internal standard, and 7.6 mL of anhydrous diethyl ether. To the resulting solution was added 1.2 g (12 mmol) of 4-methoxy-3-buten-2-one.[7] The reaction mixture was stirred for 24 h at 25 °C and then quenched with 0.61 g (10 mmol) of ethanolamine. A precipitate of 9-BBN-ethanolamine adduct was formed almost immediately. After the resulting slurry was stirred for 1 h, the reaction mixture was centrifuged. Analysis of the supernatant by GC revealed that *trans,trans*-3,5-tridecadien-2-one was formed in 100% yield.[8] The supernatant was decanted from the solid and the volatiles were removed in vacuo. There remained 1.85 g (95%) of *trans,trans*-tridecadien-2-one, >95% pure by GC.[8] An analytically pure sample was obtained by preparatory GC:[8] IR (neat) 1685, 1667, 1630, 1592, 1250, 995 cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.6–1.0 (t, 3 H), 1.0–2.0 (m, 10 H), 1.9–2.4 (m, 2 H), 2.23 (s, 3 H), 5.9–6.3 (m, 3 H), 6.9–7.3 (m, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 198.34, 145.57, 143.85, 129.01, 128.89, 33.20, 32.28, 31.89, 29.22, 28.86, 27.12, 22.70, 14.08; exact mass calcd for $C_{13}H_{22}O$ 194.167, found 194.167.

An exploratory experiment under the same conditions attempting to utilize the organoborane from 3-hexyne and 9-BBN failed to yield the desired product. We did not attempt to force the reaction by utilizing more drastic conditions.

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(7) The reagent is available from Aldrich Chemical Co., distilled prior to use, bp 70 °C (15 mmHg).

(8) GC analyses were carried out with a Hewlett-Packard 5750 chromatograph using a 6 ft × 0.25 in. column packed with 10% SE-30 on Chromosorb W. For preparative GC, a 6 ft × 0.5 in. column packed with 10% SE-30 on Chromosorb W was used.

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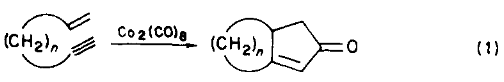
Synthesis of the Angularly Fused Triquinane Skeleton via Intramolecular Organometallic Cyclization

Summary: Preparation and cyclization of 5-pentynyl-1-cyclopentene to tricyclo[6.3.0.0^{4,8}]undec-1-en-3-one with $Co_2(CO)_8$ followed by conversion to a bisnorisocomene are described. Isocomene itself is not accessible in reasonable yield by this route, however.

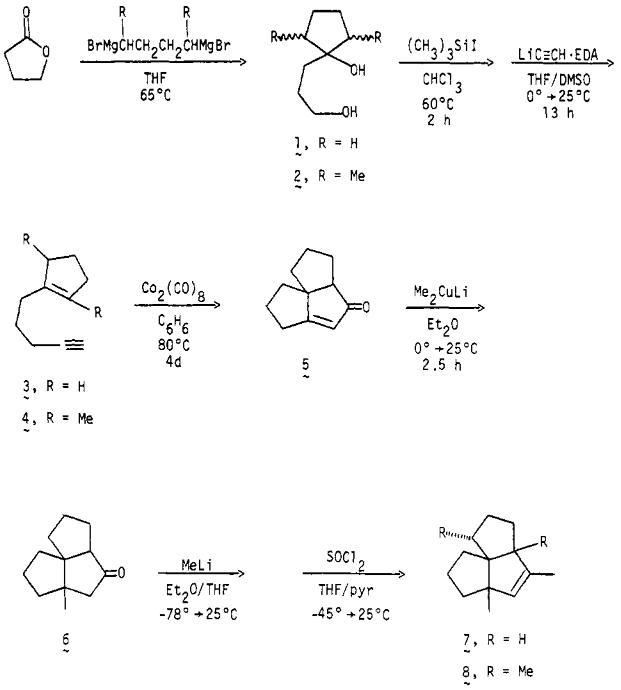
Sir: In 1981 we reported[1] the first intramolecular examples (eq 1) of the $Co_2(CO)_8$-promoted cyclopentenone preparation discovered a decade ago by Pauson and Khand.[2]



(1)

Very recently Magnus and co-workers have described the elaboration of this methodology to the total synthesis of coriolin, a linearly fused triquinane.[3] We report herein the first attempts to extend this process to the *angularly* fused triquinane system, using synthetic schemes *which completely avoid the use of carbocyclic starting materials.* Scheme I illustrates the overall sequence that was examined as an approach to the synthesis of the natural product isocomene (8).[4,5]

Scheme I



Diol 1 was prepared in 88% yield from butyrolactone via a literature process.[6] Initial attempts to convert 1 to 3 involved conversion to 1-(3-chloropropyl)cyclopentene with CCl_4/PPh_3, followed by reaction with lithium acetylide–EDA complex in Me_2SO. Low yields (<30%) in the first reaction led us to try the procedure shown. Thus 1 (3.22 g) was added to excess Me_3SiI (from 22.88 g of I_2 and 9.63 mL of hexamethyldisilane) in $CHCl_3$ (100 mL), yielding 7.95 g (98%) of a mixture of diiodide and iodoalkenes,[7] which was treated directly with lithium acetylide–EDA (5.42 g) in 1:1 THF/Me_2SO (40 mL). Enyne 3 was isolated in 38% yield (1.28 g), together with 5% of its exocyclic olefin isomer.

Treatment of 3 (1.63 g) with $Co_2(CO)_8$ (5.03 g) in C_6H_6 (40 mL) yielded enone 5 (0.70 g, 35%), a colorless oil showing IR bands at 1630 and 1690 cm^{-1}, and a singlet in the 360-MHz H^1 NMR at δ 5.82. This is therefore the first example of the generation of a quaternary carbon at a multiple ring fusion via this sort of methodology. Addition of 5 (0.12 g) to the reagent prepared from CuI (0.65 g) and MeLi (6.8 mmol) in ether (20 mL) afforded 6 (0.12 g, 90%). Characterization of the latter rests partially on spectroscopic comparisons with the dimethyl derivative prepared by Pirrung[8] (compound 8 in that reference). Both have

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(1) Schore, N. E.; Croudace, M. C. *J. Org. Chem.* **1981**, *46*, 5436.

(2) Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E.; Foreman, M. I. *J. Chem. Soc., Perkin Trans. 1*, **1973**, 977.

(3) Exon, C.; Magnus, P. *J. Am. Chem. Soc.* **1983**, *105*, 2477.

(4) Isolation: Zalkow, L.; Harris, R.; Van der Veer, D.; Bertrand, J. *J. Chem. Soc., Chem. Commun.* **1977**, 456. Bohlmann, F.; LeVan, N.; Pickardt, J. *Chem. Ber.* **1977**, *110*, 3777.

(5) Syntheses: Paquette, L.; Han, Y. K. *J. Org. Chem.* **1979**, *44*, 4014. Pirrung, M. C. *J. Am. Chem. Soc.* **1979**, *101*, 7130. Oppolzer, W.; Bättig, K.; Hudlicky, T. *Helv. Chim. Acta* **1979**, *62*, 1493.

(6) Canonne, P.; Foscolos, G. B.; Bélanger, D. *J. Org. Chem.* **1980**, *45*, 1828. This route is far superior to approaches involving addition of organometallics to cyclopentenone.

(7) A 3.26:1.00:1.05 mixture of 1-(3-iodopropyl)-1-iodocyclopentane, 1-(3-iodopropyl)cyclopentene, and (3-iodopropylidene)cyclopentane, by 360-MHz NMR.

0022-3263/84/1949-5025$01.50/0

IR bands at 1730 cm^{-1}. In the NMR spectrum, **6** shows a methyl singlet δ 1.08 and an AB pattern (δ 2.27, J = 18 Hz) for the methylene adjacent to the ketone; the Pirrung compound shows similar signals at δ 1.10 and 2.27 (J = 17 Hz). Ketone **6** also displays a signal at δ 2.31 (dd, J = 5, 11 Hz) for the methine on the other side of the carbonyl group.

Completion of the synthesis of **7** proceeds in a straightforward manner with addition of **6** (0.085 g) to MeLi (1.6 mmol) in THF (25 mL) to produce a mixture of tertiary alcohols (0.085 g, 91%), of which 0.066 g was converted without further purification to **7** by treatment with $SOCl_2$ (0.83 g) in 2:1 THF/pyridine (1.5 mL). The yield of **7** (a "bisnorisocomene") was 66% (0.052 g). The NMR spectrum of **7** is virtually identical with that of isocomene itself,[8] save for the absence of two high-field methyl signals and the presence of a broad doublet (J = 9 Hz) at δ 2.46 for the ring-fusion proton (cf. NMR of pentalenene[9]). A 28% yield of the exocyclic olefin isomer was also formed. As this pathway from **6** to **7** would not actually be applicable to isocomene itself,[8] no attempt at optimization of either yield of isomer ratio was made.

Adaptation of this general synthetic scheme to isocomene requires (1) that **4** be accessible in a manner similar to **3**, (2) that cyclization of **4** proceed satisfactorily to a dimethyl analogue of **5**, and (3) that the dimethyl analogue of **6** be convertible in some way to **8**.[10] Synthesis of **4** in fact proceeds quite satisfactorily. Addition of the bis-Grignard of 2,5-dibromohexane[11] to butyrolactone gave an 86% yield of isomeric diols **2**, which were converted via the two-step procedure shown to enyne **4** in 27% overall yield.[12] At this stage several attempts to effect cyclization of **4** with $Co_2(CO)_8$ were made without success. Even though suggestive spectroscopic (IR, NMR) evidence for a cyclopentenone moiety was reproducibly obtained in every run, the compound(s) responsible could not be isolated in pure form and, in any event, were present only in the most miniscule quantities. With the successful cyclization of **3**, therefore, we have reached the apparent practical limit of this reaction to overcome steric and strain-related obstacles to the ring-closure process. The capabilities of the reaction are nevertheless still quite intriguing, since the modest yields of the original model reactions (eq 1) have been found to be greatly enhanced by remote substitution (Thorpe–Ingold effect[1,3]). Given the methodological efficiency of this process, which is now shown to be capable of converting inexpensive and essentially acyclic precursors to complex tricyclics in as few as four steps, we are currently involved in developing approaches to related systems[9,13] which will utilize these features to the greatest advantage.

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Supplementary Material Available: Spectroscopic and analytical data for all new compounds (2 pages). Ordering information is given on any current masthead page.

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(8) Pirrung, M. C. *J. Am. Chem. Soc.* **1981**, *103*, 82.

(9) Paquette, L. A.; Annis, J. D. *J. Am. Chem. Soc.* **1983**, *105*, 7358.

(10) (a) Simple Wittig methylenation (Ph_3PCH_2/Me_2SO) is compatible with both highly hindered cyclohexanones[8] and cyclopentanones.[10b] (b) Lund, E. C.; Schore, N. E., unpublished results.

(11) Kornblum, N.; Eicher, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2259.

(12) Enyne **4** has also been synthesized in 84% yield from 2-(3-chloropropyl)-1,3-dimethylcyclopentene. The latter, unfortunately, is only available in minute (ca. 1–2%) yields from CCl_4/PPh_3 treatment of **2**.

(13) Paquette, L. A.; Galemmo, R. A., Jr.; Springer, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 6975 and references therein.

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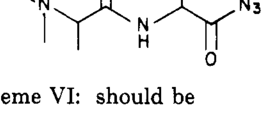
Additions and Corrections

Ruth F. Nutt, Kau-Ming Chen, and Madeleine M. Joullié*. Synthesis of Dihydromauritine A, a Reduced Cyclopeptide Alkaloid.

Page 1014. Structure **1a**, **1b**: a H is missing from ring NH.

Page 1015. Compounds **13a,b**, **15a,b**: an extra bond in the heterocyclic ring should be deleted. Second column, line 18. product **10b** should be **10a**.

Page 1016. Scheme IV, structure **21**: a carbonyl group is missing:



Page 1017. Scheme VI: should be

$$\mathbf{29} \xrightarrow{\text{pH 12}} \mathbf{31}$$

Page 1018. Structures **1b**, **1c**: NH is missing from the ring.

Alan P. Kozikowski* and Arun K. Ghosh. Diastereofacial Selection in Nitrile Oxide Cycloaddition Reactions. The Anti-Directing Effect of an Allylic Oxygen and Some New Results on the Ring Metalation of Isoxazolines. A Synthesis of (±)-Blastmycinone.

Page 2771.

Acknowledgment

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