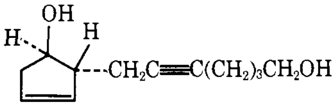
Treatment of **11** with an ethereal solution of triethylamine (10 equiv, room temperature, 2 hr) gave the hydroxyenone **12** (85% yield after silica gel chromatography; ir ν 3480, 1710, 1590 cm^{-1}; NMR δ 4.97 (b s, 1 H), 6.22 (d of d, J_1 = 5.5 Hz, J_2 = 1.5 Hz, 1 H), 7.63 (d of d, J_1 = 5.5 Hz, J_2 = 2 Hz, 1 H)).

Isomerization of **12** to **13** was carried out by addition of 1.1 equiv of anhydrous chloral in ether. This leads to the formation of the chloral hemiacetal of **12** (typical α- and β-vinyl protons of cyclopentenone in the NMR spectrum), which upon addition of triethylamine in excess was transformed extremely rapidly into **13** (disappearance of the α-vinyl proton and appearance of a new β-vinyl proton) via the intermediate acetal. Isolation (preparative thin layer chromatography on silica) gave the desired **13,** free of starting material, in 78% yield: ir ν 3350, 1710, 1650 cm^{-1}; NMR δ 2.87 (d of d J_1 = 19 Hz, J_2 = 5 Hz) and 3.02 (s or t, J = 2.5 Hz, 4 H), 4.90 (m, 1 H), 7.39 (m, 1 H); *m/e* (M + H)$^+$ 193.

The prostaglandin intermediate **16** was prepared in a similar manner, starting with alkylation of the lithium salt of **8** with the ethoxyethyl ether of 4-bromobutanol, followed by removal of the protecting groups with aqueous acetic acid. The cyclopentenol **14** was thus obtained in 82% yield after silica gel chromatography (bp 100-105° (0.3 mm); ir ν 3290, 1065 cm^{-1}; NMR δ 3.5-3.76 (m, 2 H), 4.23 (d of t, J_d = 7 Hz, J_t = 4 Hz, 1 H), 5.72 (~s, 2 H); mass spectrum *m/e* (M + H)$^+$ 195).



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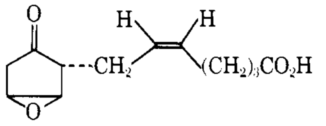

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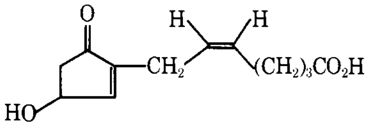

16

Peracid oxidation, as for **9** to **10,** gave the related epoxide[9] (bp 140-145° (0.05 mm); ν 3340, 1070, 840; NMR δ 3.4-3.9, (m, 5 H); mass spectrum *m/e* (M + H)$^+$ 211). The acetylenic bond was reduced at this stage (5% palladium on barium sulfate-trace of quinoline) and the resulting cis olefin (78% yield; bp 140-150° (0.15 mm); ν 3320, 1065, 838 cm^{-1}; NMR δ 34-3.6 (m, 5 H), 5.2-5.4 (m, 2 H); mass spectrum *m/e* (M + H)$^+$ 213) was oxidized with 3.6 equiv of Jones reagent to produce in 90% yield, the epoxyketoacid **15** (ir ν 3400-2700, 1750, 1715, 835 cm^{-1}; NMR δ 3.5-3.8 (m, 2 H), 5.3-5.5 (m, 2 H)). Rearrangement of **15** was carried out, without isolation of the intermediate enone of type **1** (cf. **11** → **12** → **13**), by treatment at room temperature in 1:1 ether-methylene chloride with triethylamine (2.5 equiv, 7 hr) followed by anhydrous chloral (1.1 equiv, 12 hr) to give **16** in 69% yield after chromatography on silica (ν 3400-2600, 1710, 1640 cm^{-1}; NMR δ 4.9 (m, 1 H), 5.49 (b t, J = 4.5 Hz, 2 H), 7.12 (b s, 1 H)). The methyl ester, *ex* diazomethane on **16** had λ_{max}^{MeOH} 220 nm, ε 7800, mass spectrum *m/e* (M + H)$^+$ 239.[10]

Addition of the lithium dialkyl cuprate derived from *trans*-1-iodo-1-octene-3-ol, protected as its α-ethoxyethyl ether produced the separable 15-epimers of PGE_2 as has already been described.[10,11]

References and Notes

(1) The use of hydroxycylopentenones of this general type in prostaglandin synthesis has been reported on several occasions; cf., inter alia, C. H. Sih, J. B. Heather, G. P. Perruzzoti, P. Price, R. Sood, and L.-F. H. Lee, *J. Am. Chem. Soc.*, **95,** 1676 (1973); A. F. Kluge, K. G. Untch, and J. H. Fried, *ibid.*, **94,** 9256 (1972); J. G. Miller, W. Kurz, K. G. Untch, and G. Stork, *ibid.*, **96,** 6774 (1974).

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(4) For an interesting use of a chloral hemiacetal in controlling the direction of acetoxymercuration, cf. L. E. Overman, *J. Chem. Soc., Chem. Commun.*, 1196 (1972).

(5) This mechanism is also supported by a recent report of the elimination of an isopropylidene analog of our acetal intermediate. (L. Gruber, I. Tomoskozi, E. Magor, and G. Kovacs, *Tetrahedron Lett.*, 3729 (1974).

(6) Cf. E. J. Corey and H. A. Kirst, *Tetrahedron Lett.*, 5041 (1968). It was, however, necessary to omit the (unessential) tetramethylethylenediamine in the formation of the anion to get satisfactory results in the epoxide opening.

(7) The stereo- and regiospecificity of the reaction leading to 7 were established by demonstrating the identity of the 2-butylcyclopentanol obtained by C-methylation and reduction of 7 with *trans*-2-butylcyclopentanol derived via hydroboration of 1-butylcyclopentene.

(8) Spectra were taken either neat (ir) or in $CDCl_3$ (NMR). The NMR values are in parts per million with tetramethylsilane as internal standard. Mass spectra were taken by chemical ionization, using methane as carrier, on a Finnigan 3300 mass spectrometer.

(9) The epoxide thus obtained was very largely one isomer. Its stereochemistry follows from the work of A. C. Darby, H. B. Henbest, and I. McClenaghan, *Chem. Ind.*, (*London*), 462 (1962).

(10) This compound has previously been synthesized by a combination of chemical and microbiological steps, in optically active form, by J. B. Heather, R. Sood, P. Price, G. P. Peruzzotti, S. S. Lee, L. F. H. Lee, and C. J. Sih, *Tetrahedron Lett.*, 2313 (1973). In a very recent publication (M. B. Floyd, *Synth. Commun.*, **4,** 317 (1974)) the isomerization of **15,** prepared by a different route, was carried out with aqueous base to **16.** In our hands, this isomerization procedure was much less satisfactory than the one described here.

(11) We thank the National Institutes of Health and the National Science Foundation for their support of this work.

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Activation of Molecular Hydrogen by a Transition Metal Carbonyl Radical Species[1]

Sir:

It has been shown that photochemical generation of a coordinatively unsaturated, 16 electron transition metal carbonyl species results in activation of molecular hydrogen.[2] In these instances it is reasonable to suppose that oxidative addition to the metal occurs, though no evidence has been proferred as to whether or not the active metal species is the 16 electron moiety. Reaction of a 17 electron transition metal species with H_2 is exemplified by the much studied $Co(CN)_5{}^{3-}$ system.[3] Despite a considerable effort, however, the intimate mechanism of the step in which H_2 undergoes reaction is not clear. It is possible, for example, that oxidative addition occurs, resulting in a seven-coordinate species with 19 electrons about cobalt. Prior dissociation of CN^- would result in a species with 15 electrons, which might then undergo the reaction with H_2,[4] but the lack of dependence on CN^- concentration in the reaction of $Co(CN)_5{}^{3-}$ with H_2[5] argues against this. The equilibrium

$$H_2 + N_2Co(PPh_3)_3 \rightleftarrows N_2 + H_2Co(PPh_3)_3$$

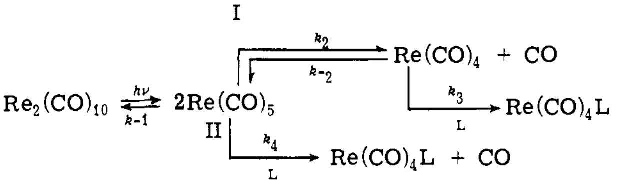
involving two 17 electron systems, has been reported.[6] There is, however, no evidence regarding the possible intermediacy of a 15 electron species.

We have recently shown that substitution of $HRe(CO)_5$

occurs via a radical chain process, in which the radical species $Re(CO)_5$ undergoes substitution by L.[7] The experiments reported here were undertaken to more clearly establish the pathway by which substitution occurs on $Re(CO)_5$, and to investigate the activation of H_2 by the 17 electron $Re(CO)_5$ species, generated photochemically by irradiation of $Re_2(CO)_{10}$ at 311, 350, or 358 nm.

When $Re_2(CO)_{10}$ is irradiated at 311 or 350 nm in the presence of tributylphosphine, PBu_3, a complex set of products, including $Re_2(CO)_8(PBu_3)_2$, $Re_2(CO)_9PBu_3$, and $Re(CO)_3(PBu_3)_2$ are formed. A 1000-W mercury-xenon lamp is used; filtering is accomplished using narrow bandwidth interference filters. Typically the experiment is carried out at 5×10^{-4} *M* $Re_2(CO)_{10}$ in hexane, with variable excess ligand concentration. At constant light flux and at ambient temperature the rate of disappearance of $Re_2(CO)_{10}$ is independent of ligand concentration. Furthermore the rate is the same when $P(OCH_3)_3$ is substituted for PBu_3. Saturation of the solution containing 5×10^{-4} *M* $Re_2(CO)_{10}$ and 3×10^{-3} *M* PBu_3 or $P(OCH_3)_3$ with CO (solubility ~0.01 *M*) causes the rate of disappearance of $Re_2(CO)_{10}$ to decrease by a factor of about 1.7.

Alternative pathways by which the $Re(CO)_5$ radical might undergo substitution are shown below as I or II.



Pathway I should show CO inhibition. Further, when [L] ≫ [CO] as is the case in the absence of added CO, the rate of formation of $Re(CO)_4L$ (and thus of stable products derived therefrom) is independent of [L]. Pathway II should show ligand dependence and independence of added CO, contrary to the observations.

When $Re_2(CO)_{10}$ is irradiated at 311 nm, using a narrow bandpass, low transmittance interference filter, in the presence of H_2 (1 atm) in hexane solution, slow formation of $HRe_3(CO)_{14}$ results. This compound is easily identified by its ir spectrum in the carbonyl region.[8] No other product is formed in substantial amount, but the ir bands due to lesser amounts of other products could easily be obscured by the dominant $HRe_3(CO)_{14}$ bands. When the narrow bandpass filter is replaced by a wider bandpass, high transmittance filter (λ_{max} 358 nm) irradiation of $Re_2(CO)_{10}$ in the presence of H_2 yielded $H_2Re_2(CO)_8$ and $HRe(CO)_5$, identified by their ir spectra.[9,10] One hour of irradiation served to completely remove $Re_2(CO)_{10}$. Continued irradiation over several hours caused decomposition of $HRe(CO)_5$ and to a lesser extent of $H_2Re_2(CO)_8$, with formation of a light brown CO-containing solid of unknown composition. Using a cutoff filter consisting only of 4.5 mm Pyrex glass, irradiation of $Re_2(CO)_{10}$ in the presence of H_2 also yields mainly $H_2Re_2(CO)_8$ as the dominant product. Other products seen in lesser amounts are $HRe_3(CO)_{14}$, $H_3Re_3(CO)_{12}$,[11] and $HRe(CO)_5$.

We suggest that the processes occurring in these systems under photolysis are as follows:

$$Re_2(CO)_{10} \underset{k_{-1}}{\overset{h\nu}{\rightleftharpoons}} 2Re(CO)_5$$

$$Re(CO)_5 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Re(CO)_4 + CO$$

$$Re(CO)_4 + H_2 \longrightarrow H_2Re(CO)_4$$

$$H_2Re(CO)_4 + Re(CO)_5 \longrightarrow HRe(CO)_5 + HRe(CO)_4$$

$$HRe(CO)_4 + Re(CO)_5 \longrightarrow HRe_2(CO)_9$$

$$HRe(CO)_5 + Re(CO)_4 \longrightarrow HRe_2(CO)_9$$

$$HRe_2(CO)_9 + Re(CO)_5 \longrightarrow HRe_3(CO)_{14}$$

$$HRe(CO)_4 + HRe(CO)_4 \longrightarrow H_2Re_2(CO)_8$$

$$H_2Re_2(CO)_8 + HRe(CO)_4 \longrightarrow H_3Re_3(CO)_{12}$$

An important element in this scheme is oxidative addition to $Re(CO)_4$. This follows in part from the substitution experiments detailed above. The product of oxidative addition should be subject to facile hydrogen abstraction by $Re(CO)_5$ as indicated.[7] This leaves $HRe(CO)_4$, a 16 electron system. While there are plausible alternatives to certain reactions in the scheme, the *major* points are that activation of molecular hydrogen is seen, and that it probably occurs via oxidation of H_2 to a 15 electron intermediate species. One of the major attractions of postulating an $HRe(CO)_4$ intermediate is that it provides a reasonable explanation for the appearance of $H_2Re_2(CO)_8$ when the photon flux is high. Under these conditions, the steady state concentration of $HRe(CO)_4$ could increase to the point where simple dimerization dominates as a reaction pathway. Reaction of $H_2Re_2(CO)_8$ with still another $HRe(CO)_4$ leads to $H_3Re_3(CO)_{12}$, observed as a minor product.[12]

One alternative to the proposed scheme is a photodissociation of CO from $Re_2(CO)_{10}$, leading to oxidative addition and subsequent reductive elimination of $HRe(CO)_5$.

$$Re_2(CO)_{10} + h\nu \longrightarrow Re_2(CO)_9 + CO$$

$$Re_2(CO)_9 + H_2 \longrightarrow H_2Re_2(CO)_9$$

$$H_2Re_2(CO)_9 \longrightarrow HRe(CO)_5 + HRe(CO)_4$$

This pathway seems to us less likely because it does not seem reasonable that the rate of photodissociation of CO from $Re_2(CO)_{10}$ at 358 nm could be rapid enough under our conditions. In addition, photolysis of $Re_2(CO)_{10}$ at 350 nm in the present of a ligand L yields little $Re_2(CO)_9L$.

Graham and coworkers have reported several interesting compounds related to $HRe_3(CO)_{14}$ resulting from photolysis of $Re_2(CO)_{10}$ in the presence of R_3SiH compounds.[13] We suggest that these compounds are probably also formed via reactions analogous to those detailed above. Photolysis of $Re_2(CO)_{10}$ in the presence of H_2 has obvious synthetic possibilities. Since 17 electron radical intermediates generated photochemically are evidently labile and their dissociation products reactive, it might be expected that these species should serve as catalysts for a variety of interesting reactions.

References and Notes

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Solvation Energies of Aliphatic Ammonium Ions in Water and Fluorosulfuric Acid

Sir:

We wish to report the heats of ionization (ΔH_i) of ammonia and 12 aliphatic amines in HSO_3F and the heats of solvation of the corresponding ammonium ions ΔH_S (BH^+) in this medium. The results allow an informative comparison with those for the same amines and their ions in water. HSO_3F is 21–22 powers of ten stronger than H_2O as a Brönsted acid toward amines;[1] nonetheless the *relative* values, $\delta\Delta H_i$ and $\delta\Delta H_S$ (BH^+), for these bases and their ions are of similar magnitude in both media. Thus the dramatic leveling of amine base strengths in water relative to those in the gas phase[2-4] is not peculiar to aqueous systems.

The heat of ionization in HSO_3F has been suggested as a useful criterion of Brönsted basicity which may be applied to most types of organic bases.[5,6] At present the amines are the only class of neutral organic base for which we also have a large collection of basicity data referred unequivocally to a standard state in water. They are therefore a natural choice for initiating studies of the solvation energies of onium ions in different media.[7]

Presented in Table I are the data necessary for determining the relative heats of solvation of ammonium ions into HSO_3F from the gas phase, $\delta\Delta H_S$ (BH^+) HSO_3F, using gas phase ionization enthalpies, ΔH_i (g), and heats of vaporization, ΔH_v, with heats of ionization in HSO_3F, ΔH_i, and the use of a Born–Haber cycle described previously.[2-4,8,9]

What we call heats of ionization are in fact heats of transfer from an "inert" solvent to HSO_3F. This device is required by the fact that in this medium the heat of solution of the neutral amine cannot be measured without ionizing it. No such difficulty arises in water where ΔH_i is obtained readily as the difference between heats of solution at low pH, where ionization is complete, and at high pH, where ionization is negligible. It is crucial for comparing ΔH_i values in HSO_3F that no specific interactions occur between the "inert" solvent and the different amines as a result of structural variation in the latter. Results presented in Table II demonstrate that for several of the smaller amines the variation in heat of solution from one solvent to another is not systematic and is on the average about ±0.5 kcal/mol.[10] Heats of solution of gaseous amines employed apparatus similar to that used by Jones[2]—liquid amines were treated as before.[5,6] We note regretfully that there is no means at present for estimating relative free energies of ionization in HSO_3F.

Figure 1 presents a comparison of the heats of solvation of ammonium ions in HSO_3F and in water. Despite the enormous difference in basicity of these media and the complete absence (by definition) of hydrophobic contributions in HSO_3F, there is a remarkably close parallel in trend *and in magnitude* between the two sets of data although the slope (0.83) shows that HSO_3F is a less discriminating solvent for these ions than is water. The points in Figure 1 are differentiated primarily in terms of the number of protons

Table I. Enthalpies of Ionization (ΔH_i), Solution (ΔH_S), and Vaporization (ΔH_{vap}) for Aliphatic Amines and Their Ammonium Ions

	$-\Delta H_S$ (HSO_3F)	ΔH_{inert}	$-\Delta H_i$ (HSO_3F)	ΔH_{vap}	ΔH_S (B)	ΔH_i(g)	$-\delta\Delta H_i$(g)	$-\delta\Delta H_i$ (HSO_3F)	$-\delta\Delta H_S$ (B)	$\delta\Delta H_S$ (BH^+)HSO_3F	$\delta\Delta H_S$ (BH^+)H_2O
1. NH_3	47.3 ± 0.7[a]	−4.0 ± 0.2[a]	43.3 ± 0.9[a]		−4.0	207[a,d]	0	0	0	0	0[d]
2. $MeNH_2$	51.7 ± 0.3[a]	−5.4 ± 0.2[a]	46.3 ± 0.5[a]		−5.4	216[a,d]	9.3	3.0	1.4	4.9	6.0[d]
3. Me_2NH	53.8 ± 0.5[a]	−6.0 ± 0.2[a]	47.8 ± 0.7[a]		−6.0	222.4[a,d]	15.4	4.5	2.0	8.9	11.2[d]
4. Me_3N	53.5 ± 0.7[a]	−6.0 ± 0.2[a]	47.5 ± 0.9[a]		−6.0	226.6[a,d]	19.6	4.2	2.0	13.4	18.6[d]
5. $EtNH_2$	52.9 ± 0.6	−6.1 ± 0.2	46.8 ± 0.8		−6.1	218.8[a,d]	11.8	3.5	2.1	6.2	6.1[d]
6. Et_2N	48.1 ± 0.3[c]	−0.42 ± 0.06	47.7 ± 0.3[c]	7.45	−7.9	227.2[a,d]	20.2	4.4	3.9	11.9	13.1[d]
7. Et_3N	49.8 ± 0.3[c]	−0.64 ± 0.08	49.2 ± 0.3[c]	8.35	−9.0	233.3[a,d]	26.3	5.9	5.0	15.4	20.3[d]
8. $PrNH_2$	45.7 ± 0.5	0.43 ± 0.05	46.2 ± 0.5	7.5	−7.0	(219.9)[e]	12.9	2.9	3.0	(7.0)[f]	(6.7)[f]
9. Pr_2NH	48.4 ± 1.0	0.19 ± 0.02	48.6 ± 1.0	9.57	−9.4	(229.5)[e]	22.5	5.3	5.4	(11.8)[f]	(13.1)[f]
10. $BuNH_2$	45.0 ± 0.4	1.15 ± 0.07	46.2 ± 0.7	8.55	−7.4	(220.4)[e]	13.4	2.9	3.4	(7.1)[f]	(6.3)[f]
11. Bu_2NH	46.7 ± 0.5[c]	−0.30 ± 0.05	46.4 ± 0.6[c]	11.8	−12.1	(230.3)[e]	23.3	3.1	8.1	(12.1)[f]	(11.7)[f]
12. *i*-$PrNH_2$	48.8 ± 0.8	0.46 ± 0.4	49.3 ± 0.8	6.60	−6.1	221.2[d]	14.2	6.0	2.1	6.1	7.9[d]
13. *t*-$BuNH_2$	48.4 ± 0.5	0.44 ± 0.06	48.8 ± 0.5	7.08	−6.6	223.3[d]	16.3	5.5	2.6	8.2	8.8[d]

[a] From E. M. Arnett and J. F. Wolf, *J. Am. Chem. Soc.*, 95, 978 (1973). [b] From E. M. Arnett and J. V. Carter, *ibid*, 93, 1516 (1971). [c] From ref 5. [d] From ref 2. [e] From ref 4; 2.4 kcal/mol has been subtracted from values in ref 2 to normalize them to same scale as those from ref *a*. [f] Calculated from adjusted values, see footnote *e*.