TABLE II

DISPERSION AND SPECIFIC DISPERSION

	Temp.	n^t_D	$n^t_{H\beta}$	n^t_{Hd}	$\Delta^t_{\beta-\alpha}$	$\delta^t_{\beta-\alpha}$
trans-cyclohexane	20°	1.4254	1.43053	1.42307	74.6×10^4	95.9×10^4
	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.*, **31**, 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).

the preparation of N-(2-nitroisopropyl)-aniline hydrochloride see Fourneau.[6]

2-Butene Product.—2-Chloro-3-nitrobutane: b.p. 45–46° (6 mm.), 8.6 g., $n^{25}{}_D$ 1.4421, $d^{25}{}_4$ 1.1835, MR_D calcd. 30.68, found 31.10; % Cl calcd. 25.59, found 25.47. Derivatives: 2,4-dinitrophenylhydrazone of chemically-reduced product, m.p. 116.5–117°, mixed m.p. with 2,4-dinitrophenylhydrazone of methyl ethyl ketone was 116–117°; benzoyl chloride derivative of catalytically-reduced product, m.p. 72–74°, mixed m.p. with authentic *s*-butylbenzamide 72–73°.

Propene Products.—Propene pseudo-nitrosite: m.p. 135–135.5°, 5 g., % N calcd. 23.72, found 23.58.

1-Nitro-2-chloropropane: b.p. 32–33° (1 mm.), 16.5 g., $n^{25}{}_D$ 1.4388, $d^{25}{}_4$ 1.2338, calcd. MR_D 26.55, mol. wt. 123.5, found, MR_D 26.32; mol. wt. 123.1 (lit.[7] b.p. 172° (749 mm.); $d^{15}{}_4$ 1.2361). Derivatives of 1-nitro-2-chloropropane: N-(2-nitroisopropyl)-aniline hydrochloride, m.p. 139–140°,[6] 2,4-dinitrophenylhydrazone of chemically reduced product, m.p. 142–148°, mixed m.p. with 2,4-dinitrophenylhydrazone of propionaldehyde, m.p. 147–148°. Benzoyl chloride derivative of catalytically reduced product, m.p. 82–83.5°, *n*-propylbenzamide.

Isobutylene Products.—Isobutylene pseudo-nitrosite; m.p. 87–88°, 8.3 g., % N calcd. 21.21, found 19.66 (lit.[8] m.p. 81°).

1-Nitro-2-chloroisobutane: b.p. 35–38° (1 mm.), 6 g., $n^{25}{}_D$ 1.4530 (reported b.p. 35–42° (2 mm.), $n^{24}{}_D$ 1.4530[3d]).

Nitro-*t*-butyl nitrite: m.p. 24.5–25.5°, b.p. 82–83° (1 mm.), 3 g., $n^{25}{}_D$ 1.4599, $d^{25}{}_4$ 1.3022.

Anal. Calcd. for $C_4H_8N_2O_4$: C, 32.43; H, 5.40; N, 18.09; MR_D, 31.91; mol. wt., 148. Found: C, 32.95; H, 5.25; N, 17.35; MR_D, 31.1; mol. wt., 141.1.

The nitrite was converted to isobutyraldehyde (2,4-dinitrophenylhydrazone, m.p. 179–181°) by chemical reduction, with or without prior alkaline treatment. This and the results of the elementary analysis are in accord with the instability ascribed to the nitrite ester function in compounds of this type.[8] Himel[3d] reported only nitro-*t*-butyl chloride as the product of this reaction.

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[6] J. P. Fourneau, *Bull. soc. chim.*, **1**, 603 (1940).

[7] L. Henry, *Chem. Zentr.*, **69**, I, 193 (1898).

[8] N. Levy, C. W. Scaife and A. E. Wilder-Smith, *J. Chem. Soc.*, **52** (1948).

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Nitryl Chloride as a Nitrating Agent[1]

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The ease of preparation of nitryl chloride from nitric acid and chlorosulfonic acid has prompted us to investigate its utility as a nitrating agent for some typical aromatic compounds. The results, summarized in Table I, indicate that its activity as a nitrating agent can be promoted with such acids as hydrogen fluoride, aluminum chloride and boron fluoride, but that its useful application seems to be limited to aromatic substances of intermediate reactivity. Highly reactive aromatics like phenol, anisole, dimethylaniline and naphthalene tend to give oxidative degradation and deactivated aromatics like nitrobenzene, benzoic acid and benzaldehyde are recovered unchanged.

Nitryl Chloride.[2]—Anhydrous nitric acid was prepared by adding 644 g. of fuming sulfuric acid (30% sulfur trioxide content) dropwise, with constant stirring, to 400 g. (5.64 moles) of fuming nitric acid (89% acid content), in a 2-liter three-necked, round-bottomed flask, cooled to 0°, equipped with a dropping funnel, a seal glass stirrer, and attached through a wide bore U-tube to a 500-cc. round-bottomed flask serving as receiver. The receiver was then cooled by a Dry Ice–isopropyl alcohol bath and 370 cc. (5.70 moles) of chlorosulfonic acid (fraction boiling at 149–152° (747 mm.) on redistillation) was added dropwise, with vigorous stirring and continued cooling, over a period of about 12 hours. After all of the chlorosulfonic acid had been introduced the cooling bath was removed from the reaction flask and the mixture stirred for one hour at room temperature; 420 g. (91%) of a dense, pale yellow liquid boiling at −16 to −15° was collected.

TABLE I

REACTION OF NITRYL CHLORIDE WITH VARIOUS AROMATICS

Reactants	Catalyst	Solvent	Product(s)
Benzene	...	...	Nitrobenzene (27–35%)
Benzene	HF[a]	HF	Nitrobenzene (70%)
Benzene	$AlCl_3$	CS_2	Nitrobenzene (89%)
Toluene	$AlCl_3$	CS_2	*o*-Nitrotoluene (47%) *p*-Nitrotoluene (24%)
p-Bromotoluene	$AlCl_3$	CS_2	2-Nitro-4-bromotoluene (23%) 3-Nitro-4-bromotoluene (16%)
Bromobenzene	$AlCl_3$	CS_2	*p*-Nitrobromobenzene (67%) *o*-Nitrobromobenzene (8%)
m-Dichlorobenzene	$AlCl_3$	CS_2	2,4-Dichloronitrobenzene (31%)
Phenol	$AlCl_3$	CS_2	*p*-Nitrophenol *o*-Nitrophenol (trace of both)
Anisole	$AlCl_3$	CS_2	*o*-Nitrophenol (trace)
Diphenyl ether	$AlCl_3$	CS_2	4-Nitrodiphenyl ether 7% Diphenyl ether 5%
N,N-Dimethylaniline	BF_3	CS_2	Tar
Naphthalene	$AlCl_3$	CS_2	1-Nitronaphthalene 31%
Naphthalene	$AlCl_3$	$C_6H_5NO_2$	1-Nitronaphthalene 26%
Salicylic acid	$AlCl_3$	$C_6H_5NO_2$	Salicylic acid 10% 5-Nitrosalicylic acid 58%
Benzoic acid	$AlCl_3$	CS_2	Benzoic acid (73%)
Benzoic acid	BF_3	CS_2	Benzoic acid (82%)
p-Chlorobenzoic acid	$AlCl_3$	$C_6H_5NO_2$	*p*-Chlorobenzoic acid (92%)
p-Toluic acid	$AlCl_3$	CS_2	*p*-Toluic acid (67%)
Nitrobenzene	$AlCl_3$	CS_2	Nitrobenzene (93%)
Nitrobenzene	BF_3	HF	Nitrobenzene (96%)
p-Nitrotoluene	$AlCl_3$	CS_2	*p*-Nitrotoluene (86%)
Benzaldehyde	$AlCl_3$	CS_2	Benzaldehyde (74%)
Acetophenone	$AlCl_3$	CS_2	Acetophenone (88%)

[a] Benzene (36 g., 0.5 mole) was added to 0.55 mole of nitryl chloride in 250 g. of liquid hydrogen fluoride in a copper beaker.

The Reaction of Benzene with Nitryl Chloride.—Nitryl chloride (0.2 mole) was allowed to distil into 50 cc. of dry benzene slowly at room temperature. The solution became yellow as the inorganic halide was added. After all of the reactant had been added the mixture was heated at reflux for 15 hours, after which the test for escaping inorganic halide was negative. Washing and distillation yielded 8.6 g. (35%) of nitrobenzene.

General Procedure for the Condensation of Nitryl Chloride with an Aromatic Compound.—The reactions were run under anhydrous conditions. The reaction flask was cooled by an ice-bath and a solution of 100 cc. of carbon disulfide and 0.2 mole of the aromatic compound added to the flask. The aluminum chloride (0.25 mole) was then added to this solution with vigorous stirring. Nitryl chloride (0.25 mole) was then allowed to distil into the reaction mixture. After all of the inorganic halide had been added the product was stirred at ice temperature for 1–2 hours, the ice-bath removed, and the reaction stirred at room temperature until inorganic halides were no longer evolved. The product was hydrolyzed by pouring into ice and concentrated hydrochloric acid mixture. The organic layer separated, was washed with water, sodium bicarbonate, again with water, and finally dried. The solvent was re-

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[2] K. Dachlauer, German Patent 509,405 (Aug. 30, 1929). We are also indebted to Prof. Harold Shechter, Ohio State University, for some helpful suggestions.