over sodium sulfate. Concentration of the extract and examination of the infrared spectrum of the residue (0.456 g) revealed that it was a mixture of aldehyde and nitroalkane. The mixture was applied to a preparative layer plate containing a 2 mm pad of silica and eluted with hexane–ether (1:1). The uppermost band, after being cut from the plate and washed with ether, produced 0.124 g of 2,3-dimethoxyphenylacetaldehyde as an oil. A 2,4-dinitrophenylhydrazone derivative was prepared quantitatively and, upon recrystallization from methanol, melted at 136–137°.

Anal. Calcd for $C_{16}H_{16}N_4O_6$: C, 53.33; H, 4.48; N, 15.55. Found: C, 53.31; H, 4.45; N, 15.84.

2-(2-Pyridyl)nitroethane (Ig) was prepared quantitatively from the corresponding nitroalkene (IIg)[10] by the general procedure for reduction. However, the compound was rather unstable to air and could be kept for prolonged periods under a nitrogen atmosphere at low temperatures. A satisfactory elemental analysis could not be obtained although its spectrum (Table II) was in total agreement with the assigned structure. Attempts to prepare a hydrochloride gave an unstable salt, mp 106–108°. A picrate salt was prepared, mp 129–130° dec.

Anal. Calcd for $C_{13}H_{11}N_5O_9$: C, 40.95; H, 2.91; N, 18.19. Found: C, 40.80; H, 2.91; N, 18.37.

Registry No.—Ia, 628-05-7; Ib, 14255-44-8; Ic, 629-37-8; Id, 6125-24-2; If, 14255-59-5; Ig, 14255-47-1; Ig hydrochloride, 14255-48-2; Ig picrate, 14255-49-3; Ih, 14255-50-6; IIa, 3156-72-7; IIb, 6065-17-4; IIc, 4550-05-4; IId, 102-96-5; IIe, 705-60-2; IIf, 2815-67-0; IIg, 14255-17-5; IIh, 14255-18-6; IIIf, 14319-56-3; 2,3-dimethoxyphenylacetaldehyde 2,4-dinitrophenylhydrazone, 14255-58-4; sodium borohydride, 1303-74-8.

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[10] K. W. Merz and H. J. Janssen, *Arch. Pharm.*, **297**, 307 (1964); *Chem. Abstr.*, **61**, 4306*d* (1964).

Addition of Nitrosyl Chloride to Olefins. Synthesis of Some Chloro Ketones[1]

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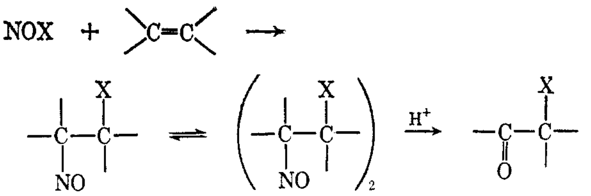
Both acyclic and cyclic α-chloro ketones have been used extensively as intermediates in various synthetic schemes as well as in reaction mechanism studies. These chloro ketones have generally been prepared by passing chlorine gas into a solution of the ketone in ethanol[2] or into an aqueous solution containing the ketone, calcium chloride, and calcium carbonate.[3] These methods usually work satisfactorily in the simple saturated ketone systems, even though significant amounts of di- and polychlorinated products are observed.[3] The above methods become less desirable in systems which are susceptible to the oxidizing action of elemental chlorine.

The addition reaction of nitrosyl halides with olefins[4] (eq 1) yields monomeric and dimeric nitroso chlorides which in most cases can be isolated in good yields as white crystalline solids. These adducts have been converted in some cases[5] to the corresponding chloro ketones by the use of strong acids. The use of strong acids for the hydrolysis step subjects this method to the same disadvantage inherent in the previously cited procedures using elemental chlorine, *i.e.*, oxidation and degradation of other vulnerable positions in the molecule. The use of strong acid for this hydrolysis step is not necessary, however, and may be avoided completely by substituting the milder method of levulinic acid hydrolysis.[6] Meinwald and coworkers[7] used the levulinic acid method of hydrolysis successfully in connection with their study of the steric course of addition of nitrosyl halides to olefins. The present study was designed to develop further the sequence of nitrosyl halide addition to olefins followed by levulinic acid hydrolysis into a useful general synthesis of chloro ketones.



(1)

Several representative olefins were chosen for study although no attempt was made to elucidate the structural requirements for the reaction. Good yields of the nitroso chloride adducts were obtained consistently; in most instances the adduct precipitated from the reaction solution as the white dimer, although in a few others very little solid was obtained. In these latter cases, an intensely blue solution was observed, indicating the nitroso chloride monomer to be present.

The adducts were hydrolyzed to the corresponding chloro ketones (eq 1), by warming with levulinic acid made 0.1 *N* in hydrochloric acid. The results of these chloro ketone preparations are summarized in Table I. The yields reported for these chloro ketones are based on the starting olefin.

TABLE I

Olefin reacted	Final product	Yield, %	Carbonyl absorption, cm^{-1} Found	Reptd
Cyclopentene	2-Chlorocyclopentanone	59	1755	1755[a]
Cyclohexene	2-Chlorocyclohexanone	63	1725	1722[a]
Cycloheptene	2-Chlorocycloheptanone	93	1715	1716[a]
trans-Stilbene	*trans*-Stilbene	. . .	. . .	. . .
cis-Stilbene	*cis*-Stilbene	. . .	. . .	. . .
Cyclopentadiene	4-Chloro-2-cyclopentenone	11	1725 1740 (sh)	. . .
Norbornene	*exo*-3-Chloronorcamphor	68	1758	1757[b]
Norbornadiene	*exo*-3-Chlorodehydronorcamphor	65	1750	1748[b]

[a] E. J. Corey, *J. Am. Chem. Soc.*, **75**, 2301 (1953). [b] See ref 7.

Cyclohexene reacts with nitrosyl chloride at 10° to give a mixture of monomeric and dimeric nitrosochlorides. Surprisingly, a significant amount of 2-chlorocyclohexanone was formed directly in this addition reaction, even before hydrolysis. *trans*-Stilbene adds nitrosyl chloride at 20° in carbon tetrachloride to give a white solid, mp 131–132°. The characteristic

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[1] Presented in part at the Southeastern Regional Meeting of the American Chemical Society, Louisville, Oct 29, 1966.

[2] M. S. Newman, M. D. Farbman, and H. Hipsher, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 188.

[3] H. W. Wanzlick, G. Gollmer, and H. Milz, *Chem. Ber.*, **88**, 69 (1955).

[4] W. A. Tilden, *J. Chem. Soc.*, **28**, 514 (1875).

[5] O. Wallach, "Terpene and Campher," 2nd ed, Viet and Co., Leipzig, 1914.

[6] C. H. DePuy and B. W. Ponder, *J. Am. Chem. Soc.*, **81**, 4629 (1959).

[7] J. Meinwald, Y. C. Meinwald, and T. N. Baker, III, *ibid.*, **86**, 4074 (1964).

blue color usually associated with nitroso monomers was not present in this addition reaction, although no attempt was made to determine whether the adduct was monomeric or dimeric. Attempted hydrolysis of this adduct led to elimination of the elements of NOCl rather than normal hydrolysis, thus yielding *trans*-stilbene as the product. In a similar manner the adduct from *cis*-stilbene liberated NOCl upon attempted hydrolysis. When nitrosyl chloride was reacted with cyclopentadiene in carbon tetrachloride at −10°, a white solid dimer, mp 130–133°, was formed. Hydrolysis of this adduct at 50° for 3 hr led to a single chloro ketone as shown by glpc analysis. Comparison of the infrared, ultraviolet, and nmr spectra of this chloro ketone with those of 4-bromo-2-cyclopentenone[8] served to identify it as 4-chloro-2-cyclopentenone.

In conclusion, the addition reaction of nitrosyl chloride with olefins, with subsequent hydrolysis of the adducts with levulinic acid made 0.1 *N* in hydrochloric acid, has been shown to be a convenient general method for converting olefins to the corresponding chloro ketones. In some cases, such as that of cyclohexene and cycloheptene, the nitrosyl chloride–levulinic acid sequence gives good yields of the corresponding α-chloro ketones even though the intermediate nitroso chloride dimers are not isolated.

Experimental Section

Infrared spectra were obtained on a Perkin-Elmer Model 337 Infracord. Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Elemental analyses were performed by Midwest Microlab, Indianapolis, Ind. Nmr spectra were obtained on a Varian HA-100 spectrometer.

Nitrosyl Chloride.—An aqueous solution of sodium nitrite was added to concentrated hydrochloric acid in a generator constructed of standard taper ground glass equipment and patterned after that suggested by Morton and Wilcox.[9] The nitrosyl chloride was collected in a cold trap, redistilled, and then added to the reaction mixture by means of a delivery tube extending below the surface of the reaction solution.

Gas–Liquid Partition Chromatography.—An Aerograph gas chromatograph, Model A-700 Autoprep, equipped with either a silicone oil column (10% DC-710, 30–60 Chromosorb P, 6 ft × 0.25 in. copper) or a Carbowax column (20% Carbowax 20M, 45–60 Chromosorb P, 6 ft × 0.25 in. copper) was used for vapor phase separations. Helium was used as the carrier gas.

General Hydrolysis Procedure.—Ten parts of the solid nitroso chloride dimer or of the concentrated monomeric nitroso chloride solution were mixed with 100 parts of levulinic acid[10] and the resulting mixture made 0.1 *N* in hydrochloric acid. This mixture was then stirred vigorously while gentle heat was applied, if necessary (about 50°), to get complete solution of any suspended solid. Normally, 3 hr or less were required for completion solution, although in two cases both the temperature and hydrolysis time had to be increased to get complete solution.

After solution was complete, the reaction mixture was cooled by dilution with water and extracted with four portions of diethyl ether. The ether extracts were washed free of levulinic acid with saturated sodium bicarbonate solution and then dried over anhydrous magnesium sulfate. The ether was then removed by evaporation at reduced pressure and the chloro ketone product recovered by distillation under nitrogen at reduced pressure.

2-Chlorocyclopentanone.—A mixture of 400 ml of carbon tetrachloride and 100 g (1.47 moles) of cyclopentene was cooled to 5° in an ice bath. With stirring, nitrosyl chloride was added at such a rate so as to keep the temperature of the solution from going over 10°. After 3 hr, a greenish slurry was obtained which was suction filtered and dried to yield 190.0 g (95%) of a white solid, mp 86–87°. An infrared spectrum showed no oxime to be present. An analytical sample, recrystallized from 1,2-dichloroethane, had mp of 88°.

Anal. Calcd for $C_{10}H_{16}Cl_2N_2O_2$: C, 44.95; H, 6.03; Cl, 26.54; N, 10.48. Found: C, 44.86; H, 5.74; Cl, 26.84; N, 10.69.

The solid dimer was hydrolyzed by the general levulinic acid procedure at 50° for 3 hr. Following the work-up, the solvent was evaporated and the product was distilled under nitrogen at 87–90° (23 mm) to yield 104.8 g (62%) of 2-chlorocyclopentanone. Samples of this ketone collected by gas–liquid partition chromatography at 130° (10% DC-710 on Chromosorb P) had the same retention time (4.8 min) and the same infrared spectrum as an authentic sample prepared by the method of Wanzlick, *et al.*[3] The carbonyl absorption was at 1755 cm^{-1} (lit.[11] 1755 cm^{-1}).

Anal. Calcd for C_5H_7ClO: C, 50.64; H, 5.96; Cl, 29.90. Found: C, 50.70; H, 6.00; Cl, 29.82.

2-Chlorocyclohexanone.—A mixture of 164 g (2.0 moles) of freshly distilled cyclohexene and 300 ml of carbon tetrachloride was cooled to 10° and nitrosyl chloride was added with stirring at such a rate so as to maintain the temperature below 20°. After 3 hr a green lachrymatory solution and a small amount of white solid (10 g, mp 154–155°) were obtained. An analysis of this crude reaction mixture by gas-liquid partition chromatography, after evaporation of the solvent, revealed the presence of approximately 30% of 2-chlorocyclohexanone, even before hydrolysis.

Hydrolysis of the crude reaction mixture was accomplished using the levulinic acid procedure for 3 hr at 50°. It is important to remove most of the carbon tetrachloride solvent before the hydrolysis step to prevent a two-phase system from being formed when the levulinic acid is added. Complete hydrolysis is hard to achieve in such a two-phase system. After work-up of the hydrolysis mixture in the usual manner, the product mixture was distilled under nitrogen to yield 167 g (63%) of 2-chlorocyclohexanone, bp 77–80° (3 mm). The chloro ketone prepared in this manner had the same retention time (7 min) on glpc analysis at 130° (10% DC-710 on Chromosorb) as an authentic sample.[12] It had carbonyl absorption at 1725 cm^{-1} (lit.[11] 1722 cm^{-1}).

Anal. Calcd for C_6H_9ClO: C, 54.38; H, 6.79; Cl, 26.75. Found: C, 54.40; H, 6.90; Cl, 27.01.

2-Chlorocycloheptanone.—A solution of 100 g (1.04 moles) of cycloheptene dissolved in 300 ml of carbon tetrachloride was cooled to 10° and nitrosyl chloride added at such a rate as to keep the temperature below 20°. After 3 hr, a green solution having a reddish oily layer on top was obtained. The oily layer was separated and, after most of the solvent had been removed from the green solution, the two portions were recombined. Hydrolysis with levulinic acid at 50° was carried out in the usual manner to yield, after work-up, 142 g (93%) of 2-chlorocycloheptanone, bp 109–111° (27 mm). The glpc retention time, 11.7 min (10% DC-710 on Chromosorb P), at 130° of this chloro ketone was identical with that of an authentic sample.[13] An analytical sample of this chloro ketone collected by gas–liquid partition chromatography showed carbonyl absorption at 1715 cm^{-1} (lit.[11] 1716 cm^{-1}).

Anal. Calcd for $C_7H_{11}ClO$: C, 57.38; H, 7.51; Cl, 24.19. Found: C, 57.42; H, 7.58; Cl, 24.49.

The Addition of Nitrosyl Chloride to *trans*-Stilbene.—*trans*-Stilbene (50 g, 0.28 mole) was dissolved in 600 ml of carbon tetrachloride at 20° and nitrosyl chloride passed into the solution over a period of 2 hr. A brownish yellow mixture was obtained which yielded, on filtration, 65.2 g (96%) of a white solid, mp 131–133°.

The solid adduct was subjected to the levulinic acid hydrolysis procedure for 3 hr at 50°. A white solid was obtained, which, after filtration and drying, had mp 123–124°. A mixture melting point determination showed that the hydrolysis reaction conditions had produced starting material, *trans*-stilbene.

The Addition of Nitrosyl Chloride to *cis*-Stilbene.—*cis*-Stilbene (5 g, 0.028 mole) and 50 ml of carbon tetrachloride were cooled to 20° and nitrosyl chloride was added over a period of 1 hr to give a yellow solution. Cooling the solution to 0° precipitated 2.05 g (30%) of a white solid which was filtered and dried. The melting point of 131–132° was the same as that of the adduct

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[8] C. H. Depuy, M. Isaks, and K. L. Eilers, *Chem. Ind.* (London), 429 (1961).

[9] J. R. Morton and H. W. Wilcox, *Inorg. Syn.*, **4**, 48 (1953).

[10] We thank the Crown Zellerback Co., Camas, Wash., for a generous gift of levulinic acid.

[11] See Table I, footnote *a*.

[12] The Aldrich Chemical Co., Milwaukee, Wis.

[13] S. Yaroslavsky and E. D. Bergman, *Tetrahedron*, **11**, 158 (1960).

of *trans*-stilbene. Attempted hydrolysis of this adduct in a manner similar to that of the *trans*-stilbene adduct led to elimination of the elements of NOCl rather than hydrolysis.

4-Chloro-2-cyclopentenone.—A solution of 122 g (1.85 moles) of freshly distilled cyclopentadiene in 500 ml of carbon tetrachloride was cooled to −10° and nitrosyl chloride was added over a period of 3 hr. The temperature of the solution was not allowed to rise above 0° during the addition. The initially formed light green solution gradually turned to a dark brown during the course of the addition. Filtration of the slurry gave a light brown solid, which, when washed with cold methanol, gave 80 g (33%) of the white nitroso chloride dimer, mp 130–133°. An infrared spectrum identified the dimer and also showed no oxime to be present.

Anal. Calcd for $C_{10}H_{12}Cl_2N_2O_2$: C, 45.66; H, 4.56; Cl, 26.96: N, 10.65. Found: C, 45.97; H, 4.76; Cl, 26.87; N, 10.88.

The solid dimer was hydrolyzed by the general levulinic acid procedure at 50° for 3 hr. Work-up in the usual manner gave 24.4 g (34.5%) of the chloro ketone as a dark red oil which was difficult to distil without decomposition. An analysis of this oil by glpc at 100° (20% Carbowax 20M on Chromosorb P) showed only one chloro ketone product to be present. An analytical sample of this chloro ketone collected by gas-liquid partition chromatography showed carbonyl absorption at 1725 cm^{-1} and a shoulder at 1740 cm^{-1}. The nmr spectrum of this compound in CCl_4 showed absorption (relative to TMS as an internal standard) at δ 2.68 (complex multiplet for two protons at C-5), 5.14 (complex multiplet for proton at C-4), 6.22 (doublet with fine splitting for olefinic proton at C-2), and 7.62 (quartet for olefinic proton at C-3). Comparison of the infrared, ultraviolet, and nmr spectra of this compound with those of 4-bromo-2-cyclopentenone[8] served to identify it as 4-chloro-2-cyclopentenone.

***exo*-3-Chloronorcamphor and *exo*-3-Chlorodehydronorcamphor.**—These preparations were carried out using the procedure of Meinwald.[7]

Registry No.—Nitrosyl chloride, 2696-92-6; 2-chlorocyclopentanone, 694-28-0; 2-chlorocyclohexanone, 822-87-7; 2-chlorocycloheptanone, 766-66-5; 4-chloro-2-cyclopentenone, 14210-15-2.

Synthesis of Δ^3-Cyclopentenone and Δ^3-Cyclopentenol

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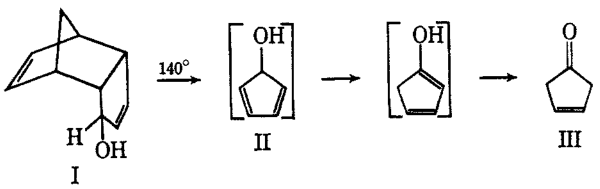
We wish to report the synthesis of Δ^3-cyclopentenone (III) and Δ^3-cyclopentenol (VI) by two independent routes, both giving isolated yields greater than 50%. Previous methods of synthesizing Δ^3-cyclopentenyl derivatives have given less satisfactory yields.[1-7]

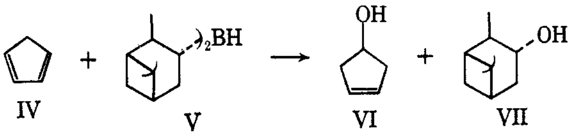
Alder and Flock[1] have reported that the vapor phase pyrolysis of 1-dicyclopentadienol (I) produces a nearly quantitative yield of Δ^2-cyclopentenone, while the vapor phase pyrolysis of the alcohol in the presence of a catalytic amount of palladium on carbon produces a mixture of cyclopentenones, 20% of which is Δ^3-cyclopentenone. Rosenblum[8] has reported that the atmospheric pressure pyrolysis of 1-dicyclopentadienol gives a 31% yield of Δ^2-cyclopentenone along with unchanged alcohol.

We have found that the atmospheric pressure pyrolysis of 1-dicyclopentadienol, using essentially the same conditions as those of Rosenblum, produces a 17% yield of Δ^2-cyclopentenone along with a 51% yield of Δ^3-cyclopentenone. Atmospheric pressure pyrolysis of the alcohol in the presence of a catalytic amount of palladium did not increase the yield of the Δ^3 ketone, but rather a 42% yield of Δ^2-cyclopentenone and a 17% yield of Δ^3-cyclopentenone were obtained.

All of these results are consistent with the view that the pyrolysis occurs *via* an initial reverse Diels–Alder reaction followed by isomerization of the 2,4-cyclopentadienol (II) to Δ^3-cyclopentenone which, depending upon the reaction conditions, is isomerized to a greater or lesser extent to the Δ^2 ketone.



Winstein and co-workers have reported that the monohydroboration of cyclopentadiene produces a 15[5]–30%[3,4] yield of 94% pure Δ^3-cyclopentenol. It has been demonstrated that the monohydroboration of cyclic dienes with alkyl-substituted boranes provides an increased yield of the corresponding unsaturated alcohol over that obtainable with borane itself.[9,10] Accordingly, we have monohydroborated cyclopentadiene with representative alkylboranes and have obtained Δ^3-cyclopentenol in greatly increased yields (Table I). Large-scale monohydroboration of cyclopentadiene with diisopinocampheylborane (V), obtained by the *in situ* hydroboration of α-pinene,[11,12] produces a 57% isolated yield of Δ^3-cyclopentenol which is greater than 99% pure by (glpc) analysis.



Consequently, the present procedures provide improved convenient synthetic routes to both Δ^3-cyclopentenone (III) and Δ^3-cyclopentenol (VI).

Experimental Section

1-Dicyclopentadienol (I) (mp 36–38°) was prepared in 56% yield by the selenium dioxide oxidation of dicyclopentadiene.[8]

Δ^3-Cyclopentenone (III).—Into a 200-ml three-necked flask, fitted with a nitrogen inlet and a Claisen head with a 6-in. side arm was placed 34.7 g (0.235 mole) of 1-dicyclopentadienol. The flask was heated over a free flame as a slow stream of dry nitrogen was passed through the alcohol. The distillate tempera-

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(1) K. Alder and F. H. Flock, *Ber.*, **89**, 1732 (1956).

(2) B. N. Dashkevich, *Proc. Acad. Sci. USSR*, **107**, 189 (1956).

(3) S. Winstein, E. L. Allred, and J. Sonnenberg, *J. Am. Chem. Soc.*, **81**, 5883 (1959).

(4) E. L. Allred, J. Sonnenberg, and S. Winstein, *J. Org. Chem.*, **25**, 27 (1960).

(5) S. Winstein, E. C. Friedrich, R. Baker, and Y.-I Lin, *Tetrahedron*, **8**, 621 (1966).

(6) P. D. Bartlett and M. R. Rice, *J. Org. Chem.*, **28**, 3351 (1963).

(7) F. Bennington and R. Morin, *ibid.*, **26**, 5210 (1961). These workers also reported that Dashkevich's synthesis could not be repeated.

(8) M. Rosenblum, *J. Am. Chem. Soc.*, **79**, 3179 (1957).

(9) G. Zweifel, K. Nagase, and H. C. Brown, *ibid.*, **84**, 183 (1962).

(10) G. Zweifel, K. Nagase, and H. C. Brown, *ibid.*, **84**, 190 (1962).

(11) G. Zweifel and H. C. Brown, *ibid.*, **86**, 393 (1964).

(12) H. C. Brown, N. R. Ayyangar, and G. Zweifel, *ibid.*, **86**, 397 (1964).