

All rate constants were corrected for volume change of the solvent from 25° to the temperature at which the rate study was made. The density measurements of Schwerts on acetone and acetone-water mixtures at various temperatures were used for these corrections.¹⁴

Acknowledgment.—The helpful discussions with Professor Saul Winstein concerning certain facets of this work are gratefully acknowledged.

(14) F. Schwerts, *J. chim. phys.*, **9**, 15 (1911).

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND PLANT NEMATOTOLOGY, UNIVERSITY OF CALIFORNIA, RIVERSIDE CALIF.]

The Role of Halide in the Reduction of Carbonium Ions by Chromium(II)

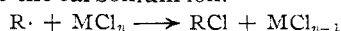
BY C. E. CASTRO

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Chromous salts alter the course of reactions that proceed by way of the 1,1-diphenylethyl cation such that dimers of this fragment are obtained rapidly and in high yield. Halide ions are essential for these transformations. This fact has been interpreted to indicate that polyarylmethyl cations are not reduced by Cr⁺⁺ but rather that a direct reduction of the intermediate organic halide occurs. In accord with this contention, benzhydryl bromide is coupled by chromous sulfate and by titanous chloride. Allyl chloride is reduced to propylene.

Introduction

The reducing power of organic free radicals¹ has been found to be of significance to synthetic² and polymer³ chemistry. Recent findings indicate that the oxidation of alkyl radicals to alkyl halides by cupric and ferric chloride⁴ most likely results from a direct radical displacement rather than prior oxidation to the carbonium ion.



The large number of reactions that proceed by way of intermediate cations suggested that a study of the converse process, that is, the reduction of carbonium ions, could be of value. In particular, the possibility of diverting these ionic reactions with metal salts such that free radical products might be obtained was attractive.

As a part of the comprehensive studies of Conant⁵ and colleagues concerning the homogeneous reduction of organic compounds, the reduction of a carbonium ion to a free radical was proposed to explain the coupling of polyarylcabinols by acidic vanadous and chromous chloride.⁶ Similar mechanisms have been suggested to accommodate the production of ditryl peroxide from the reaction of ferrocene with trityl chloride in nitromethane⁷ and the coupling of benzyl chloride upon exposure to a boiling water suspension of iron powder.⁸ This process now has been examined by exposing the 1,1-diphenylethyl cation to Cr^{II} and Ti^{III} under a variety of conditions. The acid-catalyzed dimerization of 1,1-diphenylethylene⁹ and the acid-catalyzed dehydration of diphenylmethylcarbinol¹⁰ were employed as model systems for this study.

(1) R. M. Haines and W. A. Waters, *J. Chem. Soc.*, 4256 (1935).

(2) J. K. Kochi, *J. Am. Chem. Soc.*, **78**, 4815 (1957).

(3) C. H. Bamford, A. D. Jenkins and R. Johnston, *Proc. Roy. Soc. (London)*, **A239**, 214 (1957).

(4) J. Kumamoto, H. E. De La Mare and F. F. Rust, *J. Am. Chem. Soc.*, **82**, 1935 (1960).

(5) For a survey with key references see J. B. Conant and H. B. Cutter, *ibid.*, **48**, 1016 (1926).

(6) J. B. Conant, L. F. Small and B. S. Taylor, *ibid.*, **47**, 1959 (1925).

(7) M. F. Hawthorne, *J. Org. Chem.*, **21**, 363 (1956).

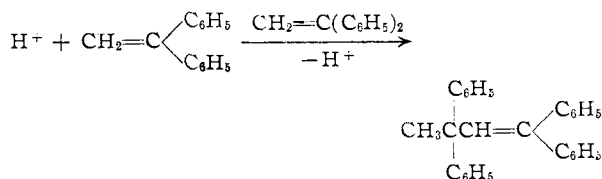
(8) K. Sisido, Y. Udô and H. Nozaki, *J. Am. Chem. Soc.*, **82**, 434 (1960).

(9) A. G. Evans, N. Jones and J. H. Thomas, *J. Chem. Soc.*, 1824 (1955).

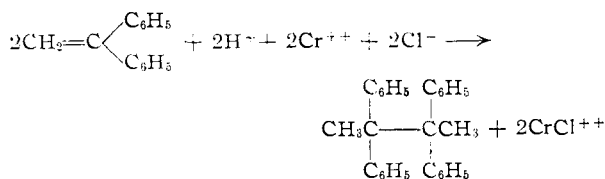
(10) C. F. H. Allen and S. Converse, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., p. 226.

Results and Discussion

The Perchloric Acid Dimerization of 1,1-Diphenylethylene.—In the absence of metal ions a stirred mixture of the olefin and 70% perchloric acid yielded 1,1,3,3-tetraphenylbutene-1 in 95% yield. Added solutions of TiCl₃ or CrSO₄ reagent¹¹ to this heterogeneous system had no effect. The metals were not oxidized.



A homogeneous solution composed of dioxane, 70% perchloric acid, an excess of the CrSO₄ reagent and 1,1-diphenylethylene after five days under nitrogen at room temperature provided only starting olefin (87%), a small yield of tetraphenylbutene (9%) and a trace of telomer.¹² That is, the typical carbonium ion products were obtained. Chromium was not oxidized.¹³ Under identical conditions except that concentrated hydrochloric was substituted for one-fourth of the perchloric acid employed, the solution immediately changed to an apple-green (CrCl⁺⁺), and 2,2,3,3-tetraphenylbutane gradually crystallized from the solution in 70% yield. Semi-quantitative analysis indicated that one mole of Cr^{II} per mole of olefin had been consumed. Thus, the addition of chloride ion to the chromous sulfate solution has altered the normal course of the acid dimerization.

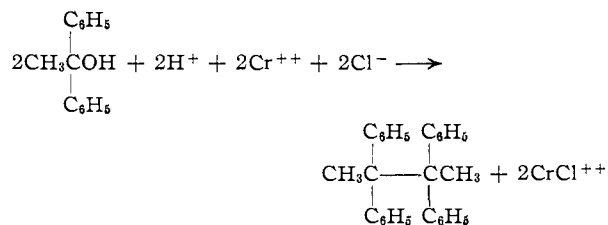


(11) From the zinc powder reduction of Cr₂(SO₄)₃·xH₂O.

(12) E. Hepp, *Ber.*, **7**, 1409 (1874); G. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, 2355 (1929).

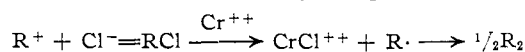
(13) At the end of this period the solution had darkened somewhat. This may have been due to a slow leak or a slow reaction with dioxane, SO₄⁼⁼ or ClO₄⁻. A blank not containing olefin also darkened slowly.

The Dehydration of Diphenylmethylcarbinol.—After five days at room temperature a homogeneous aqueous dioxane solution containing diphenylmethylcarbinol, perchloric acid and chromous and zinc sulfate afforded 1,1-diphenylethylene (95%), a small amount of 1,1,3,3-tetraphenylbutene-1 and a telomer. The solution had darkened¹³ slowly. In another experiment in which chloride ion was present, an immediate reaction ensued and 2,2,3,3-tetraphenylbutane was obtained quantitatively.



These results portray the essential role of halide ions in these transformations. It is therefore concluded that *arylmethyl cations are not reduced by Cr⁺⁺ at an appreciable rate.*

Two paths of reaction are consonant with the facts: (i) Reaction proceeds *via* the direct reduction of the intermediate organic halide to the radical¹⁴ which subsequently couples to product.

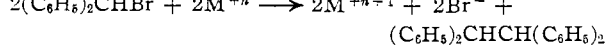


(ii) Electron transfer does occur from a chloride complex of Cr^{II} to the cation.

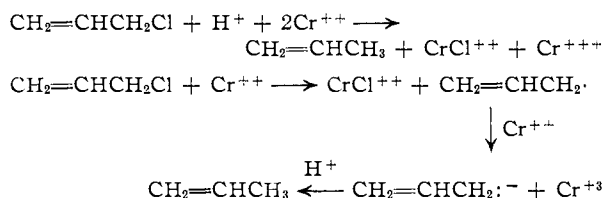


Although (ii) cannot be rigorously eliminated at this time, path i is certainly more attractive, since it bears a formal resemblance to the cleavage of carbon tetrachloride by cobaltacene¹⁵ and chromous perchlorate.¹⁶ Moreover, it is in complete accord with the mechanisms of oxidation-reduction reactions of many inorganic systems in which the role of atom transfer has been delineated.¹⁷ A particularly analogous case is that of the reduction of the cobalt(III) pentammine chloride ion by chromous for which the direct transfer of Cl from $5\text{H}^+ + \text{Co}(\text{NH}_3)_5\text{Cl}^{++} + \text{Cr}^{++} \longrightarrow \text{CrCl}^{++} + \text{Co}^{++} + 5\text{NH}_4^+$

cobalt to chromium has been cleanly demonstrated.¹⁸ Two additional observations favor path i. We have found that in homogeneous aqueous acetone media benzhydryl bromide is rapidly and nearly quantitatively coupled by either chromous sulfate or titanous chloride. Furthermore, in aqueous media allyl chloride is reduced rapidly



to propylene (108%); two moles of chromous are consumed. This latter reaction can be rationalized in terms of the sequence¹⁹



The difference in behavior of these halides might be ascribed to an inherent difference in the oxidation-reduction properties of allyl and benzhydryl radicals, or it may be the result of the inability of the allyl radical to coordinate with Cr⁺⁺⁺ or Zn⁺⁺.¹⁴ An unequivocal proof that the benzhydryl bromide coupling is in fact an example of (i) must await a kinetic investigation. However, the rapidity of the allyl chloride reduction renders the intermediacy of a carbonium ion unlikely in this case.²⁰

Acknowledgment.—I happily express my gratitude to Dr. J. K. Kochi for many helpful and encouraging discussions during the course of this work.

Experimental

Materials. Preparation of the Chromous Sulfate Reagent.—In a 4-l. 3-neck round-bottom flask equipped with a magnetic stirring bar, nitrogen inlet, mercury trap, and a coarse filter stick were placed 500 g. of hydrated chromium sulfate, ca. 3.2 l. of water and 130 g. of purified zinc powder. The mixture was stirred overnight at room temperature.²¹ The excess zinc powder was allowed to settle and the clear blue solution was filtered into a 3-l. flask that was swept with nitrogen during the operation. The batches of chromous sulfate-zinc sulfate prepared in this way had $N\text{Cr}^{II} \sim 0.71\text{--}0.75\text{ N}$ and $\text{pH} \sim 3.5$. The storing flask was equipped with a nitrogen inlet and a serum cap. All transfers were accomplished employing a nitrogen preflushed glass syringe. The stock Cr^{II} solution was standardized by injecting 10-ml. aliquots into an aqueous solution of excess FeCl₃ under nitrogen. The ferrous solution was then titrated with 0.100 N Ce(SO₄)₂ to the green ferric phenanthroline end-point. Reaction solutions were analyzed in a similar fashion except that smaller aliquots were withdrawn.

Titanous Chloride.—Fisher titanous chloride solution was employed directly.

Benzhydryl Bromide.—Benzhydryl bromide was prepared in good yield by the photobromination of diphenylmethane in an excess of the hydrocarbon. The substance employed had b.p. 170° (11 mm.) and m.p. 44°.

Allyl chloride was freshly distilled before use.

Diphenylmethylcarbinol was prepared according to the method of Gilman²²; m.p. 81°.

1,1-Diphenylethylene was obtained in 90% yield from the carbinol by a formic acid dehydration; b.p. 123° (5 mm.),⁸ $n_D^{20} 1.6081$.

Dioxane was distilled from LiAlH₄ and stored under nitrogen.

The Coupling of Benzhydryl Bromide with Cr^{II}.—To a solution of 50 ml. of acetone and 10 ml. of 0.71 N CrSO₄ reagent was added 1.0 g. of benzhydryl bromide (0.0040 mole) dissolved in 5 ml. of acetone. The homogeneous blue solu-

(14) Perhaps no free radicals exist in this medium, and the coupling may occur within a metal complex. The ion $\text{C}_6\text{H}_5\text{CH}_2\text{Cr}(\text{H}_2\text{O})_5^{++}$ has been reported to result from the interaction of benzyl halides with chromous perchlorate; F. A. L. Anet and E. Leblanc, *J. Am. Chem. Soc.*, **79**, 2649 (1957).

(15) S. Katz, J. F. Weiher and A. E. Voigt, *ibid.*, **80**, 6459 (1958).

(16) F. A. L. Anet, *Can. J. Chem.*, **37**, 58 (1959).

(17) H. Taube, in "Advances in Inorganic and Radiochemistry," edited by H. J. Emeléus and A. G. Sharpe, Academic Press, Inc., New York, N. Y., 1959, p. 12.

(18) H. Taube and H. Myers, *J. Am. Chem. Soc.*, **76**, 2103 (1954).

(19) The reduction of a free radical to its anion finds precedent in the inhibition of the radical induced polymerization of vinyl monomers by Ti^{III} and Cr^{II}; E. Collinson, F. S. Dainton, D. R. Smith, G. J. Trudel and S. Tazuke, *Disc. Faraday Soc.*, **29**, 188 (1960); F. S. Dainton and D. G. L. James, *Trans. Faraday Soc.*, **54**, 649 (1958).

(20) The rate of dissociation of allyl chloride in water at 25° is reported as $1.1 \times 10^{-6} \text{ sec.}^{-1}$ ($t_{1/2} \sim 170 \text{ hr.}$); P. J. C. Fierens and P. Kruys, *Bull. soc. chim. Belges*, **65**, 736 (1956).

(21) The reaction is exothermic.

(22) H. Gilman, R. E. Fothergill and H. H. Parker, *Rec. trav. chim.*, **48**, 750 (1929).

tion immediately began to change green. The solution was allowed to stand under nitrogen at room temperature overnight. Analysis for Cr^{II} showed that 0.0041 mole had been consumed. The solution was concentrated on the steam-bath and allowed to cool. The oil floating atop the aqueous phase crystallized. The almost colorless crystals were filtered off, to provide 0.60 g. (90%) of *sym*-tetraphenylethane, m.p. 209–210°. The substance was recrystallized from chloroform; m.p. 211°. ²³ *Anal.* Calcd. for C₂₆H₂₂: C, 93.5; H, 6.5. Found: C, 93.6; H, 6.7. The substance did not absorb bromine in carbon tetrachloride.

With Ti.^{III}—In a manner similar to that described above except that the solution consisted of 55 ml. of acetone, 5 ml. of H₂O, 5 ml. of 2.0 *N* TiCl₃ and 1.0 g. of benzhydryl bromide, *sym*-tetraphenylethane was obtained in 85% yield, m.p. and mixed m.p. with the above sample 211°.

Ineffective Metal Species.—Under the conditions described for Cr^{II}, stannous chloride, ferrous chloride and ferrocene were not effective in promoting the coupling reaction. In all cases the inorganics were recovered and benzhydrol²⁴ was the organic product as it was in the absence of metal ions.

The Reduction of Allyl Chloride.—In a 1-l. flask equipped with a dropping funnel, nitrogen inlet, magnetic stirring bar and a gas reservoir connected to a manometer was placed 200 ml. of 0.71 *N* chromous sulfate reagent. The apparatus was swept thoroughly with nitrogen during the entire operation. A solution of 4.60 g. of allyl chloride (0.060 mole) in 5 ml. of tetrahydrofuran was added to the dropping funnel. The whole system was then partially evacuated. The allyl chloride solution was added all at once to the stirred Cr⁺⁺ solution at 5°. The evolution of gas commenced after 5 minutes and the solution gradually became dark green (Cr^{III}). The whole was allowed to stir overnight at room temperature. Samples for g.l.c. and mass spectrometric analyses were taken directly from the gas reservoir. Propylene was identified qualitatively by its characteristic emergence time on a 50-ft. dimethyl sulfolane²⁵ column. Its presence was corroborated by the mass spectrum of the product gases. The calculated yield of propylene obtained in this manner was 108%. A total of 0.11 mole of Cr^{II} was oxidized. The aqueous solution was saturated with ammonium sulfate and extracted three times with ether. The ether extracts were dried over sodium sulfate and analyzed by g.l.c. employing a 6-ft. dimethyl sulfolane column. In this way 0.005 mole of unreacted allyl chloride was detected.

The Perchloric Acid Dimerization of 1,1-Diphenylethylene.—In the absence of metal ions a mixture of 1.8 g. of 1,1-diphenylethylene and 60 ml. of 70% perchloric acid was stirred for 1 day at room temperature. The mixture was diluted with 500 ml. of water and extracted three times with ether. The ether extracts were washed once with water and twice with saturated sodium bicarbonate and dried over potassium carbonate. The dried ether solution was concentrated and the residue crystallized; wt. 1.7 g. (95%) of

1,1,3,3-tetraphenylbutene-1, m.p. 112°. A portion of the material was recrystallized from hot ethanol and had m.p. 114° (lit.²⁶ 114°). *Anal.* Calcd. for C₂₈H₂₄: C, 93.2; H, 6.8. Found: C, 92.7; H, 6.7. The substance rapidly absorbed bromine in carbon tetrachloride.

The addition of 5 ml. of 2.0 *N* TiCl₃ solution to the above heterogeneous mixture had no effect. The tetraphenylbutene was isolated in 94% yield, m.p. and mixed m.p. 114°.

In a similar experiment, except that 15 ml. of 0.71 *N* CrSO₄ reagent was added, no reaction occurred after 12 hours.

A homogeneous solution consisting of 70 ml. of dioxane, 20 ml. of 70% perchloric acid, 10 ml. of 0.71 *N* CrSO₄ reagent and 0.625 g. of 1,1-diphenylethylene (0.00348 mole) was allowed to stand under nitrogen for 4 days. By this time the blue solution had darkened to some extent, but only a very small amount of Cr^{II} had been oxidized. The solution was concentrated *in vacuo* and the residue containing inorganic salts was poured into 500 ml. of water and extracted four times with ether. The ethereal solution was washed once with water and twice with saturated sodium bicarbonate and dried over potassium carbonate. A very small amount 0.05 g. (9%) of crystalline 1,1,3,3-tetraphenylbutene-1 was isolated from the oily residue by adding a few drops of ethanol. After filtering off the butene and re-concentrating the solution there was left 0.54 g. (87%) of starting 1,1-diphenylethylene, *n*_D²⁰ 1.6075, which had an infrared spectrum that was identical with that of the starting olefin.

Under conditions identical with those described above except that only 15 ml. of 70% perchloric acid and 5 ml. of concentrated hydrochloric acid was employed, addition of the substrate olefin at 5° with stirring caused an immediate blue to apple-green color change of the reaction solution. Concomitantly a white solid began to crystallize. After 10 minutes, semiquantitative analysis for Cr^{II} indicated 0.0032 mole had been consumed. The solid was filtered from the reaction solution and air-dried to afford 0.44 g. (70%) of 2,2,3,3-tetraphenylbutane having a crude m.p. 123–124°. Recrystallization from benzene-ethanol yielded colorless crystals, m.p. 126° (lit.²⁷ 126°). *Anal.* Calcd. for C₂₈H₂₆: C, 92.8; H, 7.2. Found: C, 92.4; H, 7.3. The substance did not absorb bromine in carbon tetrachloride.

The Dehydration of Diphenylmethylcarbinol.—After 5 days at room temperature under nitrogen a homogeneous solution consisting of 70 ml. of dioxane, 20 ml. of 70% perchloric acid, 10 ml. of 0.71 *N* CrSO₄ reagent and 0.685 g. (0.00345 mole) of diphenylmethylcarbinol was worked up in the manner described above. There was obtained 0.65 g. of 1,1-diphenylethylene (95%), 0.01 g. of 1,1,3,3-tetraphenylbutene-1, and a trace of telomer, m.p. 189–190° (lit.¹⁰ 190°). Chromous was not oxidized.

Under the same conditions as described immediately above except that 15 ml. of 70% perchloric acid and 5 ml. of concentrated hydrochloric acid was employed, an immediate reaction ensued and 2,2,3,3-tetraphenylbutane crystallized from the reaction solution in quantitative yield (0.625 g.), crude m.p. 124°. Recrystallization from ethanol-benzene yielded colorless crystals, m.p. and mixed m.p. with the above sample 126°.

(23) P. Sabatier and M. Murat, *Compt. rend.*, **157**, 1497 (1900).

(24) In the FeCl₃ experiment some dibenzhydryl ether also was isolated.

(25) Firebrick was used as the adsorbent.

(26) W. Schmidt-Nickels, *Ber.*, **62**, 917 (1929).

(27) K. Ziegler and B. Schnell, *Ann.*, **437**, 232 (1924).