TABLE I
HNCS ADDITIONS TO OLEFINS

Olefin	% yield I	% yield NaSCN/H+
Norbornylene	85[a]	85[a]
α-Methylstyrene	87	66[b]
Ethyl acrylate	25	38[b]
Cyclohexene	0	0

[a] Total addition products. [b] Reported yield; see ref. 4.

With ethyl acrylate, the product of both methods was ethyl β-thiocyanatopropionate in yields of 25% from I, and 38%[4] from the reported method. Both procedures, when applied to cyclohexene, gave an orange resin, with none of the expected addition products isolable. Presumably, the mode of addition of hydrothiocyanic acid to olefins is essentially the same for both methods, further indicating that the acid proton is, at best, only loosely bound to the carbamate moiety. The addition of I to olefins is considered superior to previously available methods, by virtue of its shorter reaction time, simpler procedure, cleaner products, and comparable yields.

The previously mentioned reaction of I with amines provides a simple route to the little-studied hydrothiocyanic acid amine salts, again demonstrating the utility of I as a carrier for hydrothiocyanic acid, and as such, its potential usefulness as a synthetic reagent.

Experimental[5]

Ethyl Dimethylcarbamate Hydrothiocyanate (I).—A suspension of 22.7 g. (0.234 mole) of potassium thiocyanate and 25 g. (0.234 mole) of dimethylcarbamoyl chloride in 100 ml. of absolute ethanol was stirred at room temperature for 72 hr. The precipitate was removed by filtration and the filtrate was concentrated to remove excess ethanol. The residue was triturated with 250 ml. of pentane. Evaporation of this solvent, followed by distillation of the crude material at 40.5–41.5° (5 mm.), afforded 24.4 g. (60%) of ethyl dimethylcarbamate hydrothiocyanate: $n^{25}D$ 1.4547; ν (CCl4) 3025, 2075, 1690, and 800 cm.$^{-1}$; $\lambda_{max}^{CH_3CN}$ 238 mμ (log ε 2.12).

Anal. Calcd.: neut. equiv., 176.2. Found: neut. equiv., 169.2.

A solution of 3.5 g. (0.02 mole) of hydrothiocyanate I in 20 ml. of ether was washed with aqueous sodium carbonate solution until neutral, dried, and concentrated. Distillation of the residue at 47–48° (15 mm.) afforded 2.2 g. (95%) of ethyl dimethylcarbamate, $n^{15}D$ 1.4166 (lit.[6] $n^{15}D$ 1.4171).

Anal. Calcd. for $C_5H_{11}NO_2$: C, 51.26; H, 9.46; N, 11.96. Found: C, 51.09; H, 9.44; N, 11.68.

Reaction of Amines with I. General Procedure.—To a solution of 5.3 g. (0.03 mole) of I in 25 ml. of benzene, was added 2.8 g. (0.03 mole) of aniline dropwise with stirring. When the addition was complete, the precipitate was collected by filtration and recrystallized from methylene chloride–ether affording 4.0 g. (89%) of aniline hydrothiocyanate, m.p. 82.5–83.5° (lit.[7] m.p. 80–81°).

Anal. Calcd. for $C_7H_8N_2S$: C, 55.24; H, 5.30; N, 18.40; S, 21.06. Found: C, 55.40; H, 5.29; N, 18.19; S, 21.12.

Reaction of Olefins with I. General Procedure.—A solution of 3.0 g. (0.25 mole) of α-methylstyrene and 4.75 g. (0.027 mole) of I in 10 ml. of benzene was heated under reflux for 2 hr. After cooling, the solution was washed with aqueous sodium bicarbonate, dried, and concentrated. Distillation of the residue afforded 2.3 g. of ethyl dimethylcarbamate, b.p. 31–34° (5 mm.), and 3.8 g. (87%) of α,α-dimethylbenzyl isothiocyanate, b.p. 67–68° (3.5 mm.), $n^{25}D$ 1.5674 (lit.[4] $n^{25}D$ 1.5678).

(5) Melting points are corrected and boiling points are uncorrected. The ultraviolet spectrum was measured on a Cary 14 recording spectrophotometer.

(6) C. W. Kenner and R. J. Stedman, *J. Chem. Soc.*, 2089 (1952).

(7) H. Krall and R. D. Gupta, *J. Indian Chem. Soc.*, **12**, 629 (1935).

Reactivity and Geometry in Allylic Systems. V. Oxygenation of Cholest-5-en-3-one[1]

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Photosensitized oxygenation of Δ^5 steroids produces the corresponding 5α-hydroperoxides with accompanying shift of the double bond to the Δ^6 position.[2] Studies with deuterium-labeled cholesterol established that the α-hydrogen at C-7 is selectively abstracted, and this result along with other considerations led to postulation of a cyclic "*cis*" mechanism for the sensitized pathway.[3] Recent work with a variety of steroid olefins has shown that the photooxygenation can be substantially blocked when the C–O bond has to develop into a 1,3-diaxial relationship to an alkyl substituent, or when the allylic hydrogen is rigidly equatorial or quasi-equatorial.[1b,4,5] The selective behavior of Δ^5 steroids is thus understandable because oxygenation at C-6 from the α or β side, or at C-5 from the β side, would encounter one or the other of these adverse features. Consequently the report[6] that cholest-5-en-3-one (part structure **1**) gave 6β-hydroperoxycholest-4-en-3-one (**2b**) by the photosensitized pathway is of special interest. This last transformation, unlike those of other Δ^5 steroids, utilized a C-4 hydrogen and suggests either that the carbonyl group profoundly alters the stereochemical requirements for the sensitized process or that the product is derived by some other mechanism.[7,8] To get information on this point we photooxygenated **1** in pyridine with and without added sensitizer.

In a 42-hr. run without sensitizer the crude hydroperoxidic product showed ultraviolet absorption at 242 ± 2 mμ, typical of an α,β-unsaturated ketone system. After reduction with sodium iodide, the ab-

(1) (a) This work was supported by the National Institutes of Health (Grant No. GM 09693) to whom we express our appreciation. (b) Part IV in this series: A. Nickon, N. Schwarz, J. B. DiGiorgio, and D. A. Widdowson, *J. Org. Chem.*, **30**, 1711 (1965).

(2) (a) G. O. Schenck, *Angew. Chem.*, **69**, 579 (1957); (b) G. O. Schenck and O. A. Neumuller, *Ann.*, **618**, 194 (1958); (c) G. O. Schenck, O. A. Neumuller, and W. Eisfeld, *ibid.*, **618**, 202 (1958).

(3) (a) A. Nickon and J. F. Bagli, *J. Am. Chem. Soc.*, **81**, 6330 (1959); (b) A. Nickon and J. F. Bagli, *ibid.*, **83**, 1498 (1961).

(4) (a) A. Nickon and W. L. Mendelson, *Can. J. Chem.*, in press; (b) J. B. DiGiorgio, Ph.D. Dissertation, The Johns Hopkins University, 1960, and unpublished results of Dr. P. J. L. Daniels.

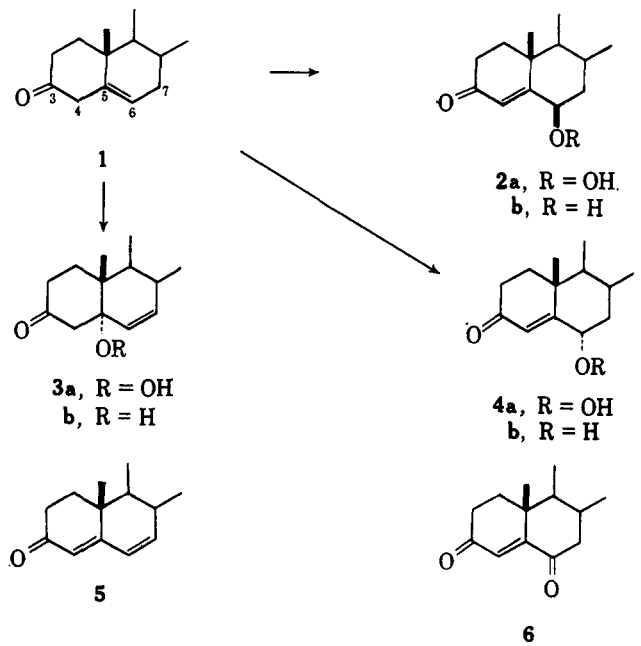
(5) The photooxygenation behavior of monocyclic olefins appears to be governed by similar factors: R. L. Kenney and G. S. Fisher, *J. Org. Chem.*, **28**, 3509 (1963); G. O. Schenck, K. Gollnick, G. Buchwald, S. Schroeter, and G. Ohloff, *Ann.*, **674**, 93 (1964).

(6) G. O. Schenck, K. Gollnick, and O. A. Neumuller, *ibid.*, **603**, 46 (1957).

(7) Fieser, *et al.*, have shown that **1** in cyclohexane readily gives a mixture of the 6β- and 6α-hydroperoxides **2a** and **3a** on treatment with oxygen in the presence of dibenzoyl peroxide and that the isomers are singularly stable to the work-up conditions. We are grateful to Professor Fieser for unpublished experimental details developed by Dr. A. J. Cox [L. F. Fieser, T. W. Greene, F. Bischoff, G. Lopez, and J. J. Rupp, *J. Am. Chem. Soc.*, **77**, 3928 (1955); L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, N. Y., 1959, p. 235].

(8) The unusual susceptibility of β,γ-unsaturated ketones to oxygenation has been emphasized by the recent work of E. L. Shapiro, T. Legatt, and E. P. Oliver [*Tetrahedron Letters*, 663 (1964)], who examined $\Delta^{5(10)}$-3-keto steroids and who noted the biological activity of the derived hydroperoxides (see also ref. 6). An example of a nonsteroid β,γ-unsaturated ketone readily oxygenated has recently been described by K. Crowshaw, R. C. Newstead, and N. A. J. Rogers [*ibid.*, 2307 (1964)].

sorption still centered around 242 mμ and no new chromophores developed on addition of a little hydrochloric acid. The reduced material was chromatographed and gave an alcoholic product (*ca.* 50% yield), shown to be a mixture of **2b** and **4b** by inspection of spectra, melting points, and optical rotations. In addition, some of the fractions (3%) contained cholest-4-ene-3,6-dione (**6**) identified by comparison with authentic material. Diketone **6** is an expected breakdown product from hydroperoxides **2a** and **4a**. The formation of **2a** and **4a** in the absence of sensitizer shows that oxygenation at C-6 occurred readily by a free-radical process during irradiation. These results parallel those of Fieser, *et al.*, who used dibenzoyl peroxide as a radical initiator.[7] By analogy to other autoxidations[9] the reaction is probably a chain process and involves generation of a mesomeric allylic radical by abstraction of a hydrogen from C-4.[10] The adjacent carbonyl group should facilitate this abstraction, and final oxygen attachment to C-6, in preference to C-4, is reasonable because it leads to a conjugated system.



When **1** was photooxygenated (42 hr.) in the presence of sensitizer (a mixture of hematoporphyrin and methylene blue) the peroxidic product showed ultraviolet absorption around 242 mμ. On careful reduction with neutral sodium iodide no new maxima appeared, but, if acetic acid was present during the reduction, or if a little acid or base was added to the reduced product, a band appeared at 285 mμ. The compound responsible for this new absorption proved to be cholesta-4,6-dien-3-one (**5**), present in the treated solutions to the extent of *ca.* 35% as judged by ultraviolet intensity. This dienone was also formed from the original reduced product during chromatography on alumina, and was isolated from the column in *ca.* 27% yield along with *ca.* 7% of the enedione **6** and *ca.* 16% of a mixture of the alcohols **2b** and **4b**.

These findings illustrate that, apart from the products derived from the competing free-radical process, the sensitized reaction produces a hydroperoxide whose corresponding alcohol is transformed easily to dienone **5** by the action of acid, base, or alumina. This is the behavior expected for alcohol **3a** derived from hydroperoxide **3a**. Contrary to views expressed in the literature,[6] we conclude that cholest-5-en-3-one (**1**) responds to photosensitized oxygenation in the same way as do other Δ^5 steroids, and that the 6α- and 6β-hydroperoxides **2a** and **4a** can arise largely, if not entirely, by the competing free-radical pathway.

Experimental[11]

General.—Photooxygenations were conducted with four 15-w. fluorescent bulbs, and hydroperoxides were reduced with sodium iodide, as described earlier,[3b] except that methanol was used in place of ethanol to avoid formation of iodoform. Fisher or Alcoa alumina (F-20, 80–200 mesh) was used for chromatography. Anhydrous sodium sulfate was the drying agent for all ether layers. Color tests for hydroperoxide involved addition of 1 drop of a saturated solution of sodium iodide in 2-propanol to the unknown (2–3 mg.) dissolved in 2 drops of acetic acid. Separate controls with authentic steroid hydroperoxides showed that formation of a deep yellow or yellow-brown color within 20 sec. constituted a positive test.

Cholest-5-en-3-one (**1**) was prepared by the method of Fieser,[12a] crystallized from ethyl acetate–methanol (*ca.* 5:1), and had m.p. 126–127°, α −2° (lit. m.p. 127°, α −4°,[13] and m.p. 124–129°, α −2°[12a]).

Photooxygenation in the Absence of Sensitizer.—A solution of cholest-5-en-3-one (**1**, 0.60 g.) in pyridine (70 ml.) was oxygenated and irradiated 42 hr. in a cold room that maintained the solution temperature at 10–15°. After conventional work-up[3b] the crude product gave a positive hydroperoxide test and showed, in the infrared spectrum, bands characteristic of α,β-unsaturated ketone (1690 cm.$^{-1}$) as well as of starting material (1725, 952, 795 cm.$^{-1}$). The ultraviolet spectrum in ethanol showed λ 244 mμ (ε 4800).[14] Addition of 2 drops of concentrated hydrochloric acid to 25 ml. of the ethanol solution increased the absorption intensity to ε 8600 (by isomerization of the starting material to cholest-4-en-3-one) but produced no new bands. After reduction with sodium iodide[3b] the product had λ 240–242 mμ (ε 10,000) with a slight shoulder at 255; addition of hydrochloric acid produced no new bands. The reduced material (0.580 g.) was dissolved in benzene and chromatographed on alumina (20 g.) after first being allowed to remain on the column for 15 min. Elution with benzene–hexane (6:1) gave oil fractions (total 0.020 g.) shown to be rich in cholest-4-ene-3,6-dione (**6**) by infrared comparison with authentic material (m.p. 124–125°) synthesized[15] by the procedure of Fieser.[12b] Elution with benzene–ether (6:1 and 3:1) gave crystalline, alcohol fractions (total 0.320 g.) containing varying proportions of cholest-4-en-6α-ol-3-one (**4b**) and cholest-4-en-6β-ol-3-one (**2b**) as evidenced from the infrared and ultraviolet spectra (λ 238–242 mμ) and from the melting points and optical rotations of individual fractions. For example, one fraction (0.060 g.) rich in **4b** had m.p. 150–155°, α +70°. The reported[16] constants for **4b**

(9) For a discussion, see C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, Chapter 9.

(10) Cholest-4-en-3-one is known to survive comparable photoxygenation conditions[4] and is therefore not an intermediate [A. Nickon and W. L. Mendelson, *J. Am. Chem. Soc.*, **85**, 1894 (1963)].

(11) Unless stated otherwise the following information applies. Melting points are corrected. Optical rotations are reported as specific rotations and were taken in chloroform solution at room temperature (21–25°) with a sodium lamp light source. Ultraviolet spectra were taken in 95% ethanol on a Beckman DK-2 or a Cary Model 11 M instrument. A standard solution of cholest-4-en-3-one was used for calibration and to check against instrumental fluctuations each time an unknown was run. Infrared spectra were recorded in carbon disulfide solution with a Perkin-Elmer Model 21 double beam spectrophotometer.

(12) L. F. Fieser, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, New York, N. Y., 1953; (a) p. 195; (b) p. 189.

(13) A. Butenandt and J. Schmidt-Thomé, *Ber.*, **69**, 882 (1936).

(14) Extinction coefficients of mixtures were calculated on the basis of a molecular weight of 400.

(15) We are grateful to Mr. A. Baum for this preparation. The constants reported by R. D. H. Heard and H. Sobel [*J. Biol. Chem.*, **165**, 687 (1946)] are λ 251.5 mμ (ε 10,600).

(16) L. F. Fieser, *J. Am. Chem. Soc.*, **75**, 4377 (1953).

are m.p. 156°, α +81°, λ 240 mμ (ϵ 17,080); and for **2b** they are m.p. 194°, α +27°, λ 237 mμ (ϵ 14,500). In this nonsensitized run no cholest-4,6-dien-3-one (**5**) was evident from the infrared or ultraviolet spectra of the fractions from chromatography.

Photosensitized Oxygenation.—A solution of **1** (0.60 g.), hematoporphyrin (0.005 g.), and methylene blue (0.005 g.) in pyridine (70 ml.) was oxygenated and irradiated 42 hr. in the cold room as before. The crude product was an oil (0.55 g.) which gave a positive test for hydroperoxide and which had λ 242 mμ (ϵ 5450). Its infrared spectrum (neat) showed strong peaks around 3330 and 1680 cm.$^{-1}$ (characteristic of OOH and α,β-unsaturated ketone, respectively); a weak shoulder at 1725 cm.$^{-1}$ and the absence of bands at 952 and 795 cm.$^{-1}$ indicated that very little starting material remained. The product was reduced with sodium iodide in the normal way except acetic acid was omitted. After reduction the product had λ 240 mμ (ϵ 6100); this maximum was overshadowed by a new maximum that appeared at 285 mμ when the ultraviolet solution was treated with a little hydrochloric acid or potassium hydroxide (ϵ 9300 and 9100, respectively). Separate runs showed that, when the acetic acid was not omitted in the sodium iodide treatment, the dienone chromaphore developed during the reduction. Based on the reported[17] values for cholesta-4,6-dien-3-one (**5**, λ 284 mμ, ϵ 26,300)[17] the acid or base treatment gave rise to *ca.* 35% of dienone **5**. A portion of the reduced material was acetylated in the usual way[3b] to esterify secondary hydroxyl groups, and the product (0.123 g.) in benzene–hexane (1:3) was chromatographed on alumina (5 g.). Dienone **5** was formed on the column and was eluted with benzene–hexane (2:5) as a solid (0.032 g.) whose melting point (75–76°) was undepressed by authentic **5** (m.p. 77–79°)[17]; the infrared spectra were also identical.

The remainder of the reduced product (0.370 g.) prior to acetylation was dissolved in benzene–hexane (1:1) and deposited on a column of alumina (13 g.), and elution with the same solvent was commenced after a 15-min. waiting period. Several solid and semisolid fractions (total 0.111 g.) were obtained whose individual infrared and ultraviolet spectra were essentially the same as that of dienone **5**. Elution with benzene gave a hardened oil (0.030 g.) whose infrared spectrum was identical with that of authentic cholest-4-ene-3,6-dione, and whose ultraviolet spectrum showed λ 253 mμ (ϵ 9600). Benzene–ether (6:1) eluted several yellow solid fractions (total 0.065 g.) whose individual melting points fell between 145 and 174°. Their ultraviolet spectra (λ 237–238 mμ, ϵ 11,200–12,000) and infrared spectra (ν 3450, 1680, 1270, 1230, 1190, 1035, 1015, 875 cm.$^{-1}$) indicated that these fractions contained varying proportions of cholest-4-en-6β-ol-3-one (**2b**) and cholest-4-en-6α-ol-3-one (**4b**). Further elution of the column with ether gave brown, gummy material (0.050 g.) that seemed polymeric and was not investigated.

Acknowledgment.—We are grateful to Mr. Anthony Baum and Mr. Zaki Abdulla for valuable laboratory assistance.

(17) A. L. Wilds and C. Djerassi, *J. Am. Chem. Soc.*, **68**, 1713 (1946). A sample of the authentic dienone was prepared by Dr. J. F. Bagli.[3b]

Synthesis of 1-Methylcyclopropene

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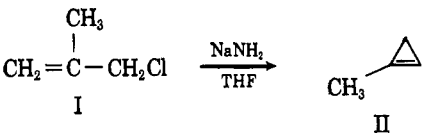
During some attempts to prepare methylenecyclopropane by γ-elimination of hydrogen chloride from methallyl chloride (I), a synthesis of the hitherto unknown 1-methylcyclopropene (II) was found. When I was treated with commercial sodamide in gently refluxing, anhydrous tetrahydrofuran and the gas evolved was passed through a wash of initially 1 *N* sulfuric acid to remove the ammonia, a readily condensed gas was obtained which gave a positive test for an acidic hydrocarbon with potassium iodomercurate (Nessler's reagent) and analyzed (C:H ratio) for C_4H_6. It showed three n.m.r. signals, δ = 0.83 (doublet, $J \sim 2$ c.p.s.), 2.13 (doublet, $J \sim 1$ c.p.s.), and 6.40 p.p.m. (partially resolved multiplet) with relative areas 2:3:1. On this basis it has been assigned the structure 1-methylcyclopropane. The chemical shifts are reasonable on the basis of similar compounds: 1,3,3-trimethylcyclopropene,[1] vinyl hydrogen at 6.65 p.p.m. and allylic methyl at 2.00 p.p.m.; and cyclopropene,[2] methylene group at 0.92 p.p.m. No yield was determined accurately, but it was approximately 50%.



I II

The reaction is probably related to the methods recently reported by Closs and co-workers,[1,3] namely, reaction of alkenyllithiums with methylene chloride, reaction of allylic halides with alkyllithium, reaction of 1,1-dihalo-2-alkenes with alkyllithium, and basic decomposition of α,β-unsaturated tosylhydrazones. All have in common an alkenylcarbene or alkenylcarbene-like intermediate[3] which closes to the cyclopropene. The present method, however, appears to complement the previous procedures, which have not been applied successfully to the preparation of cyclopropenes unsubstituted in the 3-position.

Closs,[3] *et al.*, have pointed out that cyclopropenes with hydrogens in the 3-position are quite unstable. 1-Methylcyclopropene, handled in a high-vacuum line, proved stable for at least 4 days in the gas phase or at liquid-nitrogen temperature. However, in carbon tetrachloride solution the material decomposed within 2 days at room temperature; the decomposition (probably some type of polymerization) was substantially complete after 1 week, no further change in the n.m.r. spectrum occurring after this time. Material stored in the liquid phase at −20° also decomposed within 2 weeks. No structure was assigned to the decomposition product.

Besides the reaction with Nessler's reagent, the only chemistry studied was the reaction of the cyclopropene with triphenylmethyl fluoroborate in acetic anhydride in an attempt to prepare methylcyclopropenium fluoroborate; no decoloration of the triphenylmethyl cation was noted.

Experimental[4]

1-Methylcyclopropene (II).—A solution of 25 ml. (23.1 g., 0.256 mole) of dry methallyl chloride in 50 ml. of anhydrous tetrahydrofuran was added dropwise to a slurry of 10.0 g. (0.256 mole) of sodamide in 50 ml. of anhydrous tetrahydrofuran. A slow stream of nitrogen was passed over the reaction mixture and then through a 6-in. column of $^3/_{32}$-in. glass helices, a washing bottle containing 200 ml. of 1 *N* sulfuric acid, a 6-in. column of calcium sulfate, and a Dry Ice trap. No noticeable gas evolution occurred at room temperature; the mixture was heated to gentle

(1) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **85**, 99 (1963).
(2) K. B. Wiberg and B. J. Nist, *ibid.*, **83**, 1226 (1961).
(3) G. L. Closs, L. E. Closs, and W. A. Böll, *ibid.*, **85**, 3796 (1963).
(4) For further details, including spectra, the Ph.D. Thesis of F. Fisher, University of Illinois, 1965, may be consulted.