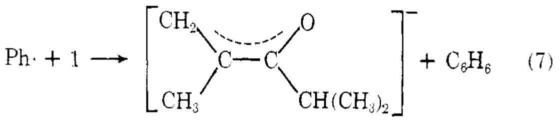
concomitant generation of an α,β-unsaturated ketone function in the side chain. Similarly, ester enolates containing β hydrogens effect reduction of aryl halides by intermolecular hydrogen atom transfer.[12]

Accordingly, we postulate that phenyl radical, besides adding to 1 (eq 3), abstracts a β hydrogen as shown in eq 7. Thereby formed are benzene and **6**, which is the radical anion of **5**.



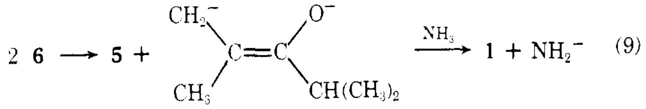
6

Being the radical anion of an α,β-unsaturated ketone, **6** is probably too stable to transfer an electron rapidly to iodobenzene, as in eq 8. Were that to happen a propagation cycle

$$\mathbf{6} + \mathrm{PhI} \not\rightarrow \mathbf{5} + [\mathrm{PhI}]^{-\cdot} \quad (8)$$

comprising steps 2, 7, and 8 would coexist with the normal $\mathrm{S_{RN}1}$ cycle of steps 2, 3, and 4, and no interpretation of the sluggishness of the overall reaction of PhI with 1 would be offered. (The very low $\mathrm{S_{RN}1}$ reactivity of acetophenone enolate ions with aryl and heteroaryl halides is probably of similar origin, the radical anion $[\mathrm{ArCH_2COPh}]^{-\cdot}$ being unable to transfer an electron rapidly enough to ArX, as in step 4, to maintain the propagation cycle.)

The sluggishness of the overall reaction of PhI with 1 suggests that termination steps accompany or follow the formation of benzene and **4**. We suggest that disproportionation of **6**, as in eq 9, is the termination step. Dianion **7** is rapidly protonated to form 1, as shown, and 1 adds to **5** to form **4** (eq 6).



7

The present results demonstrate for the first time that intermolecular hydrogen atom transfer can be a significant competing process in photostimulated reactions involving ketone enolates and carboaromatic substrates. With halogenated aromatic azines, however, this mode of reductive dehalogenation plays a less important role.[2]

Acknowledgment. We are pleased to acknowledge financial support of the National Science Foundation under Grant No. CHE 74-20520 at Virginia Polytechnic Institute and State University and Grant No. CHE 76-11364 at the University of California, Santa Cruz.

References and Notes

(1) J. F. Bunnet and J. E. Sundberg, *J. Org. Chem.*, **41**, 1702 (1976).
(2) A. P. Komin and J. F. Wolfe, *J. Org. Chem.*, **42**, 2481 (1977).
(3) J. V. Hay and J. F. Wolfe, *J. Am. Chem. Soc.*, **97**, 3702 (1975)
(4) J. V. Hay, T. Hudlicky, and J. F. Wolfe, *J. Am. Chem. Soc.*, **97**, 374 (1975).
(5) S. Hoz and J. F. Bunnett, *J. Am. Chem. Soc.*, **99**, 4690 (1977).
(6) J. K. Kim and J. F. Bunnett, *J. Am. Chem. Soc.*, **92**, 7463 (1970).
(7) We observed that negligible reaction occurred in the dark (2% in 3 h).
(8) NMR spectra were obtained at 100 MHz for ^{1}H NMR and at 25.15 MHz for ^{13}C NMR from $\mathrm{CDCl_3}$ solutions using $\mathrm{Me_4Si}$ as an internal standard.
(9) This compound [bp 80–83 °C (0.6 Torr); IR (neat) 1705 cm^{-1} (C=O)] gave a satisfactory combustion analysis.
(10) The saturated carbon absorbances and their tentative assignments are as follows: δ 18.7 and 18.9 (C-2 and/or C-8 $\mathrm{CH_3}$), 19.9 (C-6 $\mathrm{CH_3}$), 20.1 and 20.3 (C-2 and/or C-8 $\mathrm{CH_3}$), 23.7 and 25.3 (C-4 $\mathrm{CH_3}$), 34.1 (C-5), 39.8 (C-6), 41.2 and 41.4 (C-2 and C-8), and 41.3 ppm (C-4).
(11) C. Chassin, E. A. Schmidt, and H. M. R. Hoffman, *J. Am. Chem. Soc.*, **96**, 606 (1974).
(12) M. F. Semmelhack and T. M. Bargar, *J. Org. Chem.*, **42**, 1481 (1977).
(13) Enone **5** was prepared from 2-bromo-2,4-dimethylpentan-3-one according to the procedure of A. Bienvenue and B. Duchatellier, *Tetrahedron*, **28**, 833 (1972).

James F. Wolfe,* Marcus P. Moon, Mark C. Sleevi
Department of Chemistry, Virginia Polytechnic
Institute and State University
Blacksburg, Virginia 24061

Joseph F. Bunnett, Raymond R. Bard
University of California
Santa Cruz, California 95064

Received November 28, 1977

Reactions in Dry Media. Ferric Chloride Adsorbed on Silica Gel. A Multipurpose, Easily Controllable Reagent[1]

Summary: $\mathrm{FeCl_3}$ adsorbed on a chromatographic type silica gel was found to be effective for rapid, high yield and selective dehydration of alcohols, as well as for pinacol and acyloin type rearrangements. The same reagent containing ca. 2% water epimerizes tertiary alcohols and converts epoxides into diols.

Sir: One of the advantages of reactions on solid adsorbents is their use as support for selective reagents which are inefficient or inactive in solution.[1,2] We report on the use of such a reagent, consisting of ferric chloride adsorbed on chromatographic grade silica gel for rapid, high yield, selective dehydration and epimerization of alcohols, epoxide openings, and rearrangements involving carbonium or oxonium ion intermediates.[3]

When silica gel (Merck Kiesegel 60, particle size 0.063–0.200 mm, 70–230 mesh) is mixed with ~10% its weight of hydrated ferric chloride ($\mathrm{FeCl_3{\cdot}6H_2O}$) dissolved in a polar volatile solvent (such as methanol, acetone, ether, etc.), followed by evaporation at ~50–60 °C under high vacuum (0.1 Torr) for ~3 h, a dry yellowish-brown powder is obtained.[4,5] This powder is an effective reagent for dehydration of allylic, tertiary, and sterically strained secondary alcohols, as exemplified in Table I.

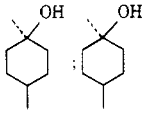
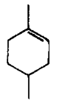
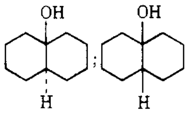
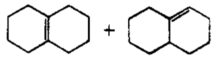
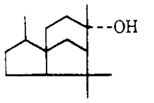
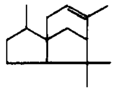
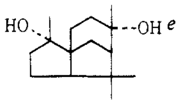
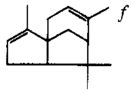
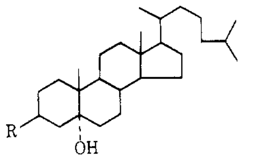
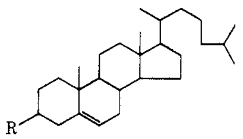
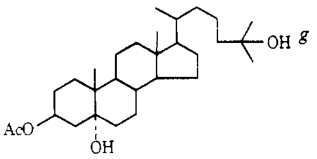
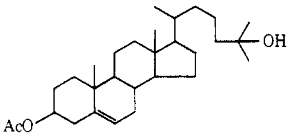
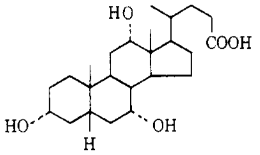
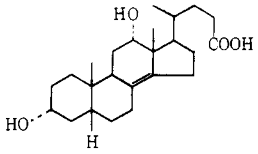
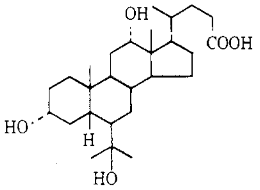
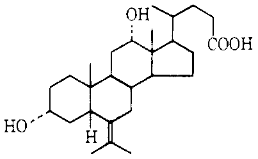
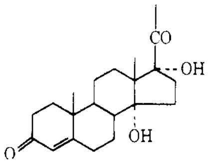
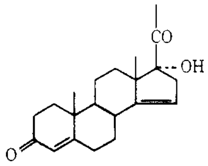
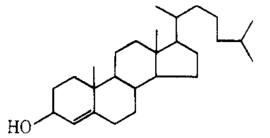
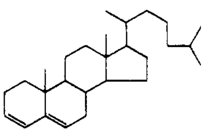
The dehydrations are performed either by dissolving the substrate in a volatile solvent, mixing it with ~100 times its weight of reagent, and evaporating to dryness under high vacuum or when the substrate is volatile, by mixing it directly with the reagent. After being left for a short time at room temperature, the products are eluted from the silica gel with an organic solvent. The dehydrations are very fast, generally taking place immediately on contact of the substrate with the adsorbed reagent, and resulting in high yields of pure products.

Addition of ~2% water by weight to the dry $\mathrm{FeCl_3}$–$\mathrm{SiO_2}$ reagent results in a bright yellow powder (wet $\mathrm{FeCl_3}$–$\mathrm{SiO_2}$ reagent) which is still capable of dehydrating allylic alcohols, and to a lesser extent, tertiary alcohols. However, high water concentration (>10%) may completely deactivate this reagent.

We have observed that the wet $\mathrm{FeCl_3}$–$\mathrm{SiO_2}$ reagent in some cases efficiently epimerizes tertiary carbinols. Thus both *cis*- and *trans*-1,4-dimethylcyclohexanols were converted quantitatively to an equilibrium mixture of the two epimers, consisting of 56% of the trans epimer.[6] When these cyclohexanols were labeled with ^{18}O, the ensuing mixture of epimers was devoid of the label. On the other hand, by using wet $\mathrm{FeCl_3}$–$\mathrm{SiO_2}$ reagent prepared by adding $\mathrm{H_2{}^{18}O}$ to the dry $\mathrm{FeCl_3}$–$\mathrm{SiO_2}$

0022-3263/78/1943-1020$01.00/0

Table I. Selective Dehydrations Carried out with $FeCl_3$ on Silica Gel

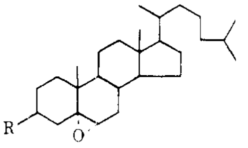
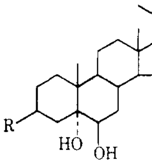
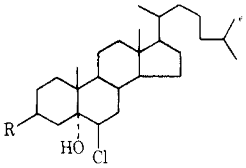
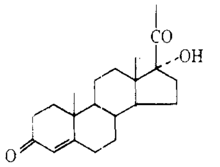
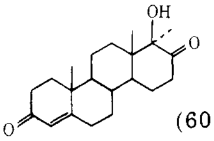
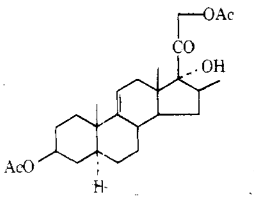
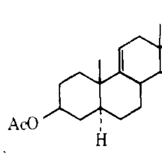
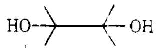
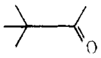
Entry	Substrate	Product	(% yield)[a,b]
1			(>90)[c]
2			(>90)[c,d]
3			(>90)[c]
4			(>90)[c]
5 R = H 6 R = OH			(80)
7			(72)
8			(75)
9 6α 10 6β			(85)[h]
11			(>90)[c,i]
12			(>90)

[a] The yields were not optimized. [b] All the known compounds were identified by a comparison with the authentic samples. [c] These conversions were almost quantitative and no other products were isolated. [d] The ratio of 9,10-octalin and 1,9-octalin was 1.4:1. [e] Prepared from cedrol with O_3 on SiO_2: E. Keinan, Ph.D. Thesis, Feinberg Graduate School, the Weizmann Institute of Science, Rehovot, Israel (1977). See also: E. Trifilieff, L. Bang, and G. Ourisson, *Tetrahedron Lett.*, 2991 (1977). [f] $[\alpha]_D$ + 10°; ^1H NMR ($CDCl_3$) δ 0.96 (s, 3 H), 1.06 (s, 3 H), and 5.3 (m, 2 H). [g] Reference 9. [h] M. Lahav, L. Leiserovitz, R. Popovitz, and Ch.P. Tang, *J. Am. Chem. Soc.*, in press. [i] B. M. Bloom, E. J. Agnello, and G. D. Laubach, *Experientia*, **12**, 27 (1956).

reagent, an incorporation of ^{18}O into both epimers was observed. Impregnation of *cis*-9-decalol into the wet $FeCl_3$–SiO_2 reagent resulted in ~85% conversion to a 1:4 mixture of alcohols and olefins consisting of *trans*- and *cis*-decalols and 9,10- and 1,9-octalines in a 4:1 and 1.4:1 ratio, respectively. An identical mixture was obtained from *trans*-9-decalol.[7]

To simplify the experimental procedure, and at the same time to control the formation of the desired products, the substrate was impregnated into the inactive $FeCl_3$–SiO_2 reagent (containing ~10% water by weight). This powder was

Table II. Epoxide Opening and Rearrangements Carried Out with $FeCl_3$ on Silica Gel

Entry	Substrate	Product (% yield)[a,b]
1 R = H 2 R = OH		 (>90)[c,d]  R = H (65)[e] R = OH (55)[f,e]
3		 (60)[g]
4		 (>90)[c,h]
5		 (70)

[a] The yields were not optimized. [b] All the known compounds were identified by a comparison with the authentic samples. [c] These conversions were almost quantitative and no other products were isolated. [d] With wet $FeCl_3$–SiO_2 reagent. [e] With dry $FeCl_3$–SiO_2 reagent. [f] Accompanied by cholestan-6-one (15%) and a rearranged product. [g] D. K. Fukushima, S. Dobriner, M. S. Heffler, T. H. Kritchevsky, F. Herling, and G. Roberts, *J. Am. Chem. Soc.*, 77, 6585 (1955). [h] D. Taub, R. D. Hoffsommer, H. L. Slates, C. H. Kuo, and N. L. Wendler, *J. Am. Chem. Soc.*, 82, 4012 (1960).

connected either to a high vacuum pump or left in a desiccator over P_2O_5. The slow water removal at room temperature gradually transformed the reagent into its active form. The concurrent reaction progress is easily followed by sampling or by the change in color from bright to brownish yellow. This reaction may be stopped at the desired stage by adding a polar solvent which dissolves $FeCl_3$, and may be resumed after removing the solvent under vacuum. Thus, *cis*- and *trans*-1,4-dimethylcyclohexanols impregnated into the inactive $FeCl_3$–SiO_2 reagent were epimerized after being left for a short time in a dessicator over P_2O_5, and were dehydrated to 1,4-dimethylcyclohexene after a longer time. The dehydration of the other alcohols listed in Table I was also performed by mixing with the inactive reagent, and then by evaporating at high vacuum, or leaving in a desiccator over P_2O_5.

The $FeCl_3$–SiO_2 reagent was found in some instances to be a highly effective Lewis-acid type reagent, converting epoxides into 1,2-diols or chlorohydrins, rearranging ketols, 1,2-diols, and epoxides as exemplified in Table II. The hydrolytic opening of the epoxides was performed with wet $FeCl_3$–SiO_2 reagent (Table II, entries 1 and 2, footnote *d*). On the other hand, the dry reagent converted the epoxides to mixtures consisting mainly of chlorohydrins[8] (Table II, entries 1 and 2, footnote *e*).

The examples in Table I show a selectivity of the $FeCl_3$–SiO_2 reagent in dehydration of polyhydroxy compounds which is normally difficult to attain in solution. These regioselective dehydrations are synthetically useful since they do not necessitate special protection of the additional hydroxyl functions present in the molecule (Table I, entries 5, 6, 7, 8, 9, 10) or specifically designed reagents (Table I, entry 8).[10]

It is also noteworthy that the rearrangement of the ketol, 17α-hydroxyprogesterone (Table II, entry 3), leads to a different product than the one obtained with Lewis acids in solution.[11] This and the previous examples suggest that the definite geometrical requirements necessary for the interaction between the adsorbed $FeCl_3$ and the oxygen function of the substrate are responsible for the specificity of this reagent.

References and Notes

(1) For previous paper in this series, see E. Keinan and Y. Mazur, *J. Am. Chem. Soc.*, **99**, 3861 (1977).

(2) F. J. Kakis, M. Fetizon, N. Douchkine, M. Golfier, P. Mourgues, and T. Prange, *J. Org. Chem.*, **39**, 523 (1974); G. H. Posner, A. W. Runquist, and M. Chapdelaine, *ibid.*, **42**, 1202 (1977); G. H. Posner, R. B. Perfetti, and A. W. Runquist, *Tetrahedron Lett.*, 3499 (1976); H. B. Kagan, *Pure Appl. Chem.*, **46**, 177 (1976); J. M. Lalancette, M. J. Fournier-Breault, and R. Thiffault, *Can. J. Chem.*, **52**, 589 (1974); S. L. Regen and Ch. Koteel, *J. Am. Chem. Soc.*, **99**, 3837 (1977); E. C. Taylor, C. S. Chiang, A. McKillop, and J. F. White, *ibid.*, **98**, 6750 (1976); H. Selig, M. Rabinovitz, I. Agranat, C. H. Lin, and L. Ebert, *ibid.*, **98**, 1601 (1976); G. Cainelli, G. Cardillo, M. Orena, and S. Sandri, *ibid.*, **98**, 6737 (1976).

(3) $FeCl_3$ in solution is used mainly as a mild oxidizing reagent (cf. L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1-5, Wiley, New York, N.Y., 1967–1975). Recently, anhydrous $FeCl_3$ in anhydrous ether was utilized for conversion of epoxides to chlorohydrins [J. Kagan, B. E. Firth, N. Y. Smith, and Ch. G. Boyajian, *J. Org. Chem.*, **42**, 343 (1977)] and anhydrous $FeCl_3$ in acetic anhydride for the cleavage of ethers [B. Ganem and V. R. Small, *ibid.*, **39**, 3728 (1974)].

(4) In this form $FeCl_3$ is physically adsorbed on the silica gel, since it may be eluted from it with polar solvents. Excessive heating transforms this reagent into dark brown powder in which $FeCl_3$ is partly decomposed and cannot be eluted either with organic solvents or with water.

(5) The reagent may also be prepared using aqueous $FeCl_3$ solution. In order to achieve a homogeneous adsorption, it is advisable to mix an equal volume of hydrated $FeCl_3$ in an organic solvent such as acetone with silica gel followed by evaporation of the solvent. Identical results were obtained using silica gel containing $FeCl_3 \cdot 6H_2O$ in concentrations between 4 and 10%.

(6) Cf. N. L. Allinger and C. D. Liang, *J. Org. Chem.*, **33**, 3319 (1968).

(7) The ratio of the decalols is in favor of the cis epimer as compared to the equilibrium ratio (P. D. Bartlett, R. E. Pincock, J. H. Rolston, W. G. Schindel, and L. A. Singer, *J. Am. Chem. Soc.*, **87**, 2590 (1965). This may be due to the more rapid dehydration of the *trans*-9-decalol.

(8) Quantitative conversion of the epoxides into chlorohydrins was achieved using more active $FeCl_3$–SiO_2 reagent prepared by heating the silica gel impregnated with $FeCl_3$ to higher temperature (>80 °C), see ref 4. To be published later.

(9) A. Rotman and Y. Mazur, *J. Chem. Soc., Chem. Commun.*, 15 (1974); Cholestane-3β,5α,25-triol 3-acetate (Table I, entry 9) is an intermediate in the synthesis of the biologically active 25-hydroxyvitamin D_3 and the direct conversion of the former to 25-hydroxycholesteryl 3-acetate simplifies the synthesis of that vitamin D.

(10) A. W. Devor and H. W. Marlow, *J. Am. Chem. Soc.*, **68**, 2101 (1946).

(11) The major products in the rearrangement of 17α-hydroxypregnan-20-ones with boron trifluoride etherate or aluminum alkoxides are the 17α-hydroxy-17β-methyl 17a-ketones (and not the 17aβ-hydroxy-17aα-methyl 17-ketones formed with $FeCl_3$–SiO_2). See: N. L. Wendler in "Molecular Rearrangement", Vol. 2, P. de Mayo, Ed., Interscience, New York, N.Y., 1964, pp 1099–1113; D. N. Kirk, and M. P. Hartshorn "Steroid Reaction Mechanisms", Elsevier, Amsterdam, 1968, p 294; D. W. Kirk and A. Mudd, *J. Chem. Soc., Perkin Trans. 1*, 1450 (1975).

Ehud Keinan, Yehuda Mazur*

Department of Organic Chemistry
The Weizman Institute of Science
Rehovot, Israel

Received December 29, 1977