**SUPPORTING
INFORMATION**

**A two-step conversion of α,β -unsaturated ketones
to their α -carbalkoxy or α -carbamoyl derivatives**

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Supporting Information

S2-S8 X-ray data for compound **2**

S9-S15 ^1H NMR spectra for compounds **1g**, **1h**, **1i**, **5f**, **5g**, **5i** and the 2,2a dehydro derivative of **3**.

Crystal Data for Compound 2

Crystal Data

Empirical Formula

 $C_{20}H_{24}O_4$

Color; Habit

Colourless needle plate fragment

Crystal Size (mm)

0.18{100}x0.76{010}x0.40{001}

Crystal System

Monoclinic

Space Group

C2/c

Unit Cell Dimensions

 $a = 18.758(3) \text{ \AA}$ $b = 10.367(1) \text{ \AA}$ $c = 17.439(2) \text{ \AA}$ $\beta = 104.808(7)^\circ$

Volume

 $3278.6(9) \text{ \AA}^3$

Z

8

Formula Weight

328.4

Density(calc.)

 1.331 g/cm^3

Absorption Coefficient

 0.91 cm^{-1}

F(000)

1408

Data Collection

Diffractometer Used	Siemens P4
Radiation	MoK α (λ = 0.71073 Å)
Temperature (K)	160
Monochromator	Highly oriented graphite crystal
2 θ Range	4.0 to 54.0 $^{\circ}$
Scan Type	ω
Scan Speed	Variable; 3.00 to 30.00 $^{\circ}$ /min. in ω
Scan Range (ω)	1.20 $^{\circ}$
Background Measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
Standard Reflections	3 measured every 100 reflections
Index Ranges	$0 \leq h \leq 23$, $0 \leq k \leq 13$ $-22 \leq l \leq 21$
Reflections Collected	3696
Independent Reflections	3586 (R_{int} = 2.36%)
Observed Reflections	2644 ($F > 6.0\sigma(F)$)
Absorption Correction	Face-indexed numerical
Min./Max. Transmission	0.9630 / 0.9848

Solution and Refinement

System Used	Siemens SHELXTL IRIS
Solution	Direct Methods
Refinement Method	Full-Matrix Least-Squares
Quantity Minimized	$\sum w(F_o - F_c)^2$
Extinction Correction	$\chi = 0.00028(2)$, where $F^* = F [1 + 0.002\chi F^2 / \sin(2\theta)]^{-1/4}$
Hydrogen Atoms	Refined isotropic U
Weighting Scheme	$w^{-1} = \sigma^2(F)$
Number of Parameters Refined	314
Final R Indices (obs. data)	$R = 3.37 \%$, $wR = 3.34 \%$
(R Indices (all data)	$R = 4.51 \%$, $wR = 3.40 \%$
Goodness-of-Fit	2.40
Largest and Mean Δ/σ	0.002, 0.000
Data-to-Parameter Ratio	8.4:1
Largest Difference Peak	0.27 eÅ ⁻³
Largest Difference Hole	-0.16 eÅ ⁻³

Table 1. Atomic coordinates ($\times 10^5$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^4$)

	x	y	z	U(eq)
C(1)	18074(9)	50520(16)	21205(9)	255(5)
C(2)	9939(9)	51831(15)	20357(10)	299(6)
C(3)	5139(9)	47280(15)	14039(10)	290(6)
C(4)	7783(8)	40794(14)	7537(9)	242(5)
C(4a)	14135(8)	48790(13)	5899(8)	210(5)
C(5)	16955(8)	43122(14)	-989(9)	241(5)
C(6)	24615(9)	45705(14)	-1006(9)	245(5)
C(7)	29664(8)	48149(14)	5674(9)	244(5)
C(7a)	28069(8)	47443(14)	13741(9)	229(5)
C(8)	34047(9)	54779(16)	19833(10)	291(5)
C(9)	33804(9)	68928(16)	18223(9)	296(6)
C(10)	27619(9)	74766(15)	14612(9)	268(5)
C(11)	20285(8)	68224(13)	12211(9)	225(5)
C(11a)	20302(8)	53250(13)	13364(8)	204(5)
C(12)	16009(8)	70560(14)	3723(9)	233(5)
O(13)	10607(6)	60565(9)	2204(6)	244(3)
C(14)	9766(9)	26588(14)	9444(10)	252(5)
C(15)	3112(9)	18609(15)	10053(11)	299(6)
C(16)	4689(8)	4393(15)	10313(9)	265(5)
O(17)	9603(8)	-604(11)	8264(9)	577(6)
O(18)	-168(6)	-2283(10)	13136(7)	356(4)
C(19)	849(12)	-16109(17)	13629(14)	402(7)
O(20)	12670(6)	37725(11)	-6489(7)	352(4)
C(21)	28784(9)	33047(16)	15983(10)	287(6)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 2. Bond lengths ($\text{\AA}$)

C(1)-C(2)	1.501(2)	C(1)-C(11a)	1.555(2)
C(2)-C(3)	1.319(2)	C(3)-C(4)	1.507(3)
C(4)-C(4a)	1.537(2)	C(4)-C(14)	1.534(2)
C(4a)-C(5)	1.547(2)	C(4a)-C(11a)	1.574(2)
C(4a)-O(13)	1.458(2)	C(5)-C(6)	1.462(2)
C(5)-O(20)	1.219(2)	C(6)-C(7)	1.324(2)
C(7)-C(7a)	1.513(2)	C(7a)-C(8)	1.535(2)
C(7a)-C(11a)	1.562(2)	C(7a)-C(21)	1.540(2)
C(8)-C(9)	1.492(2)	C(9)-C(10)	1.317(2)
C(10)-C(11)	1.494(2)	C(11)-C(11a)	1.565(2)
C(11)-C(12)	1.512(2)	C(12)-O(13)	1.426(2)
C(14)-C(15)	1.524(2)	C(15)-C(16)	1.502(2)
C(16)-O(17)	1.189(2)	C(16)-O(18)	1.334(2)
O(18)-C(19)	1.446(2)		

Table 3. Bond angles ($^{\circ}$)

C(2)-C(1)-C(11a)	113.1(1)	C(1)-C(2)-C(3)	120.6(2)
C(2)-C(3)-C(4)	120.1(2)	C(3)-C(4)-C(4a)	108.6(1)
C(3)-C(4)-C(14)	111.9(1)	C(4a)-C(4)-C(14)	113.7(1)
C(4)-C(4a)-C(5)	112.0(1)	C(4)-C(4a)-C(11a)	116.4(1)
C(5)-C(4a)-C(11a)	115.4(1)	C(4)-C(4a)-O(13)	104.4(1)
C(5)-C(4a)-O(13)	100.5(1)	C(11a)-C(4a)-O(13)	105.9(1)
C(4a)-C(5)-C(6)	117.6(1)	C(4a)-C(5)-O(20)	119.9(1)
C(6)-C(5)-O(20)	122.2(2)	C(5)-C(6)-C(7)	121.0(2)
C(6)-C(7)-C(7a)	122.8(1)	C(7)-C(7a)-C(8)	109.7(1)
C(7)-C(7a)-C(11a)	110.3(1)	C(8)-C(7a)-C(11a)	110.3(1)
C(7)-C(7a)-C(21)	104.9(1)	C(8)-C(7a)-C(21)	107.7(1)
C(11a)-C(7a)-C(21)	113.8(1)	C(7a)-C(8)-C(9)	112.0(1)
C(8)-C(9)-C(10)	121.5(1)	C(9)-C(10)-C(11)	124.1(1)
C(10)-C(11)-C(11a)	116.3(1)	C(10)-C(11)-C(12)	114.9(1)
C(11a)-C(11)-C(12)	105.5(1)	C(1)-C(11a)-C(4a)	111.6(1)
C(1)-C(11a)-C(7a)	110.5(1)	C(4a)-C(11a)-C(7a)	113.7(1)
C(1)-C(11a)-C(11)	107.5(1)	C(4a)-C(11a)-C(11)	102.0(1)
C(7a)-C(11a)-C(11)	111.0(1)	C(11)-C(12)-O(13)	103.9(1)
C(4a)-O(13)-C(12)	107.8(1)	C(4)-C(14)-C(15)	112.3(1)
C(14)-C(15)-C(16)	112.1(1)	C(15)-C(16)-O(17)	125.5(2)
C(15)-C(16)-O(18)	111.9(1)	O(17)-C(16)-O(18)	122.7(1)
C(16)-O(18)-C(19)	116.4(1)		

Table 4. Anisotropic displacement coefficients ($\text{\AA}^2 \times 10^4$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	315(9)	250(8)	216(8)	15(7)	96(7)	24(7)
C(2)	390(9)	241(8)	337(9)	56(7)	221(8)	34(7)
C(3)	277(9)	240(8)	403(10)	36(7)	176(8)	49(7)
C(4)	208(8)	218(8)	300(8)	1(6)	65(7)	15(6)
C(4a)	224(7)	168(7)	243(8)	27(6)	66(6)	15(6)
C(5)	292(8)	197(7)	233(8)	18(6)	65(7)	9(6)
C(6)	307(8)	215(8)	247(8)	14(7)	131(7)	-22(6)
C(7)	227(8)	222(8)	303(8)	17(6)	104(7)	-15(6)
C(7a)	226(8)	226(8)	232(8)	17(6)	51(6)	-1(6)
C(8)	254(9)	344(9)	260(9)	14(7)	37(7)	-30(7)
C(9)	321(9)	329(9)	237(8)	-86(8)	68(7)	-74(7)
C(10)	390(9)	223(8)	202(8)	-60(7)	95(7)	-38(6)
C(11)	297(8)	185(7)	217(8)	20(6)	107(6)	-4(6)
C(11a)	241(8)	186(7)	200(7)	12(6)	85(6)	3(6)
C(12)	271(8)	173(8)	259(8)	-3(6)	72(7)	14(6)
O(13)	243(6)	190(5)	284(6)	19(4)	38(4)	42(4)
C(14)	236(8)	209(8)	318(9)	-4(7)	83(7)	17(7)
C(15)	255(9)	255(8)	389(10)	-6(7)	89(8)	36(7)
C(16)	270(8)	264(8)	258(8)	-59(7)	65(7)	-15(7)
O(17)	701(10)	256(6)	1010(12)	-53(6)	648(9)	-83(7)
O(18)	281(6)	252(6)	569(8)	-24(5)	169(6)	70(5)
C(19)	428(11)	249(9)	564(13)	-76(8)	190(10)	12(9)
O(20)	350(6)	395(7)	297(6)	-40(5)	59(5)	-119(5)
C(21)	277(9)	260(9)	322(10)	74(7)	71(8)	37(7)

The anisotropic displacement factor exponent takes the form:

$$-2\pi^2 (h^2 a^{*2} U_{11} + \dots + 2klb^* c^* U_{23})$$

Table 5. H-Atom coordinates ($\times 10^4$) and isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$)

	x	y	z	U
H(1x)	1967(8)	4148(15)	2325(9)	27(4)
H(1y)	2088(8)	5634(15)	2532(9)	25(4)
H(2)	838(9)	5600(16)	2475(10)	36(5)
H(3)	-18(9)	4802(15)	1334(9)	32(5)
H(4)	384(9)	4130(14)	259(9)	25(4)
H(6)	2576(9)	4511(16)	-609(10)	33(4)
H(7)	3482(9)	4937(15)	575(10)	33(4)
H(8x)	3356(9)	5293(15)	2506(10)	34(5)
H(8y)	3889(9)	5131(15)	1971(10)	34(5)
H(9)	3830(9)	7368(16)	1988(10)	37(5)
H(10)	2767(8)	8409(16)	1364(9)	29(4)
H(11)	1729(8)	7190(14)	1553(9)	25(4)
H(12x)	1329(8)	7904(14)	306(8)	20(4)
H(12y)	1901(8)	7000(14)	-10(9)	24(4)
H(14x)	1363(9)	2579(15)	1439(9)	28(4)
H(14y)	1175(8)	2281(15)	529(9)	25(4)
H(15x)	-103(10)	1987(16)	550(11)	44(5)
H(15y)	133(9)	2086(16)	1464(10)	34(5)
H(19x)	545(13)	-1835(21)	1748(14)	76(8)
H(19y)	94(13)	-1957(22)	875(15)	80(8)
H(19z)	-332(13)	-1962(22)	1513(13)	79(8)
H(21x)	2482(9)	2775(15)	1266(9)	29(4)
H(21y)	2877(9)	3144(16)	2153(11)	39(5)
H(21z)	3359(9)	2992(16)	1558(10)	35(5)

S9

proton, 16 scans

1g

Current Data Parameters
NAME hssamide1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

Date_ 20001014
Time 20.43
INSTRUM Avance300
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 16
DS 2
SWH 4005.410 Hz
FIDRES 0.244532 Hz
AQ 2.0447731 sec
RG 143.7
OW 124.800 usec
DE 5.00 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====

NUC1 1H
P1 5.40 usec
PL1 0.00 dB
SF01 300.1318044 MHz

F2 - Processing parameters

SI 8192
SF 300.1300022 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters

CX 20.00 cm
F1P 7.450 ppm
F1 2236.07 Hz
F2P 0.561 ppm
F2 168.25 Hz
PPMCM 0.34449 ppm/cm
HZCM 103.39124 Hz/cm

S11

proton, 16 scans

Current Data Parameters
NAME hssnapmor
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20001030
Time 20.30
INSTRUM Avance300
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 16
DS 2
SWH 4006.410 Hz
FIDRES 0.244532 Hz
AQ 2.0447731 sec
RG 101.6
DW 124.800 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 5.40 usec
PL1 0.00 dB
SF01 300.1318044 MHz

F2 - Processing parameters
SI 8192
SF 300.1300154 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 7.652 ppm
F1 2296.72 Hz
F2P 0.865 ppm
F2 259.67 Hz
PPHCH 0.33936 ppm/cm
HZCM 101.85267 Hz/cm

Chemical structure of 2,2-dimethyl-4-(diethylamino)-6-oxocyclohex-2-en-1-one (5g) is shown. The structure is a cyclohexenone ring with a diethylamino group at position 4 and two methyl groups at position 2. The carbons are numbered 1 through 6, starting from the carbonyl carbon (C1) and proceeding clockwise.

CCN(CC)C1=C(C)CC(=O)CC1=O

5g

Chemical shift (ppm) values are listed on the left side of the spectrum:

- 1.03039
- 1.05408
- 1.07771
- 1.11801
- 1.12146
- 1.13567
- 1.14582
- 1.15110
- 1.16301
- 1.17894
- 1.19745
- 1.18271
- 1.19299
- 2.46623
- 2.49012
- 2.51177
- 2.55457
- 2.57850
- 2.60206
- 2.62595
- 2.65002
- 2.67377
- 2.71533
- 2.74029

The spectrum shows a series of peaks corresponding to these chemical shifts, with a large peak at approximately 2.6 ppm and a smaller peak at approximately 2.7 ppm. The x-axis is labeled from 1 to 6 ppm.

50

Current Data Parameters	
NAME	fs-2-feb
EXPNO	1
PROCNO	1
F2 - Acquisition Parameters	
Date_	20010217
Time	23.42
INSTRUM	Avance300
PROBHD	5 mm QNP 1H/1
PULPROG	zg30
TD	16384
SOLVENT	CDCl3
NS	16
DS	2
SWH	4006.410 Hz
FIDRES	0.244532 Hz
AQ	2.0447731 sec
RG	114
DW	124.800 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
===== CHANNEL f1 =====	
NUC1	1H
P1	5.40 usec
PL1	0.00 dB
SFO1	300.1318044 MHz
F2 - Processing parameters	
SI	8192
SF	300.1300064 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00
1D NMR plot parameters	
CX	20.00 cm
CY	12.50 cm
F1P	7.000 ppm
F1	2100.91 Hz
F2P	0.500 ppm
F2	150.07 Hz
PPMCM	0.32500 ppm/cm
HZCM	97.54225 Hz/cm

sl

proton, 16 scans

ppm

1.20395

1.81888
1.89896
1.87250

2.03302
2.00009
2.04487

3.21834
3.20158
3.18526

3.70690
3.68465
3.63418
3.61800
3.60208

5i

Integral

1.0000

6.3644

2.0837

2.1127

2.1249

6.3534

ppm

S15

RC412.001
DATE 30-1-97
TIME 14: 56

SOLVENT CDCl3
SF 250.133
SF0 250.130
SF02 250.130
SF2 250.133

SY 0.0
O1 4000.000
SI 16384
TD 16384
SM 2994.012
SM2 2994.012
HZ/PT 365
VD 0.0

PW 10.5
RD 2.000
RG 2.736
RG 200
NS 33
TE 297
DE 237.1
DR 12
DW 167
FW 3800
O2 3200.000
DP 63L PD

LB 0.0
GB 0.0
NC 2
CX 35.00
CY 0.0
F1 8.000P
F2 501P
MI 02
DC 1.000
HZ/CM 53.590
PPM/CM 1.214
IS 1
SR 2852.76

2,2a dehydro derivative of 3.