

## Structure of the Product Formed *via* Regiospecific Cyclopropanation of *exo*-6-Methoxycarbonyltricyclo[5.2.1.0<sup>2,6</sup>]deca-4,8-dien-3-one with Dimethylsulfoxonium Methylide (Corey's Reagent)

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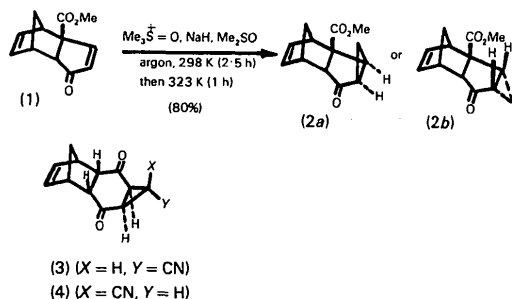
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(Received 2 September 1988; accepted 14 November 1988)

**Abstract.** Compound (2a), methyl 3-oxotetracyclo[6.2.1.0<sup>2,7</sup>.0<sup>4,6</sup>]undec-9-ene-7-carboxylate, C<sub>13</sub>H<sub>14</sub>O<sub>3</sub>, *M<sub>r</sub>* = 218.25, triclinic, *P* $\bar{1}$ , *a* = 6.470 (1), *b* = 7.523 (1), *c* = 12.967 (1) Å,  $\alpha$  = 74.50 (1),  $\beta$  = 88.97 (1),  $\gamma$  = 64.50 (1)°, *V* = 545.5 (1) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.329 g cm<sup>-3</sup>,  $\lambda$ (Mo *K*α) = 0.71073 Å,  $\mu$  = 0.88 cm<sup>-1</sup>, *F*(000) = 232, *T* = 300, *R* = 0.0448 for 1587 independent reflections. Compound 2(a) is composed of three fused five-membered rings and a three-membered ring. Molecular mechanics calculations indicate the system has about 268 kJ mol<sup>-1</sup> of strain energy. Although substitution of the norbornene moiety is asymmetric, the bond lengths across the ring system are statistically equivalent. The cyclopropane bond lengths range from 1.479 (2) to 1.512 (3) Å. The double-bond system of the norbornene moiety is folded along the C(9)–C(10) bond and deviates from planarity by 9 (2)°. The H atoms are bent away from the methylene bridge.

(2a), m.p. 354–355 K, was obtained by fractional recrystallization from pentane. A colorless crystal of dimensions 0.23 × 0.40 × 0.43 mm was mounted on a Nicolet R3M/μ update of a *P*2<sub>1</sub> diffractometer; data collected in the ω scan mode (3.0 ≤ 2θ ≤ 50°), variable scan rate (4–29.3° min<sup>-1</sup>), graphite-monochromated Mo *K*α radiation; lattice parameters from a least-squares refinement of 25 reflections (25.3 ≤ 2θ ≤ 29.7°), intensity statistics were consistent with space group *P* $\bar{1}$ ; monitored reflections  $\bar{3}1\bar{2}$  and  $\bar{1}4\bar{2}$  show no significant changes in intensities; 1920 independent reflections measured (−7 ≤ *h* ≤ 7, −8 ≤ *k* ≤ 8, 0 ≤ *l* ≤ 15), 1587 ≥ 3σ(*I*); Lorentz–polarization corrections, ψ-scan-based empirical absorption correction (transmission factors 0.816–0.858); structure solved by direct-methods techniques, block-cascade least-squares refinement, H atoms refined with isotropic thermal parameters; *R* = 0.0448, *wR* = 0.0569 for 201

**Experimental.** Under the reaction conditions shown in the scheme, a single product was obtained in 80% yield;



however, the reaction product might possess either structure (2a) or (2b). A single crystal of compound

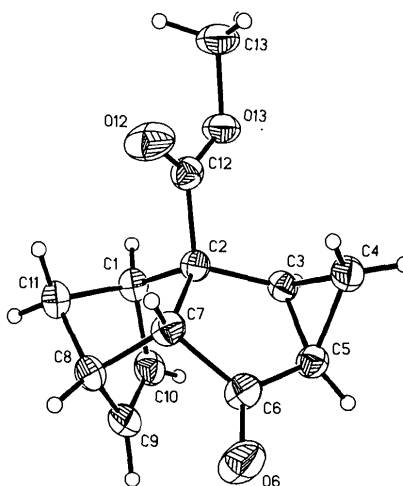


Fig. 1. Drawing of compound (2a) with thermal ellipsoids drawn at the 35% probability level. H atoms are represented by spheres of arbitrary size.

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Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ )

$U_{eq}$ defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.	$U_{eq}$			
	$x$	$y$	$z$	
C(1)	-228 (3)	3327 (3)	6527 (1)	48 (1)
C(2)	403 (3)	1440 (2)	7555 (1)	40 (1)
C(3)	2533 (3)	-496 (2)	7537 (1)	42 (1)
C(4)	3017 (3)	-2313 (3)	8468 (1)	54 (1)
C(5)	1795 (3)	-2091 (3)	7425 (1)	47 (1)
C(6)	-724 (3)	-1192 (3)	7366 (2)	53 (1)
O(6)	-1896 (3)	-1977 (2)	7174 (2)	88 (1)
C(7)	-1670 (3)	944 (3)	7508 (1)	47 (1)
C(8)	-3245 (3)	2641 (3)	6486 (2)	60 (1)
C(9)	-1978 (3)	2177 (3)	5529 (2)	64 (1)
C(10)	-190 (3)	2552 (3)	5559 (1)	57 (1)
C(11)	-2826 (3)	4452 (3)	6558 (2)	59 (1)
C(12)	625 (3)	2107 (3)	8531 (1)	48 (1)
O(12)	-804 (3)	2568 (3)	9137 (1)	81 (1)
O(13)	2619 (2)	2185 (2)	8628 (1)	60 (1)
C(13)	3045 (4)	2821 (4)	9528 (2)	76 (1)

parameters and 1587 reflections ( $R = 0.0544$  and  $wR = 0.0586$  for all 1920 reflections),  $S = 1.528$ ,  $(\Delta/\sigma)_{\max} = 0.035$ ; largest peaks in the final difference map of  $0.19$  and  $-0.24 \text{ e \AA}^{-3}$ ;  $\sum w(|F_o| - |F_c|)^2$  minimized with  $w = [\sigma^2(F_o) + 0.00074F_o^2]^{-1}$ . All computer programs supplied by Nicolet Instrument Corporation (1986) for Desktop 30 Microeclipse and Nova 4/C configurations; atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). The MM2 molecular mechanics program was used to calculate strain energies (Allinger & Yuh, 1980). Fig. 1 is a drawing of compound (2a). Table 1 lists atomic positional parameters, and Table 2 gives interatomic distances and valence angles.\*

**Related literature.** *endo*-Tricyclo[5.2.1.0<sup>2,6</sup>]dec-8-en-3-ones are of interest as intermediates in the synthesis of polyquinane natural products (Smith, Marchand, Suri & Jin, 1986; Marchand & Vidyasagar, 1988). Corey & Chaykovsky (1965) reported the use of dimethylsulfoxonium methylide in cyclopropanation reactions. The results of a study of [4 + 2] Diels-Alder cycloaddition of substituted homobenzoquinones to cyclopentadiene have been reported recently (Adam, Kliem, Lucchini, Peters, Peters & von Schnering, 1988). The crystal structures of the two related Diels-Alder cycloadducts (3) and (4) were reported. The deviations

\* Lists of H-atom coordinates, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51610 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths ( $\text{\AA}$ ) and valence angles ( $^\circ$ )

C(1)-C(2)	1.571 (2)	C(1)-C(10)	1.514 (3)
C(1)-C(11)	1.528 (2)	C(2)-C(3)	1.520 (2)
C(2)-C(7)	1.545 (3)	C(2)-C(12)	1.512 (3)
C(3)-C(4)	1.479 (2)	C(3)-C(5)	1.509 (3)
C(4)-C(5)	1.512 (3)	C(5)-C(6)	1.466 (2)
C(5)-O(6)	1.207 (3)	C(6)-C(7)	1.516 (3)
C(7)-C(8)	1.565 (2)	C(8)-C(9)	1.510 (3)
C(8)-C(11)	1.525 (4)	C(9)-C(10)	1.307 (4)
C(12)-O(12)	1.198 (2)	C(12)-O(13)	1.326 (3)
O(13)-C(13)	1.446 (3)		
C(2)-C(1)-C(10)	106.9 (1)	C(2)-C(1)-C(11)	99.9 (1)
C(10)-C(1)-C(11)	100.1 (2)	C(1)-C(2)-C(3)	115.4 (1)
C(1)-C(2)-C(7)	102.2 (1)	C(3)-C(2)-C(7)	106.3 (2)
C(1)-C(2)-C(12)	108.3 (1)	C(3)-C(2)-C(12)	110.9 (1)
C(7)-C(2)-C(12)	113.6 (1)	C(2)-C(3)-C(4)	115.1 (1)
C(2)-C(3)-C(5)	108.8 (1)	C(4)-C(3)-C(5)	60.8 (1)
C(3)-C(4)-C(5)	60.6 (1)	C(3)-C(5)-C(4)	58.6 (1)
C(3)-C(5)-C(6)	108.0 (1)	C(4)-C(5)-C(6)	115.4 (2)
C(5)-C(6)-O(6)	125.4 (2)	C(5)-C(6)-C(7)	110.0 (2)
O(6)-C(6)-C(7)	124.5 (2)	C(2)-C(7)-C(6)	106.6 (1)
C(2)-C(7)-C(8)	102.9 (1)	C(6)-C(7)-C(8)	112.2 (2)
C(7)-C(8)-C(9)	106.5 (1)	C(7)-C(8)-C(11)	100.4 (2)
C(9)-C(8)-C(11)	99.9 (2)	C(8)-C(9)-C(10)	107.8 (2)
C(1)-C(10)-C(9)	107.6 (2)	C(1)-C(11)-C(8)	93.8 (1)
C(2)-C(12)-O(12)	125.9 (2)	C(2)-C(12)-O(13)	111.1 (1)
O(12)-C(12)-O(13)	123.0 (2)	C(12)-O(13)-C(13)	116.8 (2)

from planarity of the double-bond systems in norbornenes and sesquinorbornenes have been reported previously (Watson, 1983).

We thank The Welch Foundation (Grants: P-074 to WHW, B-963 to APM), the Air force Office of Scientific Research (Grant AFOSR-88-0132 to APM), and the Faculty Research Committees of Texas Christian University and the University of North Texas for financial support of this study.

#### References

- ADAM, W., KLIEM, U., LUCCHINI, V., PETERS, E.-M., PETERS, K. & VON SCHNERING, H. G. (1988). *Chem. Ber.* **121**, 1063-1067.
- ALLINGER, N. L. & YUH, Y. H. (1980). *MMP* and *MMPI* subroutines for IBM PC. Updated by L. C. ROHREN (1984); adapted by J. J. GAGAWSKI & K. E. GILBERT from copy supplied by O. NELSON & C. SCOTT OWEN. Obtained from Serena Software, 489 Serena Lane, Bloomington, IN 47401, USA.
- COREY, E. J. & CHAYKOVSKY, M. (1965). *J. Am. Chem. Soc.* **87**, 1353-1364.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- MARCHAND, A. P. & VIDYASAGAR, V. (1988). *J. Org. Chem.* In the press.
- Nicolet Instrument Corporation (1986). *SHELXTL* for Desktop 30 (Microeclipse), PN-269-1040340. Nicolet Instrument Corporation, Madison, WI, USA.
- SMITH, W. B., MARCHAND, A. P., SURI, S. C. & JIN, P.-W. (1986). *J. Org. Chem.* **51**, 3052-3054.
- WATSON, W. H. (1983). Editor. *Stereochemistry and Reactivity of Systems Containing  $\pi$ -Electrons*. Deerfield Beach, FL: Verlag Chemie International.