

served for the corresponding oxygenated species. The NO adduct in frozen Me₂SO yields a complicated EPR spectrum that is consistent with the patterns that have been observed for square-pyramidal geometry. From the hyperfine splittings the adduct bonding appears to be to the N of an axially symmetric nitric oxide ligand.

The 2:1 ligand-to-metal stoichiometry of the product from the reaction under argon has been confirmed by a spectrophotometric titration. The UV-vis absorption spectra for **1** and for the adducts that are formed by O₂, NO, and CO are illustrated in Figure 1. An absorption band at 750–800 nm is attributed to a semiquinone contaminant, while the band at 400 nm is due to a green species which results from further oxidation of the catechol. When the solutions of the NO and CO adducts are exposed to O₂, they decolorize to yield pale yellow solutions. The purple color of the NO adduct can be regained by purging the solution of oxygen and reintroducing NO. This cycle can be repeated several times without apparent decomposition of the vanadium complex.

The loss of color on exposure of the NO adduct to oxygen indicates that the vanadium undergoes oxidation. Regeneration of the purple species by NO addition implies that the vanadium is reduced to the +4 oxidation state by NO. Thus, by this cycle the complex appears to have a catalytic effect on the oxidation of NO.

Perhaps the most interesting characteristic of **1** is the apparent tetrahedral geometry of the catechol oxygens around the vanadium(IV) center. This conclusion is supported by the infrared spectrum for **1**, which does not have a V=O stretching band in the 950–1050-cm⁻¹ region.¹⁵ Hence, **1** is unlike the bis(acetylacetonato)oxovanadium(IV) complex, which does exhibit this characteristic stretching frequency because of its axial oxygen. Apparently the more basic character of the catechol ligands enhances their coordination to cause the displacement of the axial oxygen. Indeed, the increased coordination strength of the catechols to the vanadium is reflected by the V—O stretching frequency in the far-infrared region: 504 compared with 480 cm⁻¹ for vanadyl acetylacetonate¹⁵ and 463 cm⁻¹ for VO(acac)₂(py).¹⁶

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References and Notes

- (1) D. A. Webb, *J. Exp. Biol.*, **16**, 499 (1939).
- (2) D. B. Carlisle, *Proc. R. Soc. London, Ser. B*, **171**, 31 (1968).
- (3) W. R. Biggs and J. H. Swinehart in "Metal Ions in Biological Systems", Vol. 6, H. Sigel, Ed., Marcel Dekker, New York, N.Y., 1976, pp 142–196.
- (4) I. Goodbody, *Adv. Marine Biol.*, **12**, 2 (1974).
- (5) N. P. Luneva, L. A. Nikonova, and A. E. Shilov, *React. Kinet. Catal. Lett.*, **5**, 149 (1976).
- (6) G. M. Husain and P. K. Bhattacharya, *J. Indian Chem. Soc.*, **46**, 875 (1969).
- (7) J. Zelinka, M. Bartusek, and A. Okac, *Collect. Czech. Chem. Commun.*, **39**, 83 (1974).
- (8) K. Kustin, S.-T. Liu, C. Nicolini, and D. P. Toppen, *J. Am. Chem. Soc.*, **96**, 7410 (1974).
- (9) K. Kustin, C. Nicolini, and D. L. Toppen, *J. Am. Chem. Soc.*, **96**, 7416 (1974).
- (10) S. P. Singh and J. P. Tandon, *Indian J. Chem.*, **13**, 1221 (1975).
- (11) E. Pelizzetti, E. Mentasti, and G. Saini, *Gazz. Chim. Ital.*, **106**, 605 (1976).
- (12) R. P. Henry, P. C. H. Mitchell, and J. E. Prue, *J. Chem. Soc. A*, 3392 (1971).
- (13) L. Vaska, *Acc. Chem. Res.*, **9**, 175 (1976).
- (14) The precipitate was collected, washed with water, air dried, and recrystallized from hot methanol. The overall yield from this reaction was 70%. Anal. Calcd for VC₂₈H₄₀O₄: V, 10.36; C, 68.42; H, 8.20. Found: V, 10.54; C, 67.93; H, 8.53.
- (15) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", Wiley-Interscience, New York, N.Y., 1970.
- (16) K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 4533 (1961).

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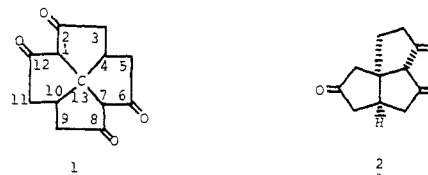
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Synthesis of a Tetraketone of the Tetracyclo[5.5.1.0^{4,13}.0^{10,13}]tridecane ("Staurane") Series

Sir:

Recent interest in cyclopentanoid ring systems has been well documented,¹ and a number of them have been synthesized; triquinacene,² peristylane,³ and the compounds of this type obtained by Paquette et al.⁴ may serve as examples. The discovery of natural compounds with ring structures based in part (retigeranic acid⁵) or entirely (hirsutic acid,⁶ the coriolins,⁷ and isocome⁸) on cyclopentanoid systems has stimulated additional interest in this area of research.

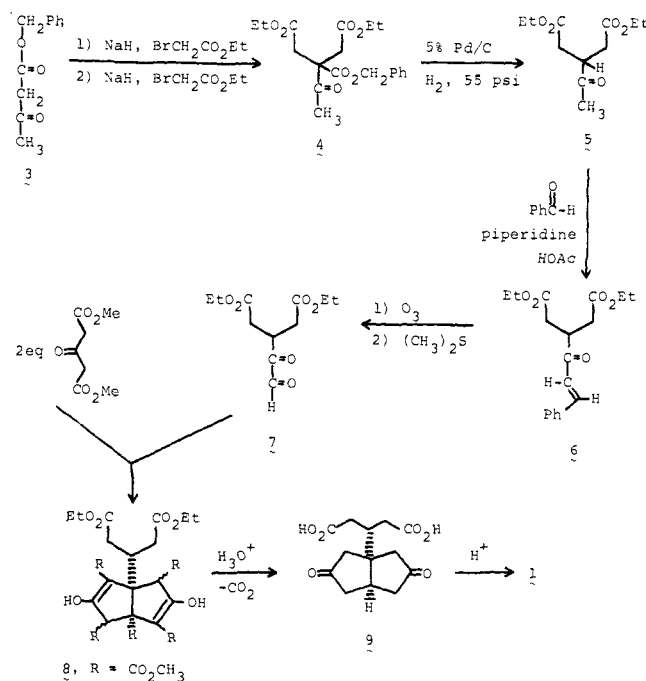


We wish to describe a simple synthesis of the tetraketone **1** from readily available starting materials. To the best of our knowledge, **1** is the first representative of the tetracyclo[5.5.1.0^{4,13}.0^{10,13}]tridecane series and we propose the name "staurane" (from Greek stauros, cross) for this highly symmetrical cyclopentanoid ring system.

Much of the synthetic work cited in ref 1–4 has been directed toward very specific targets. In contrast, our own efforts in this field⁹ have been concerned with a general method: reaction of dimethyl 3-ketoglutarate with 1,2-dicarbonyl compounds. This reaction is a convenient source of enolic β -keto esters derived from bicyclo[3.3.0]octane-3,7-dione;^{9,10} moreover, this methodology has recently been employed¹¹ to prepare the tricyclic triketone **2**, the parent ring system of isocome,⁸ and a modification has now permitted the synthesis of **1**.

Initially, several routes to **1** were considered, including conversion of the triketone **2** to **1**; however, these were cast aside in favor of a pathway which would take advantage of the C_{2v} symmetry inherent in the tetraketone **1**. The immediate goal, therefore, was preparation of the diacid **9** which was accomplished with remarkable ease from benzyl acetoacetate **3**, as illustrated in Scheme I. Dialkylation of the ester **3** with

Scheme I



ethyl bromoacetate¹² in two steps gave **4**¹³ in over 80% yield. Catalytic debenzoylation of the triester **4** over Pd/C,¹⁴ followed by loss of carbon dioxide, furnished the diester **5**¹⁵ (93%) which was converted in excellent yield to the benzylidene derivative **6**¹⁶ by Knoevenagel condensation with benzaldehyde in refluxing benzene.¹⁷

Treatment of **6** with ozone, followed by decomposition of the ozonide with dimethyl sulfide,¹⁸ provided the oily α -ketoaldehyde **7**¹⁹ in 80% yield. Since this compound darkened very rapidly, it was converted at once to the 1:2 adduct **8**²⁰ by stirring with 2 mol of dimethyl β -ketoglutarate in aqueous sodium bicarbonate (pH 8.3) at room temperature for 7 days. Acidification of the resulting solution to pH 1 precipitated **8**: mp 135–137 °C (from methanol); yield of recrystallized product, 51%.²¹ Hydrolysis of the ester functions of **8** in refluxing acetic acid–hydrochloric acid solution, followed by loss of carbon dioxide from the β -keto acid functions, gave the key diacid **9**²² in 51% yield,²¹ mp 180–185 °C (from ethyl acetate).

With the diketo diacid **9** in hand we now turned our attention to its conversion to the tetraketone **1**. Synthesis of **1** from the diester of **9** by the usual base-catalyzed methods was avoided because of the extreme alkali sensitivity of cyclopentanoid β -diketones; this sensitivity has been observed by Eaton in similar β -diketones²³ and by us in **2**.¹¹ Heating **9** in a refluxing benzene–dioxane solution with catalytic amounts of naphthalene-1-sulfonic acid²⁴ gave mixtures of products; pyrolysis, in vacuo, at 200 °C was similarly unsatisfactory. However, stirring **9** (0.6 g) with naphthalene-1-sulfonic acid (0.5 g) for 4 days in refluxing cumene–diglyme (2:1) provided **1** as a light gray, microcrystalline powder in 78% yield. The tetraketone proved quite insoluble in the usual organic solvents²⁵ other than pyridine and dimethyl sulfoxide; therefore, it was purified by sublimation at 190 °C (0.02 mm) to furnish a white solid, mp 288 °C dec. The molecular formula was established by high-resolution mass spectrometry (M^+ , calcd for $C_{13}H_{12}O_4$ 232.0736, found 232.0739) and the identity of **1** was confirmed by IR ($\nu(\text{CO})$ 1765 cm^{-1}) and other spectroscopic data.²⁶ The ¹³C NMR spectrum of **1** was particularly informative, for it contained only five signals with the chemical shifts (δ 37.5, 44.8, 62.5 (quaternary carbon), 65.8 and 207 (C=O)) quite consistent with carbon atoms contained in **1**, on the basis of values observed for related compounds.^{11,23}

The tetraketone **1** is more strained than bicyclic ketones related to **9** as evidenced by comparison of their carbonyl absorptions, ν 1765 and 1743, respectively; however, the Dreiding model of **1** can be assembled without undue difficulty.

The relative ease with which tetracyclo[5.5.1.0^{4,13}.0^{10,13}]-tridecane 2,6,8,12-tetraketone **1** (C_{2v} symmetry) can be prepared by the route presented here demonstrates the feasibility of extending this method to the synthesis of other polycyclic cyclopentanoid systems; we plan to examine such possibilities, and to study the chemistry of staurane derivatives²⁷ in greater detail.

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References and Notes

- I. T. Jacobson, Ph.D. Thesis, University of Lund, 1973.
- Cf., *inter alia*, R. B. Woodward, T. Fukunaga, and R. C. Kelly, *J. Am. Chem. Soc.*, **86**, 3162 (1964); R. Russo, Y. Lambert, and P. Deslongchamps, *Can. J. Chem.*, **49**, 531 (1971).
- P. E. Eaton, R. H. Mueller, G. R. Carson, D. A. Cullison, G. F. Cooper, T.-C. Chou, and E. P. Krebs, *J. Am. Chem. Soc.*, **99**, 2751 (1977); P. E. Eaton and R. H. Mueller, *ibid.*, **94**, 1014 (1972).
- L. A. Paquette, M. J. Wyratt, O. Schallner, D. F. Schneider, W. J. Begley, and R. M. Blankenship, *J. Am. Chem. Soc.*, **98**, 6744 (1976); L. A. Paquette and M. J. Wyratt, *ibid.*, **96**, 4671 (1974), and **96**, 2433 (1974).
- E. Kaneda, R. Takahashi, Y. Iitaka, and S. Shibata, *Tetrahedron Lett.*, 4609 (1972).
- F. W. Comer, F. McCapra, I. H. Qureshi, and A. I. Scott, *Tetrahedron*, **23**, 4761 (1961).
- S. Takahashi, H. Naganawa, H. Yinuma, T. Takita, K. Maeda, and H. Umezawa, *Tetrahedron Lett.*, 1955 (1971).
- L. H. Zalkow, R. N. Harris III, D. Van Derveer, and J. A. Bertrand, *J. Chem. Soc., Chem. Commun.*, 456 (1977).
- U. Weiss and J. M. Edwards, *Tetrahedron Lett.*, 4885 (1968); S. Yang-Lan, M. Mueller-Johnson, J. Oehdrich, D. Wichman, J. M. Cook, and U. Weiss, *J. Org. Chem.*, **41**, 4053 (1976).
- D. Yang and J. M. Cook, *J. Org. Chem.*, **41**, 1903 (1976); R. Weber and J. M. Cook, *Can. J. Chem.*, in press.
- J. Oehdrich, J. M. Cook, and U. Weiss, *Tetrahedron Lett.*, 4549 (1976).
- M. D. Soffer, R. A. Stewart, J. C. Cavanaugh, H. E. Gellerson, and E. A. Bowler, *J. Am. Chem. Soc.*, **72**, 3704 (1950).
- 4**: bp 135–138 °C at 0.06 mmHg; IR (neat) 2980, 1730, and 1710 cm^{-1} ; NMR (CDCl_3) δ 1.20 (6 H, t, $J = 7$ Hz), 2.20 (3 H, s), 3.15 (4 H, s), 4.05 (4 H, q, $J = 7$ Hz), 5.10 (2 H, s), and 7.30 (5 H, s); M^+ at m/e 364.
- J. D. Hobson, J. Raines, and R. J. Whiteoak, *J. Chem. Soc.*, 3495 (1963).
- 5**: bp 95–96 °C at 0.1 mmHg; IR (neat) 2980, 1735, and 1710 cm^{-1} ; NMR (CDCl_3) δ 1.30 (6 H, t, $J = 7$ Hz), 2.65 (3 H, s), 2.55 (4 H, d of d, $J = 6$ Hz), 3.35 (1 H, quin, $J = 6$ Hz), and 4.20 (4 H, q, $J = 7$ Hz); M^+ at m/e 230.
- 6**: oil; IR (neat) 2980, 1735, 1685, 1655, and 1605 cm^{-1} ; NMR (CDCl_3) δ 1.20 (6 t, $J = 7$ Hz), 2.65 (4 H, d of d, $J = 6$ Hz), 3.75 (1 H, quin, $J = 6$ Hz), 4.15 (4 H, q, $J = 7$ Hz), 6.80 (1 H, d, $J = 16$ Hz), 7.45 (5 H, m), and 7.75 (1 H, d, $J = 16$ Hz); M^+ at m/e 318.
- S. Zaheer, I. Zacker, and N. Rao, *Chem. Ber.*, **89**, 351 (1956).
- J. Pappas, W. P. Keaveney, E. Gancher, and M. Berger, *Tetrahedron Lett.*, 4273 (1966).
- 7** as the geminate diol: oil; IR (neat) 3680–3120 (br), 2980, and 1730 cm^{-1} (br); NMR (CDCl_3) δ 1.30 (6 H, t, $J = 7$ Hz), 2.75 (4 H, d of d, $J = 6$ Hz), 3.70 (1 H, quin, $J = 6$ Hz), 4.10 (4 H, q, $J = 7$ Hz), and 7.25 (2 H, s, geminate diol); M^+ at m/e 244.
- 8**: mp 135–137 °C, (CH_3OH); IR (KBr) 3500–2950 (br), 1740–1610 cm^{-1} (br ester and enol absorptions); NMR (CDCl_3) δ 1.25 (6 H, t, $J = 7$ Hz), 2.50 (5 H, m), 3.80 (14 H, 4 \times OCH_3 groups overlapping with two other protons), and 4.05 (4 H, q, $J = 7$ Hz); M^+ at m/e 556.
- No attempts to maximize this yield have been made to date.
- 9**: white solid; mp 180–185 °C (EtOAc); IR (KBr) 3500–2800, 1730, 1710, and 1400 cm^{-1} ; NMR ($\text{Me}_2\text{SO}-d_6$) δ 2.40 (14 H, m) 12.0 (2 H, br s); M^+ at m/e 268.
- P. E. Eaton, C. Giordano, G. Schloemer, and U. Vogel, *J. Org. Chem.*, **41**, 2238 (1976).
- H. Loewenthal and Z. Neuwirth, *J. Org. Chem.*, **32**, 517 (1967).
- Compound **2** was converted to methyl bicyclo[3.3.0]octane-3,7-dione 1-propionate merely on stirring in methanol; recrystallization of **1** was therefore not attempted.
- 1** precipitated from the cumene–diglyme reaction medium and was purified by sublimation in vacuo: mp 288 °C dec; IR (KBr) 2960, 1765 (intense), 1710 (sh, weak), and 1400 cm^{-1} ; M^+ at m/e 232 (100), 204 (4), 190 (13), 170 (5), 163 (20), 162 (33), 161 (16), 149 (5), 148 (7), 147 (6), 137 (12), 136 (34), 135 (21), 134 (25), 122 (18), 121 (17), 120 (15), 105 (28), 94 (12), and 91 (22).
- The parent hydrocarbon, staurane, would belong to the D_{2d} point group.

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