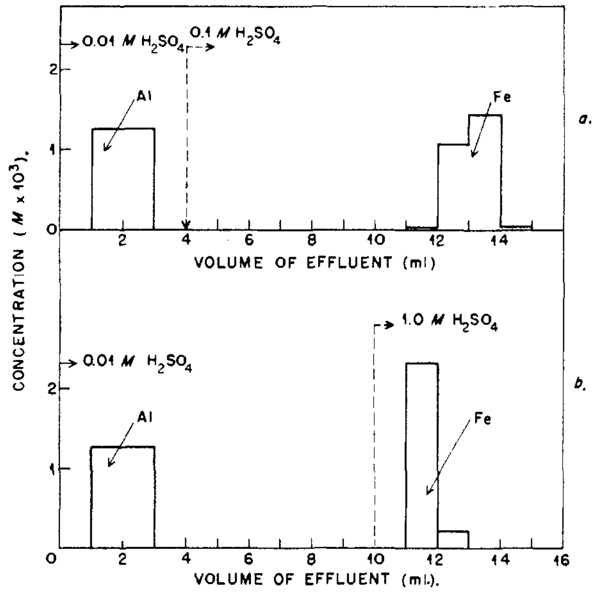

Fig. 1.—Separation of Al(III) and Fe(III) by anion exchange in sulfate solutions (0.187 cm.² × 9.3 cm. Dowex-1 column).

Al(III) rapidly appeared in the effluent while Fe(III) was adsorbed (iron concentration in effluent < 10^{-6} M). The appearance of Fe(III) in the effluent is considerably delayed when elution is carried out with 0.1 M H_2SO_4, (Fig. 1a) but is quite rapid when elution is carried out with 1.0 M H_2SO_4. In both experiments, the Fe(III) band is narrow and shows little tailing. The long delay in the appearance of the Fe(III) band in the effluent with 0.1 M H_2SO_4 is probably connected with the adsorption of sulfuric acid by the resin and its partial conversion to the bisulfate form. The sulfuric acid concentration thus remains considerably less than that of the eluent until the column has been equilibrated with the new medium.

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The Refractive Indices and Molecular Dispersion of *cis*- and *trans*-Decahydronaphthalene

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In the course of a series of measurements dealing with the physical-chemical properties of *cis*- and *trans*-decahydronaphthalene it became desirable to ascertain their refractive indices in the temperature range of 0 to 85°.

For this purpose a Pulfrich refractometer was used with two sources of light, a bunsen burner sodium chloride flame for the D line and a guild type of hydrogen tube for the C(Hα) and F(Hβ) lines. The results are given in the form of graphs in Figs. 1 and 2.

The refractive index–temperature relationship is linear for the *trans* compound within the limits of accuracy obtainable. In the case of the *cis* compound there appeared to be a slight change in slope above 50°. It should be noted that between 50.0 and 50.9° for this compound no readings of the refractive index could be made because of a persistent turbidity, normally associated with all measurements when the temperature of the liquid in the test cup was not constant. This observation appeared significant because other physical properties indicated some change in liquid structure between these temperature regions in the case of the *cis* isomer.

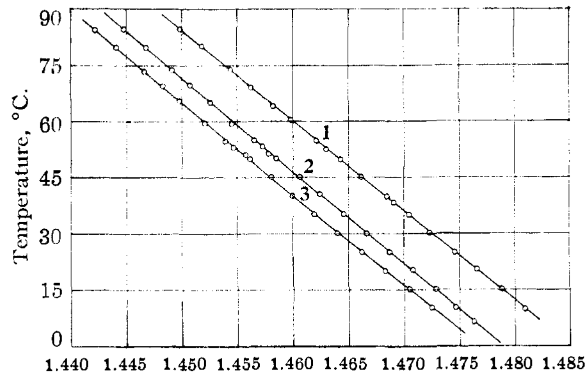

Fig. 1.—Refractive index of *trans*-decahydronaphthalene: 1, n^t_F; 2, n^t_D; 3, n^t_C.

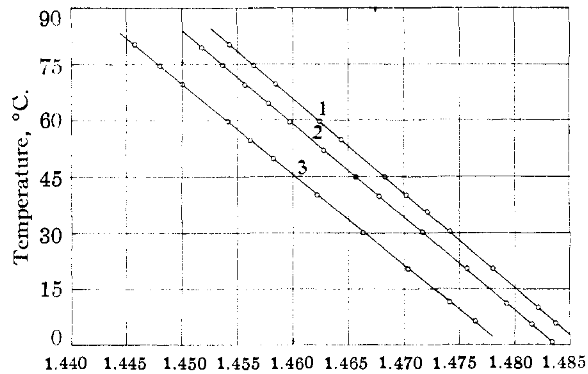

Fig. 2.—Refractive index of *cis*-decahydronaphthalene: 1, n^t_F; 2, n^t_D; 3, n^t_C.

The refractive indices of the *trans* isomer over the temperature interval from 10–90° were used to test the validity of the molar refraction R as calculated from the Gladstone–Dale (R_G), Lorentz–Lorenz (R_L) and Eykman (R_e) equations. The drift in the value of R per degree with rise in temperature for all three wave lengths is shown in Table I.

TABLE I

	n_C	n_D	n_F
$\Delta R_G \times 10^{-3}$	1.6	6.4	5.9
$\Delta R_L \times 10^{-3}$	4.0	6.2	8.1
$\Delta R_e \times 10^{-3}$	52.0	59.0	60.6

Thus for this compound Eykman's empirical equation is far less valid than the other two. Attempts have been made to correlate refractive index with surface tension, notably by Tripathi.[1] However, his equation cannot hold for *trans*-decahydronaphthalene for the molar refraction R increases with temperature while that of the parachor decreases 0.075 unit per degree.[1] Using Eisenlohr's values of carbon and hydrogen the

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(1) R. C. Tripathi, *J. Indian Chem. Soc.*, **18**, 411 (1941).

TABLE II

DISPERSION AND SPECIFIC DISPERSION

	Temp.	$n^t{}_D$	$n^t{}_{H\beta}$	$n^t{}_{H\alpha}$	$\Delta^t{}_{\beta-\alpha}$	$\delta^t{}_{\beta-\alpha}$
trans-cyclohexane	20°	1.4254	1.43053	1.42307	74.6 × 10⁴	95.9 × 10⁴
	80°	1.3953	1.40022	1.39345	67.7	93.9
trans-decalin	20°	1.46934	1.47501	1.46669	83.2	95.6
	80°	1.44577	1.45109	1.44297	81.2	98.3
cis-decalin	20°	1.48098	1.48694	1.47844	85.0	91.6
	80°	1.45841	1.46353	1.45582	77.1	90.5

value of R_D calculated by the Lorentz–Lorenz formula was 43.98. Based on the refractive indices as measured at 20° that of the *trans* isomer was 44.25 and 43.87 for the *cis* isomer. Whether this difference is significant in respect to ring structure is at this time uncertain.

It is interesting to compare the dispersion, Δ, the specific dispersion δ and the temperature-refractive index coefficient of these bicyclic saturated hydrocarbons with those compounds listed by Grosse and Wackher.[2]

In the case of both hydrocarbons the temperature coefficients of Δ and δ are extremely small.

[2] A. V. Grosse and R. C. Wacker, *Ind. Eng. Chem.*, *Anal. Ed.*, **11**, 614 (1939).

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The Addition of Nitryl Chloride to Some Simple Olefins[1,2]

BY CHARLES C. PRICE AND CARLTON A. SEARS[2]

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The addition of nitryl chloride to a number of unsaturated compounds has been reported in the literature.[3] In many cases, the reaction is complicated by addition of the elements of chlorine, N_2O_3 or N_2O_4 across the double bond, depending on the solvent used and the olefin studied.

In the simple examples reported herein, all of these reactions have been observed, suggesting that nitryl chloride can easily disproportionate to chlorine and N_2O_4.

$$2ClNO_2 \rightleftarrows N_2O_4 + Cl_2$$

$$N_2O_4 \longrightarrow N_2O_3 + \text{oxidation}$$

In general, we found dry ether as a solvent superior to carbon tetrachloride or no solvent. We do not have an explanation for the wide difference in the nature of products formed from the four simple olefins studied, but since the work has been discontinued we wish to report the results obtained.

Experimental

The Addition of Nitryl Chloride to Cyclohexene.—A solution of 24.6 g. (0.3 mole) of cyclohexene in 200 cc. of anhydrous ether was added to the reaction flask and 0.35 mole of nitryl chloride was distilled in over a period of two hours at ice temperature. After addition of the inorganic halide the solution was allowed to come slowly to room temperature. The solvent was removed and the cyclohexene pseudo-nitrosite isolated by filtration, 1.2 g. After recrystallization from glacial acetic acid, it melted at 149–150° dec. (lit.[4] m.p. 152° dec.).

The liquid fraction was vacuum distilled and two products were isolated; b.p. 62–73° (6 mm.), 13.4 g. and b.p. 109–114° (6 mm.), 16.3 g.

A pure sample of the lower-boiling fraction was prepared in the following manner. The liquid was cooled in a Dry Ice–isopropyl alcohol bath and white crystals formed. The supernatant liquid was decanted. The white crystals, which liquified on warming to room temperature, were diluted with an equal volume of alcohol and recooled. The white crystals which formed were quickly separated by filtration and washed with Dry Ice-cooled alcohol. The product was quickly transferred to a clean dry watch glass; $n^{25}{}_D$ 1.4835, $d^{25}{}_4$ 1.1655, MR_D calcd., 37.53, found, 37.44. Values reported for 1,2-dichlorocyclohexane are b.p. 75° (15 mm.), $n^{16.6}{}_D$ 1.4886, corrected to $n^{25}{}_D$ 1.4834.[5]

The higher boiling fraction proved to be 1-chloro-2-nitrocyclohexane, $n^{25}{}_D$ 1.4887, $d^{25}{}_4$ 1.2184, MR_D calcd., 38.20, found, 38.52 (lit.[3a] b.p. 121–122° (9 mm.). Steinkopf and Kuhnel[3a] reported only the chloronitrocyclohexane as the product of this reaction.

Chemical Reduction of 1-Chloro-2-nitrocyclohexane.—Approximately 0.5–1.0 cc. of the product was treated with two drops of 25% sodium hydroxide solution. This was then acidified with a 50% hydrochloric acid solution and a small amount of mossy tin added. The mixture was refluxed for 10 to 15 minutes and the product steam distilled. The distillate was treated with 2,4-dinitrophenylhydrazine in the usual manner. A yellow derivative settled, was separated by filtration, and was recrystallized from alcohol, m.p. 161–163°. A mixture with an authentic sample of cyclohexanone 2,4-dinitrophenylhydrazone melted at 161–162°.

Catalytic Reduction of 1-Chloro-2-nitrocyclohexane.—The reduction was run in a low pressure hydrogenator at room temperature in alcohol as solvent and Raney nickel as catalyst. The reduction was discontinued after six hours at which time the pressure was constant. The Raney nickel was separated by filtration and washed with 95% ethanol. The alcoholic filtrate was made acid with dilute sulfuric acid. The alcohol was distilled from the acidic solution until about 5–10 cc. of brown colored liquid remained. One half of this solution was made alkaline and filtered. The filtrate was treated with benzoyl chloride. A curdy precipitate was formed which was recrystallized from alcohol, m.p. 143–147°. The mixed melting point with the derivative of authentic cyclohexylamine was 144–148°.

General Procedure for the Addition of Nitryl Chloride to 2-Butene, Propene and Isobutylene.—The olefin (*ca.* 0.25 mole) was passed into a solution of 200 cc. of dry ether and 0.25 mole of nitryl chloride, for about three hours. The ice-bath was then removed and the reaction product came slowly to room temperature. The solvent was removed at the water pump. Any dimeric pseudo-nitrosite was separated by filtration and the oily filtrate distilled. The physical constants for the products and derivatives are recorded below. The derivatives were prepared in a similar manner as described for the cyclohexene derivatives. For

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[1] Abstracted from a thesis presented by Carlton A. Sears in partial fulfillment of the requirements for the Ph.D. degree at the University of Notre Dame.

[2] This work was presented in part at the 119th National Meeting of the American Chemical Society at Cleveland, Ohio. We are indebted to the Navy Department, Bureau of Ordance, for a Grant, Contract NOrd-10273, which made this work possible.

[3] (a) W. Steinkopf and M. Kuhnel, *Ber.*, **75**, 1323 (1942); (b) Brintzinger and K. Pfannsteil, *Z. anorg. Chem.*, **256**, 324 (1948); (c) M. Kuhnel, German Patent 739,533 (July 25, 1940); (d) C. M. Himel, U. S. Patent 2,511,915 (June 20, 1950).

[4] H. Wieland and E. Blumich, *Ann.*, **424**, 8 (1921).

[5] M. Mousseron and R. Granger, *Compt. rend.*, **205**, 327 (1937).