Bridged Ionic Intermediates in the Acylation of Cyclopropanes[1,2]

Harold Hart and Richard H. Schlosberg

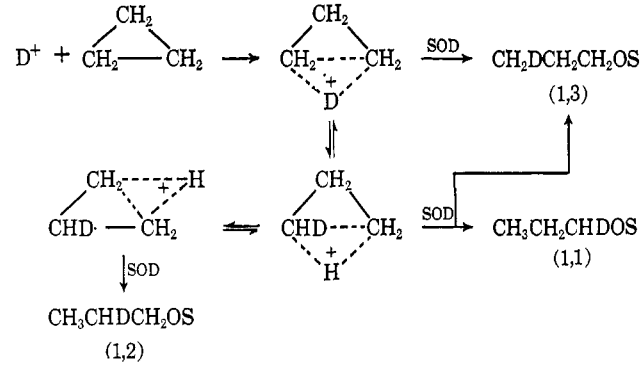
Contribution from the Department of Chemistry, Michigan State University, East Lansing, Michigan 48823. *Received March 13, 1968*

Abstract: Acetylation of cyclopropane gave four products, 5-chloro-2-pentanone (**1**), 4-chloro-3-methyl-2-butanone (**2**), and the corresponding unsaturated ketones 3-methyl-3-buten-2-one (**3**) and 3-chloro-2-pentanone (**4**). These correspond to the addition of acetyl chloride in a 1,2 and 1,1 as well as the expected 1,3 manner. Each product is formed directly and not from one of the others. Acetylcyclopropane is not a reaction intermediate and does not suffer ring opening with hydrogen chloride and aluminum chloride under the mild conditions comparable to those of acetylation. A conventional carbonium ion mechanism encounters difficulty in explaining the observed products. All the results are nicely accommodated by a mechanism (Scheme III) involving protonated cyclopropane intermediates. Consistent with this scheme are the observations that polar solvents or inverse addition (acetylating agent to cyclopropane) favor products **2** and **3** relative to **1** and **4**. 1,1-Dimethylcyclopropane, on acetylation, gives 4-chloro-3,4-dimethyl-2-pentanone (**11**) and 3,4-dimethyl-3-penten-2-one (**12**). Protonated cyclopropanes are not involved. The mechanism suggested involves isomerization of 1,1-dimethylcyclopropane to 2-methyl-2-butene which is then acetylated in the expected manner. Methylcyclopropane gives as acetylation products 5-chloro-2-hexanone (**7**), 4-chloro-3-methyl-2-pentanone (**8**), and 3-methyl-3-penten-2-one (**9**). These can be accounted for by a conventional mechanism involving reaction by two competing paths—1,3 addition to give **7** (eq 9) and isomerization to 2-butene which is acetylated conventionally to **8** and **9** (eq 10)—or by a single mechanism (Scheme IV) involving the most stable protonated cyclopropane intermediates. A choice between these two alternatives awaits further experiments.

It was first clearly established in the pioneering work of Baird and Aboderin[3] that electrophilic attack of a proton on the cyclopropane ring leads to *n*-propyl products which are best explained as arising from protonated cyclopropanes.[4] Treatment of cyclopropane with 57% (8.43 *M*) D_2SO_4 led to 1-propanol with deuterium incorporated into all three positions of the carbon skeleton. Equilibration prior or subsequent to the hydrolysis was eliminated as an explanation. A simple carbonium ion mechanism involving proton addition to give a 1-propyl cation which is then captured by solvent is untenable because it would give label only at the 3 position. The results can be rationalized *via* protonated cyclopropanes, according to Scheme I. In a sense, these results can be discussed in terms of the addition of deuteriosulfuric acid to cyclopropane not only in a 1,3 but also in a 1,2 and 1,1 manner; the anion always takes position 1, and the cation (deuterium) takes position 3, 2, or 1 with appropriate hydrogen migration.

Some years ago we observed[5] that the acylation of cyclopropane with acetyl chloride gave not only 5-chloro-2-pentanone (**1**), the expected 1,3-addition product, but also 4-chloro-3-methyl-2-butanone (**2**). At the time no plausible mechanism for the formation of **2** presented itself, and indeed until recently, the result was described as "curious . . . difficult to account for."[6] It now seems clear that this result is another manifestation of the intermediacy of protonated cyclopropanes, but with attack initiated by an acyl cation rather than a proton. Thus **1** and **2** can be considered as products of 1,3 and 1,2 addition of acetyl chloride to cyclopropane, with the nucleophile (chloride) always taking position 1.

Scheme I



We have reinvestigated the reaction with the aid of modern analytical weapons. The earlier work has been confirmed and extended, and evidence is presented for the progressive formation of protonated cyclopropane intermediates in order of increasing thermodynamic stability. Evidence is also presented for the formation of such intermediates in the acylation of methylcyclopropane, but not 1,1-dimethylcyclopropane.

Results

Most acylations were carried out by bubbling cyclopropane into a homogeneous solution of a 1:1 acetyl

(1) (a) For a preliminary communication of some of these results, see H. Hart and R. H. Schlosberg, *J. Am. Chem. Soc.*, **88**, 5030 (1966); (b) for a closely related communication, see N. C. Deno and D. N. Lincoln, *ibid.*, **88**, 5357 (1966).

(2) We are indebted to the National Science Foundation and the National Institutes of Health for financial support of this research.

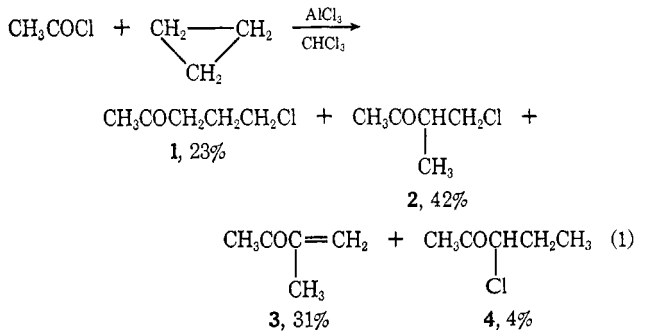
(3) R. L. Baird and A. A. Aboderin, *J. Am. Chem. Soc.*, **86**, 252 (1964); A. A. Aboderin and R. L. Baird, *ibid.*, **86**, 2300 (1964).

(4) Similar intermediates have been suggested in amine deaminations, in the reactions of alkoxides with carbenes, in solvolysis reactions, and in the reaction of alkyl halides with electrophiles. In contrast with the present work, however, only a small fraction of the products of these reactions arises from protonated cyclopropanes. For leading references see G. J. Karabatsos, C. E. Orzech, Jr., and S. Meyerson, *ibid.*, **87**, 4394 (1965); C. C. Lee and J. E. Kruger, *Tetrahedron*, **23**, 2539 (1967); O. E. Edwards and M. Lesage, *Can. J. Chem.*, **41**, 1592 (1963); P. S. Skell and I. Starer, *J. Am. Chem. Soc.*, **82**, 2971 (1960); M. S. Silver, *ibid.*, **82**, 2971 (1960); C. C. Lee and J. E. Kruger, *Can. J. Chem.*, **44**, 2343 (1966); J. H. Bayless, F. D. Mendicino, and L. Friedman, *J. Am. Chem. Soc.*, **87**, 5790 (1965); J. A. Berson and P. W. Grubb, *ibid.*, **87**, 4016 (1965); G. J. Karabatsos, J. L. Fry, and S. Meyerson, *Tetrahedron Letters*, 3735 (1967). For a theoretical discussion see R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964).

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

(6) R. Breslow in "Molecular Rearrangements," P. de Mayo, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, p 256.

chloride–aluminum chloride complex in a solvent, the temperature being maintained near 0°. Reactions were clean and remained homogeneous; work-up involved hydrolysis with hydrochloric acid and ice, extraction, and isolation by preparative vpc. The products with yields are shown in eq 1 for reaction in chloroform, and



in Table I for several solvents.

Table I. Per Cent Yield of Products from the Acylation of Cyclopropane in Several Solvents[a]

Solvent	1	2	3	4
$CHCl_3$	23 ± 2	42 ± 3	31 ± 3	4 ± 1
CCl_4	35 ± 1	40 ± 1	21 ± 1	4 ± 1
CS_2	38 ± 5	28 ± 4	25 ± 4	9 ± 1
CH_2Cl_2	25 ± 1	53 ± 2	17 ± 3	5 ± 1
$C_6H_5NO_2$	18 ± 2	48 ± 3	30 ± 3	5 ± 1

[a] Yields are the average of at least two runs, all determined from vpc traces. Normal addition sequence (cyclopropane added to acylating mixture) was followed.

The structures of **1** and **3** had been established chemically in previous work[5] and were confirmed by nmr and mass spectroscopy (see the Experimental Section). The structure of **2** was deduced from its spectra.[7] In particular, the nmr spectrum showed a singlet at τ 7.85 (3 H, CH_3CO), a multiplet at τ 7.18 (1 H, methine), a doublet at τ 8.80 (3 H, J = 7.0 Hz, CH_3CH), and a multiplet at τ 6.45 (2 H, CH_2Cl; not a simple doublet due to the adjacent asymmetric center[8]). Infrared and mass spectra support the structure.

Compound **4** went previously undetected, among the acylation products. It was consistently produced in a variety of solvents (Table I). Its structure rests on spectral properties and independent synthesis. The mass spectrum showed, in addition to parent peaks (*m/e* 120, 122), prominent fragmentation peaks at *m/e* 92, 94 ($CH_3C(OH)=CHCl^+$) and *m/e* 43 (CH_3CO^+). The nmr spectrum showed the acetyl methyl at τ 7.75 (singlet, 3 H) and another methyl at τ 8.97 (triplet, J = 7.1 Hz, 3 H). The methine hydrogen appeared as two doublets, τ 5.96, J = 7.4 Hz (note that the adjacent methylene protons are not equivalent, being next to an asymmetric center), and the methylene protons as a multiplet at τ 8.12.

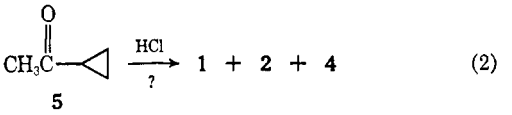
(7) In earlier work,[5] with techniques available at the time, compound **2** was not in fact isolated from the reaction mixture, since direct distillation led to appreciable decomposition. Consequently the reaction mixture was dehydrohalogenated directly with 20% sodium carbonate, and **1** and **3** were characterized. It was deduced that **3** arose from **2**; the present work shows (*vide infra*) that *both* **2** and **3** are direct acetylation products of cyclopropane.

(8) G. M. Whitesides, D. Holtz, and J. D. Roberts, *J. Am. Chem. Soc.* **86**, 2628 (1964).

Chlorination of 2-pentanone with sulfuryl chloride gave a product[9] identical (retention time, ir, nmr) with **4** obtained from the cyclopropane acetylation.

When the homogeneous acylation reaction mixture in carbon tetrachloride was subjected to direct nmr examination it was clear that all four products (**1–4**) were present prior to work-up. Integration of selected nonoverlapping peaks (see Experimental Section) established the ratio of **2**:**1** as 1.20; this same ratio determined from vpc traces after work-up was 1.17. Independent experiments showed that the dehydrohalogenation **2** → **3** was negligible under the vpc conditions used. Thus **3** is formed directly in the acylation, and not from **2** during work-up.

It is conceivable that **1**, **2**, and **4** might arise from the addition of HCl to acetylcyclopropane (**5**) as a reaction

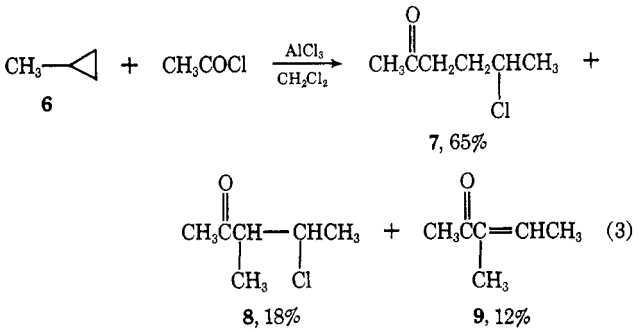


intermediate. To test this possibility, acetylcyclopropane was treated with aluminum chloride and hydrogen chloride in CH_2Cl_2 at 5° for 1 hr. Vpc analysis of the product showed only recovered, unchanged starting material (retention time, ir, nmr). In a more direct test, acetylcyclopropane was recovered (92%) from attempted acylation under the usual conditions used for cyclopropane; only 8% of acylation products different from **1–4** were obtained. Finally, the acetylation of cyclopropane was carried out in the presence of initially added acetylcyclopropane. The acetylcyclopropane was recovered (96%) and the remaining product distribution was as expected (Table II).

To examine the possible interconversion of the three halo ketones during acetylation, various amounts of **1**, **2**, and **4** were initially added to a cyclopropane acetylation reaction mixture. The results, given in Table II, show that the added chloro ketones are recovered unchanged in each case, and hence are presumably not interconverted during the reaction.

For reasons which will be discussed below, it became important to carry out several product studies on acetylations performed with inverse addition. A solution of the 1:1 acetyl chloride–aluminum chloride complex was slowly added to a cold solution of cyclopropane in the same solvent. The results are given in Table III.

Methylcyclopropane was acetylated in methylene chloride at about 0°, by adding the cyclopropane to the acylating medium. The products are shown in eq 3. The structure of the major product, **7**, was indicated



(9) E. R. Buchman and E. M. Richardson, *ibid.*, **67**, 395 (1945).

Table II. Cyclopropane Acetylation with Added Chloro Ketones or Acetylcyclopropane

Cyclopropane, mol	Solvent	Added reactant, mol	Products	% No added reactant	% Expd	% Obsd
0.010	CCl_4	**1**, 0.0044	**1**	35	55	57
			2	40	28	24
			3	21	14	16
			4	4	3	3
0.005	CCl_4	**2**, 0.0017	**1**	35	26	28
			2	40	55	48
			3	21	16	20
			4	4	3	4
0.010	CH_2Cl_2	**4**, 0.0077	**1**	25	15	16
			2	53	31	28
			3	17	10	11
			4	5	44	45
0.050	CH_2Cl_2	**5**, 0.050	**1**	25	12	11
			2	53	28	32
			3	17	8	7
			4	5	2	2
			5	0	50	48

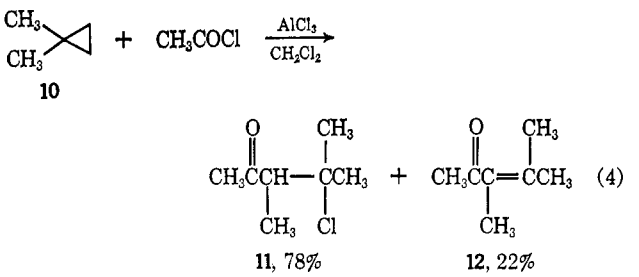
Table III. Per Cent Yield of Products from the Acylation of Cyclopropane by Inverse Addition

Solvent	1	2	3	4
CCl_4	20 ± 1	59 ± 2	18 ± 1	3 ± 1
CH_2Cl_2	4 ± 1	74 ± 4	20 ± 2	2 ± 1

by its nmr spectrum. The methyl ketone singlet appeared τ 7.92, and the other methyl group as a doublet at τ 8.48, J = 6.5 Hz. The methylene protons adjacent to the carbonyl function formed a triplet at τ 7.38, J = 7.0 Hz. Multiplets at τ 6.02 and 8.04 were assigned to the methine proton and the remaining methylene group, respectively.

The nmr spectra of the minor products were also consistent with the assigned structures. Compound **8** showed a singlet at τ 7.82 (3 H, methyl ketone) and two doublets at τ 8.50 and 8.87 (J = 6.5 and 7.0 Hz, respectively) for the remaining two methyl groups, the former being assigned, from its chemical shift, to the methyl attached to the chlorine-bearing carbon. The two methine protons were multiplets centered at τ 5.80 (C*H*Cl) and τ 7.32 (C*H*C=O). The unsaturated ketone **9** had a singlet at τ 8.00 for the methyl ketone. The remainder of the spectrum was complicated, possibly by the presence of *cis* and *trans* isomers, and also by long-range coupling. Signals of the correct areas were readily accounted for, however, as follows: one vinyl proton, quartet of quartets (J = 7.0 Hz and 1.4 Hz) centered at τ 3.68, multiplet centered at τ 8.25 (3 H, methyl near carbonyl), and an eight-line resonance at τ 8.58 (3 H, methyl group split by adjacent proton and by other allylic methyl group). Ketone **9** was synthesized by acetylation of 2-butene, and found to be identical with the product from methylcyclopropane.

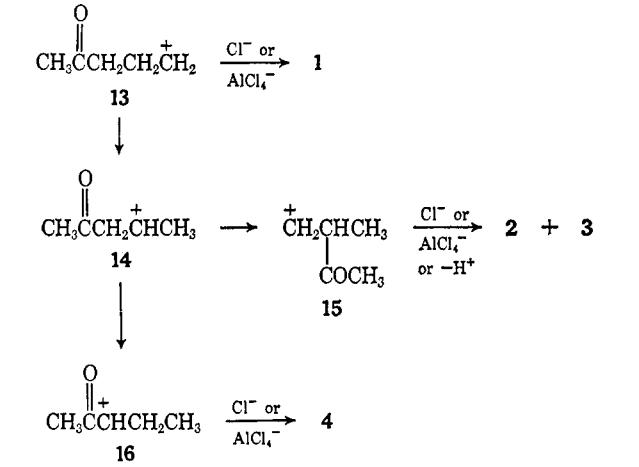
Previous work[10] on acetylation of 1,1-dimethylcyclopropane reported a 59% yield of 4-chloro-3,4-dimethyl-2-pentanone (**11**). Reexamination of this reaction with the aid of modern techniques confirmed the formation of **11**, but in 78% yield. The other product was the corresponding α,β-unsaturated ketone **12** (eq 4). The structure of **11** was proved chemically;[10] the nmr spectrum determined here was consistent with the assigned structure (see Experimental Section). The structure of **12** followed directly from its ir and nmr spectra (the latter showed three singlets at τ 7.95, 8.17, and 8.27 with relative areas 1:2:1) and from its synthesis from **11** by reflux with 20% sodium bicarbonate.



Discussion

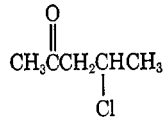
It is difficult to rationalize the formation of products **2–4** from acetyl chloride and cyclopropane using a conventional carbonium ion mechanism (Scheme II). For example, if the electrophile is considered to be the acetyl cation (or a complex which furnishes such a species), the first formed carbonium ion should be **13**. Capture of chloride ion would lead to the 1,3-adduct **1**, the expected product. To rationalize the formation of **2** and **3**, ion **13** must first undergo hydride shift to **14**, a not unreasonable step leading to a secondary car-

Scheme II



(10) H. Hart and G. Levitt, *J. Org. Chem.*, **24**, 1261 (1959).

bonium ion. The next step, acyl migration, leads once again to a primary carbonium ion, **15**, and should be energetically unfavorable. Although some acyl migrations are known in carbonium ion chemistry,[11] this one seems unlikely. Furthermore, if ion **14** were an intermediate one might expect to find **17** or **18** among the reaction products. In fact acetylation of propene does



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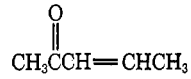

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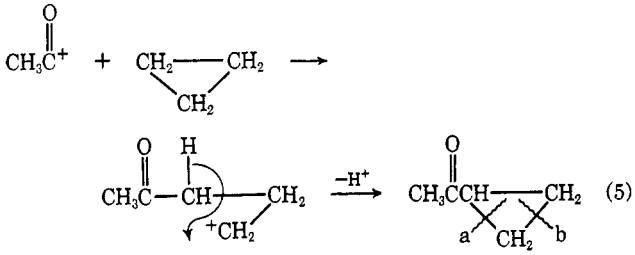
lead to these compounds under conditions identical with those used in the present acetylations.[5] Ion **14** would be the expected intermediate in that reaction, and no **2** or **3** is produced when propene is acetylated.

To rationalize **4** *via* conventional carbonium ions is even more difficult. Hydride shift in **14** to give **16** is required; this is certainly an uphill step energywise, since the positive charge is adjacent to a carbonyl group in **16**.

From this discussion it is clear that a scheme involving ions **13**–**16** is unlikely as a rationalization for the observed products. So too is the suggestion that cyclopropane isomerizes to propene prior to acylation; this would give[5] **17** and **18**, which were not observed reaction products. Such isomerizations may be important for substituted cyclopropanes (*vide infra*).

Another possible way of rationalizing the observed products would be *via* addition of hydrogen chloride to acetylcyclopropane, which conceivably could be formed *via* some route such as eq 5. Addition of HCl across



(5)

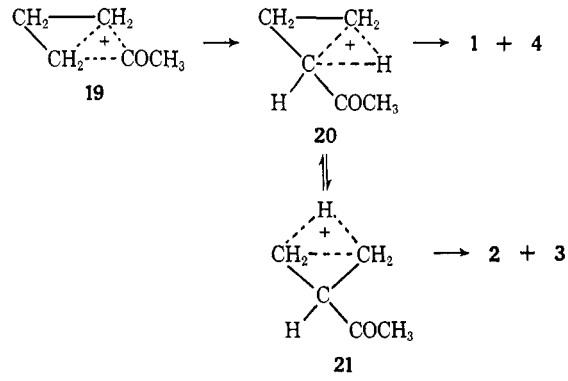
bond a in two different manners could give **1** or **4**; addition across bond b would give **2** which might lead to **3** by elimination. Several experiments already described argue against this mechanism, the most cogent being that when acetylcyclopropane was added to the acetylating medium (Table II) it was recovered unchanged. Also, HCl did not add to acetylcyclopropane in the presence of aluminum chloride, under conditions otherwise similar to those used in the acetylation.

Several attempts were made to promote the formation of acetylcyclopropane as an acetylation product, and these are described in detail in the Experimental Section. Three relatively nonnucleophilic bases (tetrahydrofuran, 2,6-lutidine, and N,N-diisopropylethylamine) were used to promote proton removal; in no case was any acetylcyclopropane detected among the products, which were the same four usually isolated. The only effect was to increase the percentage of **3** at the expense of **2**, to varying degrees.

(11) For leading references, see H. Hart and L. Lerner, *J. Org. Chem.*, **32**, 2669 (1967).

Scheme III, which involves bridged protonated cyclopropanes, does rationalize our results nicely. Initial

Scheme III



attack of the electrophile leads to **19** which by formation of a C–C σ bond and rotation about one of the ring C–C bonds leads to protonated cyclopropane **20**. Because of the smaller size of the proton, overlap should be much better in **20** than in **19**. The first formed protonated cyclopropane, then, is bridged between the carbon holding the acyl group and a methylene carbon. This ion is not symmetrical, and most of the charge is probably on the carbon furthest from the carbonyl function. Reaction of **20** with nucleophile occurs predominantly at this carbon, giving **1**, but some **4** is also formed from attack at the carbon bearing the carbonyl function.

Migration of bridging around the ring in protonated cyclopropane itself is facile.[3] A similar course here leads to ion **21** which has a plane of symmetry; attack of nucleophile at either positive carbon gives **2**. Alternatively, **21** may lose the methine proton α to the carbonyl group, leading directly to **3**. This proton should be quite acidic because it is not only α to a carbonyl group but also α to two partially positive carbon atoms. Evidence was presented above which shows that **3** is present in the reaction mixture prior to workup. Furthermore, addition of **2** to the acetylating mixture did not lead to appreciably greater yields of **3** (Table II). Thus although not proved conclusively, it seems likely that **3** is a direct reaction product, and is not produced by the dehydrohalogenation of **2**.

It is expected that if equilibrium were attained between **20** and **21**, the latter would predominate, because the positive charge is most remote from the carbonyl carbon atom. The data in Table I show that products from **21** did predominate in all solvents; the ratio [(**2** + **3**)/(**1** + **4**)] varied from as low as 1.13 in carbon disulfide to as high as 3.4 in nitrobenzene. The ratio seems to increase with increasing solvent polarity (CCl_4, 1.56; CH_2Cl_2, 2.33; $CHCl_3$, 2.7), suggesting either that equilibrium between **20** $\rightleftharpoons$ **21** is more closely approached the more polar the solvent or that equilibrium is always attained, but that the extent to which **21** predominates increases in more polar solvents.

Most of the acylations (Tables I and II) were performed with an excess of nucleophile always present; that is, cyclopropane was slowly added to a molar equivalent of the 1:1 acetyl chloride–aluminum chloride complex. It was thought that if the addition were carried out in an inverse manner, there would be less nucleophile available at any instant and this would favor

attainment of equilibrium **20** ⇌ **21**. Since the first-formed ion is presumably **20**, this procedure should increase the yield of **2** + **3** at the expense of **1** + **4**. The results are given in Table III. In CCl_4 the ratio of [(**2** + **3**)/(**1** + **4**)] increased from 1.56 to 3.34, and in methylene chloride the comparable change was from 2.33 to 15.6! *In the latter solvent, only 6% of the product was derived from the first-formed ion.* We consider these results to constitute strong supporting evidence for the mechanism in Scheme III and to demonstrate the sequential formation of structurally different protonated cyclopropanes. These results also support the view that increased solvent polarity allows closer approach to equilibrium between **20** and **21** (see previous paragraph).[12]

Alkylcyclopropanes. One reason why protonated cyclopropanes might be preferred intermediates in electrophilic ring openings of cyclopropane itself is that the alternative conventional carbonium ion would have to be primary. Alkyl substitution provides the possibility that the conventional ion would be secondary or tertiary (for 1,1-dialkylcyclopropanes); this might swing the energy balance away from bridged ions in favor of reaction *via* ordinary carbonium ions. To test this possibility, we examined the acetylation of methylcyclopropane (**6**) and 1,1-dimethylcyclopropane (**10**).

The products from **10** are shown in eq 4. Their structures are identical with the acetylation products of 2-methyl-2-butene.[10] Had reaction occurred by a conventional carbonium ion route, one would have expected 5-chloro-5-methyl-2-hexanone (**23**) to be the major product, *via* ion **22** (eq 6). The same product

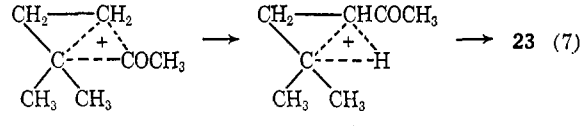
10 + $CH_3\overset{+}{C}O$ ⟶

$$CH_3COCH_2CH_2\overset{+}{C}(CH_3)_2 \longrightarrow CH_3COCH_2CH_2C(CH_3)_2 \quad (6)$$

22 → **23** (Cl)

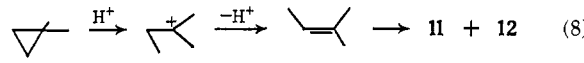
might have been expected if bridged ions (**24** and **25**) were involved. In fact, no 1,3 adduct such as **23** was

10 + $CH_3\overset{+}{C}O$ ⟶



24 → **25** → **23** (7)

obtained; the only products were **11** and **12**. Presumably 1,1-dimethylcyclopropane is rapidly isomerized by acid present in the acylating medium to 2-methyl-2-butene, which then gives the observed products (eq 8).



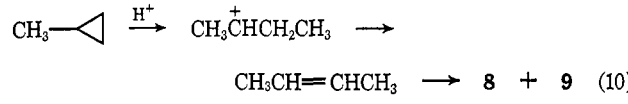
This reaction path was ruled out for cyclopropane itself (*vide supra*) but clearly becomes important when substitution on the cyclopropane facilitates isomerization to the less strained alkene.

Methylcyclopropane provides an instructive intermediate case; the products are summarized in eq 3. Had reaction occurred by a conventional carbonium ion route, one would have expected 5-chloro-2-hexanone (**7**) to be the major product, *via* ion **26** (eq 9) in

$$\mathbf{6} + CH_3\overset{+}{C}O \longrightarrow CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{+}{C}HCH_3 \longrightarrow \mathbf{7} \quad (9)$$

26

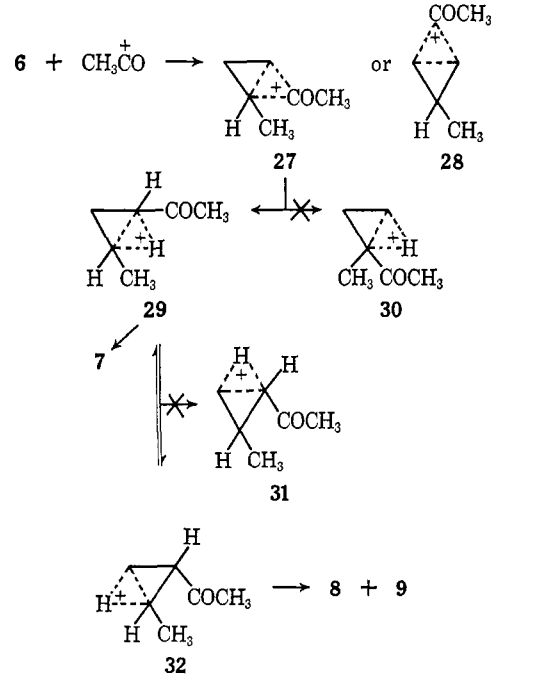
which the cyclopropane ring has opened to give the most stable carbonium ion (secondary). Compound **7** was in fact the major product, but it was accompanied by appreciable amounts of **8** and **9**. These could arise by isomerization of methylcyclopropane to 2-butene, which is then acetylated (eq 10). The products can be



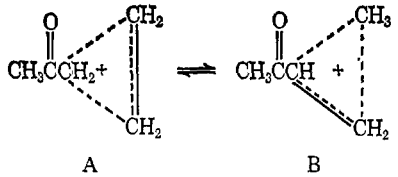
accounted for if the methylcyclopropane reacts two-thirds by eq 9 and one-third by eq 10.

Alternatively one can account for all three observed products as those most likely to arise if the entire reaction proceeded *via* the most stable protonated cyclopropanes, as shown in Scheme IV. Of the first two possible intermediates, **27** is much preferred to **28** (approximately the same energy difference as primary *vs.* secondary carbonium ions). In converting to a pro-

Scheme IV



(12) A referee has suggested that our data may also be rationalized in terms of equilibrium A ⇌ B; these lead to products: A ⟶ **1** and B ⟶ **2**



A B

+ **3** + **4**. Product **4** is now allied with (**2** + **3**) rather than with **1**. This does not alter the ratios markedly since the amount of **3** produced is small relative to the three other products.

If this mechanism were correct, presumably A would be formed before B. Inverse addition should therefore favor **4** whereas in fact less **4** was produced (in CCl_4, 3% *vs.* 4%, and in CH_2Cl_2, 2% *vs.* 5%). Admittedly the differences are probably too small to rule out the A ⇌ B mechanism, but the results seem more consistent with the edge-protonated mechanism (Scheme III). For stronger evidence for edge protonation, see papers by Lee and Kruger (1966) and Karabatsos, Fry, and Meyerson (1967) cited in ref 4.

tonated cyclopropane, **27** has the option of **29** or **30**; since most of the charge will be on the carbon most remote from the carbonyl group, **29** is preferred over **30** (again, secondary > primary). If **29** reacts with a nucleophile (Cl^- or $AlCl_4^-$) the major expected product (1,3 addition) will be **7**, as observed. The other possible product at this stage would be 3-chloro-2-hexanone which is expected in only trace amounts. This type of product (**4**) was only observed to the extent of about 5% with cyclopropane, and should perhaps be less important here because the competing carbon is secondary rather than primary.

Instead of reacting with a nucleophile, **29** might be converted to another protonated cyclopropane, **31** or **32**. Conversion to **31** would be an uphill process energywise (primary *vs.* secondary), and no products derived from **31** were observed. However, **32** should be formed, since this removes the positive charge from a position adjacent to a carbonyl group. Reaction of **32** with nucleophile at the preferred secondary carbon gives **8**, or loss of the α-methine proton to give the most stable alkene furnishes **9**.

Scheme IV thus furnishes a rational scheme for all the products observed from acetylation of methylcyclopropane. It is also reasonable that here a greater percentage of the product (about 68%) comes from the first-formed protonated cyclopropane (**29**) than in the acetylation of cyclopropane itself (30% from **20** in CH_2Cl_2) since **29** should be more stable relative to **32** than is **20** relative to **21**, due to the secondary carbon in **29**.

Although all of the data for acetylation of methylcyclopropane are consistent with Scheme IV, it is not proved. Experiments now under way with appropriately labeled methylcyclopropane will hopefully distinguish between Scheme IV, a suitable combination of eq 9 and 10, or some alternate mechanism not yet considered.

In summary, the acetylation of cyclopropane is difficult to rationalize by a conventional carbonium ion mechanism, but is nicely accommodated with hydrogen-bridged or protonated cyclopropanes. Predictions based on this mechanism were fulfilled, and the sequential formation of structurally different isomeric protonated cyclopropanes in order of increasing thermodynamic stability was demonstrated. 1,1-Dimethylcyclopropane does not acetylate in this manner, but methylcyclopropane may. It is to be expected that other electrophilic ring openings of cyclopropane (see ref 1b) will follow a similar pattern.

Experimental Section

General Procedures. All nmr spectra were measured with a Varian A-60 or Jeolco C-60H spectrometer. Chemical shifts are reported as τ values measured from tetramethylsilane or methylene chloride as an internal standard. Vpc analyses were carried out on 5- or 10-ft columns packed with 20% SE-30 on Chromosorb W, 20% FFAP on Chromosorb W, or 20% SF-96 on Chromosorb P at approximately 130–140°. Infrared spectra were obtained on a Unicam Model SP-200 spectrometer and were calibrated against a polystyrene film. Ultraviolet spectra were measured with a Unicam Model SP-800 or a Beckman Model DB spectrophotometer. Mass spectra of the chloro ketones from the acylation of cyclopropane were obtained by S. Meyerson and E. Bednar, American Oil Company, Whiting, Ind. Other mass spectra were obtained by Dr. H. Harris and Dr. J. Wettaw of this department with a Consolidated Electrodynamic Corporation 21-103C instrument operating at an ionizing potential of 70 V.

Acetylation of Cyclopropane. The procedure was similar to that of Hart and Curtis.[5] A solution of 16.49 g (0.210 mol) of acetyl chloride in 50 ml of methylene chloride was added over a 1-hr period to a mixture of anhydrous aluminum chloride (26.67 g, 0.200 mol) in 50 ml of methylene chloride. After addition of the acetyl chloride solution the mixture was stirred for an additional hour, then filtered through a sintered glass funnel into a flask equipped with a Dry Ice condenser, stirrer, gas-inlet tube, and pressure-equalizing dropping funnel. While the clear, pale yellow solution was maintained below 10° cyclopropane (11 ml, 7.9 g, 0.19 mol), previously condensed in a trap cooled to −79°, was bubbled into the acylating medium over a 45-min period. After addition was completed, the reaction mixture was stirred for 1 hr at 3–6°. During this time the solution took on a deep orange-brown color. The reaction mixture was hydrolyzed by slowly pouring it with stirring onto a mixture of 100 ml of concentrated HCl and 250 g of crushed ice. The organic layer was separated and washed successively with 50-ml portions of water, 10% sodium bicarbonate solution, and water and dried over anhydrous sodium sulfate. After removal of the solvent, the yield of crude acetylated product was 21.8 g. Vpc analysis on a 5-ft SE-30 column at 115° with a helium flow rate of 40 cc/min indicated that the product consisted of 14% of C_5H_8O (retention time 0.80 min) and 86% of C_5H_9OCl material (retention time 2.2, 4.8, and 7.5 min). On this basis there was a 96% yield of monoacetylated product. The reaction products were separated by preparative scale vpc. The yields in this experiment are those given in eq 1. The results of similar acetylations in other solvents are given in Table I.

Product Identification. 5-Chloro-2-pentanone (1). This compound had a retention time of 7.5 min and bp 75–77° (23 mm) (lit.[5] 77–78° (22 mm)). It was a clear, colorless liquid which quickly darkened and decomposed upon standing at room temperature. Its ir spectrum (liquid film) showed principal bands at 1710 ($\nu_{C=O}$) and 760 cm^{-1} (ν_{C-Cl}). The mass spectrum indicated parent peaks at *m/e* 120 and 122 and peaks at *m/e* 84 (P − HCl), 58 ($CH_3C(OH)=CH_2^+$), and 43 (CH_3CO^+). The nmr spectrum (neat) consisted of a sharp singlet at τ 7.89 (3 H), a triplet (J = 6.5 Hz) at τ 7.38 (2 H), a complex multiplet centered at τ 7.89 (2 H), and a triplet (J = 6.0 Hz) at τ 6.42 (2 H), assigned to the protons of C-1, C-3, C-4, and C-5, respectively.

4-Chloro-3-methyl-2-butanone (2). The retention time of this chloro ketone was 4.8 min. It was a clear, colorless liquid which quickly darkened and decomposed overnight at room temperature. The principal ir bands (liquid film) appeared at 1710 ($\nu_{C=O}$) and 758 cm^{-1} (ν_{C-Cl}). The mass spectrum indicated, in addition to the parent peaks at *m/e* 120 and 122, intense peaks at *m/e* 85 (P − Cl), 84 (P − HCl), and 42 (CH_2CO^+). The nmr spectrum (neat) showed a sharp singlet at τ 7.85 (3 H; methyl ketone), complex multiplets centered at τ 7.18 (1 H; methine proton) and τ 6.45 (2 H; methylene protons), and a doublet (J = 7.0 Hz) at τ 8.80 (3 H; methyl group on C-3).

3-Methyl-3-buten-2-one (3). The α,β-unsaturated ketone had a retention time of 0.80 min and bp 44–45° (98 mm) (lit.[5] 45–46° (98 mm)). It was a clear, colorless liquid wth $\lambda_{max}^{95\%\ EtOH}$ 218 mμ (log ϵ 3.84) (lit.[13] $\lambda_{max}^{95\%\ EtOH}$ 218 mμ). Its ir spectrum (CCl_4) displayed prominent bands at 1678 ($\nu_{C=O}$) and 1635 cm^{-1} ($\nu_{C=C}$). The nmr spectrum (CCl_4) consisted of a sharp singlet at τ 7.71 (3 H; methyl ketone), complex multiplets centered at τ 4.10 (1 H, H_{trans}) and τ 4.25 (1 H; H_{cis}), and a three-line absorbance centered at τ 8.15 (3 H; allylic methyl).

3-Chloro-2-pentanone (4). This compound had a retention time of 2.2 min. The principal ir bands (liquid film) appeared at 1718 ($\nu_{C=O}$) and 758 cm^{-1} (ν_{C-Cl}). The mass spectrum had prominent peaks at *m/e* 120, 122 (P), 92, 94 ($CH_3C(OH)=CHCl^+$), and 43 (CH_3CO^+). The nmr spectrum (neat) showed a sharp singlet at τ 7.75 (3 H), two doublets (J = 7.4 Hz) centered at τ 5.96 (1 H), a complex multiplet centered at τ 8.12 (2 H), and a triplet (J = 7.1 Hz) at τ 8.97 (3 H).

Synthesis of 3-Chloro-2-pentanone (4). Sulfuryl chloride (27 g, 0.20 mol) was dropped into a stirred solution of 17.2 g (0.200 mol) of 2-pentanone diluted with 20 ml of dry benzene over a period of 20 min while the reaction temperature was maintained below 24° by means of external cooling. The clear, colorless solution was stirred for an additional 50 min at 22°, then quickly poured onto approximately 100 g of crushed ice. About 20 ml of methylene

(13) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 100.

chloride was added and the combined organic layers were separated and dried over anhydrous sodium sulfate. After removal of the solvent *in vacuo*, the organic material was vacuum distilled and 4.1 g (17%) of a product with a boiling point of 57–58° (49 mm) was collected. This clear, colorless liquid darkened and decomposed slowly upon standing at room temperature, but appeared to be stable indefinitely when kept in the dark at 0°. It was identical in all respects (retention time, ir and nmr spectra) with the acetylation product **4**.

Acetylation of Cyclopropane with Added 1, 2, 4, or 5. These reactions were carried out using normal acylating conditions except that known quantities of 5-chloro-2-pentanone (**1**), 4-chloro-3-methyl-2-butanone (**2**), 3-chloro-2-pentanone (**4**), or acetylcyclopropane (**5**) were added to the solvent prior to the addition of the acylating reagent. The results of these experiments are summarized in Table II.

Acetylation of Cyclopropane with Inverse Addition. To a stirred mixture of 6.66 g (0.050 mol) of aluminum chloride and 50 ml of methylene chloride acetyl chloride (3.96 g, 0.050 mol) was slowly added, and the mixture was stirred for 20 min. The pale green solution was filtered through sintered glass and kept dry in a flask fitted with a drying tube. Into a flask equipped with a stirrer, gas-inlet tube, pressure-equalizing dropping funnel, and Dry Ice condenser and cooled by means of a salt–ice bath was placed 50 ml of methylene chloride. Cyclopropane (29 ml, 21 g, 0.50 mol) was condensed in a trap cooled to −79°, and then slowly bubbled over a 1-hr period into the methylene chloride. Finally the solution of acetylating reagent was dropped into the flask over a 1-hr period at a rate that maintained the reaction temperature below 10°, and the reaction mixture was stirred for an additional hour at 4–7°. During this time the solution took on a very deep cherry red color. The reaction mixture was slowly poured onto a mixture of 40 ml of concentrated HCl and 100 g of crushed ice, and the organic layer was washed successively with 50-ml portions of water, 10% sodium bicarbonate solution, and water and dried over anhydrous sodium sulfate. Product composition was determined by vpc analysis on a silicone column at 120° with the helium flow rate at 40 cc/min. The results of this experiment, and a similar one using carbon tetrachloride as solvent, are summarized in Table III.

Nmr Study of a Homogeneous Solution of Acetyl Chloride–Aluminum Chloride Complex and Cyclopropane in Carbon Tetrachloride. The procedure was identical with that employed for the normal acetylation of cyclopropane in carbon tetrachloride. A sample of the reaction mixture was placed in an nmr tube immediately after all the cyclopropane was added to the acetylating reagent. The methyl doublet (J = 7.0 Hz) of $CH_3COCH(CH_3)$-CH_2Cl appeared at τ 8.62 before work-up and at τ 8.80 after hydrolysis. The methylene α to the chlorine in $CH_3COCH_2CH_2$-CH_2Cl appeared as a triplet (J = 6.0 Hz) at τ 6.30 in the complex and at τ 6.42 in the isolated compound. Integration of the doublet of 4-chloro-3-methyl-2-butanone (**2**) and the triplet of 5-chloro-2-pentanone (**1**) gave (after statistical correction) a ratio of β-:γ-chloro ketone of 1.20:1; the vpc ratio after work-up was 1.17:1 (see Table I).

Separate experiments showed that **2** is stable under the vpc conditions employed in this study. When a sample of **2** was injected onto a column at the conditions normally used (130° at a helium flow rate of 40 cc/min), no peak due to **3** was observed.

Acetylation of Cyclopropane with Added Relatively Nonnucleophilic Bases. Tetrahydrofuran. Cyclopropane (2.1 g, 0.050 mol) was acetylated as previously described except that an equimolar amount of tetrahydrofuran was added to the methylene chloride solvent prior to the addition of acetylating agent. The products were 5-chloro-2-pentanone (17%), 4-chloro-3-methyl-2-butanone (47%), 3-methyl-3-buten-2-one (34%), and 3-chloro-2-pentanone (2%) as determined by vpc analysis. No acetylcyclopropane was produced, as indicated by a comparison of the crude product with the vpc retention time of an authentic sample of acetylcyclopropane.

2,6-Lutidine. The acetylation of cyclopropane (0.4 g, 0.01 mol) with an equimolar amount of 2,6-lutidine added to the methylene chloride solvent prior to addition of the acetylating agent produced 5-chloro-2-pentanone (24%), 4-chloro-3-methyl-2-butanone (52%), 3-chloro-2-pentanone (4%), and 3-methyl-3-buten-2-one (20%). No acetylcyclopropane was present.

N,N-Diisopropylethylamine. This experiment was identical with the inverse addition acetylation of cyclopropane in methylene chloride except that an equimolar amount of N,N-diisopropylethylamine was added to a methylene chloride solution of cyclopropane (2.1 g, 0.050 mol) prior to the addition of the acetylating solution. The products were 5-chloro-2-pentanone (8%), 4-chloro-3-methyl-2-butanone (42%), 3-chloro-2-pentanone (3%), and 3-methyl-3-buten-2-one (47%). No acetylcyclopropane was present.

Reaction of Acetylcyclopropane with Hydrogen Chloride and Aluminum Chloride. A mixture of 6.66 g (0.050 mol) of anhydrous aluminum chloride and 38 ml of methylene chloride was placed in a flask equipped with a liquid nitrogen condenser. Hydrogen chloride (1.5 ml, 1.8 g, 0.050 mol) was condensed in a trap cooled with liquid nitrogen and was bubbled slowly into the reaction flask. Finally acetylcyclopropane (4.2 g, 0.050 mol) was slowly added to the solution which was cooled by means of an ice bath. After the clear pale brown solution was stirred for 45 min, it was slowly poured onto a mixture of 40 ml of concentrated hydrochloric acid and 100 g of crushed ice. The organic layer was successively washed with 50-ml portions of water, 10% sodium bicarbonate solution, and water and dried over anhydrous sodium sulfate. Vpc analysis of the clear, pale yellow solution on a 5-ft SE-30 column at 120° with a helium flow rate of 25 cc/min showed the presence of a single peak (retention time = 3.2 min) which was shown to be identical (retention time, ir and nmr spectra) with authentic acetylcyclopropane. There were no other peaks.

Acetylation of Acetylcyclopropane under Normal Conditions. The usual acetylation procedure was used, except that the substrate was added by means of a pressure equilibrating dropping funnel rather than *via* the gas-inlet tube used in the acetylation of cyclopropane. After the addition of the acetylcyclopropane the reaction mixture was stirred for an additional hour at 3–6° before work-up. The gas chromatogram showed two peaks due to unreacted starting material (92%) and to some acetylation product(s) (8%).

Under Forcing Conditions. A solution of acetyl chloride in 20 ml of methylene chloride was slowly dropped into a stirred mixture of 13.33 g (0.100 mol) of anhydrous aluminum chloride in 20 ml of methylene chloride, and the solution was stirred for 25 min. The acetylating reagent was filtered through sintered glass. To this clear reagent there was added a solution of acetylcyclopropane (8.4 g, 0.10 mol) in 40 ml of methylene chloride over a 25-min period while the reaction temperature was maintained below 40°, and the reaction mixture was stirred for an additional 48 hr at room temperature. During this time the solution slowly acquired a fairly intense cherry red color. The reaction mixture was poured onto a mixture of 55 ml of concentrated hydrochloric acid and 100 g of crushed ice, and the organic layer was washed with water, twice with saturated sodium bicarbonate solution, and water, and the resultant clear, pale yellow solution was dried over anhydrous sodium sulfate. After removal of the solvent *in vacuo* vpc analysis indicated that about 40% of the acetylcyclopropane remained unreacted.

Of the reacted material more than 95% proved to be a mixture of three chloro ketones. These compounds were collected by preparative scale vpc and submitted to mass spectrometric analysis, Each of the compounds showed parent peaks at *m/e* 162 and 164, corresponding to $C_7H_{11}O_2Cl$. The first compound had a retention time of 1.2 min on a 5-ft Lexan (polycarbonate resin) column at 130° with a helium flow rate of 80 cc/min and was formed in 30% yield. This compound had a complex group of bands in the ir spectrum (liquid film) centered at 1713 cm^{-1}. The compound was not characterized. The second chloro ketone, formed in 33% yield, had a retention time of 2.9 min and had a sharp carbonyl stretch at 1715 cm^{-1}. The nmr spectrum (CCl_4) consisted of a one-proton triplet (J = 6.1 Hz) at τ 6.40, a two proton quartet (J = 6.1 Hz) at τ 7.48, a six-proton singlet at τ 7.88, and a complex two-proton multiplet at τ 7.95. On the basis of these data 3-chloroheptane-2,6-dione is tentatively assigned as the structure. The third chloro ketone had a retention time of 3.8 min and was formed in 32% yield. The ir spectrum (CCl_4) showed the carbonyl band at 1710 cm^{-1}. The nmr spectrum (CCl_4) had a multiplet accounting for two protons centered at τ 6.42, a six-proton singlet at τ 7.83, and a two-proton multiplet at τ 7.80. A tentative structure of 3-chloromethylhexane-2,5-dione is assigned. The 12-line spectrum expected for the C-3 proton at about τ 7.2 was not detected in the nmr spectrum.

Acetylation of 1,1-Dimethylcyclopropane. The usual procedure for acetylating a liquid substrate was followed. The reaction was carried out in a 0.10 M scale (7.0 g of 1,1-dimethylcyclopropane) in methylene chloride for 45 min at 5°. After work-up, vpc analysis indicated the presence of two products: 4-chloro-3,4-dimethyl-2-pentanone (**11**, 78%) and 3,4-dimethyl-3-penten-2-one (**12**, 22%). The infrared spectrum of **11** (liquid film) showed principal bands at 1710 ($\nu_{C=O}$), 1370 and 1390 ($\nu_{(CH_3)_2C}$), and 760 cm^{-1} (ν_{C-Cl}). The nmr spectrum (CCl_4) consisted of a quartet (J = 7.0 Hz) at τ 7.01 for the methine proton, a three-proton resonance at

τ 7.79 for the methyl ketone protons, a sharp six-proton singlet at τ 8.34 for the *gem*-dimethyl group, and a methyl doublet (J = 7.0 Hz) at τ 8.79.

The infrared spectrum (CCl_4) of **12** showed absorbances indicative of an α,β-unsaturated ketone at 1680 ($\nu_{C=O}$) and 1625 cm^{-1} ($\nu_{C=C}$). The nmr spectrum (CCl_4) showed three singlets at τ 7.95, 8.17, and 8.27 in the area ratio 1:2:1. The two high-field resonances were slightly broadened due to long-range coupling.

A separate experiment showed that treatment of 1.0 g (0.0066 mol) of **11** with a 20% solution of sodium carbonate (20 ml, 4 g, 0.04 mol) for 15 min at reflux in 15 ml of carbon tetrachloride led to a clean conversion to 0.67 g (0.0060, 91%) of **12**.

Acetylation of Methylcyclopropane. Since methylcyclopropane is a gas (bp 4°) this acetylation was run using the procedure outlined for the normal acetylation of cyclopropane. Methylcyclopropane (Chemical Procurement Laboratories) was purified by slowly passing it through a trap containing saturated, neutral potassium permanganate solution, then through a trap containing anhydrous calcium sulfate (Drierite) and collecting the gas in a vessel cooled in a Dry Ice–acetone bath. The resultant material showed only a single vpc peak and was free of alkenes. A 0.10 M scale reaction (5.5 g of methylcyclopropane) in 50 ml of methylene chloride was carried out at 0° for 1 hr. The reaction was monitored by vpc using a 5-ft QF-1 column at 130° with a helium flow rate of 70 cc/min. Three major products with retention times of 0.70, 3.0, and 4.0 min were observed.

The compound with the retention time of 0.70 min, formed in 12% yield, was a clear, colorless liquid. It was identical with the unsaturated ketone formed in the acetylation of 2-butene, *i.e.*, 3-methyl-3-penten-2-one (**9**). The ir spectrum (CCl_4) had principal bands at 1670 ($\nu_{C=O}$) and 1640 cm^{-1} ($\nu_{C=C}$). The nmr spectrum (C_6D_6 solution) showed a quartet of quartets (J_{gem} = 7.0 Hz, J_{vic} = 1.4 Hz) at τ 3.68 for the vinyl proton, a singlet at τ 8.00 for the methyl ketone protons, a three-proton multiplet centered at τ 8.25 (C-3 methyl group), and an eight-line resonance at τ 8.58 for the remaining methyl group.

The second product, retention time 3.0 min, was formed in 18% yield. The structure was shown to be 4-chloro-3-methyl-3-pentanone (**8**) on the basis of its ir and nmr spectra. The carbonyl band in the ir spectrum (CCl_4) appeared at 1710 cm^{-1}. The nmr spectrum (CCl_4) consisted of a one-proton multiplet centered at τ 5.80 (C-4 proton), a one-proton multiplet at τ 7.32 (C-3 proton), a singlet for the methyl ketone protons at τ 7.82, a doublet (J = 6.5 Hz) at τ 8.50 (C-4 methyl), and a doublet (J = 7.0 Hz) at τ 8.87 (C-3 methyl).

The major product, formed in 65% yield, had a retention time of 4.0 min. It was shown to be 5-chloro-2-hexanone (**7**) by its ir and nmr spectra. The ir spectrum (CCl_4) had the carbonyl stretch at 1710 cm^{-1}. The nmr spectrum (CCl_4) showed a one-proton multiplet centered at τ 6.02 (methine proton), a triplet (J = 7.0 Hz) at τ 7.38 for the two protons adjacent to the carbonyl function, a singlet at τ 7.92 for the methyl ketone protons, a complex multiplet centered at τ 8.08 for the C-4 methylene protons, and a doublet (J = 6.5 Hz) at τ 8.48 for the C-6 methyl protons.

Formation and Oxidation of Alkyl Radicals by Cobalt(III) Complexes

Sheldon S. Lande and Jay K. Kochi

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received April 3, 1968*

Abstract: The homolysis of Co^{III} carboxylates, formed by metathesis of Co^{III} acetate in a carboxylic acid medium, follows first-order kinetics. The products derived from the decarboxylation of the acid arise from an alkyl radical precursor. Primary and secondary propyl radicals from *n*-butyric and isobutyric acids, respectively, afford principally propane by hydrogen transfer from solvent. Oxidation by Co^{III} is a minor reaction. These radicals are, however, readily intercepted by catalytic amounts of Cu^{II} salts and propylene is generated in quantitative yields. On the other hand, *t*-butyl radicals from the decarboxylation of pivalic acid are readily oxidized by Co^{III}. *t*-Butyl radicals are trapped efficiently by oxygen, and the regeneration of Co^{III} from Co^{II} by reaction with *t*-butylperoxy and *t*-butoxy radicals allows for the catalytic oxidative decarboxylation of pivalic acid. Strong acids markedly enhance the rates of both decarboxylation and oxidation of alkyl radicals by Co^{III}. Cationic carboxylatocobalt(III) complexes, proposed as the reactive species responsible for facile homolysis, are also capable of the oxidation of primary and secondary alkyl radicals as well as alkenes. Carboxylate salts also promote decarboxylation by Co^{III} *via* anionic carboxylatocobaltate(III) complexes. The latter, however, are ineffective toward primary and secondary alkyl radicals. A mechanism for the oxidation of alkyl radicals by various Co^{III} complexes is proposed.

A variety of transition metal complexes catalyze the autoxidation of organic compounds in nonaqueous media by an oxidation–reduction process.[1] Prominent among these are cobalt compounds, which function between the Co^{II} and Co^{III} oxidation states. In order to examine the mechanisms of these complex and interesting catalytic processes, it is desirable to elucidate some fundamental reactions between the metal species and the organic substrate.

Co^{III} complexes have been utilized as oxidants for a number of types of functional groups.[2] The decarboxylation of aliphatic acids induced by cobaltic ion in aqueous perchloric acid solutions has been examined by Waters and coworkers,[3] who found an inverse acid dependence of rate. They proposed a mechanism which involves the reversible replacement of water on the Co^{III} nucleus by carboxylato ligands, and subsequent homolysis to Co^{II}, carbon dioxide, and alkyl radical. The latter participated in the induced oxidation of toluene.

(1) (a) For a review see E. Denisov and N. Emanuel, *Russ. Chem. Rev.*, **29**, 645 (1960); also "Liquid Phase Oxidation of Hydrocarbons," Plenum Press, New York, N. Y., 1967; (b) "Oxidation of Organic Compounds," Vol. II, Advances in Chemistry Series, No. 72, American Chemical Society, Washington, D. C., 1968.

(2) (a) W. Waters and J. Littler, "Oxidation in Organic Chemistry," K. Wiberg, Ed., Academic Press Inc., New York, N. Y., 1965, p 186 ff.

(3) (a) A. Clifford and W. Waters, *J. Chem. Soc.*, 2796 (1965); (b) T. Cooper, A. Clifford, D. Mills, and W. Waters, *ibid.*, *B*, 793 (1966).