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Ketone Pyramidalization in a Tetracyclic Perpendicular Enone Derivative

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Abstract. *endo,exo*-11,11-Dimethoxytetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-9-en-12-one (1), C₁₄H₁₈O₃, *M_r* = 234.30, monoclinic, *P*₂₁/*n*, *a* = 14.113 (2), *b* = 10.032 (1), *c* = 17.086 (2) Å, β = 103.55 (1)°, *V* = 2351.74 Å³, *Z* = 8, *D_x* = 1.323 g cm⁻³, λ(Cu Kα) = 1.54056 Å, μ = 7.038 cm⁻¹, *F*(000) = 1008, *T* = 133 K, *R* = 0.0433 and *wR* = 0.0435 for 4255 unique reflections. The molecule contains a norbornanone unit fused to a substituted norbornene. The ring C atom of the ketone is significantly pyramidalized. Possible factors contributing to this deformation include incipient nucleophilic attack by the π electrons at the carbonyl C atom, polarization of the π system, relief of bond-angle compression, and steric effects.

Introduction. Structural deformations of C=C double bonds have received considerable attention in recent years (Luef & Keese, 1991; Borden, 1989). Although experimental structures are known of many compounds containing C=N and C=O double bonds, few authors have focused on pyramidalization in these groups. X-ray diffraction data show that pyramidalization in C=N double bonds (Hollenstein & Laube, 1990; Carrupt, Vogel, Mison, Eddaïf, Pellissier, Faure & Loiseleur, 1986) is small (less than 5°). Similarly, neutron diffraction data for amides, amino acids or dipeptides (Jeffrey, Houk, Paddon-Row, Rondan & Mitra, 1985) show that carbonyl pyramidalization in these functional groups is no larger than 5°. Significant carbonyl pyramidalizations have been observed in cyclic structures containing nucleophilic functional groups (Bürgi & Dunitz, 1983; Cossu, Bachmann, N'Guessan, Viani,

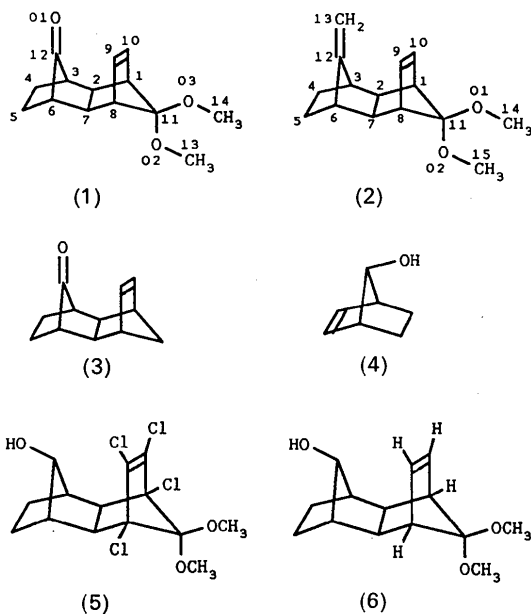
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Lapasset, Aycard & Bodot, 1987). However, to the best of our knowledge, no intramolecular Nu...C=O interactions (resulting in nonplanarity at the carbonyl C atom) have been reported for structures in which the incipient nucleophile (Nu) is alkenic.

The low-temperature X-ray crystal structure of (2), in which the ring C atom C(12) of the exocyclic double bond is significantly pyramidalized, was recently reported (Lloyd, Arif & Allred, 1992). This study led us to investigate the isoelectronic compound (1) that might have significant C-atom pyramidalization at the ketone. Tetracyclic ketone (3) is known (Haywood-Farmer, Malkus & Battiste, 1972; Paddon-Row, Patney & Warrenner, 1979) and its UV photoelectron spectrum is consistent with through-space interaction between the C=C double bond and the ketone (Paddon-Row, Patney & Brown, 1982). It seemed likely that this electronic effect would result in deformations of the double bonds.

Although enone (3) is a solid at 298 K, it was reported to be somewhat unstable (Haywood-Farmer, Malkus & Battiste, 1972). For this reason, and to facilitate comparison with the diene ketal (2), the dimethoxy derivative (1) was synthesized and its structure was determined by X-ray diffraction.



Experimental. The synthesis of (1) is similar to that reported (Haywood-Farmer, Malkus & Battiste, 1972) for (3). 7-Norbornenone (bicyclo[2.2.1]hept-2-en-7-one) was made by the standard method (Gassman & Marshall, 1973). The ketone was reduced (Franzus & Snyder, 1965; Gassman & Pape, 1964) to bicyclo[2.2.1]hept-2-en-anti-7-ol (4). Diels-Alder reaction of (4) with dimethoxytetrachlorocyclop-

tadiene in refluxing xylenes afforded exclusively the *endo,exo*-adduct (5), which was purified by chromatography on Florisil (pentane/CH₂Cl₂) and recrystallization from ether/pentane (77% yield): m.p. 403–404 K; ¹H NMR (90 MHz, CDCl₃) δ 1.05–1.35 (*m*, 2H), 1.37 (*bs*, 1H), 1.93–2.17 (*m*, 2H), 2.17–2.29 (*m*, 2H), 2.55 (*s*, 2H), 3.53 (*s*, 3H), 3.59 (*s*, 3H), 4.06 (*bs*, 1H). Adduct (5) was dechlorinated with sodium/ethanol (Lap & Paddon-Row, 1979) to give (6). Crude (6) was purified by vacuum sublimation at 383 K and 30 Pa (71% yield) then recrystallization from ether/pentane: m.p. 384–386 K; ¹H NMR (300 MHz, CDCl₃) δ 1.06–1.22 (*m*, 2H), 1.83–1.98 (*m*, 4H), 2.11 (*s*, 1H), 2.19 (*s*, 2H), 2.80–2.90 (*m*, 2H), 3.06 (*s*, 3H), 3.16 (*s*, 3H), 4.92 (*s*, 1H), 6.15 (*t*, 2H). The —OH group of (6) was then oxidized (Ratcliffe & Rodehorst, 1970) to the ketone (1), which was purified by chromatography on Florisil (pentane/CH₂Cl₂, 88% yield), and recrystallization three times from ether/pentane (37% yield purified): m.p. 386.7–387.7 K; ¹H NMR (300 MHz, CDCl₃) δ 1.41–1.58 (*m*, 2H), 1.62–1.82 (*m*, 4H), 2.33–2.48 (*m*, 2H), 2.91–3.03 (*m*, 2H), 3.12 (*s*, 3H), 3.23 (*s*, 3H), 6.05 (*t*, 2H); ¹H decoupled ¹³C NMR (75 MHz, CDCl₃) δ 22.27, 41.11, 42.68, 48.23, 49.72, 51.96, 119.41 [C(11)], 134.17 [C(9), C(10)], 214.89 [C(12)].

A crystal of (1) suitable for X-ray structure analysis was obtained by vacuum sublimation in a 11 mm × 0.5 m Pyrex tube in a temperature gradient (298–353 K) tube heater (10 Pa); crystal dimensions 0.30 × 0.28 × 0.16 mm. Intensity measurements were collected at 133 K on an Enraf-Nonius CAD-4 diffractometer, using $\theta/2\theta$ scans. (4 to 130°). Lattice parameters were calculated from least-squares refinement of 25 reflections in the range $11 \leq 2\theta \leq 40^\circ$. An empirical absorption correction was applied (minimum transmission 95.6, maximum 99.3%). The maximum value of $\sin\theta/\lambda$ was 0.587 \AA^{-1} . A total of 4436 reflections were measured ($0 \leq h \leq 16$, $0 \leq k \leq 11$ and $-20 \leq l \leq 20$), of which 4255 were unique ($R_{\text{int}} = 0.022$), and 3345 with $I \geq 3\sigma(I)$ were used in the final cycle of refinement. Standard reflections 51 $\bar{2}$ and $2\bar{2}\bar{2}$ showed variations in intensity of less than 3%, and no decay correction was applied. The structure was solved and refined using the direct-methods *SDP* package (Frenz, 1978). *F* magnitudes were used in the least-squares refinement. H atoms were located and refined with fixed isotropic thermal parameters. The number of parameters refined in the final cycle was 416 (C and O anisotropic, unit weighting), yielding $R = 0.0433$, $wR = 0.0435$, $S = 1.103$, $(\Delta/\sigma)_{\text{max}} = 0.001$. The highest peak in the final difference map was 0.404 e \AA^{-3} . Primary- and secondary-extinction values were used, and atomic scattering factors f' and f'' were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). There were two independent molecules in the asymmetric unit

Table 1. Atomic coordinates and isotropic or equivalent isotropic thermal parameters (\AA^2)

H atoms were refined with fixed isotropic thermal parameters. For C and O atoms $B_{\text{eq}} = (1/3)\sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$.

	x	y	z	$B_{\text{iso}}/B_{\text{eq}}$
O(1)	0.1288 (1)	-0.5084 (2)	0.1619 (1)	2.75 (3)
O(2)	0.2305 (1)	-0.0091 (2)	0.02147 (9)	1.86 (3)
O(3)	0.1248 (1)	0.0685 (2)	0.09617 (9)	1.89 (3)
C(1)	0.0946 (1)	-0.1547 (2)	0.0432 (1)	1.60 (4)
C(2)	0.1626 (1)	-0.2644 (2)	0.0227 (1)	1.53 (4)
C(3)	0.1317 (2)	-0.4095 (2)	0.0291 (1)	1.82 (4)
C(4)	0.2076 (2)	-0.4985 (2)	0.0015 (1)	2.26 (5)
C(5)	0.3019 (2)	-0.4832 (2)	0.0715 (1)	2.10 (5)
C(6)	0.2698 (2)	-0.3881 (2)	0.1320 (1)	1.81 (4)
C(7)	0.2579 (1)	-0.2496 (2)	0.0930 (1)	1.51 (4)
C(8)	0.2320 (2)	-0.1310 (2)	0.1431 (1)	1.58 (4)
C(9)	0.1511 (2)	-0.1772 (2)	0.1812 (1)	1.88 (4)
C(10)	0.0707 (2)	-0.1927 (2)	0.1224 (1)	1.87 (4)
C(11)	0.1713 (1)	-0.0449 (2)	0.0741 (1)	1.54 (4)
C(12)	0.1658 (2)	-0.4396 (2)	0.1187 (1)	1.92 (4)
C(13)	0.1778 (2)	0.0523 (3)	-0.0514 (1)	2.77 (5)
C(14)	0.1906 (2)	0.1680 (2)	0.1370 (2)	2.48 (5)
H(1)	0.040 (2)	-0.127 (4)	-0.002 (2)	4.0
H(3)	0.064 (2)	-0.429 (4)	0.004 (2)	4.0
H(6)	0.309 (2)	-0.394 (4)	0.188 (2)	4.0
H(8)	0.290 (2)	-0.086 (4)	0.179 (2)	4.0
H(9)	0.159 (2)	-0.194 (4)	0.246 (2)	4.0
H(10)	0.004 (2)	-0.233 (4)	0.127 (2)	4.0

Table 2. Bond distances (\AA) and bond angles ($^\circ$)

C(1)—C(2)	1.554 (3)	C(1)—C(10)	1.519 (3)
C(1)—C(11)	1.547 (3)	C(2)—C(3)	1.532 (3)
C(2)—C(7)	1.586 (3)	C(3)—C(4)	1.551 (3)
C(3)—C(12)	1.523 (3)	C(4)—C(5)	1.574 (3)
C(5)—C(6)	1.550 (3)	C(6)—C(7)	1.534 (3)
C(6)—C(12)	1.522 (3)	C(7)—C(8)	1.558 (3)
C(8)—C(9)	1.513 (3)	C(8)—C(11)	1.549 (3)
C(9)—C(10)	1.337 (3)	C(11)—O(3)	1.408 (2)
C(11)—O(2)	1.410 (2)	C(12)—O(1)	1.215 (3)
C(14)—O(3)	1.430 (3)	C(13)—O(2)	1.432 (3)
C(11)—O(3)—C(14)	113.8 (2)	C(11)—O(2)—C(13)	113.5 (2)
C(2)—C(1)—C(10)	107.6 (2)	C(2)—C(1)—C(11)	99.3 (2)
C(10)—C(1)—C(11)	99.2 (2)	C(1)—C(2)—C(3)	117.1 (2)
C(1)—C(2)—C(7)	102.8 (2)	C(3)—C(2)—C(7)	103.9 (2)
C(2)—C(3)—C(4)	107.2 (2)	C(2)—C(3)—C(12)	103.4 (2)
C(4)—C(3)—C(12)	96.5 (2)	C(3)—C(4)—C(5)	103.5 (2)
C(4)—C(5)—C(6)	103.9 (2)	C(5)—C(6)—C(7)	106.7 (2)
C(5)—C(6)—C(12)	96.5 (2)	C(7)—C(6)—C(12)	103.8 (2)
C(2)—C(7)—C(6)	103.4 (2)	C(2)—C(7)—C(8)	102.8 (2)
C(6)—C(7)—C(8)	118.0 (2)	C(7)—C(8)—C(9)	107.4 (2)
C(7)—C(8)—C(11)	99.6 (2)	C(9)—C(8)—C(11)	99.2 (5)
C(8)—C(9)—C(10)	107.9 (2)	C(1)—C(10)—C(9)	108.2 (2)
O(2)—C(11)—O(3)	110.4 (2)	C(1)—C(11)—O(3)	109.5 (2)
O(2)—C(11)—C(1)	115.8 (2)	O(3)—C(11)—C(8)	117.1 (2)
O(2)—C(11)—C(8)	108.8 (2)	C(1)—C(11)—C(8)	94.6 (2)
C(3)—C(12)—C(6)	98.7 (2)	O(1)—C(12)—C(3)	130.0 (2)
O(1)—C(12)—C(6)	129.7 (2)		

cell. Table 1 lists the atomic positional parameters while Table 2 gives bond lengths and bond angles for one of the molecules.*

* Complete lists of atomic coordinates, bond distances, bond angles, least-squares planes, torsion angles, thermal parameters, and structure factors, as well as a cell-packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55544 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1005]

Discussion. ORTEPII (Johnson, 1976) and PLUTO (Motherwell & Clegg, 1978) side-view drawings of one of the molecules are shown in Figs. 1 and 2, respectively. Differences between the corresponding bond lengths and bond angles for the two independent molecules are $\leq 0.009 \text{\AA}$ and $\leq 0.8^\circ$, respectively. There are no intermolecular contacts closer than 3.5\AA except five O...H distances calculated ($2.5\text{--}2.6 \text{\AA}$) to be near the van der Waals contact of 2.6\AA (Gordon & Ford, 1972). Comparison of the two independent molecules suggests that structural consequences of the O...H interactions are small.

Analysis of least-squares planes and torsion angles shows that twisting of the tetracyclic hydrocarbon framework is small. Excluding the ketal group, a single molecule contains an approximate noncrystallographic mirror plane. Differences between symmetry-related pairs of bond lengths and bond angles in the tetracyclic hydrocarbon framework are $\leq 0.006 \text{\AA}$ and $\leq 1.1^\circ$, respectively.

The most interesting feature of the structure (revealed in Fig. 2) is the pyramidalized C(12) atom.

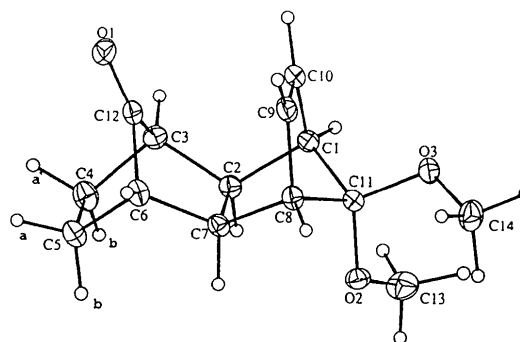


Fig. 1. ORTEPII (Johnson, 1976) drawing of one of the two independent molecules of (1) with thermal ellipsoids at the 30% probability level and spherical H atoms of arbitrary size.

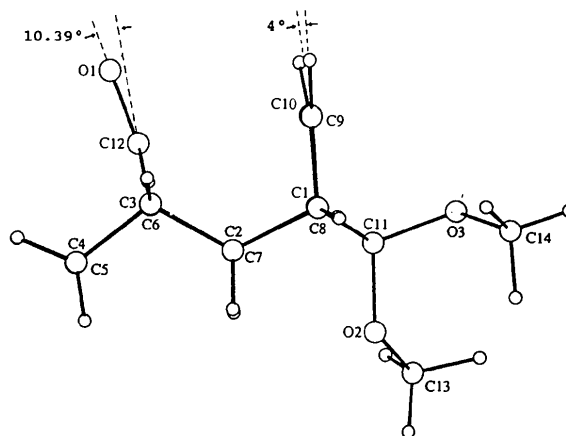


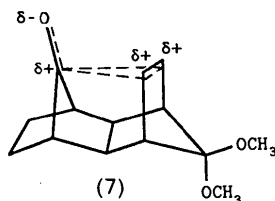
Fig. 2. PLUTO (Motherwell & Clegg, 1978) side view of (1) looking down the C(7)—C(2) and C(5)—C(4) bonds.

The O(1) atom lies 0.219 (2) Å out of the C(3)—C(12)—C(6) plane. The angle between the C(12)—O(1) bond and the C(3)—C(12)—C(6) plane is 10.39°. The analogous parameters for the second molecule are 0.197 (2) Å and 9.31°, respectively.

The angle between the H(9)—C(9)—C(10)—H(10) and C(8)—C(9)—C(10)—C(1) least-squares planes is 4°. Although this value is not statistically significant, it is in the same direction (*endo*) and is not far from the accurate measurement of 7.4° for a pyramidalized double bond in a simple norbornene derivative (Ermer, Bell & Mason, 1989).

Pyramidalization at C(12) is not likely a result of relief of the usual type of angle strain because the C(3)—C(12)—O(1) and C(6)—C(12)—O(1) bond angles are much larger than 100° (Borden, 1989). Nor is it a result of alleviation of torsional (eclipsing) repulsions because C(12) has no substituents that can interact sterically with H(3) or H(6).

From the ketone standpoint, the C(9)=C(10) π bridge is an incipient intramolecular nucleophile (Bürgi & Dunitz, 1983; Cossu, Bachmann, N'Guessan, Viani, Lapasset, Aycard & Bodot, 1987), and bending of O(1) is in the direction expected on this basis. The C(9)⋯C(12) and C(10)⋯C(12) distances [2.866 (3) and 2.825 (3) Å, respectively] are well within the van der Waals contacts (3.4 Å) (Bondi, 1964), and are consistent with π - π and/or π - π^* interactions in (1). NMR data suggest that the π system is somewhat polar, *i.e.* it may have partial homocyclopropenyl carbocation character (Winstein & Hansen, 1960), as in structure (7). The greater electronegativity of O(1) in structure (1) *versus* C(13) in structure (2) is consistent with greater polarization of the π system in (1) *versus* (2), and more pyramidalization at C(12) in (1) *versus* (2).



Another factor may contribute to C(12) pyramidalization. Bond-angle compression between C(3)—C(12), C(6)—C(12) and partial σ bonds from C(12) to C(9) and C(10) would be mitigated if C(12) were rehybridized towards sp^3 . The observed 'outward' bending of O(1) is also consistent with this idea.

Further, steric repulsions between O(1) and the C(9)=C(10) bridge could cause the O(1) atom to bend outward, since C(9)⋯O(1) and C(10)⋯O(1) distances [3.346 (3) and 3.301 (3) Å, respectively] are near van der Waals contacts (Bondi, 1964).

Differences between corresponding bond lengths and bond angles in structure (1) *versus* structure (2) are not large, but are sometimes significant. Bonds C(2)—C(3) and C(6)—C(7) are shorter by an average of 0.013 Å in (1) *versus* (2), while bonds C(3)—C(12), C(6)—C(12), C(4)—C(5) and C(2)—C(7) are longer by an average of 0.013 Å. Bond C(9)—C(10) is longer by 0.011 Å in (1) *versus* (2), while the O(1)—C(12) bond of (1) is shorter than the C(12)—C(13) bond of (2) by 0.112 Å (as expected for ketone *versus* methylene). The interbridge bond angles C(2)—C(1)—C(10), C(7)—C(8)—C(9), C(1)—C(2)—C(3), C(6)—C(7)—C(8), C(2)—C(3)—C(12), C(7)—C(6)—C(12), C(4)—C(3)—C(12) and C(5)—C(6)—C(12) are smaller by an average of 1.6° for (1) *versus* (2), while most of the other bond angles are slightly larger in (1) *versus* (2). The C(12)⋯C(9) and C(12)⋯C(10) nonbonding distances are shorter (by an average of 0.113 Å) in (1) *versus* (2).

Qualitatively, the differences between structures (1) and (2) can be explained if the π - π interaction were dominant in (2), and the π - π^* interaction were dominant in (1) (Paddon-Row, Patney & Brown, 1982). The π - π interaction is consistent with repulsion between the C(12) and C(9)=C(10) bridges, while the π - π^* interaction is consistent with less repulsion (or even attraction) between the C(12) and C(9)=C(10) bridges. The tetracyclic hydrocarbon structure, within the limits of its rigidity, apparently flexes so as to minimize repulsion and/or maximize attraction between π bridges of each structure. Similar observations have been made for other systems (McCabe, Milne & Sim, 1989). *Ab initio* calculations are in progress to investigate these possibilities.

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A Twisted Pentacyclic Ketone Derivative

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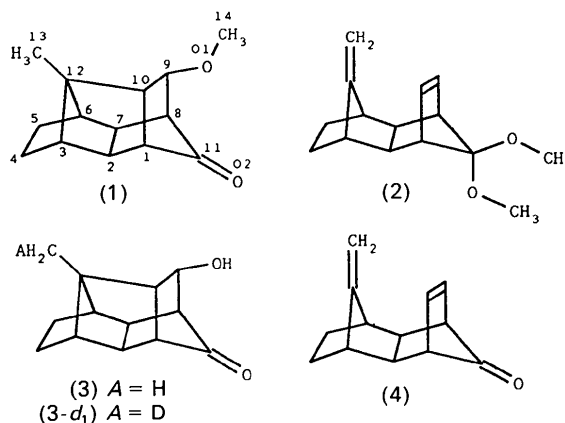
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Abstract. *exo*-11-Methoxy-9-methylpentacyclo[6.3.1.0^{3,10}.0^{4,12}.0^{5,9}]dodecan-2-one (1), C₁₄H₁₈O₂, *M_r* = 218.30, orthorhombic, *Pbca*, *a* = 7.288 (1), *b* = 12.432 (3), *c* = 24.392 (2) Å, *V* = 2209.88 Å³, *Z* = 8, *D_x* = 1.311 g cm⁻³, λ(Cu Kα) = 1.54056 Å, μ = 6.425 cm⁻¹, *F*(000) = 944, *T* = 148 K, *R* = 0.0547 and *wR* = 0.0552 for 1602 unique reflections. The molecule consists of a 'twisted' pentacyclic hydrocarbon ring system with methyl and methoxy substituents and a ketone functional group.

Introduction. The preparation and X-ray crystal structure of diene ketal (2) were recently reported (Lloyd, Arif & Allred, 1992). In an effort to hydrolyze the dimethoxy ketal to the ketone (4), compound (2) was subjected to aqueous acids. Normally ketals can be acid hydrolyzed in the presence of alkene functional groups to unrearranged ketones in high yields (Bertsch, Grimme, Reinhardt, Rose & Warner, 1988; Fessner, Sedelmeier, Spurr, Rihs & Prinsbach, 1987; Gassman & Marshall, 1973). However, chemical behavior is apparently influenced by the π–π interaction in (2). Attempted

hydrolysis of (2) with strong aqueous acids yielded mostly the ring-closed 'twisted' products (1) and (3).‡



Experimental. Compound (2) was stirred with excess 5% H₂SO₄/H₂O (Gassman & Marshall, 1973) for 18 h at 296 K. After neutralization of the reaction mixture with NaHCO₃, ether extraction, drying (Na₂SO₄), and evaporation of the solvent, the

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‡ Nonstandard numbering of atoms was used in structure (1) in order to facilitate comparison with structure (2).