solvent or with the nucleophilic bromide leading to **3** and **5**. The rearrangement to form the cyclopropylidenemethyl bromide (**6**) occurs in the solvent separated ion pair **7**. The addition of the excess of tetraethylammonium bromide made the special salt effect possible and the cation **7** had enough time to rearrange and capture the more nucleophilic bromide. This result is in agreement with our earlier work in the solvolysis reactions of other substituted cyclopropylidenemethyl bromides and homopropargyl sulfonates.[9] **5** and **6** are stable under the conditions of solvolysis (75 °C). To bring them to solvolysis, higher temperatures than 75 °C are required.[9]

The next higher homologue of **1**, cyclopenten-1-yl nonaflate and also cyclopenten-1-yl triflate, were recovered practically unchanged even after heating them in an ampule with absolute TFE containing triethylamine as buffer at 100 °C for 10 days. Apparently, cyclopenten-1-yl nonaflate and triflate do not solvolyze with formation of a vinyl cation in TFE, but with an oxygen–sulfur cleavage in the more nucleophilic ethanol/water system.[6]

Acknowledgment. We thank Deutsche Forschungsgemeinschaft for the financial support of this work and the Bayer AG, Leverkusen, for a generous supply of nonafluorobutanesulfonyl fluoride.

References and Notes

(1) Vinyl Cations. 24: K. P. Jäckel and M. Hanack, *Chem. Ber.*, in press.
(2) M. Hanack, *Acc. Chem. Res.*, **9**, 364 (1976); L. R. Subramanian and M. Hanack, *J. Chem. Educ.*, **52**, 80 (1975).
(3) L. R. Subramanian and M. Hanack, *Angew. Chem., Int. Ed. Engl.*, **11**, 714 (1972).
(4) H. Fischer, K. Hummel, and M. Hanack, *Tetrahedron Lett.*, 2169 (1969).
(5) Y. Apeloig, P. v. R. Schleyer, J. D. Dill, J. B. Collins, and J. A. Pople, paper presented at the 170th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1975; J. B. Collins and P. v. R. Schleyer, private communication.
(6) L. R. Subramanian, M. Hanack, P. v. R. Schleyer, L. W. Chang, F. Effenberger, W. Kurtz, P. J. Stang, and T. E. Dueber, *J. Org. Chem.*, in press.
(7) The total yield of **3** and **4** from the solvolysis is 91% besides 9% cyclobutanone which was probably formed owing to the adventitious moisture present in the system; other possible products like 3-butynetrifluoroethyl ether and cyclopropylidenemethyl trifluoroethyl ether could not be detected.
(8) Solvolysis of **1** in 80% TFE buffered with TEA containing a tenfold excess of tetraethylammonium bromide gave identical products except for the formation of more cyclobutanone and less of the trifluoroethyl ketal. The other rearranged product, $HC{\equiv}CCH_2CH_2Br$, could not be detected by GC.
(9) M. Hanack, T. Bässler, W. Eymann, W. E. Heyd, and R. Kopp, *J. Am. Chem. Soc.*, **96**, 6686 (1974).

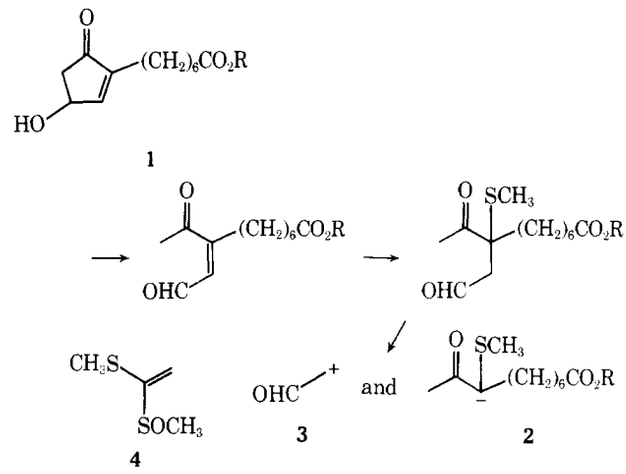
L. R. Subramanian, M. Hanack*
Institut für Organische Chemie der Universität Tübingen, Lehrstuhl für Organische Chemie II 74 Tübingen, Germany
Received September 8, 1976

Prostaglandins. An Efficient Synthesis of a 2-Alkyl-4-hydroxycyclopentenone

Summary: The preparation of a 2-alkyl-4-hydroxycyclopentenone precursor to PGE_1 is described. This construction is technically simple to achieve and proceeds in good overall yield.

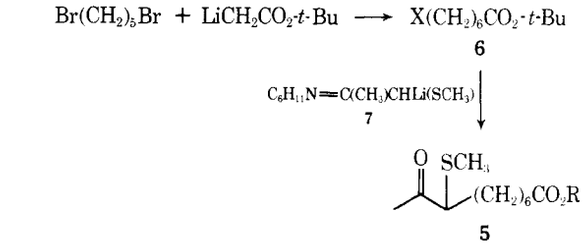
Sir: Hydroxycyclopentenones of type **1** have been shown to be among the most useful of prostaglandin intermediates.[1] We outline here a method for synthesis of **1**, an intermediate leading to PGE_1 and derivatives thereof.

Our construction of **1** arose from the following retro-synthetic consideration which ultimately led to the ketone enolate **2** and the enolonium ion **3**.[2] Efficacy with this scheme has been achieved using the ketene thioacetal monoxide **4**, an experimentally viable equivalent form of enolonium ion **3**.[3]



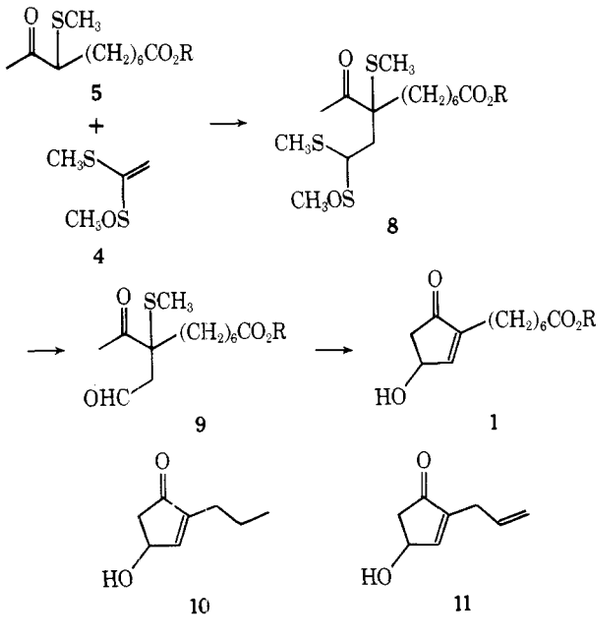
R = CH_3 or *t*-Bu

The synthesis of **1** (R = CH_3 or *t*-Bu) starts with the ketone ester **5** (R = CH_3 or *t*-Bu) which was conveniently prepared in the following manner. Lithium *tert*-butyl acetate (1 equiv, 1 M in THF, −78 °C)[4] was treated with 1,5-dibromopentane (2 equiv) followed immediately by hexamethylphosphoramide (HMPA, 2 equiv). After the mixture was stirred for 10 min at −78 °C, the temperature of the reaction was raised to 0 °C over 2 h and then quenched with saturated ammonium chloride solution. Standard workup followed by distillation from calcium metal gave the bromo ester **6** (X = Br, bp 80 °C at 0.15 Torr) in 65% yield. This material was converted into the corresponding iodide **6** (X = I, bp 65 °C at 5×10^{-4} Torr) in 97% yield using standard methods.[5] Reaction of **6** (X = I, 0.9 equiv) with the lithium imine salt **7**[6] (1 equiv, 1 M in THF) at −78 °C for 10 h followed by hydrolysis with a mixture of sodium acetate, acetic acid, and water at 25 °C for 45 min gave the ketone ester **5** (R = *t*-Bu) in 86% distilled yield (bp 85 °C at



5×10^{-4} Torr). Treatment of this material with thionyl chloride in THF/CH_3OH solution (1:1) afforded the ketone ester **5** (R = CH_3, bp 65 °C at 5×10^{-4} Torr) in essentially quantitative yield.

The conversion of **5** into the hydroxycyclopentenone **1** was accomplished by the three-step reaction sequence outlined below. Compound **5** (R = CH_3, 1 equiv) was added to a 1 M solution of *tert*-butyl alcohol containing potassium *tert*-butoxide (0.1 equiv). After the mixture was stirred for 10 min at 25 °C, the ketene thioacetal monoxide **4** (1.06 equiv) was added and the resulting mixture stirred for 1 h at 25 °C. Workup with saturated ammonium chloride solution gave the adduct **8** (R = CH_3) in quantitative crude yield.[7] Without purification, **8** (1 equiv) was treated with 48% HBF_4 (0.025 equiv) dissolved in acetonitrile (0.76 M with respect to **8**) at 21–22 °C for 2 h. The reaction mixture was quenched at 0 °C with saturated sodium bicarbonate and the resultant keto aldehyde **9** (R = CH_3) was isolated, again in essentially quantitative yield.[7] The crude keto aldehyde was then cyclized into the hydroxycyclopentenone **1** (R = CH_3) using a phase-transfer technique.[8] Thus, compound **9** (1 equiv) dissolved in benzene (1×10^{-2} M) was treated with a mixture of saturated



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.

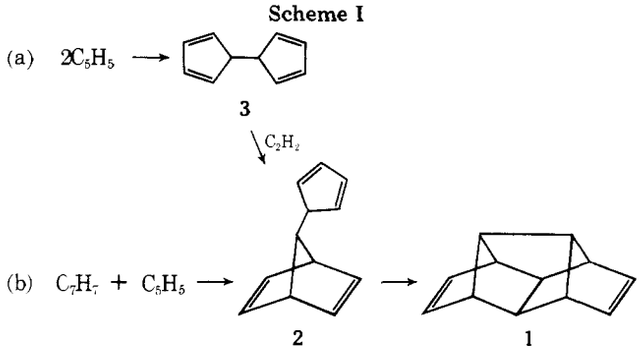
G. R. Kieczykowski,[12] C. S. Pogonowski[13]
J. E. Richman,[14] Richard H. Schlessinger*
Department of Chemistry, University of Rochester
Rochester, New York 14627
Received September 7, 1976

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.**

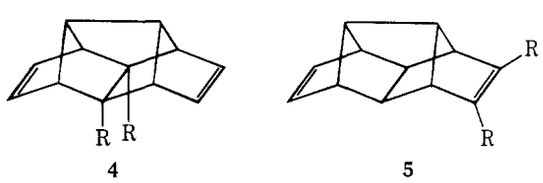
Sir: The novel $C_{12}H_{12}$ hydrocarbon, hexahydro-3,4,7-methenocyclopenta[*a*]pentalene (1),[2] may be formally considered to derive from the combination of two cyclopentadienyl (C_5H_5) residues with acetylene (C_2H_2) or alternatively from the coupling of 7-norbornadienyl (C_7H_7) and cyclopentadienyl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

Scheme I



of either pathway is the rapid intramolecular [4 + 2] cycloaddition of the intermediate 7-(5-cyclopentadienyl)norbornadiene (**2**).

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



4 5

R = CO_2Me

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