similar to that described by Weissberger.[9] The sample was introduced into the evacuated and outgassed isoteniscope and outgassed to constant vapor pressure at 20° through a bypass which was later sealed off. Mercury was used in the U-tube rather than the liquid under investigation because of the high solubility of the latter in all of the common stopcock greases. Both the mercury levels in the U-tube and in the mercury manometer were observed by means of a cathetometer to ±0.1 mm. The temperature was obtained by means of a rapidly stirred water bath, which was contained in a clear-walled Dewar flask and was observed by means of an Anschutz melting point thermometer to ±0.1°.

Melting points. The melting points listed in Table II were determined by suspending samples sealed in evacuated pyrex tubes of about 5 mm. o.d. and 15 cm. long in a rapidly stirred ethanol-ether bath contained in a half-gallon Dewar flask. The bath was cooled with liquid nitrogen sufficiently below the melting point to cause the samples to crystallize. They tended to supercool by 20–30°. Heating was accomplished by natural conduction at a rate slightly less than 1°/min. Temperatures were measured with an iron-constantan thermocouple and a 10-mv. Varian model G-10 recorder.[10]

Acknowledgment. The authors are indebted to Dr. Bert E. Holder for the nuclear-magnetic resonance determination of D/H ratios, to Mr. Richard W. Crawford for burning a sample of our tetrahydrofuran-d_8 and to Miss Patricia A. Cogswell for its mass spectral analysis.

LIVERMORE, CALIF.

(9) A. Weissberger, *Physical Methods of Organic Chemistry*, Interscience Publishers, Inc., New York, 1949, Vol. I, Part I, pp. 173–5.

(10) Varian Associates, Palo Alto, Calif.

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY]

Cyclopropane Chemistry. VI. Acylation of Some Substituted Cyclopropanes[1,2]

HAROLD HART AND GEORGE LEVITT

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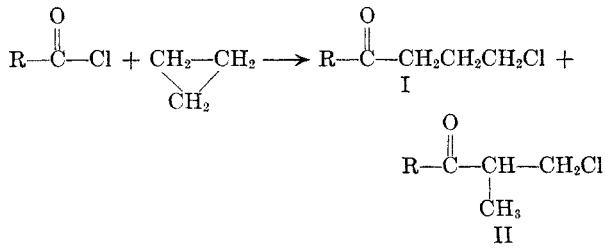
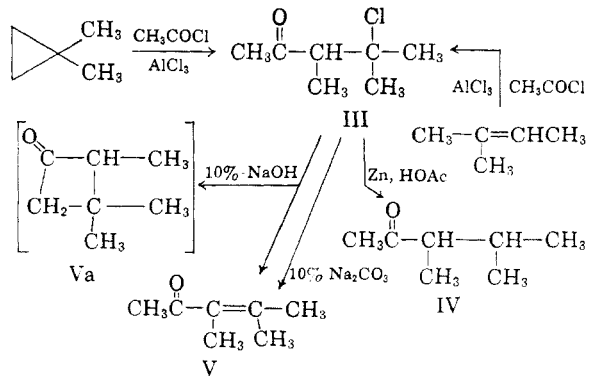
A previously reported[3] rearrangement in the acylation of cyclopropanes has been confirmed and extended to certain substituted cyclopropanes. 1,1-Dimethylcyclopropane and acetyl chloride gave mainly 4-chloro-3,4-dimethyl-2-pentanone (III). Chlorocyclopropane and acetyl chloride gave, after dehydrohalogenation of the initial product, 4-chloro-3-methyl-3-butene-2-one (VII). Both of these products are branched chain β-chloroketones; no products corresponding to "normal" addition (*i.e.*, γ-chloroketones) were identified. Chloracetyl chloride and cyclopropane gave both the normal product [1,5-dichloro-2-pentanone (XI)] and, after dehydrohalogenation 1-chloro-3-methyl-3-butene-2-one (XII) corresponding to the β-chloroketone or abnormal product. Acetylation of the phenyl ring predominated with phenylcyclopropane, *p*-cyclopropylacetophenone being isolated in good yield. Acetyl perchlorate in nitromethane was not a satisfactory acetylating agent for cyclopropanes. 1,1-Dichlorocyclopropane was acetylated only slowly in refluxing chloroform, several sulfonyl halides were unreactive toward cyclopropane, and *t*-butyl chloride and cyclopropane gave a mixture of C_7 alkyl chlorides in poor yield.

The acylation of cyclopropane was recently shown[3] to take a rather unusual course, for in addition to the anticipated γ-chloroketones (I), there were also obtained β-chloroketones with a branched structure (II). Indeed, products with the latter



structure predominated; the ratio of II/I was approximately 2 when R = ethyl, isopropyl, or phenyl. Previous studies[3] were limited to cyclopropane itself, and to lower acyl halides and benzoyl chloride. In the present work, the reaction is extended to several substituted cyclopropanes to determine the direction of ring opening, and to certain additional acylating agents.

1,1-Dimethylcyclopropane. A single chloroketone, which proved to be 4-chloro-3,4-dimethyl-2-pentanone (III), was obtained (crude yield 59%; fractionated, 49%) from the reaction of 1,1-dimethylcyclopropane with a 1:1 acetyl chloride–aluminum chloride complex in chloroform at 0 to



Scheme 1

(1) For the previous paper in this series, see H. Hart and J. M. Sandri, *J. Am. Chem. Soc.* **81**, 320 (1959).

(2) Taken from a portion of the Ph.D. thesis of George Levitt, 1957.

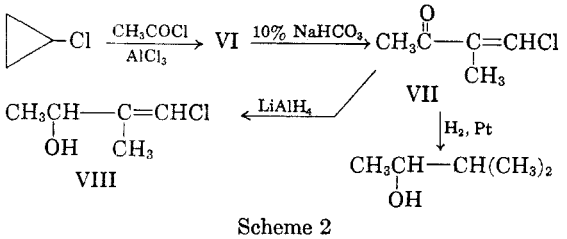
(3) H. Hart and O. E. Curtis, Jr., *J. Am. Chem. Soc.* **79**, 931 (1957).

10°. The structure proof is outlined in Scheme 1. The carbon skeleton and position of the carbonyl group was demonstrated by reduction with zinc and acetic acid (68% yield) to 3,4-dimethyl-2-pentanone (IV), semicarbazone m.p. 113–114°.[4] Dehydrohalogenation with 10% sodium carbonate gave 3,4-dimethyl-3-pentene-2-one (V),[4] but with 10% sodium hydroxide, the ketonic product showed, in addition to α,β-unsaturated ketone bands at 1690 and 1620 cm.$^{-1}$, an intense, sharp band at 1780 cm.$^{-1}$ This is attributed to a cyclobutanone impurity,[5] probably 2,3,3-trimethylcyclobutanone (Va).[6] Finally, III synthesized directly from acetyl chloride and trimethylethylene was identical in all respects with the product from 1,1-dimethylcyclopropane.

In addition to III, unidentified polymeric material was also obtained from this acylation. When the reaction was carried out at −50° and −15°, the yield of ketone was reduced (to 5% and 20%, respectively) and more polymer was produced.

A solution of acetyl perchlorate, prepared from acetyl chloride and silver perchlorate in nitromethane according to Burton and Praill,[7] was treated for one hour at 0° with 1,1-dimethylcyclopropane. Although acylation with acetyl chloride–aluminum chloride under these conditions was virtually instantaneous, no product boiling above solvent was isolated from the acetyl perchlorate reaction. The last cuts of solvent apparently contained traces of V however, for they gave its 2,4-dinitrophenylhydrazone derivative.

Chlorocyclopropane. Chlorocyclopropane reacted slowly (18 hr.) and slightly exothermically at room temperature with acetyl chloride–aluminum chloride in chloroform. The initial product (VI) decomposed when distillation (3 mm.) was attempted, and was therefore dehydrohalogenated directly by refluxing with 10% sodium bicarbonate. The product (23% over-all yield) was shown to be 4 - chloro - 3 - methyl - 3 - butene - 2 - one (VII). See Scheme 2. The branched structure and position of the carbonyl was demonstrated by hydrogenation over platinum to 3-methyl-2-butanol. The ultraviolet and infrared spectra of VII were consistent with an α,β-disubstituted α,β-unsaturated ketone. Reduction of VII with lithium aluminum hydride gave an unsaturated chlorine-containing alcohol which did not react with 5% alcoholic silver nitrate under conditions where allyl chloride gave an immediate silver chloride precipitate. This alcohol must contain vinylic chlorine and therefore be 4-chloro-3-methyl-3-butene-2-ol (VIII); the corresponding ketone must have structure VII. Possible structures of VI are considered in the discussion.

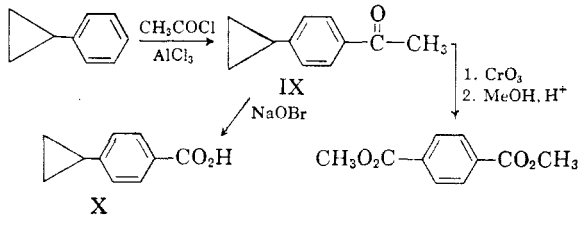


Scheme 2

A small yield (about 5%) of a slightly higher boiling ketonic product was not identified. Much unidentified tar, insoluble in isopropyl alcohol, was recovered from the water layer after the initial dehydrohalogenation.

1,1-Dichlorocyclopropane. Even after 1 hr. in refluxing chloroform, 67% of unchanged 1,1-dichlorocyclopropane was recovered from a reaction with the acetyl chloride–aluminum chloride complex. The structure of the small quantity of unstable unsaturated carbonyl compound which was obtained was not investigated.

Phenylcyclopropane. Acetylation of phenylcyclopropane was exothermic and hydrogen chloride evolved rapidly at 4°; even at −25 ± 5° hydrogen chloride was produced steadily. The major product (48%) was *p*-cyclopropylacetophenone (IX), m.p. 35–36°:



Scheme 3

Chromic acid oxidation followed by esterification with methanol gave dimethyl terephthalate, establishing the *para* orientation. Hypobromite oxidation gave *p*-cyclopropylbenzoic acid (X), m.p. 157–158°, in 88% yield.[8] A slightly higher boiling liquid product (about 10%) which appeared to be an isomeric acetophenone was also obtained as an acylation product, but not identified. A tarry residue was also not identified.

The ultraviolet absorption spectrum of IX is worthy of special comment. It is known that *p*-alkyl substituents cause a small bathochromic shift in the principal absorption of acetophenone[9,10]; the magnitude varies somewhat with the alkyl group,[10] but for methyl is about 9 mμ (from 243

(4) J. Colonge and K. Mostafavi, *Bull. soc. chim.* 6, 335 (1939).

(5) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen and Co., Ltd., 1954, p. 128.

(6) See, for example, J. Colonge and D. Joly, *Ann. chim.* (*Paris*) **18**, 306 (1943).

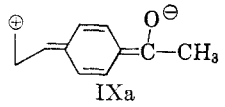
(7) H. Burton and P. F. G. Praill, *J. Chem. Soc.* 827 (1953).

(8) An authentic sample had the same melting point; private communication from Professor N. Lichtin, Boston University.

(9) E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3754 (1955).

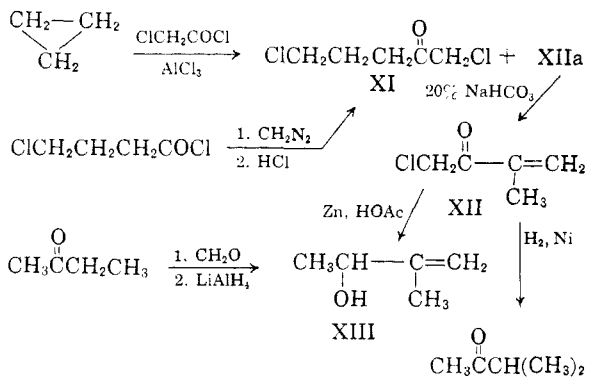
(10) W. M. Schubert, J. Robins and J. L. Haun, *J. Am. Chem. Soc.* **79**, 910 (1957).

mμ to 252 mμ). In 95% ethanol, IX showed a principal absorption band with λ_{max} at 265 mμ (ϵ = 16,000), a bathochromic shift of 22–23 mμ from acetophenone. Since inductive electron release seems to be less for the cyclopropyl group than for methyl (σ^{*}[11] + 0.11[12] on a scale where methyl = 0.00), there apparently is considerable resonance interaction between the cyclopropyl and the carbonyl, as formally represented by structures such as IXa.



IXa

Chloracetyl chloride and cyclopropane. It was not possible to fractionate the chloroketones, which were direct reaction products, because of instability. After refluxing for 1 hr. with 20% sodium bicarbonate, fractionation gave a γ-chloroketone (XI) and an α,β-unsaturated chloroketone (XII), as shown in Scheme 4:



Scheme 4

The structure of the "normal" product, 1,5-dichloro-2-pentanone (XI), was proved by synthesis from γ-chlorobutyryl chloride. The "abnormal" or rearranged product (XII) gave 3-methyl-2-butanone on reduction with hydrogen and Raney nickel, establishing the carbon skeleton and location of the carbonyl group. Zinc and acetic acid reduced XII to 3-methyl-3-butene-2-ol (XIII), identical with authentic material synthesized from methyl ethyl ketone as shown. An attempt to synthesize 1,4-dichloro-3-methyl-2-butanone, the presumed precursor (XIIa) of (XII) from β-chloroisobutyryl chloride and diazomethane gave inconclusive results.

Miscellaneous acylations of cyclopropane. Several experiments were designed to determine whether β-chloroketones (II) are direct acylation products or arise by rearrangement of γ-chloroketones (I). When 5-chloro-2-pentanone (I, R = CH_3) was stirred for 1 hr. with a four-fold excess of acetyl chloride–aluminum chloride in chloroform at 0–10°, 80% was recovered; no β-chloroketone (II, R = CH_3) or its dehydrohalogenation product was isolated. Furthermore, the yield of II (R = CH_3) was unaffected in an acylation run in the presence of an excess of I (R = CH_3).

Several sulfonyl chlorides (methane, ethane, butane, and *p*-toluene) did not give significant yields of cyclopropane acylation products (0–25°, chloroform). *t*-Butyl chloride and cyclopropane gave a mixture of alkyl halides corresponding approximately to $C_7H_{15}Cl$, but no single pure compound was separated or identified.

DISCUSSION

It is clear from experiments described here and previously[3] that β-chloroketones produced when cyclopropanes are acylated do not arise from abnormal addition of hydrogen chloride to acylcyclopropanes,[3] from isomerization of cyclopropane to propylene[3] nor by rearrangement of the γ-chloroketone co-product which is found when cyclopropane itself is acylated. It is indeed interesting that with two substituted cyclopropanes (1,1-dimethyl and monochloro) no product corresponding to a γ-chloroketone could be isolated. If, for example, addition of acetyl chloride to 1,1-dimethylcyclopropane had proceeded according to Markownikoff's rule,[13] one might have expected 5-chloro-5-methyl-2-hexanone to be the major product. Instead, only the β-chloroketone III was isolated.

This same product (III) was obtained when trimethylethylene, a possible isomerization product of 1,1-dimethylcyclopropane, was acetylated. 1,1-Dimethylcyclopropane polymerizes rapidly over aluminum bromide, even at −50°,[16] and an increase in refractive index of the not unrelated 1,1,2-trimethylcyclopropane over aluminum chloride has been attributed[17] to isomerization and polymerization. Several experiments were designed to determine whether acylation of 1,1-dimethylcyclopropane proceeded *via* prior isomerization to trimethylethylene. When an excess of 1,1-dimethylcyclopropane was used, neither it nor an isomerization product, but only polymer could be recovered, in addition to the same yield of ketonic product. Acylation at −50° or by reverse addition at 0° (*i.e.*, adding a chloroform solution of acylating complex to a chloroform solution of 1,1-dimethylcyclopropane) reduced the yield of ketone, and much polymer was produced. It appears that acylation and polymerization are competing reactions, that acylation is the slower of the two and only competes favorably at 0° or above. Acylation therefore probably does not depend on the isomerization and/or polymerization of the 1,1-dimethylcyclopropane.

With chlorocyclopropane also, no γ-choloroketone was isolated. The immediate reaction product was unstable, but

(11) R. W. Taft, Jr., in M. S. Newman "Steric Effects in Organic Chemistry," J. Wiley and Sons, Inc., New York, 1956, p. 618.

(12) T. L. Brown, *J. Am. Chem. Soc.* **80**, 6489 (1958).

(13) Cyclopropanes generally give Markownikoff addition, as for example the formation of 2-bromo-2,3-dimethylbutane from 1,1,2-trimethylcyclopropane and hydrogen bromide,[14] though much of the work upon which this generalization is based is rather old. Special conformational effects may bring about non-Markownikoff addition.[15]

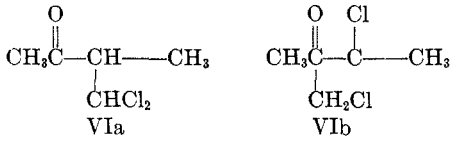
(14) N. Kizhner and G. Khonin, *J. Russ. Phys. Chem. Soc.* **45**, 1775 (1911).

(15) G. Büchi and D. M. White, *J. Am. Chem. Soc.* **79**, 751 (1957).

(16) H. Pines, W. D. Huntsman, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **75**, 2315 (1953).

(17) R. G. Kelso, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Am. Chem. Soc.*, **74**, 287 (1952).

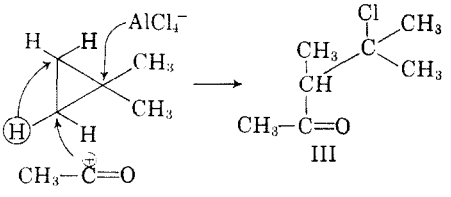
its dehydrohalogenation product VII presumably arose from VIa or VIb:



VIa VIb

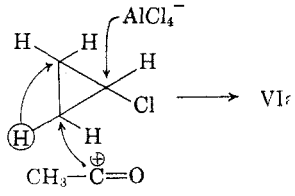
Although VIb could give two dehydrohalogenation products, one of which was not found, it cannot be rigorously excluded for the allylic halide from VIb may have hydrolyzed to a hydroxyketone during the dehydrohalogenation, and been lost in the water layer. Rearrangement of chlorocyclopropane to allyl chloride prior to acylation can be excluded because the acylation product from the former was not obtained from a direct acylation of the latter. Isomerization to 1-chloropropene, while it might explain the product, appears implausible.

The electrophilic nature of the attack in these acylations of cyclopropanes is evident from the decreased rate of the reaction as electron-withdrawing substituents are placed on the ring. Thus much 1,1-dichlorocyclopropane was recovered from an acylation in refluxing chloroform, monochlorocyclopropane required several hours at room temperature, while cyclopropane and dimethylcyclopropane reacted rapidly at 0°. Also, benzoyl chloride was less reactive[8] toward cyclopropane than aliphatic acid chlorides. Attack was primarily on the benzene ring of phenylcyclopropane. Presumably the cyclopropyl group acts as an electron donor activating the benzene ring,[18] whereas the inductive effect of the phenyl group deactivates the cyclopropane ring. Simple attack by an acyl carbonium ion does not lead, however, to an entirely satisfactory explanation of the acylation reaction, for when cyclopropane or 1,1-dimethylcyclopropane was treated with acetyl perchlorate (presumably a source of acetyl cations) only a trace of acylation product was detected. One can rationalize, however, which β-chloroketone will be produced from a substituted cyclopropane by assuming attack of an acyl cation or related species on the most negative ring carbon, transfer of hydrogen from that carbon to the more negative of the remaining ring carbons, and attack of chloride ion (or $AlCl_4^-$) at the most positive ring carbon. Thus, with the two cases studied,



III

and similarly



VI?

In the latter case, as with vinyl halides,[19] orientation is governed by electromeric release from chlorine.

(18) Note, for example, the ultraviolet absorption spectrum of *p*-cyclopropylacetophenone (*vide supra*).

(19) For a brief discussion, see E. E. Royals "Advanced Organic Chemistry," Prentice-Hall, Inc., New York, 1954, p. 364.

EXPERIMENTAL[20]

Acetylation of 1,1-dimethylcyclopropane. Acetyl chloride (157 g., 2 moles) was added slowly at 0–5° to a slurry of 266 g. (2 moles) of aluminum chloride in 1 l. of chloroform. The resulting solution was filtered (scintered glass) and to it there was added 100 g. (1.43 moles) of 1,1-dimethylcyclopropane[22] at a rate to maintain the temperature at 0–10°. Some hydrogen chloride was evolved during the addition. After standing for 1 hr., the mixture was poured onto 1500 g. of ice and 300 ml. of concentrated hydrochloric acid. The chloroform layer was washed with 500-ml. portions of water, 10% sodium bicarbonate, and water, then dried over calcium chloride. The crude product (108 g., b.p. 40–70° at 3 mm.) was fractionated through a helices-packed column, giving 91 g. (49%) of 4-chloro-3,4-dimethyl-2-pentanone (III), b.p. 44–49° at 4 mm., n_D^{20} 1.4398–1.4408 (lit. values,[4] b.p. 60–64° at 14 mm., n_D^{16} 1.4440); 2,4-DNP,[23] recrystallized from methanol, m.p. 130.5–131°.

Anal. Calcd. for $C_{13}H_{17}O_4N_4Cl$: C, 47.50; H, 5.22; N, 17.03. Found: C, 47.50; H, 5.27; N, 17.21.

In addition to III, there was obtained 33 g. of polymer.[24] When the acylation was carried out at −50° and −15° the yield of ketone was reduced to 5% and 20%, respectively, and more polymer was obtained. Attempts to recover unchanged 1,1-dimethylcyclopropane or an isomer thereof were unsuccessful.

Structure proof of 4-chloro-3,4-dimethyl-2-pentanone (III). a. *Reduction with zinc and acetic acid.* To a vigorously stirred suspension of 15 g. (0.23 mole) of zinc dust in 60 ml. of acetic acid and 30 ml. of water there was added 12 g. (0.081 mole) of III. After gently refluxing for 3 hr., the mixture was poured over 50 g. of ice, extracted with three 25-ml. portions of ether, the combined extracts were neutralized by stirring with aqueous potassium carbonate, then dried over anhydrous potassium carbonate. After solvent was removed, there was obtained 6.3 g. (68%) of 3,4-dimethyl-2-pentanone (IV), b.p. 135–140°, n_D^{20} 1.4198, semicarbazone m.p. 113–114° from 50% ethanol (lit. value[4] 113–114°).

b. *Dehydrohalogenation with sodium hydroxide.* III (15 g., 0.1 mole) was added dropwise to 78 ml. of stirred, refluxing 10% sodium hydroxide. After 1 hr. of reflux, the mixture was cooled in an ice bath, extracted with ether, and the extracts dried over magnesium sulfate. After removal of solvent, 5.6 g. (49%) of 3,4-dimethyl-3-pentene-2-one (V) was obtained b.p. 145–149°, n_D^{20} 1.4462–1.4474 (lit. values[4] b.p. 146–147°, n_D^{14} 1.4506). The infrared bands at 1690 and 1620 cm.$^{-1}$ are characteristic of an α,β-unsaturated ketone,[25] but a sharp intense band at 1780 cm.$^{-1}$ is attributed to a cyclobutanone impurity,[5] probably 2,3,3-trimethylcyclobutanone (Va). The semicarbazone melted initially at 176–180°; when recrystallized in small amounts, the derivative melted at 179–180°; a larger sample, after several recrystallizations from 50% ethanol, melted at 191–192°. All of these melting

(20) Microanalyses by Geller Microanalytical Laboratories, Hackensack, N. J. or Micro-Tech Laboratories, Skokie, Ill. Chlorine analyses on liquid products were by G. L., using the method of Umhoefer.[21] Melting points are uncorrected.

(21) R. Umhoefer, *Anal. Chem.* **15**, 383 (1943).

(22) R. W. Shortridge, R. A. Craig, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Am. Chem. Soc.* **70**, 946 (1948).

(23) All 2,4-DNP derivatives in this paper were prepared using the method of D. G. Johnson, *J. Am. Chem. Soc.*, **73**, 5888 (1951).

(24) A similar polymer (9 g.) was obtained when 10 g. (0.142 mole) of 1,1-dimethylcyclopropane was added dropwise at 0° to a suspension of 26.6 g. (0.2 mole) of aluminum chloride in 100 ml. of chloroform.

(25) Ref. 5, pp. 36, 117.

points have been recorded previously,[4,26-28] and the variation has been attributed[4] to small amounts of 3,4-dimethyl-4-pentene-2-one.

c. *Dehydrohalogenation with sodium carbonate.* III (13 g., 0.087 mole) was refluxed for 2 hours with 200 ml. of 10% sodium carbonate. The product, b.p. 145–149°, n_D^{20} 1.4442–1.4456, isolated as above, had an infrared spectrum identical with V above, except that the cyclobutanone band at 1780 cm.$^{-1}$ and a weaker band at 1037 cm.$^{-1}$ were absent. The semicarbazone, m.p. 191–192° (50% ethanol) did not depress the m.p. of the semicarbazone from the preceding experiment.

d. *Synthesis from acetyl chloride and 2-methyl-2-butene.* Acetyl chloride–aluminum chloride complex was prepared as above, from 1 mole of each reagent in 500 ml. of chloroform. To this solution there was added at −20°, dropwise, 70 g. (1.0 mole) of 2-methyl-2-butene (Phillips Tech. grade, 95% min., which had been fractionated through a large column). After 1 hr., hydrolysis over 750 g. of ice and 150 ml. of concentrated hydrochloric acid, and work-up in the usual way gave 90 g. (53%) of III, b.p. 46–49° at 3 mm., n_D^{20} 1.4400, infrared spectrum identical with the product from 1,1-dimethylcyclopropane. Derivatives, reduction products, and their derivatives were identical in all respects with those from 1,1-dimethylcyclopropane.

1,1-Dimethylcyclopropane and acetyl perchlorate. To a filtered solution of acetyl perchlorate (prepared[7] from 41 g. (0.2 mole) of silver perchlorate and 17.2 g. (0.22 mole) of acetyl chloride in 200 ml. of nitromethane) there was added, at 0°, 14 g. (0.2 mole) of 1,1-dimethylcyclopropane. The mixture was stirred 1 hr., then poured into 200 ml. of 5% sodium bicarbonate. Ether extracts were dried over magnesium sulfate; no product boiling above 100° (nitromethane) was collected, but the last fractions of distillate gave a 2,4-DNP, m.p. 129–130° which did not depress the melting point of this derivative of authentic 3,4-dimethyl-3-pentene-2-one.

A similar experiment using cyclopropane in place of 1,1-dimethylcyclopropane gave no acylation product.

Acetylation of chlorocyclopropane. To acetylating mixture prepared as above from 266 g. of aluminum chloride, 200 g. of acetyl chloride and 2 l. of chloroform there was added, at room temperature, 153 g. (2 moles) of chlorocyclopropane.[29,30] The temperature rose to 35° after 1–2 hr., then gradually dropped to room temperature. After 18 hr., the mixture was poured onto 1500 g. of ice; the chloroform layer and extracts of the amber aqueous layer were washed with water, dried over calcium chloride, and solvent stripped *in vacuo*. The residue (202 g.) which appeared to decompose on attempted distillation at 3 mm., was added to 500 ml. of 10% sodium bicarbonate and refluxed with vigorous stirring for 2 hr. An ether extract gave, after drying over magnesium sulfate and removal of the solvent, 63 g. (23%) of 4-chloro-3-methyl-3-butene-2-one (VII), b.p. 32–36° at 3 mm., n_D^{25} 1.4694–1.4704.

Anal.[31] Calcd. for C_5H_7OCl: Cl, 29.9. Found: Cl, 29.1, 28.8. Bands at 1687 and 1615 cm.$^{-1}$ are typical of α,β-unsaturated ketones[25] and a strong band at 822 cm.$^{-1}$ is characteristic of a trisubstituted ethylene.[32] The ultraviolet absorption spectrum of VII in 95% ethanol showed a single band, λ_{max} 234 mμ (ϵ = 1790) consistent with an α,β-disubstituted α,β-unsaturated ketone.[33] The 2,4-DNP, recrystallized from ethyl acetate, melted at 204–205°.

Anal. Calcd. for $C_{11}H_{11}O_4N_4Cl$: C, 44.23; H, 3.72; N, 18.73; Cl, 11.87. Found: C, 44.18; H, 3.78; N, 18.50; Cl, 11.95.

The semicarbazone, recrystallized from 50% ethanol, melted at 181–181.5°.

Anal. Calcd. for $C_6H_{10}ON_3Cl$: C, 41.04; H, 5.74; N, 23.93. Found: C, 40.71; H, 5.90; N, 24.64.

In addition to VII, there was obtained 9.2 g. of liquid, b.p. 62–65° at 3 mm., n_D^{25} 1.4760. Bands for an α,β-unsaturated ketone (1615, 1685 cm.$^{-1}$) and for a non-conjugated, unsaturated ketone (1630, 1725 cm.$^{-1}$) were present, but purification by fractionation was unsuccessful.

The water layer from the dehydrohalogenation of crude product (*vide supra*) was evaporated, leaving a residue; digestion of the latter with isopropyl alcohol did not give any soluble product. Also, no unreacted chlorocyclopropane could be recovered from the original reaction mixture.

Structure proof of 4-chloro-3-methyl-3-butene-2-one (VII).

a. *Reduction with lithium aluminum hydride.* To a stirred suspension of 3.8 g. (0.1 mole) of lithium aluminum hydride in 50 ml. of anhydrous ether was added 10 g. (0.085 mole) of VII. After stirring for 4 hr., the mixture was hydrolyzed and worked up in the usual manner, giving 9.2 g. (90%) of 4-chloro-3-methyl-3-butene-2-ol (VIII), b.p. 65° at 3 mm., n_D^{25} 1.4670.

Anal. Calcd. for C_5H_9OCl: C, 49.82; H, 7.52; Cl, 29.5. Found: C, 49.73; H, 7.73; Cl, 29.6.

In addition to hydroxyl and olefin bands, VIII showed a strong trisubstituted olefin band[32] at 814 cm.$^{-1}$ One ml. of VIII in 50 ml. of 80% ethanol containing 5% silver nitrate gave no precipitate of silver chloride. The 1-naphthylurethane of VIII, recrystallized from petroleum ether, melted at 97–98°.

Anal. Calcd. for $C_{16}H_{16}O_2NCl$: C, 66.31; H, 5.56; N, 4.84; Cl, 12.33. Found: C, 66.48; H, 5.68; N, 5.11; Cl, 12.20.

b. *Hydrogenation of VII.* A solution of 5 g. (0.042 mole) of VII in 25 ml. of anhydrous ether was hydrogenated (50 p.s.i.) over platinum oxide (0.2 g.) in 0.5 hr. Distillation gave 2.4 g. (65%) of 3-methyl-2-butanol, b.p. 106–110°, n_D^{25} 1.3942. The phenylurethane and 1-naphthylurethane melted at 65–67° and 107–108°, respectively (lit. values[34] 68° and 112°), and showed no depression when mixed with authentic samples.

Acetylation of allyl chloride. Allyl chloride (74 g., 1.0 mole) was added dropwise at 5° to acetylation mixture prepared from 133 g. of aluminum chloride, 120 g. of acetyl chloride and 800 ml. of chloroform. The bright red solution was hydrolyzed and worked up in the usual manner. The product could not be distilled without decomposition at 3 mm. It was refluxed for 1 hr. with 300 ml. of 20% sodium bicarbonate, but product from this step also decomposed above 60° at 3 mm. This material was very viscous, and not investigated further.

Acetylation of 1,1-dichlorocylopropane. To a solution of 22 g. (0.275 mole) of acetyl chloride and 33 g. (0.25 mole) of aluminum chloride in 300 ml. of chloroform prepared as above there was added 28 g. (0.25 mole) of 1,1-dichlorocyclopropane.[35] After 5 hr. reflux, the mixture was hydrolyzed with 500 g. of ice and 100 ml. of concentrated hydrochloric acid. Work-up gave some recovered 1,1-dichlorocyclopropane and 5 g. of an unstable product, b.p. 70–80° at 3 mm. Bands at 1611 cm.$^{-1}$ and 1725 cm.$^{-1}$ indicated unsaturation and a carbonyl, but this material was not further investi-

(26) L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, 816 (1941).

(27) G. K. Estok and J. H. Sikes, *J. Am. Chem. Soc.* **75**, 2745 (1953).

(28) H. Favre and H. Schinz, *Helv. Chim. Acta*, **35**, 2388 (1952).

(29) J. D. Roberts and P. H. Dirstine, *J. Am. Chem. Soc.* **67**, 1281 (1945).

(30) V. A. Slabey, *J. Am. Chem. Soc.*, **74**, 4928 (1952).

(31) Chlorine analyses on these compounds are often a bit low[21]; for other examples, see ref. 3.

(32) Ref. 5, p. 44.

(33) R. B. Woodward, *J. Am. Chem. Soc.*, **64**, 76 (1942).

(34) R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 4th ed., 1956, p. 280.

(35) Obtained as a by-product from the preparation of chlorocyclopropane. B.p. 75–75.5°, n_D^{25} 1.4378 (lit. values[30] b.p. 75.5°, n_D^{25} 1.4377).

gated. In another run for 1 hr. 67% of the 1,1-dichlorocyclopropane was recovered unchanged.

Acetylation of phenylcyclopropane. To the acetylation mixture prepared as above from one mole each of acetyl chloride and aluminum chloride in 750 ml. of chloroform was added at 4° 118 g. (1 mole) of phenylcyclopropane.[36] After several milliliters had been added, the temperature rose gradually and hydrogen chloride evolved. The mixture was then cooled to −25 ± 5° and the addition completed, accompanied by slow hydrogen chloride evolution. After stirring for 1 additional hr. the mixture was hydrolyzed with 750 g. of ice and 200 ml. of concentrated hydrochloric acid. Work-up in the usual manner gave 104 g. of crude product, b.p. 120–130° at 2–4 mm. Fractionation gave 78 g. (48%) of *p*-cyclopropylacetophenone (IX), b.p. 114–119° at 2.5–2.9 mm., m.p. 35–36° from ethanol or petroleum ether by cooling to 0°.

Anal. Calcd. for $C_{11}H_{12}O$: C, 82.47; H, 7.55. Found: C, 82.27; H, 7.56.

The 2,4-DNP, recrystallized from ethyl acetate, melted at 219–220°.

Anal. Calcd. for $C_{17}H_{16}N_4O_4$: C, 59.98; H, 4.73; N, 16.46. Found: C, 59.88; H, 4.90; N, 16.25.

IX had a carbonyl band at 1680 cm.$^{-1}$ and in 95% ethanol, showed ultraviolet absorption with λ_{max} 265 mμ, ϵ = 16,000. Another 9.5 g. of product, b.p. 125–131° at 2.8 mm., n_D^{20} 1.5668–1.5532 contained chlorine, carbonyl and aromatic bands, but did not crystallize and was not further investigated.

Structure proof of p-cyclopropylacetophenone (IX). a. *Oxidation to p-cyclopropylbenzoic acid* (X). To a solution containing 20 ml. of water, 20 ml. of dioxane, 12 g. (0.3 mole) of sodium hydroxide and 9 g. (0.11 mole) of bromine was added 1 g. (0.006 mole) of (IX) and the whole stirred for 5 hr. The dioxane was extracted with ether, the water layer acidified with hydrochloric acid, decolorized with sodium bisulfite, and filtered yielding 0.9 g. (88%) of *p*-cyclopropylbenzoic acid (X), m.p. 157–158°[8] (aqueous ethanol). Neutralization equivalent Calcd.: 162.2; Found: 164.0.

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.03; H, 6.21. Found: C, 73.82; H, 6.36.

b. *Chromic acid oxidation.* A mixture of 33 g. (0.33 mole) of chromic oxide, 100 ml. of 50% acetic acid and 6 g. (0.0375 mole) of IX was refluxed 8 hr., poured onto 100 g. of ice and filtered. The precipitate was washed with water, warmed with 20 ml. of ethanol for 0.5 hr., filtered and the precipitate washed with ether, giving 3.8 g. (61%) of terephthalic acid, subl. 280–300°, neutralization equivalent 85, 86 (Calcd. 83). The dimethyl ester, recrystallized from methanol, melted at 141°.[37]

Chloroacetyl chloride and cyclopropane. Following the general procedure of Hart and Curtis,[3] from 246 g. (2 moles) of chloroacetyl chloride, 266 g. (2 moles) of aluminum chloride and 90 g. (2.2 moles) of cyclopropane in 800 ml. of chloroform there was obtained 247.5 g. (69%) of a mixture of chloroketones, b.p. 70–90° at 3 mm., which was refluxed for 1 hr. with 500 ml. of 20% sodium bicarbonate. The organic layer and ether extracts of the aqueous layer were combined and gave 55 g. (16.5%) of 1-chloro-3-methyl-3-butene-2-one (XII), b.p. 56–57° at 3 mm., n_D^{25} 1.4692–1.4700.

Anal. Calcd. for C_5H_7OCl: Cl, 29.9. Found: Cl, 29.9, 29.6.

Characteristic α,β-unsaturated ketone bands were present (1700, 1630 cm.$^{-1}$) and XII gave a positive iodoform test. The 2,4-DNP, recrystallized from methanol, melted at 121–122°.

Anal. Calcd. for $C_{11}H_{11}O_4N_4Cl$: C, 44.23; H, 3.72; N, 18.76; Cl, 11.87. Found: C, 44.03; H, 3.94; N, 18.53; Cl, 11.84. There was also obtained 52 g. (14%) of 1,5-dichloro-2-pentanone (XI), b.p. 76–79° at 3 mm., n_D^{25} 1.4761–1.4770.

Anal. Calcd. for $C_5H_8OCl_2$: Cl, 45.8. Found: Cl, 44.9, 44.7. The 2,4-DNP, recrystallized from methanol, melted at 105–105.5°

Anal. Calcd. for $C_{11}H_{12}O_4N_4Cl_2$: C, 39.43; H, 3.61; N, 16.72; Cl, 21.16. Found: C, 39.47; H, 3.66; N, 16.87; Cl, 21.10.

Structure proof of 1-chloro-3-methyl-3-butene-2-one (XII). a. *Hydrogenation.* Hydrogenation of 6 g. (0.05 mole) of XII using Raney nickel and hydrogen at 50 p.s.i. and room temperature absorbed 0.1 mole of hydrogen in 40 minutes and gave, on distillation, 2.2 g. (51%) of 3-methyl-2-butanone, b.p. 94–97°, n_D^{25} 1.4204, 2,4-DNP m.p. 117–118° which did not depress the m.p. of an authentic sample. b. *Reduction with zinc.* To a vigorously stirred suspension of 20 g. of zinc dust in 50 ml. of 50% acetic acid was added slowly 11 g. (0.09 mole) of XII. After 1 hour the mixture was filtered. Combined ether extracts were neutralized by stirring with aqueous sodium carbonate, dried over anhydrous potassium carbonate and distilled, giving 5 g. (65%) of 3-methyl-3-butene-2-ol (XIII), b.p. 111–114°, n_D^{25} 1.4225. The phenylurethane melted at 66–66.5° (petroleum ether).

Anal. Calcd. for $C_{12}H_{15}O_2N$: C, 70.23; H, 7.36; N, 6.83. Found: C, 70.00; H, 7.30; N, 7.52.

The 1-naphthylurethane melted at 97–98° (petroleum ether).

Anal. Calcd. for $C_{16}H_{17}O_2N$: C, 75.28; H, 6.71; N, 5.49. Found: C, 75.40; H, 6.67; N, 5.63.

Authentic XIII prepared by lithium aluminum hydride reduction of 3-methyl-3-butene-2-one[38] in the conventional manner gave identical derivatives and the alcohol samples from the two sources had identical infrared spectra.

An attempted synthesis of XII by treatment of β-chloroisobutyryl chloride successively with diazomethane, hydrogen chloride and sodium bicarbonate gave some products which were not identical with XII and require further investigation.

1,5-Dichloro-2-pentanone (XI). To an anhydrous ether solution containing about 16.8 g. (0.4 mole) of diazomethane there was added an ether solution of 21 g. (0.15 mole) of 4-chlorobutyryl chloride (prepared in 50% yield from butyrolactone and phosphorus pentachloride) at such a rate as to maintain gentle reflux. After standing for 2 hr., the solution was cooled to 0° and anhydrous hydrogen chloride was passed in for 25 min., after which the yellow solution became colorless. After 1 hr. water was added, the ether layer washed with 10% sodium bicarbonate, water, and dried. Distillation gave 16 g. (69%) of 1,5-dichloro-2-pentanone (XI), b.p. 80–85° at 3 mm., n_D^{25} 1.4766–1.4772.

Anal. Calcd. for $C_5H_8OCl_2$: Cl, 45.8. Found: Cl, 46.6, 46.2.

The 2,4-DNP and infrared spectrum were identical with the product from chloroacetyl chloride and cyclopropane (*vide supra*).

Sulfonyl chlorides and cyclopropane. To a solution of 54.3 g. (0.5 mole) of methanesulfonyl chloride, 67 g. (0.5 mole) of aluminum chloride and 500 ml. of chloroform, prepared as usual, was added 25 g. (0.6 mole) of cyclopropane and the whole maintained at 0° for 1 hr. and room temperature for 12 hr., then worked up as usual. Only recovered sulfonyl chloride and about 1 g. of product, b.p. 120–150° at 3 mm. was obtained. Ethanesulfonyl chloride, butanesulfonyl chloride, and *p*-toluenesulfonyl chloride under similar and more strenuous conditions failed to yield significant amounts of acylation products.

Attempted isomerization of 5-chloro-2-pentanone (I, R = CH_3). To a solution of 78 g. (1 mole) of acetyl chloride and 133 g. (1 mole) of aluminum chloride in 1 l. of chloroform was added 30 g. (0.25 mole) of 5-chloro-2-pentanone. The solution was stirred at 0–10° for 1 hr., then worked up as usual giving 24 g. (80%) of unchanged 5-chloro-2-pentanone. No 3-methyl-3-butene-2-one was obtained.

(36) N. Kizhner, *J. Russ. Phys. Chem. Soc.* **45**, 949 (1911).
(37) M. E. Smith, *J. Am. Chem. Soc.*, **43**, 1920 (1921).
(38) E. Landau and E. P. Irany, *J. Org. Chem.*, **12**, 422 (1947).

Acetylation of cyclopropane in the presence of 5-chloro-2-pentanone (I, R = CH_3). In several acetylations of cyclopropane on a 1 mole scale, 25–27 g. (31–33%) of 3-methyl-3-butene-2-one was isolated. In two experiments in which 0.3–0.4 mole of 5-chloro-2-pentanone was added to the original reaction mixture, the yield of 3-methyl-3-butene-2-one remained 24–27 g. Furthermore, the yield of 5-chloro-2-pentanone corresponded to that normally found (30–33 g.) plus that initially added.

t-Butyl chloride and cyclopropane. The procedure was similar to that which Schmerling used[39] for addition of alkyl halides to olefins. A solution of 212 g. (2 moles) of *t*-butyl chloride in 100 ml. of chloroform was cooled to −50°, 90 g. (2.2 moles) of cyclopropane was added followed by 7 g. (0.053 mole) of aluminum chloride. After 10 min. the aluminum chloride was entirely dissolved and the solution was amber. After 2 hr., during which the temperature was allowed to rise to 0°, 25 ml. of 50% methanol was added. The chloroform layer, after washing with water and drying over potassium carbonate, gave 50 g. of product boiling over the range 40–110° at 92 mm. Careful fractionation into 19 cuts gave a major flat at 70–74° with variable refractive index (n_D^{20} 1.4258–1.4301). Fractions over the entire range corresponded approximately to $C_7H_{15}Cl$, but no single pure isomer was isolated.

Anal. Calcd. for $C_7H_{15}Cl$: C, 62.47; H, 11.24; Cl, 26.4. Found: Frac. 5 (53–55° at 92 mm., n_D^{20} 1.4181): C, 61.32; H, 11.13; Cl, 27.25. Frac. 8 (67–70° at 92 mm., n_D^{20} 1.4230): C, 62.90; H, 11.29; Cl, 25.6. Frac. 14 (74° at 92 mm., n_D^{20} 1.4301): C, 63.36; H; 11.28; Cl, 25.85.

(39) L. Schmerling, *J. Am. Chem. Soc.*, **67**, 1152 (1945).

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Cyclopropane Chemistry VII. Acetylation of Nortricyclene[1,2]

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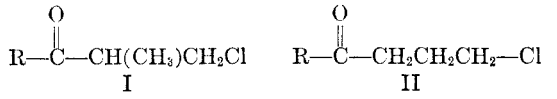
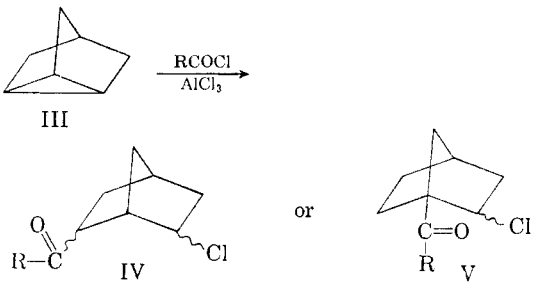
Nortricyclene reacts with acetyl chloride–aluminum chloride complex to give 2-chloro-6-acetylnorbornane (IV) which readily loses hydrogen chloride to give 1-acetylnortricyclene (VI), over-all yield 40–50%. The structure of the latter was proved by conversion to the known 1-methyl derivative. A number of 1-substituted nortricyclenes were prepared for the first time, from VI; correlations of their infrared spectra are discussed, with particular attention to bands in the 11.7μ and 12.7μ regions. A procedure is described for preparing VI from norbornene in 30–35% over-all yield.

The acylation of cyclopropane[3] and certain substituted cyclopropanes[1] was found to give predominantly β-chloroketones (I) and their related α,β-unsaturated ketones rather than the anticipated γ-chloroketones (II). I is formally produced by migration of a hydrogen from the carbon of the cyclopropane ring to which the acyl group becomes attached to one of the two remaining ring carbons, the chlorine becoming bound to the third. Because it is conceivable that both sides of the plane of the three-membered ring might be required for this shuffling of bonds, it seemed desirable to acylate a cyclopropane ring, one side of which was blocked from reaction by a cage. Nortricyclene (III) fulfilled this requirement, and was potentially of interest for several other reasons. If acylation of III were reasonably normal, one might learn something of the stereochemistry of additions to three-membered rings, a problem which has not yet been investigated. Furthermore, some of the anticipated acylation products might have intrinsic value for other mechanistic studies.



Normal addition to the three-membered ring of III would give 2-chloro-6-acylnorbornanes (IV) whereas the rearrangement observed in previous cyclopropane acylations[1,3] would be expected to give the β-chloroketones V. This paper describes the acetylation of III, a reaction which, as will be seen, has lead to a rather convenient approach to the previously inaccessible 1-substituted nortricyclenes.



Acetylation of nortricyclene (III). When pure nortricyclene[4] was acylated at 0–5° with the 1:1 acetyl chloride–aluminum chloride complex in methylene chloride, there was obtained (69%) a single chloroketone which decomposed with loss of hydrogen chloride on attempted fractionation at 14 mm. (85–95°) but could be distilled rapidly at 0.8 mm. (76–80°). Storage at Dry Ice temperature, at which the chloroketone was a solid, was possible, but dehydrohalogenation was rapid on storage at room

(1) For the previous paper, see H. Hart and G. Levitt, *J. Org. Chem.*, **24**, 1261 (1959).

(2) A portion of this work was sponsored by the Office of Ordnance Research, Contract No. DA-20-018-ORD-16492.

(3) H. Hart and O. E. Curtis, Jr., *J. Am. Chem. Soc.*, **79**, 931 (1957).

(4) J. D. Roberts, E. R. Trumbell, Jr., W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).