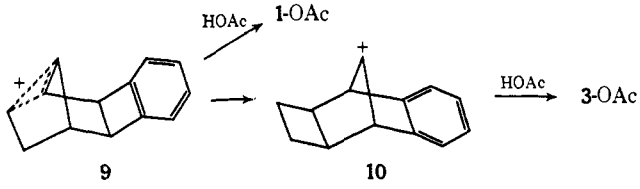
The product situation with regard to **2**-OBs (240°; seven half-lives) was considerably more complex with at least 17 components detected by glpc analysis. Of the various products, five were isolated in pure form by preparative glpc and identified by their spectral properties as **1** (19%), **2** (6%), **3** (28%), 5,6-benzindan[8] (18%), and 5,6-benzindene (2%). Although the acetates **1**-OAc, **2**-OAc, and **3**-OAc are stable to the acetolysis conditions (HOAc containing NaOAc; 240°), considerable charring with resulting variation in the relative yields of the above products occurred on prolonged heating of the actual acetolysis solution.

The formation of **3** from **1**-OBs requires a double Wagner–Meerwein rearrangement with ion **9** visualized as the first intermediate. This ion may either react with solvent to give retained acetate or rearrange further *via* a phenonium ion shift to give the more stable benznorbornenyl ion **10**. Although it is unlikely that



9 10

10 is formed concertedly from **1**-OBs, it is conceivable that formation of ion **9** is electronically assisted by overlap of the incipient p orbital at C-1 with the π orbitals of the aromatic ring.[9]

Acknowledgment. Financial support of this work by the Air Force Office of Scientific Research and the National Science Foundation is gratefully acknowledged.

(8) S. C. Sen-Gupta, *Current Sci.*, **5**, 133 (1936); *Chem. Abstr.*, **31**, 5789 (1937).

(9) Mechanistic speculation on the origin of products obtained from **2**-OBs is not warranted at this time, although it is reasonable to assume that **1**-OAc and **3**-OAc are formed after leakage to **9** from an ion originally generated by backside participation of the C-1–C-2 bond in the ionization step.

(10) Alfred P. Sloan Foundation Fellow, 1967–1969.

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Received July 22, 1969

Synthesis of Chlorobiumquinone

Sir:

The isolation and characterization of chlorobiumquinone as a 2-methyl-3-(1′-alkenyl)-1,4-naphthoquinone (**1**), $C_{45}H_{62}O_2$, has been reported.[1] Subsequently mass spectrometry established the molecular weight as 662, requiring 28 mass units more than in the proposed structure. Based on similar mass spectral observations and similarity in the uv of chlorobiumquinone and 2-acetyl-1,4-naphthoquinone, a 1′-oxomenaquinone-7 (**2**), $C_{46}H_{62}O_3$, structure was proposed for chlorobiumquinone.[2] Although uv analogies in this series can be misleading (*e.g.*, the close similarity of vinylquinones[3] to chlorobiumquinone), nevertheless structure **2** is reasonable for chlorobiumquinone. We have turned to synthesis for proof and now report the synthesis of both **1** and **2**, utilizing as a common side-chain intermediate *all-trans*-farnesylfarnesylacetone (**20**).[4]

Geraniol (**4**)[5] was converted to geranylacetone (**5**),[6] homogeneous by glpc,[7b,8] and treatment with ethylene glycol and *p*-toluenesulfonic acid in benzene afforded ethylene ketal **6**. Selective epoxidation of the terminal double bond of **6** was achieved using N-bromosuccinimide[9] to give the bromohydrin **7** followed by KOH–methanol to give epoxide **8** in 79% yield. The nmr spectrum showed six methyl hydrogens at δ 1.2 and 1.23 (s), three methyl hydrogens on a *trans* double bond at 1.64, and one α-epoxy hydrogen at 2.62 (t, J = 7 Hz).[10]

Treatment of **8** with acetic acid–sodium acetate–acetic anhydride (8:1:1) gave the monoacetate **9** in 77% yield; nmr δ 2.08 (s, 3), 4.86 (b, 1), consistent with the acetate ester being at C-9. Hydrolysis in KOH–methanol gave glycol **10** (87% yield) which was cleaved to aldehyde **11** (97% yield) with sodium periodate in aqueous dioxane; δ 10.45 (t). Reduction of aldehyde **11** with sodium borohydride gave alcohol **12** in 43% overall yield from ethylene ketal **6**. Alternatively alcohol ethylene ketal **12** was obtained from diene ketal **6** in methanol at −78° with 1 equiv of O_3 followed by reduction with sodium borohydride–sodium hydroxide.[11] The desired alcohol **12** was obtained in 25% yield after separation of the complex product mixture and was homogeneous by glpc;[7a] nmr: two methylene hydrogens at δ 3.5 (t, J = 6 Hz), three methyl hydrogens on a *trans* double bond at δ 1.62.

Alcohol **12** was converted to *p*-toluenesulfonate **13**, iodoketal **14**, and triphenylphosphonium salt **15** by standard procedures. The ylide **16** was generated from salt **15** in dimethyl sulfoxide by addition of butyllithium and allowed to react with ketone **5** at 25°. Geranylgeranylacetone ethylene ketal (**17**) was isolated in 73%

(4) G. I. Samokhalov and E. A. Obol'nikova, *Usp. Khim.*, **36**, 413 (1967), and references therein.

(5) A generous gift of Givaudan Corp.

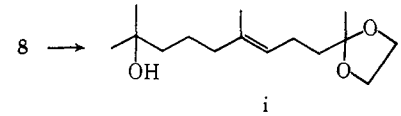
(6) O. Isler, R. Ruegg, L. Chopard-dit-Jean, H. Wagner, and K. Bernhard, *Helv. Chim. Acta*, **39**, 897 (1956).

(7) Glpc analyses were performed on (a) 30% QF-1 on acid-washed, DMCS-treated, 60–80 Chromosorb P, 10 ft × 0.25 in.; (b) 20% Carbowax 20 M on 60–80 Firebrick, 10 ft × 0.25 in.; (c) Apiezon J on 60–80 Chromosorb P, 5 ft × 0.25 in.; (d) Apiezon L, capillary column, 100 ft × 0.1 mm.

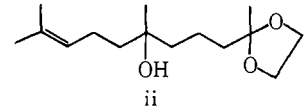
(8) Satisfactory elemental analyses and confirmatory mass spectral data were obtained for all compounds. Structures assigned are consistent with ir and nmr spectra (δ values in $CDCl_3$) and homogeneity was established by glpc[7] and tlc (ethyl acetate–benzene on Kiesel Gel G). All final purifications were by column chromatography on silica gel, eluting with ethyl acetate–benzene.

(9) E. E. van Tamelen and T. J. Curphey, *Tetrahedron Letters*, 121 (1962); E. E. van Tamelen and K. B. Sharpless, *ibid.*, 2655 (1967).

(10) The isomeric purity of **8** was established by conversion to i with lithium aluminum hydride in tetrahydrofuran [H. C. Brown, P. M Weissman, and N. M. Yoon, *J. Am. Chem. Soc.*, **88**, 1458 (1966)] and glpc[7a] comparison of the trimethylsilyl ether with the ethers of a mixture of i and ii.



i



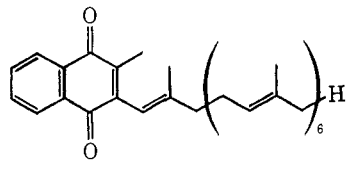
ii

(11) C. G. Overberger and H. Kaye, *ibid.*, **89**, 5640 (1967).

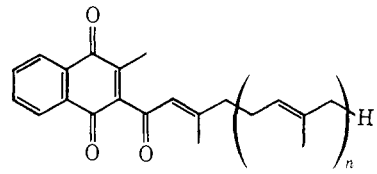
(1) B. Frydman and H. Rapoport, *J. Am. Chem. Soc.*, **85**, 823 (1963).

(2) R. Powls, E. R. Redfearn, and S. Trippett, *Biochem. Biophys. Res. Commun.*, **33**, 408 (1968); R. Powls and E. R. Redfearn, *Biochim. Biophys. Acta*, **172**, 429 (1969).

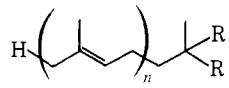
(3) W. E. Bondinell, S. J. Di Mari, B. Frydman, K. Matsumoto, and H. Rapoport, *J. Org. Chem.*, **33**, 4351 (1968).



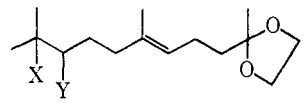
1



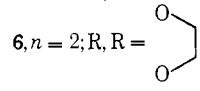
2, $n = 6$
3, $n = 1$



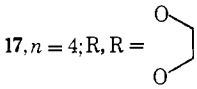
5, $n = 2$; R, R = =O



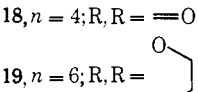
7, X = OH; Y = Br
8, X, Y = >O
9, X = OH; Y = OAc
10, X = Y = OH



6, $n = 2$; R, R =

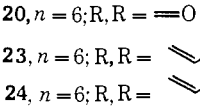


17, $n = 4$; R, R =



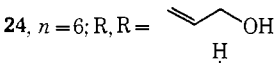
18, $n = 4$; R, R = =O

19, $n = 6$; R, R =

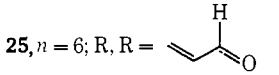


20, $n = 6$; R, R = =O

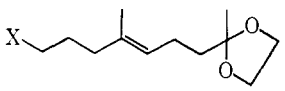
23, $n = 6$; R, R =



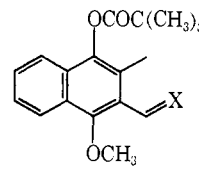
24, $n = 6$; R, R =



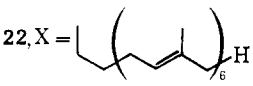
25, $n = 6$; R, R =



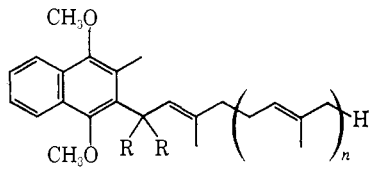
11, X = =O
12, X = OH
13, X = OTs
14, X = I
15, X = $P(C_6H_5)_3^+$
16, X = =$P(C_6H_5)_3$



21, X = $P(C_6H_5)_3$



22, X =



26, $n = 6$; R, R = H, OH
27, $n = 6$; R, R = =O
28, $n = 1$; R, R = =O

yield after chromatography followed by molecular distillation at 70° (3 mm) to remove unreacted **5** (17%) and then at 110° (20 μ). The ketal was a 3:2 mixture of *cis* and *trans* Δ^9 isomers by glpc[7c] comparison with the pure isomers. *all-trans*-**17** was obtained in 21% yield from the mixture (as well as 41% of Δ^9-mono-*cis*-**17**) by thiourea inclusion from methanol.[12] Hydrolysis with phosphoric acid in aqueous acetone gave a 97% yield of *all-trans*-geranylgeranylacetone (**18**).[13]

Reaction of *all-trans*-geranylgeranylacetone (**18**) with ylide **16** gave farnesylfarnesylacetone ethylene ketal (**19**) (74% yield) as a 3:2 mixture of *cis* and *trans* Δ^9 isomers by glpc.[7d] *all-trans*-**19** was isolated from the mixture in 39% yield by thiourea inclusion (along with 59% of Δ^9-mono-*cis*-**19**) and hydrolyzed quantitatively to give *all-trans*-farnesylfarnesylacetone (*all-trans*-**20**).

Reaction of *all-trans*-farnesylfarnesylacetone (**20**) with excess ylide **21**[3] for 72 hr in refluxing toluene gave a mixture of *cis*- and *trans*-**22** (50% yield) which was treated with lithium aluminum hydride to cleave the pivalate ester. The resulting hydroquinone monomethyl ether was oxidized with ferric chloride, giving a mixture of *cis*- and *trans*-**1**, purified by tlc; uv $\lambda_{max}^{isooctane}$ 248 nm (ϵ 23,000), 264 (14,000), 280–350 (3370); ir (neat) 1660, 1596, 1578 cm^{-1}; mass spectrum (70 eV) *m/e* 634 (M^+).[14]

To effect the synthesis of **2**, *all-trans*-C_{33}-ketone **20** was extended two carbon atoms by condensation with triethyl phosphonoacetate, yielding α,β-unsaturated ester **23** with a *cis*:*trans* ratio of 3:7 at the Δ^2 position. Crude ester **23** was reduced ($LiAlH_4$–$AlCl_3$) to C_{35}-allylic alcohol **24** which was then oxidized with manganese dioxide to α,β-unsaturated aldehyde **25** obtained pure as the *cis*–*trans* mixture in 50% overall yield from ketone **20**.

2-Methyl-3-lithio-1,4-dimethoxynaphthalene, prepared by transmetalation of 2-methyl-3-bromo-1,4-dimethoxynaphthalene[15] and butyllithium, was condensed with aldehyde **25** to give the allylic alcohol **26** which upon heating in chloroform with manganese dioxide was oxidized to hydroquinone dimethyl ether **27**, in 60% yield from **25**. Chromatography effected resolution into pure *cis* and *trans* components (1:2.5).

Converting hydroquinone dimethyl ester **27** to quinone **2** was accomplished by a facile oxidative demethylation[16] utilizing argentic oxide in dioxane–phosphoric acid.[17] Model oxidations using the simpler isoprenolog **28** prepared as above starting with citral established that the reaction proceeded essentially with retention of stereochemistry about the $\Delta^{2'}$ position as assayed by nmr ($COC{=}CCH_3$: *trans*, δ 2.24; *cis*, δ 1.93). Pure *trans*-**28** yielded quinone **3** containing 5% of the *cis* isomer while *cis*-**28** gave *cis*-quinone **3** containing 15% *trans* material. The *cis*- and *trans*-hydroquinone dimethyl ethers **27** were oxidized separately yielding quinones **2**, which were purified by column chromatography and obtained stereochemically pure (as assayed with tlc) by recrystallization from petroleum ether; *trans*-**2**: mp 50°; uv $\lambda_{max}^{isooctane}$ 250 nm (ϵ 32,000), sh 245 (31,000), sh 255 (31,000), sh 265 (22,000), 325 (3000); ir (neat) 1660, 1610, 1595 cm^{-1}; nmr δ 1.58 (b, $=CCH_3-$), 1.93 (b, $-CH_2CH_2$), 2.08 (s, $ArCH_3$), 2.28 (d, J = 2 Hz, $COC{=}CCH_3-$), 5.05 (b, $-CH{=}$), 6.15 (b, $COCH{=}$), 7.8 (m, ArH); mass spec-

(12) R. W. Schiessler and D. Flitter, *J. Am. Chem. Soc.*, 74, 1720 (1952).

(13) Identical with a sample kindly supplied by Hoffmann-LaRoche and prepared by a different procedure.

(14) Nmr of *cis,trans*-**1**: δ 2.05 (m, $ArCH_3$, *trans*-$ArC{=}CCH_3$, *cis*-$ArC{=}CCH_2CH_2-$), 2.3 (unsym d, *trans*-$ArC{=}CCH_2CH_2-$), 6.00 (b, *cis*-$ArCH{=}$), 6.15 (b, *trans*-$ArCH{=}$).

(15) R. Adams, T. A. Geissman, B. R. Baker, and H. M. Teeter, *J. Am. Chem. Soc.*, 63, 528 (1941).

(16) This mild reaction which easily accomplishes a previously difficult demethylation of the hydroquinone dimethyl ether will be the subject of a future publication.

(17) L. Syper, *Tetrahedron Letters*, 4193 (1967).

trum: *m/e* (rel intensity) 664 ($M^+ + 2$, 7), 662 (M^+, 2), 241 (44), 201 (57), 200 (65), 81 (44), 69 (100). *Anal.* Found: C, 83.1; H, 9.3.

The ir, uv,[18] and nmr[19] spectra of chlorobiumquinone, *cis,trans*-**1**, and *trans*-**2** were very similar. The mass spectra of chlorobiumquinone and *trans*-**2** were superimposable, whereas that of *cis,trans*-**1** was distinctly different, possessing a molecular ion at *m/e* 634. Tlc confirmed the dissimilarity of chlorobiumquinone and *cis,trans*-**1** while *trans*-**2** was coincident with the natural material. Therefore, chlorobiumquinone is *all-trans*-1′-oxomenaquinone-7 (**2**).

(18) Although the uv spectra of chlorobiumquinone and 1′-oxomenaquinone-7 are qualitatively identical, a quantitative disparity exists; that is, we find an extinction coefficient at 250 nm of 32,000 *vs.* a reported value of 16,000.[1] A possible explanation is that this quinone series is particularly photolabile and exposure of spectrophotometric solutions to laboratory light even briefly before measurement could effect such a diminution.

(19) Whereas the nmr spectrum of *trans*-**2** and that reported[1] for chlorobiumquinone are identical, there is a discrepancy with the assignments reported in ref 2, where the ring methyl and conjugated vinyl methyl absorptions have been reversed. These assignments will be discussed in detail in our full paper.

(20) National Institutes of Health Predoctoral Fellow.

(21) This research was supported in part by Grant AI-04888 from the National Institutes of Health, U. S. Public Health Service.

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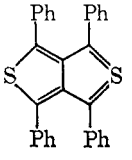
Department of Chemistry, University of California
Berkeley, California 94720
Received August 29, 1969

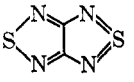
The Synthesis of Two Nonclassical Thienothiadiazoles

Sir:

Recently, syntheses of the stable nonclassical ten-π-electron heterocycles tetraphenylthieno[3,4-*c*]thiophene (**1**)[1] and 1,2,5-thiadiazolo[3,4-*c*]-1,2,5-thiadiazole (**2**)[2] have been described. These compounds are of considerable interest because of the unusual tetracovalent sulfur bonding found in them. In this regard, we wish to describe the preparation of 2,5-diphenylthieno[3,4-*c*]-1,2,5-thiadiazole (**3**) and the generation of 2,5-diphenylthieno[3,4-*e*]-2,1,3-benzothiadiazole (**4**), two novel sulfur-containing heterocyclic systems which are electronically similar to both thiophene **1** and thiadiazole **2**.



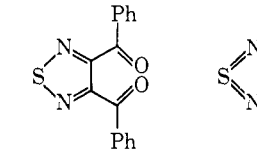
1



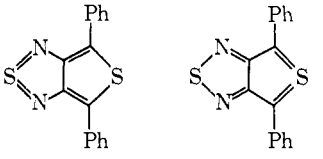
2

Treatment of 3,4-dibenzoyl-1,2,5-thiadiazole (**5**)[3] with phosphorus pentasulfide in dioxane solution at 110° for 5 hr gave heterocycle **3** as brilliant purple needles (mp 146°, 78% yield).[4] Heterocycle **3** shows ultraviolet and visible absorption maxima at $\lambda_{max}^{CH_2Cl_2}$ 275 nm (ϵ 16,700), 312 (21,600), 330 (19,900), and 558 (8650). The nmr spectrum of **3** closely resembles that of diketone **5** with proton resonance appearing as two complex multiplets centered at δ 7.5 (3 H) and 8.2 (2 H), suggesting that the phenyl substituents lie in the plane of the thienothiadiazole ring system. An extremely simple mass spectrum of the heterocycle was obtained with peaks at *m/e* 294 (100%, parent ion of **3**) and 121 (30%, ion of C_7H_5S).

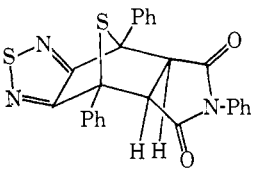
Heterocycle **3** undergoes a sluggish Diels–Alder reaction at 140° with N-phenylmaleimide giving rise in 71% yield to a 2:1 mixture of the adducts **6** and **7**, respectively. The *exo* adduct **6**, mp 217°, shows a sharp singlet resonance for the two protons α to the imide carbonyl groups at δ 4.8, while the *endo* adduct **7**, mp 213°, exhibits singlet resonance for these protons at δ 3.8.[5] Both **6** and **7** undergo retro-Diels–Alder fragmentation on electron impact.



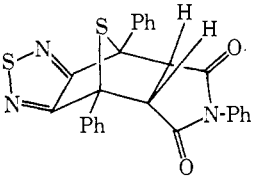
5



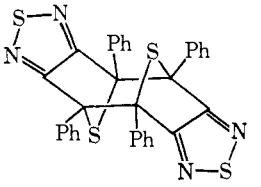
3



6



7



8

Irradiation of 0.1 *M* solutions of the heterocycle in rigorously degassed methylene chloride gave the insoluble white crystalline dimer, **8**, mp 100° dec (30% yield), along with unreacted **3** (68% yield). This result is in marked contrast to other stable tetracovalent sulfur systems which have been found to be photochemically inert under these conditions.[6] The ultraviolet and infrared spectra of the dimer show only the presence of a thiadiazole ring system. Compound **8** gives the correct parent ion (*m/e* 588) in the mass spectrum with the major fragment representing retrodimerization into heterocycle **3**.[7] In addition, thermal cracking of the dimer readily occurs in a variety of organic solvents when gently warmed.

Heterocycle **4** has been prepared starting from the readily available 5,6-dimethyl-2,1,3-benzothiadiazole (**9**).[8] Bromination of **9** with N-bromosuccinimide in

(1) M. P. Cava and G. E. M. Husbands, *J. Amer. Chem. Soc.*, **91**, 3952 (1969).

(2) M. Carmack, R. W. Street, and R. Y. Wen, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, Abstract ORGN-54.

(3) L. M. Weinstock and P. I. Pollak, *Advan. Heterocyclic Chem.*, **9**, 136 (1968).

(4) All melting points are uncorrected. Satisfactory analyses were obtained for all new compounds.

(5) For a detailed discussion relating the chemical shifts of these protons to conformation in similar adduct systems, see ref 1.

(6) For examples, see I. S. Ponticello and R. H. Schlessinger, *J. Amer. Chem. Soc.*, **90**, 4190 (1968).

(7) The geometric assignment given to the dimer (head to tail) must be considered tentative.

(8) V. G. Pesin, V. A. Sergeev, and A. M. Khaletskii, *J. Gen. Chem. USSR*, **34**, 1261 (1962).