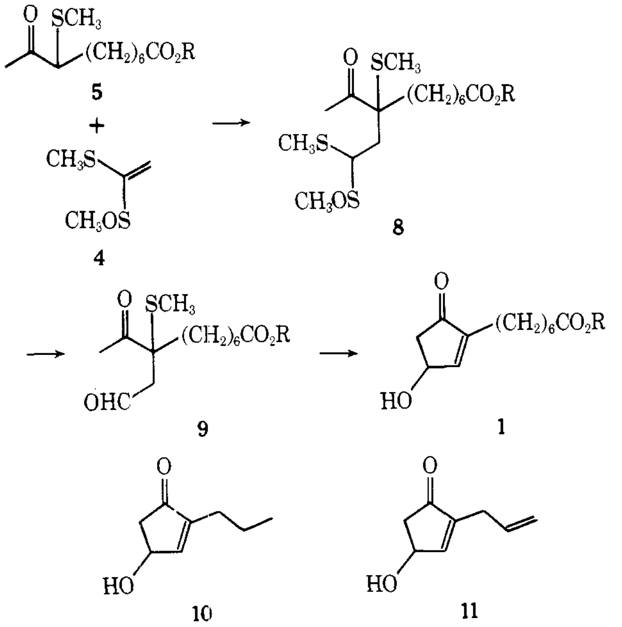

R = $CH_3$ or *t*-Bu

lithium hydroxide (2 equiv) and Adogen 464 (1 equiv)[9] at 40 °C for 20 min. Evaporation of the benzene solution gave a colorless oil which on vaccum filtration through silica gel followed by crystallization from ether/petroleum ether afforded pure 1 (R = $CH_3$, mp 45.5–47.5 °C)[10] in 55% overall yield from 5.[11] The identical reaction sequence gives an overall yield of 50% for 1 where R = *t*-Bu (oil). In addition, the hydroxycyclopentenones 10 and 11 have been prepared by this method in overall yields of 70 and 50%, respectively.

We intend to prepare other hydroxycyclopentenones related to 1 using this technically simple reaction sequence.

**Acknowledgment.** We thank the National Institutes of Health and the Hoffmann La-Roche Corporation for support of this work.

**Supplementary Material Available:** Experimental procedures for reactions described (6 pages). Ordering information is given on any current masthead page.

## References and Notes

(1) For leading references on the preparation and use of hydroxycyclopentenones in prostaglandin synthesis, see A. F. Kluge, K. G. Untch, and J. H. Fried, *J. Am. Chem. Soc.*, **94,** 9256 (1972); C. H. Sih, J. B. Heather, G. P. Perruzzoti, P. Price, R. Snood, and L. F. H. Lee, *ibid.*, **95,** 1676 (1973); J. G. Miller, W. Kurz, K. G. Untch, and G. Stork, *ibid.*, **96,** 6774 (1974); and G. Stork, C. Kowalski, and G. Garcia, *ibid.*, **97,** 3258 (1975).
(2) A similar synthetic strategy has been outlined for the preparation of rethrolone systems by R. F. Romanet and R. H. Schlessinger, *J. Am. Chem. Soc.*, **96,** 3701 (1974).
(3) For a preparation of this compound amenable to large-scale application, see J. L. Herrmann, G. R. Kieczykowski, R. F. Romanet, P. J. Wepplo, and R. H. Schlessinger, *Tetrahedron Lett.*, 4711 (1973).
(4) Prepared by reaction of *tert*-butyl acetate with lithium diisopropylamide as described by R. J. Cregge, J. L. Herrmann, C. S. Lee, J. E. Richman, and R. H. Schlessinger, *Tetrahedron Lett.*, 2425 (1973).
(5) The conversion of 6 (X = Br) into 6 (X = I) was accomplished using sodium iodide in acetone. Satisfactory spectral and physical data were obtained for all new compounds with reported boiling points or melting points. The preparation of these *tert*-butyl esters has also been reported by D. A. Evans, T. C. Crawford, T. T. Fujimoto, and R. C. Thomas, *J. Org. Chem.*, **39,** 3176 (1974).
(6) The imine analogue of 7 (bp 62 °C at 0.2 Torr) was prepared from thiomethylacetone and cyclohexylamine by azeotropic distillation in benzene containing *p*-toluenesulfonic acid. A preparation of thiomethylacetone has been reported by C. K. Bradsher, F. C. Brown, and R. J. Grantham, *J. Am. Chem. Soc.*, **76,** 114 (1954). The lithium salt 7 was generated using lithium diisopropylamide as the base. For examples of lithium imine salts in alkylation reactions, see G. Stork and J. Benaim, *ibid.*, **93,** 5938 (1971), and references cited therein.
(7) The yield of this compound was determined by NMR and no attempt was made to purify the material.
(8) For an excellent review of phase-transfer reactions, see E. V. Dehmlow, *Angew. Chem., Int. Ed. Engl.*, **13,** 170 (1974).
(9) Available from the Aldrich Chemical Co., Inc.
(10) Literature mp 48–49. 5 °C reported by F. S. Alvarez, D. Wren, and A. Prince, *J. Am. Chem. Soc.*, **94,** 7823 (1972).
(11) We thank Dr. K. G. Untch of the Syntex Research Institute for a generous sample of racemic compound 1 (R = $CH_3$).
(12) Sherman-Clarke fellow of the University of Rochester and Hooker fellow of the University of Rochester.
(13) Postdoctorate associate supported by NIH grant HL 17341.
(14) Hooker fellow of the University of Rochester.

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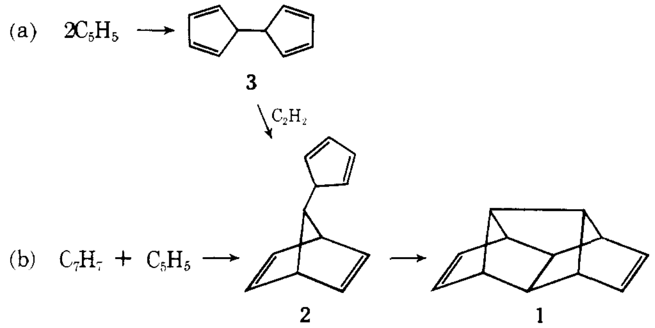
## The Reaction of 7-Chloronorbornadiene with Thallium Cyclopentadienide. A Convenient One-Step Synthesis of Hexahydro-3,4,7-methenocyclopenta[*a*]pentalene[1]

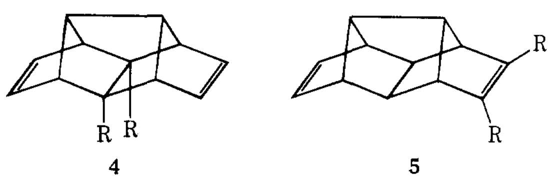
*Summary:* The thermally promoted reaction of thallium cyclopentadienide with 7-chloronorbornadiene provides a convenient, single-stage, preparative route to the title hydrocarbon (1) accompanied by minor amounts of dihydro-*as*-indacenes 7–9.

*Sir:* The novel $C_{12}H_{12}$ hydrocarbon, hexahydro-3,4,7-methenocyclopenta[*a*]pentalene (1),[2] may be formally considered to derive from the combination of two cyclopentadienyl ($C_5H_5$) residues with acetylene ($C_2H_2$) or alternatively from the coupling of 7-norbornadienyl ($C_7H_7$) and cyclopentadienyl ($C_5H_5$) residues as depicted in Scheme I. Critical to the success of either pathway is the rapid intramolecular [4 + 2] cycloaddition of the intermediate 7-(5-cyclopentadienyl)norbornadiene (2).

Scheme I



In practice the synthetic feasibility of path a has been demonstrated recently by Paquette[2] and Hedaya[3] and their co-workers employing a reactive acetylenic dienophile. Thus, the reaction of preformed 9,10-dihydrofulvalene (3) with dimethyl acetylenedicarboxylate afforded the 1:1 cycloadducts 4 and 5 in 23.2 and 16.8% yield, respectively. By a sequence of reduction, hydrolysis, and oxidative decarboxylation the minor adduct 5 was subsequently converted[2] to the parent diene 1 in an overall yield of 7.3%.[4] In an effort to expedite the synthesis of 1 for further synthetic and mechanistic studies



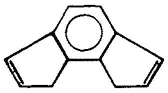
4 5

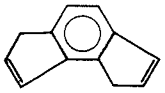
R = $CO_2Me$

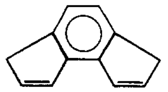
of polyfused cyclopentanoid systems we have examined the preparative value of path b in Scheme I and now wish to report our preliminary findings which detail a convenient one-step synthesis of **1** in 8–12% yield from commercially available starting materials.

Generation of tetraene **2** by path b would appear to require a reaction between 7-norbornadienyl cation and cyclopentadienyl anion; however, for convenience we favored the in situ formation of these reactive partners from appropriately stabilized precursors in a moderately polar aprotic solvent. Thallium cyclopentadienide (TlCp) was chosen as the cyclopentadienyl anion precursor on the basis of thermal stability and possible catalytic role of the metal ion on ionization of a suitable 7-norbornadienyl substrate, e.g., 7-norbornadienyl chloride (**6**-Cl). Accordingly, solutions of **6**-Cl in dry diglyme containing 10–80% molar excess of suspended TlCp were heated at 150 °C for 3–4 h under nitrogen and the reaction products separated from the thallium salts. Chromatography of the crude reaction product on silica gel with pentane afforded an initial fraction containing only diene **1** and dicyclopentadiene, a side product from decomposition of TlCp. Preparative GLC separation afforded pure **1**: $^1$H NMR ($CDCl_3$) $\delta$ 5.79 (t, 4 H, $J$ = 2.0 Hz), 2.85 (q, 4 H, $J$ = 2 Hz), 2.43 (m, 2 H), and 1.80 (t, 2 H, $J$ = 2.2 Hz); $^{13}$C NMR ($CDCl_3$) 49.08, 60.58, 61.64, and 132.51 ppm from TMS; mass spectrum (70 eV) *m/e* (rel intensity) 156 (16.4), 155 (28.6), 154 (4.8), 152 (16.7), 141 (22.2), 128 (20.6), 115 (29.7), 91 (100), and 78 (21.5). The mass spectrum of **1** was unusual in that it indicated successive loss of one, two, and four hydrogen atoms from the parent ion to form a $C_{12}H_8$ ion (accurate mass) which most reasonably has the acenaphthylene structure.

The later pentane fractions from the original silica gel chromatography contained a third material along with minor contaminants which were removed by preparative GLC separation. Analysis of the separated material on a capillary column revealed at least two incompletely separated components in ~1:1 ratio. The proton spectrum ($CDCl_3$) showed an aromatic two proton singlet at $\delta$ 7.16, a set of complex, but sharply defined, two-proton olefinic multiplets at 6.7–7.0 and 6.2–6.6, and a pair of allylic triplets ($J$ = 1.7 Hz) at 3.35 and 3.24 integrating for a total of four protons. This spectrum compares favorably with the published[5] spectrum for a mixture of dihydro-*as*-indacenes **7** and **8** (and possibly **9**). The mass spectrum [70 eV, *m/e* (rel intensity) 154 (82.5), 153 (100), 152 (45.4), 77 (10.8), 76.5 (8.4), and 76 (31.6)] is entirely consistent with this assignment.


**7**

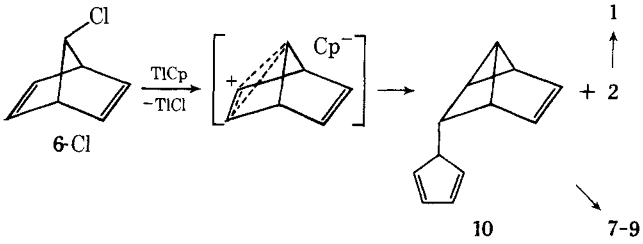

**8**


**9**

Altogether some six–eight reactions were carried out in diglyme (150 °C) according to the described procedure and employing 0.5 g, 1.0 g, or 2.0 g of **6**-Cl. Despite variations in the workup procedure the yield of diene **1** after silica gel chromatography consistently averaged ~100 mg/g of **6**-Cl (NMR or GLC analysis).[6] Thus the preparation of **1** on the gram scale by this method is entirely feasible. Furthermore, if analytical grade **1** is not required, material of at least 90–95% purity can be obtained by careful chromatography on silica gel with pentane, **1** eluting just prior to dicyclopentadiene.

Although the yield of diene **1** was consistent in the above reactions the total number of hydrocarbon products and the yield of the dihydro-*as*-indacenes appeared to vary with the age and quality of the TlCp reagent. With aged and slightly discolored samples of TlCp the ratio (NMR) of **1** to **7**, **8**, or **9** in the crude hydrocarbon product was 3–4:1. In experiments using freshly obtained TlCp[7] the yield of **7–9** was considerably reduced and a new hydrocarbon component, tentatively identified as a tetrahydro-*as*-indacene isomer, was detected by GLC and NMR.

The formation of diene **1**, together with the dihydro-*as*-indacenes **7–9**, may be satisfactorily rationalized by invoking initial generation of an intimate 7-norbornadienyl cation–cyclopentadienyl anion ion pair which suffers immediate and stereospecific ion collapse at either the C-7 or C-2 positions of the cation skeleton to afford **2** and the tricyclic hydrocarbon **10**. The latter hydrocarbon should undergo a cascading series of sigmatropic rearrangements to eventually afford an isomeric mixture of tetrahydro-*as*-indacenes which may be expected to at least partially dehydrogenate under the reaction conditions to give **7–9**.



Further exploration of this facile route into a complex series of $C_{12}$ hydrocarbons is planned with particular emphasis on the reaction of preformed 7-norbornadienyl cations with cyclopentadienyl metal derivatives.

**Acknowledgment.** We are grateful to the National Science Foundation for financial support of this work.

### References and Notes

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(2) L. A. Paquette and M. J. Wyvratt, *J. Am. Chem. Soc.*, **96**, 4671 (1974).

(3) D. McNeil, B. R. Vogt, J. J. Sudol, S. Theodoropulos, and E. Hedaya, *J. Am. Chem. Soc.*, **96**, 4673 (1974).

(4) Calculated from the yield data quoted in ref 2.

(5) T. J. Katz, V. Balogh, and J. Schulman, *J. Am. Chem. Soc.*, **90**, 734 (1968).

(6) The reaction may also be conducted at lower temperatures (e.g., refluxing glyme); however, extended reaction times are required (2–3 days) with no significant improvement in yields.

(7) Commercial grade TlCp was employed as received from Aldrich Chemical Co.

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## Novel Substitution Reactions of 4-Chloro-4*H*-pyrazole Derivatives[1]

*Summary:* 4-Chloro-4*H*-pyrazoles and their mono and di-*N*-oxides have been prepared by treatment of the parent pyrazole with *tert*-butyl hypochlorite or chlorine. Treatment of these chlorides with methanolic base yields 4-methoxymethyl- or 3-methoxymethylpyrazoles, depending upon the structure of the starting materials.

*Sir:* Recently the synthesis of a 4-chloro-4*H*-pyrazole 1-oxide was reported.[2] We now have prepared the corresponding 4*H*-pyrazole and 4*H*-pyrazole 1,2-dioxide as well as some homologues and have observed some interesting substitution reactions of these compounds.

The series, 3,5-diphenyl-4-methyl-4-chloropyrazole (**1**)[3] and the corresponding 1-oxide (**2**) and 1,2-dioxide (**3**), has been