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CYCLOPROPANONES—IX

REACTIONS OF ACIDS AND AMINES WITH CYCLOPROPANONE AND SOME ALKYL CYCLOPROPANONES[1,2,*]

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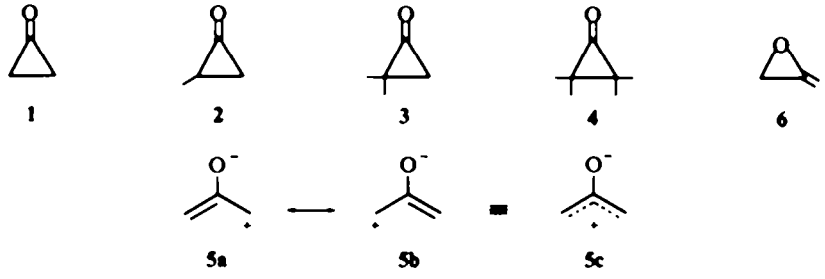
Abstract—The reactions of cyclopropanone (**1**) and several alkyl cyclopropanones (**2**, **3** and **4**) with acids and amines are described. Although ring-closed adducts are the major products from **1**, ring opened products generally form when alkyl cyclopropanones are treated with acids or amines

INTRODUCTION

Cyclopropanone (**1**) and several alkyl cyclopropanones (**2**, **3**, and **4**) have been prepared.[2] These compounds were shown to possess the ring closed structures on the basis of physical and chemical evidence.[2] However, the possibility that cyclopropanone reactions may proceed via a ring opened dipolar intermediate (e.g. **5**) is indicated by both theoretical calculations[3] and isolation of products best explained on the basis of a dipolar intermediate.[4]



1 **2** **3** **4** **6**

5a **5b** **5c**

In addition, alleneoxides (e.g. **6**) have been proposed as potential intermediates in reactions presumed to proceed via cyclopropanones.[4]

The dipolar species **5** is of further interest because of the prediction that **5** should be formed by a disrotatory opening[5] and that cycloaddition reactions of **5** can proceed in a concerted manner (and hopefully with low activation energy).

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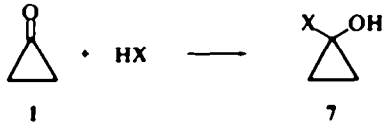
A high energy content and high reactivity also is expected for cyclopropanones because they incorporate features of highly strained molecules.

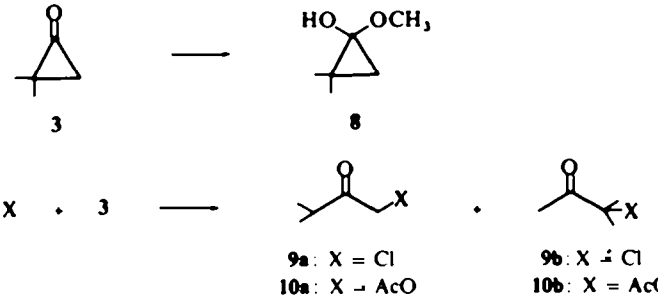
Addition of carbonyl reagents. Consideration of the large amount of "I-strain" of cyclopropanones,[6] suggests that reactions which convert the sp^2 carbon atom into an sp^3 hybridization should proceed rapidly and the equilibrium of such reactions should lie far to the right. Addition of methanol,[7] dry hydrochloric acid,[8] water,[9] acetic acid,[8] aniline and N-methylaniline[10] to methylene chloride solutions lead to high yields of adducts of general structure 7. Only in the case of water in methylene chloride does polymerization of 1 compete with formation of the hydrate 7c.



1 7

7a: X = OCH_3, 100% 7d: X = CH_3CO, 100%
7b: X = Cl, 65% 7e: X = C_6H_5NH, 95%
7c: X = OH 7f: X = $C_6H_5NCH_3$, 100%

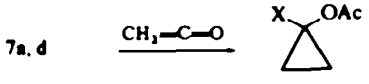
Although addition of methanol to 2,2-dimethylcyclopropanone (3) yields the hemiketal 8 in quantitative yield,[8] addition of dry hydrochloric acid[8] or acetic acid[11] to 3 results in formation of the two keto-chlorides **9a** (58%) and **9b** (42%) and ketoacetates **10** (> 90), respectively.



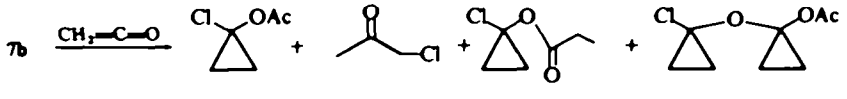
3 8

9a: X = Cl 9b: X = Cl
10a: X = AcO 10b: X = AcO

Characterization of the carbonyl adducts **7a–e** and **8**. The hemiketal **7a** was characterized by NMR, IR and mass spectra (Experimental). Reaction of **7a**, **b**, or **d** with ketene yields the 1-acetoxycyclopropanes **11a** and **b**, and **d**; however, the chloride adduct also yields the rearrangement product **12**, in addition to **13** and **14**.

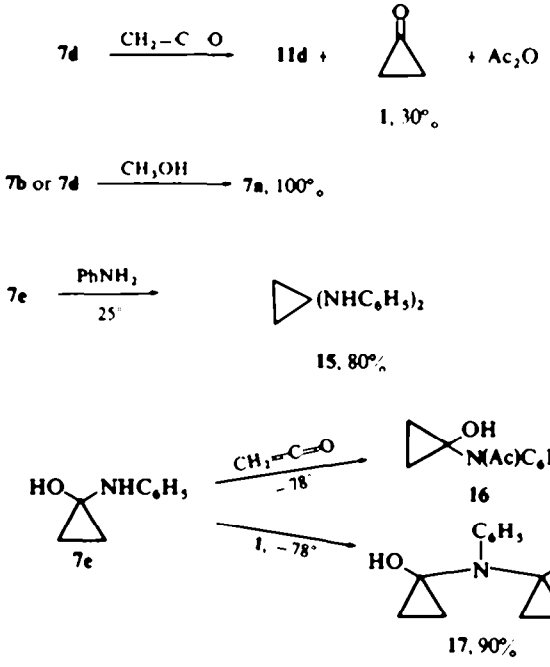


11a: X = OCH_3, 98%
11d: X = CH_3CO, 62%



11b, 34% 12, 13, 14,

Addition of ketene to **7d** yields **1** and acetic anhydride in addition to **11d**. The addition of acetic acid to **1** is therefore reversible. The addition of methanol to **7b** or **7d** resulted in their smooth conversion to **7a**, which rearranges further to methyl propionate under the acidic conditions. The addition of aniline to **7e** yields 1,1-dianilinocyclopropane[10,12] **15**. The amine function of **7e** may be acylated with ketene or cyclopropanone to yield **16** and **17** respectively. Compound **7e** rearranges at high temperatures (VPC, 230°) or on silica gel to propionanilide.

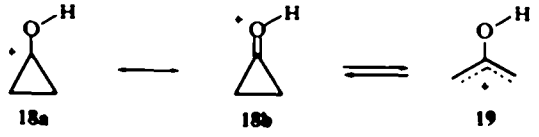


DISCUSSION

In spite of the high reactivity of cyclopropanones, the reactions reported here are relatively clean and free of side reactions.

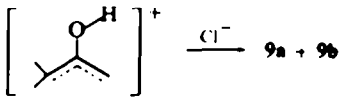
The addition of acids to cyclopropanones can occur by attack of a proton on the cyclopropane ring or by protonation of the carbonyl group. The ring opening of cyclopropanes by acids is well known.[13] The carbonyl protonated cyclopropanones are of interest because they are formally hydroxycyclopropyl cations. Cyclopropyl cations are predicted to open[14] with exceeding rapidity to allyl cations.[15]

Cyclopropanone itself is relatively resistant to ring opening by hydrochloric acid or acetic acid. It is interesting to note that Olah[16] has found that the 1-hydroxycyclopropyl cation, **18**, exists *in equilibrium* with the 2-hydroxyallyl cation **19** in FSO_3H - SO_2 solution at $-80°$.



The fact that cyclopropanone does not undergo rapid ring opening may be attributed to the contribution of resonance form **18** which localizes the bulk of the electron deficiency on oxygen rather than carbon.

On the other hand, 2,2-dimethylcyclopropanone yields *only* ring opened products when its CH_2Cl_2 solutions are treated with hydrochloric or acetic acids. These results are consistent with the more stable 1,1-dimethylallyl cation **20** formed when carbonyl protonated **3** undergoes ring opening. The greater stability of **20** over **19** should lower the activation for ring opening.[18]* Also, the methyl groups of **3** might make ring carbon atoms more nucleophilic and thereby promote a change in mechanism to protonation of the C_2–C_3 bond.



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The addition of alcohol to cyclopropanones does not result in ring opening. In addition, cyclopropanone yields ring closed carbonyl adducts in good yields when treated with amines,[10] again a somewhat surprising result.†

EXPERIMENTAL

IR spectra were taken on a Perkin Elmer 137 spectrometer or a Perkin Elmer 421 grating spectrometer. NMR spectra were taken on a Varian A-60 or A-60 Analytical High Resolution NMR spectrometer. Chemical shifts are reported in δ (ppm) from internal TMS (δ 0·00) or from internal CH_2Cl_2 (δ 5·30) unless specified. Mass spectra were taken on a Hitachi Perkin–Elmer RMU-6D Mass spectrometer. VPC was performed on an aerograph A90P gas chromatograph. Elemental Analyses performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York. Unless specified, yields are based on NMR integrations of product absorption *vs* CH_2Cl_2. All commercial chemicals were reagent quality.

Preparation of 1-methoxy-1-hydroxycyclopropane (**7a**) and 1,1-dihydroxycyclopropane (**7c**) were accomplished as described previously.[2]

Reaction of **1** *with hydrogen chloride and acetyl chloride*

1-Hydroxy-1-chlorocyclopropane (**7b**) *and 1-acetoxy-1-chlorocyclopropane* (**11b**), *1-chlorocyclopropyl propionate* (**13**) *and 1-(1-chlorocyclopropoxy) cyclopropylpropionate* (**14**). To a soln of HCl gas (20 mmoles) in CH_2Cl_2 (3 ml) at −95° was added a soln of cyclopropanone (8·25 mmoles) in CH_2Cl_2 (15 ml). NMR showed a complex absorption between 0·9 and 1·4 accounting for 90% of the added cyclopropanone. A sharp singlet for **7b** at 1·2 accounted for 65% of the added cyclopropanone. Acetyl chloride (3 ml, 42 mmoles) was added to the soln which was stored at 25° for 3 days. After washing with $NaHCO_3$ aq and drying, the CH_2Cl_2 soln of products was analyzed by quantitative VPC on a 10 ft βββ column at 135°. Bromocyclohexane was used as an internal standard. The major products were isolated and identified by their spectral properties:

Compound **11b**, (2·48 mmoles, 34%), IR $\lambda_{max}^{CCl_4}$ (cm^{-1}) 3015 (cyclopropane C–H), 1775, 1760 sh, (C=O), 1210 (acetate), 1030 (cyclopropane C–C); NMR (CCl_4) δ 1·37 (s, 4H), 2·10 (s, 3H); mass spec. *m/e* (%) 136, 134 (trace), 121, 119 (trace), 99 (4), 77 (trace), 75 (2), 56 (37), 43 (100), 28 (31). Compound **12** (1·07 mmoles, 15%); identical with commercially available material. Compound **13** (0·88 mmoles, 12%); IR $\lambda_{max}^{CCl_4}$ 1770 cm^{-1}, NMR (CCl_4), δ 1·24 (t, J = 7 c.s, 3H) 1·40 (broad s, 4H), 2·35 (qu, J = 7 c.s, 2H), mass spec. *m e*

* For a proposal of zero activation energy for the cyclopropyl cation to allyl cation rearrangement see Ref. 17.

† Hemiketals of cyclopropanones also may be used as a source of cyclopropanones.[2,19]

(%) 150, 148 (trace), 77, 75 (trace), 57 (100), 56 (10), 39 (4), 29 (62), 28 (18). Compound **14** (0·16 mmoles, 2%); IR $\lambda_{max}^{CCl_4}$ (cm^{-1}) 1770 (C=O); NMR (CCl_4) δ 0·85 to 1·55 (complex 11H), 2·25 (qu, J = 8 c/s, 2H); mass spec. *m/e* (%) 206, 2·4 (parent, trace), 177, 175 (trace), 113 (18), 57 (100), 56 (10), 39 (7), 29 (42), 28 (29), low voltage *m/e* 113 (base peak).

Reaction of **7b** *with methanol*

Hydrogen chloride was bubbled into a soln of **1** (0·45M) in CH_2Cl_2 at −78° for 2 mins and the resulting soln was stored overnight at room temp. Analysis of the soln showed a broad absorption between δ 0·9 and 1·4 with a sharp singlet (**7b**, 60%) at δ 1·2 accounting for all of the original cyclopropanone. On addition of MeOH (30 microliters) to an NMR sample of the soln (0·5 ml) the singlet at δ 1·2 disappeared. A new singlet at δ 0·8 (assigned to **7a**) formed and slowly disappeared being replaced by a triplet at δ 1·08 and a quartet at δ 2·20 for methyl propionate.

Reversible formation of **7b** *from* **1**

A CH_2Cl_2 soln (12 ml) of **1** (7·2 mmoles) was treated with HCl gas (155 ml at STP, 7 mmoles) at −78°. An NMR spectrum of the soln showed a complex absorption between δ 1·0 and 1·5 with a singlet at δ 1·20 (**7b**, 50%). Ketene (0·1 ml) was distilled into an NMR sample of the above soln (0·5 ml) at −78° and scanned rapidly by NMR at room temp. A peak at δ 1·65 (**1**) was initially observed which quickly disappeared leaving a complex absorption between δ 0·8 and 1·5

Preparation of 1-*acetoxy*-1-*hydroxycyclopropane* (**7d**)

Cyclopropanone (6·6 mmoles) in CH_2Cl_2 at −95° was treated with AcOH (0·5 ml, 8·8 mmoles) containing 2% Ac_2O and warmed to room temp. The resulting soln showed a broad singlet at 1·0 in the NMR attributed to **7d**. **7** (δ 1·65) was completely absent. After ½ hr at room temp ketene (1 ml, 13 mmoles) was added to the soln at −130° and allowed to react for 1 hr at −78°. Removal of the excess ketene on the vaccum line, a 4 ft βββ column at 150° afforded two major products:

Compound **7d**: IR $\lambda_{max}^{CCl_4}$ (cm^{-1}) 1750, 1730 sh (C=O), 1230 (acetoxy); NMR (CCl_4) δ 2·10 (s, 3H), 4·55 (s, 1H); identical with authentic material synthesized by another route.[20]

Compound **11d**: m.p. 60·61° (subl); IR $\lambda_{max}^{CCl_4}$ (cm^{-1}) 1760 (C=O), 1220 (acetoxy), NMR (CCl_4) δ 1·24 (s, 2H), 2·13 (s, 3H); mass spec. *m/e* (%), 159 (M^+ + 1, trace), 56 (17%), 43 (100%), 28 (18%). (Found: C, 53·84, 53·54; H, 6·46, 6·44. Calc for **11d**: C, 53·16, H, 6·37%).

Reversible reaction of **1** *with acetic acid*

A soln of **1** (4 mmoles) in CH_2Cl_2 (9 ml) at −95° was treated with AcOH (0·3 ml, 5·5 mmoles) followed by ketene (40 mmoles). After 5 days at −78° the ketene was removed on the vacuum line. The resulting soln contained **1** (δ 1·65, 0·03 M), **11d** (δ 1·12, 0·28 M) in part due to **7d** in the NMR. The NMR of the reaction mixture after addition of MeOH (0·2 ml, 5 mmoles) showed only singlets at δ 1·12 (**11d**, 0·28 M) and δ 0·8 (hemiketal **7a**, 0·15 M) in the region between δ 0·0 and 1·8

Preparation of 1,1-*diacetoxycyclopropane* (**11d**)

To a soln of cyclopropanone (8·25 mmoles) in (15 ml) at −78° was added AcOH (0·85 ml, 15 mmoles) followed by ketene (65 mmoles). After reacting for 3 days at −78° the ketene and solvent were removed under vacuum. The resulting yellow oil was sublimed to yield 0·29 g (65%) **11d** (m.p. 56·57°). Resublimation produced a white solid (m.p. 60·61°) identical to the material reported above as **11d** (98%).

Reaction of cyclopropanone with aniline

1-*aniline*-1-*hydroxycyclopropane* (**7e**) *and* N,N-*bis*(1-*hydroxycyclopropyl*) *aniline* (**17**). *Treatment of* **1** *with one equivalent of aniline.* To a soln of **1** (3 mmoles) in CH_2Cl_2 (5 ml) at −78° was added one equiv aniline (0·27 ml, 3 mmoles). Compounds **7e** and **17** were formed in a ratio of 2 to 1 and in combined quantitative yield.*

Attempts to isolate 1-*hydroxy*-1-*anilinocyclopropane* (**7e**). Aniline (1·5 ml, 16·5 mmoles) was added to a CH_2Cl_2 soln (10 ml) of **1** (10 mmoles) to give **7e** in 85% yield (NMR) characterized by a symmetrical A_2B_2 pattern centered at δ 1·05 in the NMR. Chromatography of crude **7e** on silica gel and florosil pro-

* Yields were measured by integration of the characteristic A_2B_2 pattern of **7e** centered at δ 1·05 and the singlet of **17** at δ 2·20 *vs* the CH_2Cl_2 absorption at δ 5·30.

duced propionanilide, identical to an authentic sample, along with unidentified oily products. VPC analysis of crude **7e** on a 4 ft carbowax 20M column at 235° (injector temp 250°) also produced propionanilide. Compound **7e** could be distilled under high vacuum (~0·1 mm, 150°) but was always contaminated by the excess aniline used in its preparation.

Preparation of N-*acetoxy*-1-*hydroxy*-1-*anilinocyclopropane* (**16**)

The soln of **7e** (3·1 mmoles) in CH_2Cl_2 (8 ml) prepared above was reacted with ketene (3 ml at −78° for 3 days. Removal of the unreacted ketene left a new compound (**16**), formed in quantitative yield. **16** was purified by chromatography on silica gel with pentane:ether and showed the following spectral properties: IR $\lambda_{max}^{CH_2Cl_2}$ (cm^{-1}) 1680 (amide C=O); NMR (CCl_4) δ 0·7–1·3 (A_2B_2, 4H), 1·95 (s, 3H), 7·1–1·6 (m, 5H); mass spec. *m/e* 191 (M^+), 149 ($M^+ - C_2H_2O$), 135 ($M^+ - C_3H_4O$). Pyrolysis of **16** on a 3 ft carbowax 20 M column at 250° produced acetanilide and propionanilide.

Preparation of bis-N,N-(1-*hydroxycyclopropyl*)*aniline* (**17**)

Aniline (0·25 ml, 2·7 mmoles) was added to a cold (−78°) CH_2Cl_2 soln (5 ml) of cyclopropanone (2·4 mmoles). Compounds **7e** and **17** were formed in a ratio of 3·5:1 and in quantitative yield (NMR) from **1**. The resulting soln was treated with an additional equiv of cyclopropanone soln (5 ml, 1·4 mmoles) to produce **17** in 85% yield (NMR) from **7**. **17** formed a milky white suspension in CH_2Cl_2 at −78° which congealed after several days at −78°. Rapid filtration allowed the isolation of **17** (0·25 g) as a sticky white solid, stable at −78° but decomposing at room temp. **17** was identified by its spectral properties: IR $\lambda_{max}^{CH_2Cl_2}$ (cm^{-1}) 3580 (sharp, OH), 3420 (broad, OH), NMR (CH_2Cl_2) δ 1·20 (s, 8H),* 3·0 (s, 2H), 6·8–7·4 (m, 5H), mas spec. *m/e* 205 (M^+), 149 ($M^+ - C_6H_8O_2$); UV $\lambda_{max}^{CH_2Cl_2}$ (mμ) 243 ($1·2 \times 10^4$), 284 ($1·4 \times 10^3$).

Reaction of **1** *with methylaniline*

1-(N-*methylanilino*)-1-*hydroxycyclopropane* (**7f**). Methylaniline (0·48 ml, 4·3 mmoles) was added to a CH_2Cl_2 soln (5 ml) of **7** (4·25 mmoles) at −78°. Compound **7b** was formed quantitatively (NMR) and isolated as a crude oil with the following spectral properties: IR $\lambda_{max}^{CH_2Cl_2}$ (cm^{-1}) 3575 (sharp, —OH), 3420 (broad, OH) 1595, 1495 (aromatic). NMR (CH_2Cl_2) δ 0·8–1·3* (A_2B_2, 4H), 1·9 (s, 3H), 7·07–0·5 (5H); mass spec. *m/e* 163 (M^+), ($M^+ - C_3H_4O$), 106 ($M^+ - C_3H_5O$).

Conversion of **7e** *and* **17** *to* 1,1-*dianilinocyclopropane* (**15**)

A CH_2Cl_2 soln (0·5 ml) of **7e** (0·07 mmoles) and **17** (0·29 mmoles) was treated with aniline (0·08 ml, 0·9 mmoles) at room temp for 6 days. After 3 days all of **17** was gone and **15** was forming. At the end of 6 days **15** had formed in 80% yield (NMR).

Attempted dehydration of **7e**

(*a*) Aniline (0·41 ml, 4·5 mmoles) was added to a cold (−78°) soln of **7** (4·5 mmoles). **7e** and **17** were produced in a ratio of 3·3 to 1. The CH_2Cl_2 was removed under vacuum and the residue dissolved in benzene (10 ml). Refluxing for 13 hr using a Dean Stark trap produced no change in the UV spectrum of the soln.† **7e** and **17** slowly disappeared and **15** was formed (NMR), no evidence for **21** (cyclopropanoneanil) was found.

(*b*) The above procedure was repeated with the addition of *p*-toluene-sulfonic acid (0·0046 g, 0·38 mmole). The benzene soln immediately turned dark and gave a complex NMR spectrum. After refluxing for 2 hr the soln showed an A_2B_2 multiplet centered at δ 1·1 and a singlet at δ 1·6. Addition of MeOH or solid $NaHCO_3$ produced no visible spectral change. The UV spectrum of the reaction mixture shifted from 2390 Å on addition of the acid and the absorption at 2840 Å disappeared.

(*c*) A soln of **7e** (2 mmoles) in methylene chloride (5 ml) was treated with pyridine (0·5 ml, 6·2 mmoles) and dicyclohexylcarbodiimide (0·8 g, 4·0 mmoles) at room temperature. After four days the NMR spectrum of this soln showed no change.

Reaction of **3** *with hydrogen chloride.*

Compound **3** was prepared from dimethylketene (2·1 g, 30 mmoles) in CH_2Cl_2 (5 ml) and diazomethane.

* The singlet at 1·20 became an A_2B_2 pattern when pyridine was added to the NMR sample.

† Acetone anil shows UV absorption at λ_{max} = 275 mμ (log ε = 3·25)[21] and the strain of a cyclopropane ring would be expected to shift the absorption to longer wavelengths for **21**.

(11·2 mmoles) in CH_2Cl_2 chloride (20 ml) at −78° HCl gas was bubbled into the cold soln (−78°) for 15 min, then the soln was warmed slowly to room temp. The IR absorption at 1820 cm^{-1} (cyclopropanone) disappeared immediately on addition of HCl. The reaction mixture was washed twice with $NaHCO_3$ aq (25 ml), dried over $MgSO_4$ and concentrated under vacuum. The products were analyzed by quantitative VPC on a 10 ft βββ column using *o*-chlorotoluene as an internal standard. Compounds **9a** and **9b** were formed in the ratio of 58 to 42 and in a combined yield of 47%, based on diazomethane. Compound **22a**, (2,2-dimethylcyclobutanone) an impurity in the preparation of **3** was not resolved from **9b**; however, it was corrected for by measuring the amount of **22b** (3,3-dimethylcyclobutanone) and assuming the ratio of **22a**:**22b** was 1·3.

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