (1965); (b) M. F. Farena and M. J. Brenner, *J. Am. Chem. Soc.*, 88, 3735 (1966).

(10) National Science Foundation Science Faculty Fellow, 1966–1967.

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New Structural and Stereochemical Aspects of the Cyclization of Olefinic Acetals

Sir:

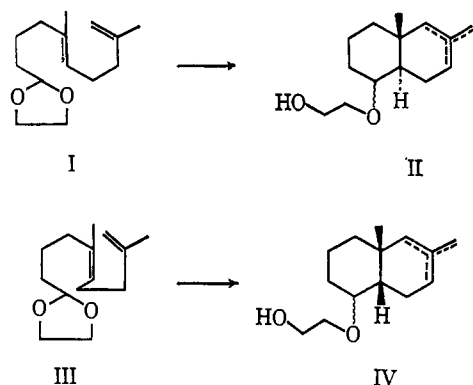
Recently we reported on the stereospecific cyclization of an acyclic trienic acetal to give tricyclic material of "natural" (*trans,anti,trans*) configuration.¹ Unanswered questions of immediate interest were (a) can this method be adapted to the production of fused-ring systems containing the angular methyl group, and (b) is the stereochemical course of the reaction dictated by the configuration of the olefinic bonds in the substrate?² The present study provides unequivocally affirmative answers to both of these questions. Thus the *trans* and *cis* dienic acetals I and III have been shown to undergo rapid stereospecific cyclization to give, in

(1) W. S. Johnson and R. B. Kinzel, *J. Am. Chem. Soc.*, 88, 3861 (1966).

(2) Cf. W. S. Johnson and J. K. Crandall, *J. Org. Chem.*, 30, 1785 (1965), for a discussion of the general stereochemical problem and its relationship to the Stork-Eschenmoser hypothesis.

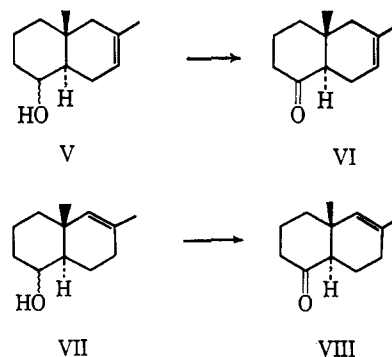
high yield, the *trans* and *cis* angularly methylated octalin derivatives II and IV, respectively.

The acetals I and III were synthesized as follows: the Grignard reagent³ of 1-ethylenedioxy-4-chlorobutane⁴ was allowed to react with acetic anhydride⁵ to give



6-ethylenedioxyhexan-2-one which was treated⁶ with the Wittig reagent from 4-methyl-4-pentenyl bromide.⁷ Preparative vpc gave pure specimens of the liquid acetals: *trans* isomer I (*Anal.* Found: C, 74.75; H, 10.6) and *cis* isomer III (*Anal.* Found: C, 74.65; H, 10.6). The nmr signals for the methyl group at C-5 appeared at 1.60⁸ and 1.68, respectively.⁹

These acetals cyclized more rapidly than the previously reported¹ trienic acetal, presumably because of the greater nucleophilicity of the olefinic bond (tri- instead of disubstituted) involved in the formation of the first ring. Thus, treatment of 0.05 *M* solutions of acetals I and III in benzene with 0.48 mole equiv of stannic chloride for 5 min at 25° effected essentially complete cyclization. The vapor phase chromatogram of the product from the *trans* acetal I showed five new peaks, comprising 91% of the total area, which corresponded to *trans* bicyclic material (II). The major product (peak area 58%) was shown to be 5 β , Δ^2 -II, and the next most abundant isomer (21%) was the 5 α epimer. The other constituents were 5 β , Δ^1 -II (7.5%), 5 α , Δ^1 -II (1%), and probably the 5 β isomer with an exocyclic double bond (3.5%). All but the last substance were isolated by preparative vpc and degraded to the octalols by removal of the hydroxyethyl group.¹ The nmr spectra of the two octalols with equatorial hydroxyl groups, *i.e.*, 5 α -V and 5 α -VII, showed signals for the angular methyl group at δ 0.79 and 0.83 and broad multiplets for the axial 5 β hydrogens centered at 3.43 and 3.55. The spectra of the axial hydroxy isomers 5 β -V and 5 β -VII showed signals for the angular methyl groups at δ 1.01 and 1.07 (shifted downfield as a result of 1,3-diaxial interactions with



the hydroxyl groups¹⁰), and relatively narrow multiplets for the equatorial 5 α hydrogens centered at δ 3.85 and 3.87. The width at half-height of the signals for the vinyl protons of the two Δ^1 isomers VII were 4.7 cps at 5.05 ppm for the 5 β epimer and 5.2 cps at 5.12 ppm for the 5 α epimer, while for the Δ^2 isomers V these values were 9.7 cps at 5.38 ppm and 9.3 cps at 5.37 ppm. The band-broadening in the case of the Δ^2 isomers results from additional coupling with the adjacent protons at C-4. Oxidation of the two Δ^2 epimers V with Jones reagent yielded a single octalone VI. Similarly both Δ^1 epimers VII yielded a single octalone VIII. The nmr spectra of the octalones exhibited singlets at δ 0.76 and 0.83, respectively, for the angular methyl groups. Wolff-Kishner reduction of the Δ^2 -octalone VI gave a 3:2 mixture of *trans*- and *cis*-2,9-dimethyl- Δ^2 -octalin.¹¹ These hydrocarbons were isolated by preparative vpc and identified by comparison with authentic materials prepared from *cis*- and *trans*-9-methyl-2-decalone¹² by reaction with methyl-lithium followed by dehydration.

The product of cyclization of the *cis* acetal III was similarly mainly composed of bicyclic material (vpc area 88.5% of total), completely different from any of the products formed in the *trans* series. The total mixture was degraded and oxidized as described above to give in 66% over-all yield a 3:7 mixture of the *cis*- Δ^1 - and Δ^2 -octalones IX and X, separated by preparative vpc. Evidence that these octalones belonged to the *cis* series was provided by the appearance of the nmr signals for the angular methyl groups at lower field (δ 1.07 for ketone IX and at 1.06 for X) than in the *trans* series.¹³ Wolff-Kishner reduction of the Δ^2 -octalone X gave a 3:2 mixture of *trans*- and *cis*-2,9-dimethyl- Δ^2 -octalin. Similarly the Δ^1 -octalone IX gave the corresponding *trans*- and *cis*- Δ^1 -octalins in a 2:3 ratio. Treatment of each of the ketones IX and X with

(10) Cf. R. F. Zürcher, *Helv. Chim. Acta*, **46**, 2054 (1963).

(11) Such isomerization during the Wolff-Kishner reduction is an established phenomenon; see, *inter alia*, C. Djerassi, T. T. Grossnickle, and L. B. High, *J. Am. Chem. Soc.*, **78**, 3166 (1956).

(12) *cis* isomer: A. J. Birch and R. Robinson, *J. Chem. Soc.*, 501 (1943); W. S. Johnson, P. J. Neustaeder, and K. K. Schmiegell, *J. Am. Chem. Soc.*, **87**, 5148 (1965). *trans* isomer: W. Nagata, I. Kikkawa, and M. Fujimoto, *Chem. Pharm. Bull. (Tokyo)*, **11**, 226 (1963); W. Nagata and I. Kikkawa, *ibid.*, **11**, 289 (1963).

(13) The observed differences in chemical shift between the *cis*- and *trans*-octalones are larger than that of 0.13 ppm between *cis*- and *trans*-9-methyldecalin: M. J. T. Robinson, *Tetrahedron Letters*, 1685 (1965). Insofar as the *cis* isomers adopt the "steroid" A/B conformation, the carbonyl group will cause an extra downfield shift of about 0.23 ppm relative to the *trans* isomers (*cf.* ref 10). In their "nonsteroid" conformations, the carbonyl group has no extra effect, but in this case the methyl group becomes equatorial to the ring containing the olefinic bond, which also results in a downfield shift: J. W. ApSimon, W. G. Craig, P. V. Demarco, D. W. Mathieson, L. Saunders, and W. B. Whalley, *Chem. Commun.*, 359 (1966); A. C. de Paulet and J. Bascoul, *Bull. Soc. Chim. France*, 939 (1966).

(3) Cf. C. Feugas and H. Normant, *Bull. Soc. Chim. France*, 1441 (1963).

(4) M. G. Pleshakov, A. E. Vasil'ev, I. K. Sarycheva, and N. A. Preobrazhenskii, *J. Gen. Chem. USSR*, **31**, 1433 (1961).

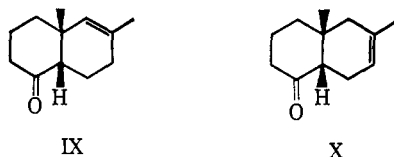
(5) Cf. M. S. Newman and W. T. Booth, Jr., *J. Am. Chem. Soc.*, **67**, 154 (1945).

(6) Cf. R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).

(7) Prepared from the corresponding alcohol: W. S. Johnson and R. Owyang, *J. Am. Chem. Soc.*, **86**, 5593 (1964).

(8) All nmr signals are given in ppm relative to tetramethylsilane = 0 at 60 Mc.

(9) These values are in agreement with those of R. B. Bates and D. M. Gale, *J. Am. Chem. Soc.*, **82**, 5749 (1960), for the methyl resonance of *trans* and *cis* substances of structure R¹CH=C(CH₃)R². Thirteen additional supporting examples have been collected by B. B. Molloy of our laboratory.



base effected partial conversion into the respective *trans* isomers, VIII and VI.

Since there is no stereochemical crossover in the cyclization of the two isomeric acetals, the process is stereospecific and must either be synchronous or involve cationic intermediates that maintain their stereochemical integrity.

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Fluorine Oxidation of Tetravalent Uranium and Neptunium to the Pentavalent State¹

Sir:

Fluorine oxidation of uranium tetrafluoride in a slurry of anhydrous liquid HF has been found to be a new and useful synthesis for pentavalent uranium compounds. We find that fluorine oxidation of UF₄ dispersed in liquid anhydrous HF proceeds readily to UF₅ but then goes only very slowly to UF₆. When both alkali fluoride and UF₄ are present in liquid HF, fluorine oxidation halts at U(V) in the form of the soluble UF₆⁻ ion. This technique is especially useful in the preparation of pure MUF₆ compounds, avoiding the separate preparation and handling of UF₅.

The pentafluorides of the heavier actinides, neptunium and plutonium, have not been prepared although the tetra- and hexafluorides of both are well known.² Therefore, after successfully preparing UF₅ by the method just described, we attempted to extend the technique to neptunium. Although oxidation of Np(IV) to Np(V) was observed in cesium hydrogen fluoride solution, NpF₅ itself could not be isolated.

Fluorine Oxidation of U(IV) to U(V). (a) We prepared UF₅ from UF₄ by stirring a suspension of high-surface-area UF₄ in liquid anhydrous HF at 25° under 10 psig of F₂. (High-surface-area UF₄ was made by dehydrating UF₄·2.5H₂O in a stream of gaseous H₂ and HF for 2 hr at 200° followed by 3 hr at 450°.) The oxidation on a 3–5-g scale essentially halted at β-UF₅ in 1–4 hr, and many more hours were required before significant quantities of UF₆ were formed.

(b) A stirred slurry of CsF and UF₄ (1:1 mole ratio) in liquid HF reacted smoothly with F₂ at 10 psig and 25°, yielding a clear blue solution of CsUF₆. (A Teflon-coated bar magnet is convenient for stirring.) On evaporation of HF, blue crystals of pure CsUF₆ were obtained; with RbF, light yellow RbUF₆ crystals were deposited.³ The UF₄ need not be of high surface area since the reaction proceeds readily to completion, probably because the MUF₆ reaction products are soluble.

(1) This work was sponsored by the U. S. Atomic Energy Commission.

(2) J. J. Katz and G. T. Seaborg, "The Chemistry of the Actinide Elements," John Wiley and Sons, Inc., New York, N. Y., 1957.

(3) G. D. Sturgeon, R. A. Penneman, F. H. Kruse, and L. B. Asprey, *Inorg. Chem.*, **4**, 748 (1965).

To avoid weighing hygroscopic, heavy alkali fluorides, the nonhygroscopic chlorides can be substituted. In this case, HF is condensed onto the alkali chloride–UF₄ mixture and the HCl, which is formed when the mixture is warmed, is vented through a trap. After this step, F₂ is admitted and the suspension is stirred. We use weighable, translucent Kel-F tubes (with a flared end for connection to a Monel line) to observe the course of the reaction. Five-gram quantities of UF₄ are conveniently oxidized to soluble MUF₆ in 30–45 min at 25°. *Caution:* Before admitting fluorine, any hydrogen frequently present in the tank of HF must be removed; this is done readily by condensing the HF and pumping off gases volatile at liquid nitrogen temperatures.

Preparation of Np(V). At 25°, a slurry of NpF₄ (0.17 g) in HF was not oxidized to NpF₅ by 10 psig of F₂. However, when 10 g of CsF was added and the excess HF pumped off, the green NpF₄ dissolved in the warm CsF·2HF melt (mp ~50°). Neptunium(IV) was then oxidized by F₂ at 70° to a soluble, magenta-colored Np(V) fluoride complex. The absorption spectrum of Np(V) in this cesium difluoride melt closely resembled that of pure CsNpF₆; in addition, CsNpF₆ was identified as the pink solid deposited from this solution.⁴ When several milliliters of liquid HF was recondensed on this Np(V) material, *disproportionation* took place leaving green NpF₄ behind and yielding orange, volatile NpF₆. This behavior contrasts with that of CsUF₆ which is completely stable in anhydrous HF.

(4) L. B. Asprey, T. K. Keenan, R. A. Penneman, and G. D. Sturgeon, *Inorg. Nucl. Chem. Letters*, **2**, 19 (1966).

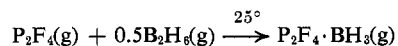
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The Basic Properties of Tetrafluorodiphosphine. The Synthesis of Tetrafluorodiphosphine Borane

Sir:

In recent papers, reactions of the new compound P₂F₄ with some Brønsted–Lowry acids of general formula HX, to give products of the forms F₂PH^{1a} and F₂PX, were mentioned very briefly.^{1b} On the basis of present evidence, a transition-state complex of the form F₂PPF₂·HX could account for the products, or a free-radical mechanism involving F₂P· radicals would be reasonable. A cleavage of the P–P bond to give F₂POPF₂ has also been reported by Lustig, Ruff, and Colburn,² but, as in the other cases, the nature of the transition state was not defined.

When a Lewis acid containing only hydridic hydrogen (*i.e.*, BH₃) is used in place of a Brønsted–Lowry acid, the complex F₂PPF₂·BH₃ is formed. The reaction can be described by the equation



No evidence for a double adduct has yet been obtained

(1) (a) Reaction of F₂PH with HI to give F₂PH HI has also been noted: R. W. Rudolph, Ph.D. Dissertation, University of Michigan, 1966; (b) R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Am. Chem. Soc.*, **88**, 3729 (1966).

(2) M. Lustig, J. K. Ruff, and C. B. Colburn, *ibid.*, **88**, 3875 (1966).