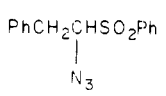

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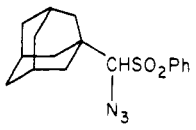

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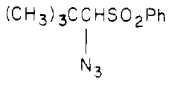

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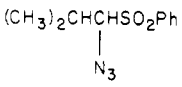

10

nitriles are produced. These reactions are somewhat limited in that many alkyl nitriles may not be stable under strongly basic conditions.[6]

Registry No. **3a**, 831-91-4; **3b**, 51229-52-8; **3c**, 7693-30-3; **3d**, 51229-54-0; **3e**, 5023-65-4; **4a**, 70891-83-7; **4b**, 70891-84-8; **4c**, 70891-85-9; **4d**, 70891-86-0; **4e**, 70891-87-1; **5a**, 70891-88-2; **5b**, 70891-89-3; **5c**, 70891-90-6; **5d**, 70891-91-7; **5e**, 70891-92-8; **6a**, 70891-93-9; **6b**, 70891-94-0; **6c**, 70891-95-1; **6d**, 70891-96-2; **6e**, 70891-97-3; **7**, 70891-98-4; **8**, 70891-99-5; **9**, 70912-36-6; **10**, 70892-00-1; benzonitrile, 100-47-0; *m*-chlorobenzonitrile, 766-84-7; *p*-chlorobenzonitrile, 623-03-0; *p*-cyanobenzonitrile, 623-26-7; *p*-methylbenzonitrile, 104-85-8; 1-adamantanecarbonitrile, 23074-42-2.

Supplementary Material Available: Analytical and spectral data on compounds **6–10** (1 page). Ordering information is given on any current masthead page.

(6) The scope of this reaction may be limited by other problems. For example, α-iodo nitriles bearing two carbon atoms at the α center give α,β-unsaturated nitriles rather than α-azido nitriles when treated with azide ion under a variety of conditions: A. D. Barone, D. L. Snitman, and D. S. Watt, *J. Org. Chem.*, **43**, 2066 (1978).

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Oxidative Rearrangements of Tertiary Cyclopropylcarbinols Leading to β,γ-Unsaturated Ketones. A Simple Approach to 1,4-Carbonyl Transposition

Summary: Oxidation of tertiary 2-alkylcyclopropylcarbinols with pyridinium chlorochromate results in oxidative homoallylic rearrangement to the corresponding β,γ-unsaturated ketones, making the overall process a synthetically useful method for 1,4-carbonyl transposition.

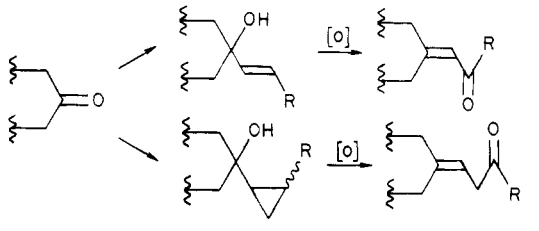
Sir: Recent communications[1] have described the direct oxidation of tertiary allylic alcohols with pyridinium chlorochromate (PCC)[2] yielding the corresponding α,β-unsaturated aldehydes or ketones,[3] which provides an efficient method for directed aldol condensation[4] and 1,3-carbonyl transposition[5] as depicted in eq 1. Despite the well-known similarity in rearrangement behavior of

Table I

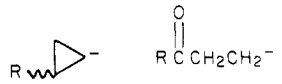
method	reagent/reaction time[a]	% yield[b] 4a	5a
A	PCC (5 equiv)/6 h	48	15
B	PCC (5 equiv) + $AgNO_3$ (10 equiv)/6 h	53	*c*
C	$C_5H_5NHCrO_3BF_4$[d] (5 equiv)/20 h	50	*c*
D	PCC (5 equiv) + H_2O (8 equiv)/6 h	60	5

[a] Time required for completion. [b] Isolated yields via column chromatography. [c] Not detected by VPC or NMR. [d] For preparation, ref 15.

cyclopropylcarbinyl systems to that of allylic ones, direct oxidation of tertiary cyclopropylcarbinols has received only scant attention.[6-8] In our continuing investigation of synthetic applications of cyclopropane rearrangements,[9] we have now found that the modified use of PCC can effect direct oxidation of tertiary 2-alkylcyclopropylcarbinols to the corresponding β,γ-unsaturated ketones as depicted in eq 2.



The interesting oxidative rearrangement appears to be an excellent method for converting ketones to the trishomologous β,γ-enones,[10,11] since the tertiary alcohols serving as substrates can be prepared by reactions of ketones with cyclopropyl organometallic reagents. The net effect of the process is an efficient method for effecting 1,4-carbonyl transposition and allows cyclopropyl anion **1** to serve as an equivalent of ketone homoenolate anion **2**.[12,13]



1 2

(1) (a) J. H. Babler and M. J. Coghlan, *Synth. Commun.*, **6**, 469 (1976); (b) W. G. Dauben and D. M. Michno, *J. Org. Chem.*, **42**, 682 (1977); (c) P. Sundraraman and W. Herz, *ibid.*, **42**, 813 (1977).

(2) Available from the Aldrich Co. For use of this reagent for oxidation of alcohols to aldehydes or ketones, see E. J. Corey and J. W. Suggs, *Tetrahedron Lett.*, 2674 (1975).

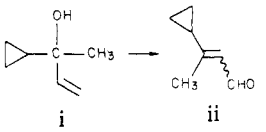
(3) For multistep transformations of allylic alcohols including secondary ones to the rearranged α,β-unsaturated carbonyl compounds, see B. M. Trost and J. L. Stanton, *J. Am. Chem. Soc.*, **97**, 4018 (1975); T. Nakai, T. Mimura, and A. Ari-izumi, *Tetrahedron Lett.*, 2425 (1977), and references cited therein.

(4) Reviews: H. Reiff, *Newer Methods Prep. Org. Chem.*, **6**, 48 (1971); A. T. Nielsen and W. J. Houlshan, *Org. React.*, **16**, 1 (1968).

(5) For a general review on carbonyl transpositions, see T. Nakai and T. Mimura, *Yuki Gosei Kagaku Kyokaishi* (*J. Synth. Org. Chem., Jpn.*), **35**, 964 (1977).

(6) Dauben and Michno (ref 1b) have briefly reported that attempted oxidation of cyclopropyldimethylcarbinol with PCC resulted in the formation of 5-chloro-2-methylpent-2-ene as the major product. In our hands, the yield of the chloro olefin was 40%.

(7) Most recently the PCC oxidation of carbinol i was found to result in oxidative allylic rearrangement to α,β-enal ii. We thank Mr. M. Nozomi in our laboratory for carrying out this experiment.



i ii

(8) For oxidation of secondary cyclopropylcarbinols with Me_2SO–BF_3 leading to the rearranged α,β-enals, see S. Nishida and F. Kataoka, *Chem. Lett.*, 1297 (1976).

(9) E. Wada, T. Nakai, and M. Okawara, *Chem. Lett.*, 1121 (1977), and our earlier papers cited therein.

(10) For a recent method for converting ketones to the trishomologous β,γ-enals, see E. J. Corey and P. Ulrich, *Tetrahedron Lett.*, 3685 (1975). This method is based on the solvolytic rearrangement of tertiary 2-methoxycyclopropylcarbinyl mesylates.

(11) For different routes to β,γ-enones, see C. Broquet and M. Simalty, *Tetrahedron Lett.*, 933 (1972); A. Pelter, C. R. Harrison, and D. Kirkpatrick, *ibid.*, 4491 (1973); K. Uehara, F. Kitamura, and M. Tanaka, *Chem. Lett.*, 279 (1973); R. Calas, J. Dunogues, J.-P. Pillot, C. Biran, F. Disciotti, and B. Arreguy, *J. Organomet. Chem.*, **85**, 149 (1975), and references cited therein.

(12) For leading references of various homoenolate anion equivalents and related species, see E. Nakamura and I. Kuwajima, *J. Am. Chem. Soc.*, **99**, 7360 (1977).

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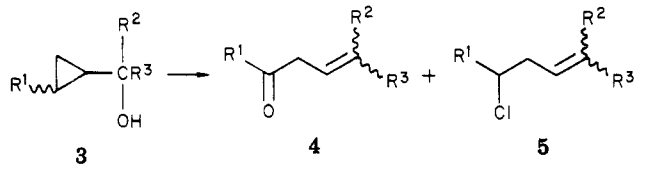
Our efforts have been directed toward oxidation of tertiary 2-alkylcyclopropylcarbinols.[6] When, for example, carbinol **3a** was treated with 5 equiv of PCC in dichloromethane for 6 h at room temperature, two products were isolated and identified[14] as the desired β,γ-enone **4a** (48%) and the chloro olefin **5a** (15%). None of the



3 **4** **5**

a, $R^1 = R^2 = R^3 = CH_3$; b, $R^1 = R^2 = CH_3$; $R^3 = C_2H_5$; c, $R^1 = R^2 = CH_3$; $R^3 = Rh$

corresponding α,β-enone could be detected. The result indicates that both the desired oxidation and the nucleophilic attack by the chloride ion take place simultaneously at the homoallylic carbon atom. In an attempt to increase the proportion of the β,γ-enone in the product, the effect of varying the ligand (or the counterion) of the chromate reagents was investigated (Table I). We found that by using PCC along with an excess of silver nitrate or by replacing the chloride ligand by tetrafluoroborate,[15] only the desired β,γ-enone was obtained. More interestingly, we observed that addition of a small amount (~8 equiv) of water not only improved the yield of **4a** but considerably depressed the formation of **5a**. The results of oxidative rearrangements of other carbinols are shown in Table II.

While the sequence shown in eq 2 can be considered to be an *intermolecular* 1,4-carbonyl transposition (homoaldol condensation), the availability of tertiary cyclopropylcarbinols via cyclopropanation of cyclic α,β-enones followed by organometallic additions[16] allows the above method to be utilized as an *intramolecular* 1,4-carbonyl (homologative 1,3-carbonyl) transposition as depicted in eq 3. The results of oxidation of epimeric mixtures of bicyclo[4.1.0]heptan-2-ols (**6**)[17] are included in Table II. The observed lower yields of the ring-enlarged β,γ-enones (**7**)[18] compared with those of open-chain ones (**4**) suggest that the stereochemistry (or the conformation) of **6** might play an important role in the oxidative rearrangement.[19]

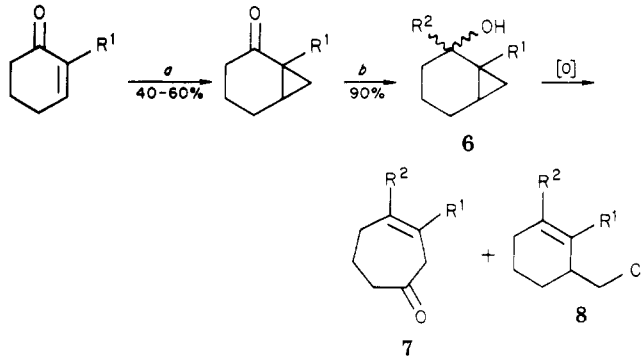
Although it is premature to speculate on the detailed

Table II

carbinol	method	β,γ-enone[a] (yield, %)[b]	other products[a] (yield, %)[b]
3b	C	**4b**[c] (50)	(**3b** (20))
	D	**4b** (62)	**5b**[c] (3)
3c	C	**4c**[c] (38)	$PhCOCH_3$[d] (20)
	D	**4c** (57)	**5c**[c] (3)
6a	A	**7a**[e] (14)	**8a**[e] (19)
	B	**7a** (22)	*f*
	D	**7a** (28)	**8a** (10)
6b	C	**7b**[e] (20)	*f*
	D	**7b** (30)	**8b**[e] (6)

[a] All products exhibited spectral (IR, NMR, and MS) data in accord with the assigned structures or with the reported values. [b] Isolated yields via column chromatography. [c] A mixture of the *E* and *Z* isomers. The ratio was not determined. [d] Formation of acetophenone has been also observed with the PCC oxidation of tertiary α-phenylallylic alcohols (ref la,b). [e] For spectral data, see ref 18. [f] Not detected by VPC or NMR. However, small amounts of the starting alcohols remained in the product mixture (by NMR).

mechanisms of this oxidation, there are two possible

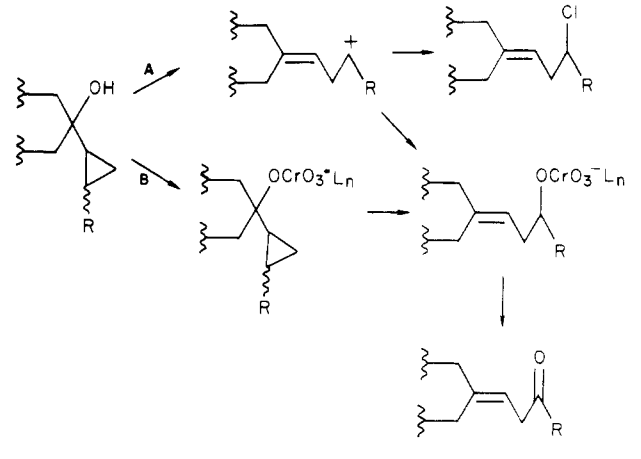


6 **7** **8**

a, $R^1 = H$, $R^2 = CH_3$; b, $R^1 = R^2 = CH_3$

[a] $[(CH_3)_3SO]^+I^-$, NaH, Me_2SO. [b] R^2MgI, Et_2O.

pathways. One involves a prior solvolysis of the tertiary alcohol to a homoallylic carbonium ion which then collapses with nucleophilic species such as chloride and



chromate ions, as in path A. Another explanation assumes the chromate ester formation prior to the rearrangement as in path B, which has been proposed favorably for the PCC oxidation of allylic alcohols.[1b,c] Presently, however, the former pathway appears to be more favorable for the present oxidative rearrangement in view of both the acidic nature of PCC and the observed effect of the nucleophilicity of anionic species present in the reaction system

(13) For examples of the reactions of homoenolate anion equivalents with carbonyl compounds, see G. Büchi and H. Wüest, *J. Org. Chem.*, **34**, 1122 (1969); K. Kondo and D. Tsunemoto, *Tetrahedron Lett.*, 1397 (1975); W. Oppolzer and R. L. Snowden, *ibid.*, 4187 (1976); K.-H. Geiss, B. Seuring, R. Pieter, and D. Seebach, *Angew. Chem.*, **86**, 484 (1974); D. Seebach, K.-H. Geiss, and M. Pohmakotr, *ibid.*, **88**, 449 (1976); D. A. Evans, G. C. Andrews, and B. Buchwalter, *J. Am. Chem. Soc.*, **96**, 5560 (1974); D. A. Evans, D. J. Baillargeon, and J. V. Nelson, *ibid.*, **100**, 2242 (1978); H. Ahlbrecht and G. Rauchschwalbe, *Synthesis*, 417 (1973).

(14) **4a**: IR (neat) 1750 cm^{-1} (C=O); NMR (CCl_4) δ 5.25 (t, 1 H), 3.00 (d, 2 H), 2.07 (s, 3 H), 1.93 (s, 3 H), 1.64 (s, 3 H). **5a**: NMR (CCl_4) δ 5.13 (t, 1 H), 3.90 (tq, 1 H), 2.33 (t, 2 H), 1.70 (s, 3 H), 1.63 (s, 3 H), 1.47 (d, 3 H); MS *m/e* 134 (M^+), 136 ($M^+ + 2$).

(15) The chromate reagent, $C_5H_5NHCrO_3BF_4$, was prepared by the reaction of CrO_3 with 21% HBF_4 following the procedure for preparation of PCC.[2] We found that oxidation of *n*-decanol using this reagent (1.5 equiv) provided an 85% yield of *n*-decanal, indicating that the oxidative power of the reagent is roughly equal to that of PCC.

(16) An alternative synthesis of carbinol **6** which involves 1,2 addition of organometallics to the α,β-enones followed by cyclopropanation via the Simmons–Smith reagent was found to fail. We thank Mr. T. Momose in our laboratory for carrying out the experiment.

(17) Obtained as epimeric mixtures (by NMR): **6a**, bp 59–60 °C (3 mmHg); **6b**, 52–53 °C (2 mmHg).

(18) **7a**: IR (neat) 1700 cm^{-1} (C=O); NMR (CCl_4) δ 5.23 (t, 1 H), 3.00 (br d, 2 H), 2.56–1.77 (m, 6 H), 1.73 (s, 3 H); 2,4-dinitrophenylhydrazone, mp 129–133 °C. **7b**: IR (neat) 1700 cm^{-1} (C=O); NMR (CCl_4) δ 3.03 (s, 2 H), 2.40 (m, 4 H), 2.00 (m, 2 H), 1.70 (s, 6 H); 2,4-D, mp 102–106 °C. **8a**: NMR (CCl_4) δ 5.28 (br s, 1 H), 3.31 (d, 2 H), 2.7–1.5 (m, 10 H); MS *m/e* 144 (M^+), 146 ($M^+ + 2$). **8b**: NMR (CCl_4) δ 3.40 (m, 2 H), 2.45–1.35 (m, 13 H).

(19) Separation of each epimer of **6** and its oxidation with PCC are of our current interest.

on the ratio of the oxidation vs. the nucleophilic substitution.

The conclusions of this preliminary study are that the PCC oxidation of tertiary 2-alkylcyclopropylcarbinols results in oxidative homoallylic rearrangement to the transposed β,γ-enones, making the overall process a synthetically useful method for 1,4-carbonyl transposition. Further improvements and applications of the method outlined here are in progress.

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A Route to Keto Acids (or Esters) or to Dicarboxylic Acids (or Esters) from α-Alkylidenecyclanones

Summary: Baeyer–Villiger oxidation of α-alkylidenecyclanones followed by hydrolysis and esterification gives keto esters; further treatment with H_2O_2 leads to dicarboxylic esters.

Sir: Baeyer–Villiger oxidation of α-alkylidenecyclanones has been shown[1] to provide primarily the lactone derived from insertion of an oxygen atom between the carbonyl and α-olefinic carbon atoms (Scheme I). Surprisingly, hydrolysis of this enol lactone has been neglected[2] as a method of generating keto acids such as **3**.

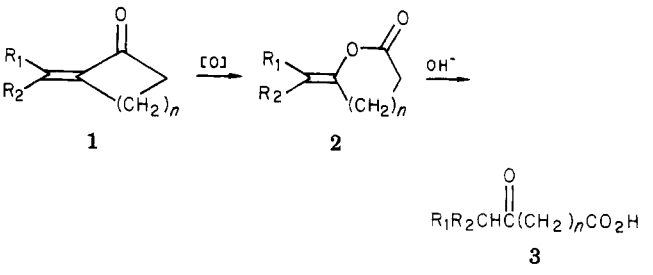
We recently observed that good yields of the keto ester **7**[3] could be obtained by treatment of the α-alkylidenecyclobutanone **4** with 40% peracetic acid,[4] followed by alkaline hydrolysis of the lactone **5**, acidification of **6**, and esterification with CH_2N_2.

When **6** was treated with additional H_2O_2, after separation of epoxide and unreacted starting material, a further oxidation took place to provide a complete conversion, after acidification, to the diacid, which was converted to the diester **8** (Scheme II).

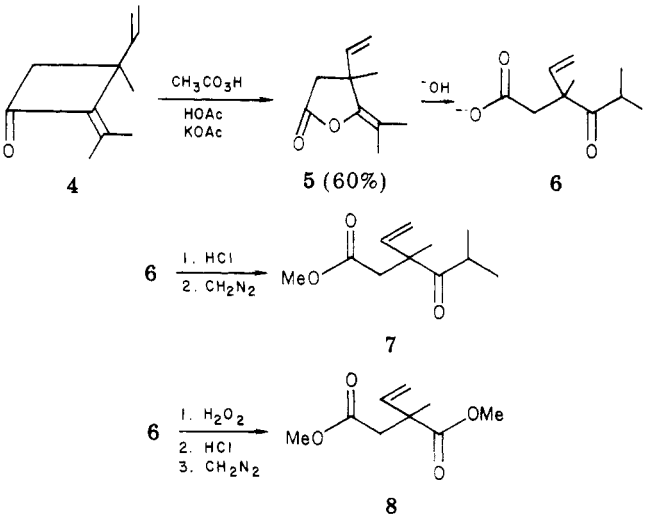
Baeyer–Villiger oxidation of pulegone **9**, followed by alkaline hydrolysis of the lactone **10**, acidification, and esterification resulted in the keto ester **11** (Scheme III). However the yield was lower than that obtained from **4** because of competing formation of the epoxides **12**; epoxidation of **9** was much more evident than epoxidation of **4**.

Presumably, further oxidation of the alkaline solution of the carboxylic acid corresponding to **11** would yield the diacid **13**. A small amount of **13**, isolated as the dimethyl ester **14**, resulted as a byproduct from residual H_2O_2 during alkaline hydrolysis of **10**. Formation of **13** was eliminated by removal of H_2O_2 with sodium thiosulfate before hydrolysis, but this reduced the yield of **11**.

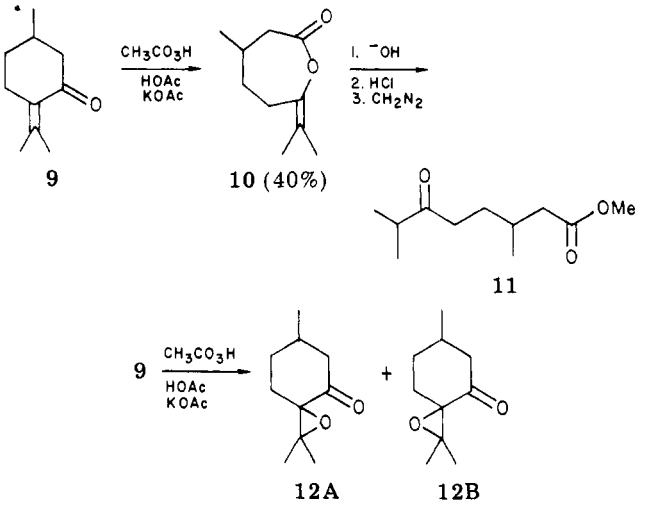
Scheme I

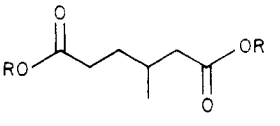


Scheme II



Scheme III





13, R = H
14, R = Me

A typical procedure is given for the case of **4**. To a solution of 500 mg (3.3 mmol) of **4** in 2.0 mL of acetic acid saturated with potassium acetate (pH 4.3–4.5)[1] was added, at 25 °C and all at once, 473 μL (3.6 mmol, 1.1 equiv) of 40% CH_3CO_3H.[4] The mixture, after stirring overnight, was

(1) H. M. Walton, *J. Org. Chem.*, **22**, 1161 (1957).
(2) Walton,[1] while investigating the reaction of 40% CH_3CO_3H with aralkylidenecyclanones, characterized the resultant enol lactones by hydrolysis to the keto acid and formation of the semicarbazone. He did not pursue the formation of the keto acids further.
(3) Identified previously as an anomalous product from an attempted Wharton rearrangement: J. R. Handley, A. A. Swigar, T. Ueda, and R. M. Silverstein, *J. Org. Chem.*, submitted for publication.
(4) F. P. Greenspan, *Ind. Eng. Chem.*, **39**, 847 (1947).
(5) NMR, IR, and mass spectra, and combustion analyses are in accord with the designated structures.

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