

sented by the last equation. If we write $T = 2C_p + \sqrt{C_p/K}$ for the total Ce(IV) content of the solution, neglecting C_p^* as compared to the bulk of the Ce(IV), the usual steady state approximation immediately produces the rate equation

$$-\frac{dT}{dt} = \frac{kC_p}{m + C_3} \quad (4)$$

where $k = 2k_1k_2/k_3$ and $m = (k_2 + k_4)/k_3$. For convenience we select $z = \sqrt{C_p/K}$ as the dependent variable and integrate (4) with the result

$$F \equiv \frac{M}{Kz} + \left(\frac{1}{K} - 4M\right) \ln z + 6z + 4Kz^2 = kt + F_0 \quad (5)$$

In this equation $M = m + a + b$, a and b being the initial total Ce(IV) and Ce(III) concentrations, respectively. In equation (5) we have a means of representing the rate data in terms of the equilibrium constant of the dimerization and the group of constants m . Unfortunately there are not available independent determinations of these constants, hence the application of (5) to the data of this paper can be considered only tentative. Comparison of the empirical equation (1) and equation (4) indicates that m is probably small with respect to C_3 and hence with respect to $a + b$. As a preliminary test of (5) we thus put $M \approx a + b$. We now have an equation with one adjustable constant, K . The data on the water oxidation at 60° can be well represented by this equation with reasonable values of K . If one chooses $K = 1.0$

and applies (5) to a run with $[ClO_4] = 7.16$, $a = 0.0830$, $b = 0.2853$, the values of $F - F_0$ fall close to a straight line with slope $k = 1.15 \times 10^{-3}$. Using the same value of K in a run with nearly the same perchlorate concentration, $[ClO_4] = 7.43$, and a widely different ratio of initial concentrations, $a = 0.1572$ and $b = 0.0315$, the straight line through the points has the slope $k = 1.17 \times 10^{-3}$. Since the only criterion for the correct choice of K is the fit of the data to a straight line, considerable latitude in the choice of K is permissible. About the most that can be said is that higher values of K must be chosen for lower perchloric acid concentrations. Thus at $[ClO_4] = 3.72$, K must be chosen in the range 2.0 to 2.5. It will be necessary to test the mechanism using independent determinations of the dimerization constants. A further interesting study will be the comparison of the rate of the deactivation reaction, given by k_3 , with the rate of the electron exchange reaction between ceric and cerous cerium.

Summary

1. Rate data are presented on the thermal reaction in perchloric acid solution between ceric cerium and water. Empirical equations summarizing these data are reported.

2. The results are examined in the light of the mechanism of Heidt and Smith for this reaction. The data are shown to be consistent with this mechanism.

RECEIVED MARCH 29, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY AND CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Chlorination of Bicyclo[2,2,1]heptane (Norbornylane)

BY JOHN D. ROBERTS,¹ L. URBANEK² AND ROSE ARMSTRONG

The nitration of bicyclo[2,2,1]heptane (norbornylane³) has been reported to give 1-nitrobicyclo[2,2,1]heptane.⁴ In the present investigation a study was made of the peroxide-catalyzed chlorination of bicyclo[2,2,1]heptane with sulfuryl chloride⁵ in an attempt to find a convenient synthesis for the 1- and 7-chlorobicyclo[2,2,1]heptanes. Both mono- and dichloro products were isolated from the chlorination of bicyclo[2,2,1]heptane in methylene chloride solution. The monochloride fraction had practically the same physical properties (Table I) and infrared

absorption spectrum (Fig. 1) as a sample of norbornyl chloride (2-chlorobicyclo[2,2,1]heptane) made by the addition of hydrogen chloride to norbornylene (bicyclo[2,2,1]2-heptene).⁶

TABLE I

PHYSICAL PROPERTIES AND SOLVOLYTIC RATE CONSTANTS

Chloride	B. p., °C.	Mm.	M. p., °C.	n_D^{20}	d_4^{20}	k_1^a , hr. ⁻¹
Product of addition of hydrogen chloride to bicyclo[2,2,1]2-heptene	97	100	-6 ^b	1.4823	1.060	0.151
Product from the chlorination of bicyclo[2,2,1]-heptane	88-89	74	..	1.4824	1.061	.152
Chlorination of bicyclo[2,2,1]heptane (after partial hydrolysis)	79	46	-4 ^b	1.4825	1.059	.116
Cyclopentyl chloride017

^a Solvolysis rate constant for aqueous alcohol (80% ethanol and 20% water by volume) at 85°. ^b Melting point of a mixture of approximately equal weights of these materials was -5°.

(6) Schmerling, *ibid.*, **68**, 195 (1946).

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(3) Bicyclo[2,2,1]heptane and its derivatives are listed by *Chemical Abstracts* as "norcamphanes." In this paper the more desirable name, norbornylane, is used for the parent hydrocarbon; cf. Komppa and Beckmann [*Ann.*, **512**, 172 (1934)].

(4) Blickenstaff and Hass, *This Journal*, **68**, 1431 (1946).

(5) Kharasch and Brown, *ibid.*, **61**, 2142 (1939).

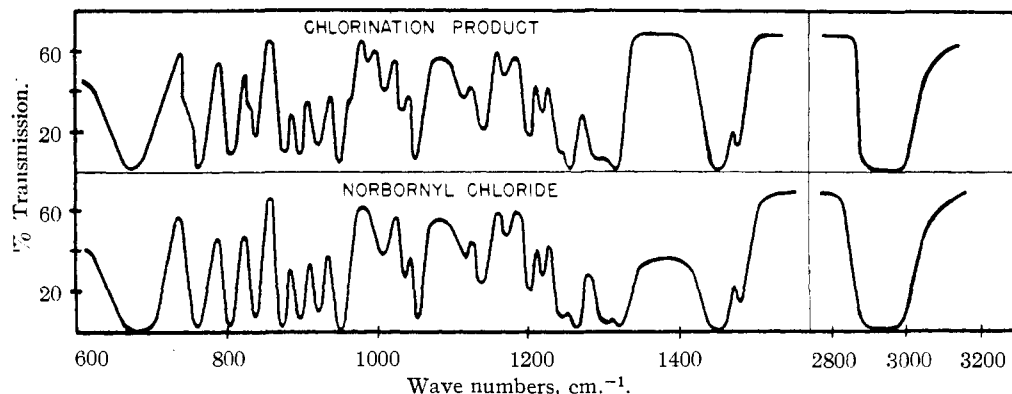
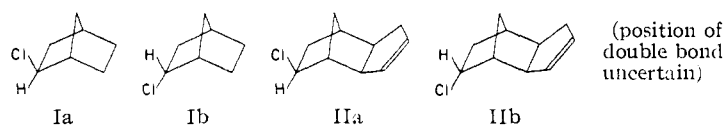


Fig. 1.—Infrared spectra.

In order to confirm the identity of the monochlorination product, the rate constant of its solvolytic reaction at 85° in aqueous alcohol (80% ethanol and 20% water by volume) was compared with that of the material prepared from norbornylene. The results are given in Table I along with the rate constant obtained for cyclopentyl chloride under the same conditions. Although the rate constant of the chlorination product was very close to that of norbornyl chloride, the presence of a small amount (5%) of less reactive chloride was indicated by the deviation from first-order kinetics in the later stages of the reaction. To concentrate any less reactive chloride, the monochlorination product was boiled for five hours with a water-acetone mixture. The physical properties of the recovered unreacted chloride were not appreciably different from those of the starting material. However, the solvolytic rate measurements (Fig. 2) showed clearly the presence of 15–25% of substances less reactive than norbornyl chloride. Since the unreacted chloride amounted to about 25% of the material taken, it is evident that only about 5% of the monochlorination product was not norbornyl chloride.⁷

The solvolytic reactivity of norbornyl chloride is nine times greater than that of cyclopentyl chloride in 80% ethanol at 85°. The very considerable reactivity of norbornyl chloride as compared to cyclopentyl chloride is particularly interesting since cyclopentyl chloride is more reactive in solvolytic reactions than most typical secondary alkyl chlorides.⁸ Furthermore, the similarly constituted chlorodihydro-*exo*-dicyclo-

pentadiene (II) has been reported to be very unreactive.⁹



The configurations (Ia and Ib or IIa and IIb) of the chlorine atoms in I and II with respect to the methylene bridges are not certain¹⁰ and may

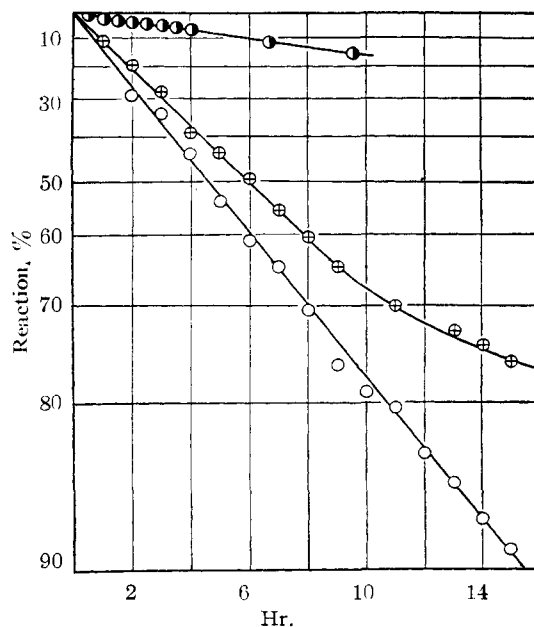


Fig. 2.—Solvolysis of chlorides at 85°: O, norbornyl chloride; ⊕, chlorination product after partial hydrolysis; ●, cyclopentyl chloride.

(9) Bruson and Riener, *THIS JOURNAL*, **67**, 726, 1178 (1945). The compound was referred to in these papers as chloro-dihydro-nor-dicyclopentadiene. See Bartlett and Schneider, *ibid.*, **68**, 6 (1946) and Bruson and Riener, *ibid.*, **68**, 8 (1946). The position of the double bond is uncertain in this substance.

(10) The *exo(cis)*-configuration (Ia) of chlorine and bridge has been assigned by Komppa and Beckman (cited in ref. 3) to the chloride resulting from the treatment of *exo*-norborneol with phosphorus

(7) The high degree of specificity in this chlorination is unusual, particularly since with the possibility of *exo-endo* isomerism (*vide infra*) substitution at only four (at the most) of the ten secondary positions of norbornylene can give equivalent chlorination products.

(8) In 50% alcohol-50% water (by volume) solutions at 90°, cyclopentyl chloride solvolyses approximately five times more rapidly than diethylcarbinyl chloride. For solvolytic reaction rate constants of other secondary alkyl chlorides, see Roberts [*THIS JOURNAL*, **71**, 1880 (1949)].

possibly account for the difference in reactivity between I and II. However, it is noteworthy that if I is a mixture of *exo*- and *endo*-forms, these must have very similar solvolytic rate constants since the solvolysis of I follows the first-order rate law to well over 90% reaction as shown by Fig. 1.

Further experiments are in progress on the determination of the mechanisms of displacement reactions of norbornyl derivatives.

Acknowledgment.—We are indebted to Dr. R. C. Lord, Jr., and Mr. R. S. McDonald for the infrared determinations.

Experimental

Chlorination of Bicyclo[2,2,1]heptane.—A mixture of 48 g. of bicyclo[2,2,1]heptane,¹¹ 34 g. of sulfuryl chloride, 0.25 g. of benzoyl peroxide and 40 ml. of methylene chlo-

pentachloride. The properties b. p. 66–67° (25 mm.), m. p. –5° of the chloride prepared by Komppa and Beckman are very similar to those obtained in the present work.

(11) The bicyclo[2,2,1]heptane was prepared by low-pressure hydrogenation in acetic acid over platinum oxide of bicyclo[2,2,1]heptene made by the method of Joshel and Butz, *THIS JOURNAL*, **63**, 3350 (1941), as modified by Thomas, *Ind. Eng. Chem.*, **36**, 310 (1944). The low pressure hydrogenation process is somewhat more convenient than that described by Thomas and gives no methylecyclohexane.

ride was refluxed (about five hours) until no further loss of weight was observed. The mixture was filtered and fractionally distilled through a 30-cm. Vigreux column. The yield of monochloride, b. p. 88–89° (74 mm.), was 23 g. (70% based on sulfuryl chloride). The weight of dichloride, b. p. 122–123° (75 mm.), was 4 g.

Anal. Calcd. for C₇H₁₀Cl₂ (dichloride): C, 50.93; H, 6.10. Found: C, 51.47; H, 6.27.

The monochloride (20 g.) was refluxed for five hours with a mixture of 50 ml. of water, 50 ml. of acetone and 50 g. of sodium carbonate. The recovered chloride amounted to 5 g., b. p. 79° (46 mm.).

Rate Determinations.—Weighed samples (0.5–1 g.) of the chlorides were made up to 50.0 ml. with aqueous alcohol (80% alcohol and 20% water by volume) at room temperature. Five-milliliter samples were sealed in soft glass test-tubes and heated in a thermostat at 85.0 ± 0.1°. The reaction rate was followed by titration of the liberated acid with standard alkali.

Summary

The peroxide-catalyzed chlorination of bicyclo[2,2,1]heptane with sulfuryl chloride was found to give norbornyl chloride as the principal monochlorination product.

Norbornyl chloride solvolyzes in 80% ethanol at 85° nine times faster than cyclopentyl chloride.

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RECEIVED OCTOBER 30, 1948

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Hydroformylation of Unsaturated Compounds with a Cobalt Carbonyl Catalyst

BY HOMER ADKINS AND GEORGE KRSEK¹

Dicobalt octacarbonyl, Co₂(CO)₈, proved to be quite effective and useful² in catalyzing the formation of aldehydes through the addition of carbon monoxide and hydrogen (H₂CO) to alkene linkages. The present paper is concerned with improvements in the method and a survey of the usefulness and of the limitations of the hydroformylation reaction. The use of a soluble cobalt catalyst was developed from the earlier work^{3–6} with a Fischer–Tropsch type of insoluble catalyst. Two publications on the use of the insoluble catalyst have appeared recently.^{7,8}

The hydroformylation reaction has given good results with unsaturated compounds of quite diverse structures. Hydrocarbons of the types RCH=CH₂ and RCH=CHR, allyl ethers, α,β-unsaturated esters such as acrylates, crotonates and fumarates, and allyl and vinyl acetates and

allylidene diacetate added the elements of formaldehyde in good to fair yields. A summary of the numerical results is given in Table I.

The yields of aldehydes reported in the tables are based upon distillation of the reaction mixtures, titration with hydroxylamine hydrochloride, determination of refractive indices, and the chromatographic separation of 2,4-dinitrophenylhydrazones, as described in the experimental part of this paper. Since it is difficult to isolate an aldehyde without considerable loss, the yields in Table I should be interpreted in consideration of the more detailed results given in the experimental part for representative syntheses.

The reactions were run at 120–125° in benzene, under a pressure of 100–150 atm. of hydrogen and 100–150 atm. of carbon monoxide, as measured at 23°. These conditions differ from those used earlier with dicobalt octacarbonyl, in that benzene rather than ether was the reaction medium, the total pressure was lower, and the ratio of carbon monoxide to hydrogen was 1:1 instead of 2:1. Benzene was chosen as the reaction medium after a comparison of several liquids. The hydroformylation of methyl undecylenate went twice as rapidly in benzene or methylcyclohexane as in diethyl ether and three times as rapidly as in methyl formate. The reaction went as rapidly

(1) Socony-Vacuum Oil Co. Fellow, July, 1947–November, 1948.

(2) Adkins and Krsek, *THIS JOURNAL*, **70**, 383 (1948).

(3) Smith, Hawk and Golden, *ibid.*, **52**, 3221 (1930).

(4) Mittasch, Winkler and Urban, German Patent 539,900, C. A., **26**, 2197 (1932).

(5) Otto Roelen, U. S. Patent 2,327,066 (1943).

(6) FIAT Final Report 1000. The Oxo Process. Issued by the Office of Military Government for Germany, through the Office of Technical Services of the U. S. Department of Commerce, PB81383.

(7) Keulemans, Kwantes and Van Bavel, *Rec. trav. chim.*, **67**, 299 (1948).

(8) Gresham, Brooks and Bruner, U. S. Patent 2,437,600 (1948).