

so far, attempts to isolate a nitrogen-coordinated complex have failed.

The addition of excess triphenylphosphine to the benzene solution interferes with the combination of molecular nitrogen; the more triphenylphosphine that is added to the solution, the weaker the band at 2143 cm^{-1} becomes. Probably in the benzene solution the triphenylphosphine-ruthenium complex is dissociated to free triphenylphosphine and a partly dissociated species, which can combine with N_2 . The addition of triphenylphosphine may interfere with the dissociation, thus preventing the coordination of N_2 to Ru. In the case of nitrogentris(triphenylphosphine)cobalt, in which the N_2 ligand is tightly bound to cobalt, the addition of excess triphenylphosphine to the benzene solution causes no change in the intensity of the N_2 stretch band.

A similar reversible reaction of the ruthenium complex is observed with molecular hydrogen. When hydrogen gas is bubbled through the benzene solution a new broad band which is ascribable to a Ru-H stretch appears at about 1910 cm^{-1} . The band disappears when argon gas is passed through the solution and the cycle can be repeated many times.

Similarly a triphenylphosphine-rhodium complex was obtained from RhCl_3 or rhodium(III) acetylacetonate by reduction with triethylaluminum in the presence of triphenylphosphine. The yellow diamagnetic complex is slightly soluble in benzene and toluene and was recrystallized from toluene, mp $162\text{--}163^\circ$, $\nu_{\text{Rh-H}} 2147\text{ cm}^{-1}$ (Nujol).

Anal. Calcd for $\text{C}_{72}\text{H}_{61}\text{P}_4\text{Rh}$: C, 75.0; H, 5.33. Found: C, 75.6; H, 5.54.

The complex liberates only a trace of H_2 on pyrolysis but releases about 0.4 mole of H_2 per Rh on acidolysis. It was converted to $\text{HRh}(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)_2$, $\nu_{\text{Rh-H}} 1907\text{ cm}^{-1}$, by a reaction with 1,2-bis(diphenylphosphino)ethane.¹⁰ The complex is considered to be identical with $\text{HRh}(\text{PPh}_3)_4$ which was prepared independently by Takesada, Yamazaki, and Hagihara¹¹ by a hydrogenolysis of (1,5-cyclooctadiene)(triphenylphosphine)phenylrhodium.

In contrast to the triphenylphosphine-cobalt and -ruthenium complexes, no indication of the N_2 coordination to the rhodium complex was observed at room temperature and atmospheric pressure of nitrogen.

The three triphenylphosphine complexes of cobalt, ruthenium, and rhodium contrast with each other in their ability to combine with molecular nitrogen.

(10) A. Sacco and R. Ugo, *J. Chem. Soc.*, 3274 (1964).

(11) M. Takesada, H. Yamazaki, and N. Hagihara, Preprint of Symposium on Organometallic Compounds, Osaka, Oct 1967, p 207. $\text{HRh}(\text{PPh}_3)_3$ was also reported by W. Keim, *J. Organometal. Chem.* (Amsterdam), 8, 25 (1967).

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The Total Synthesis of Racemic Bulnesol

Sir:

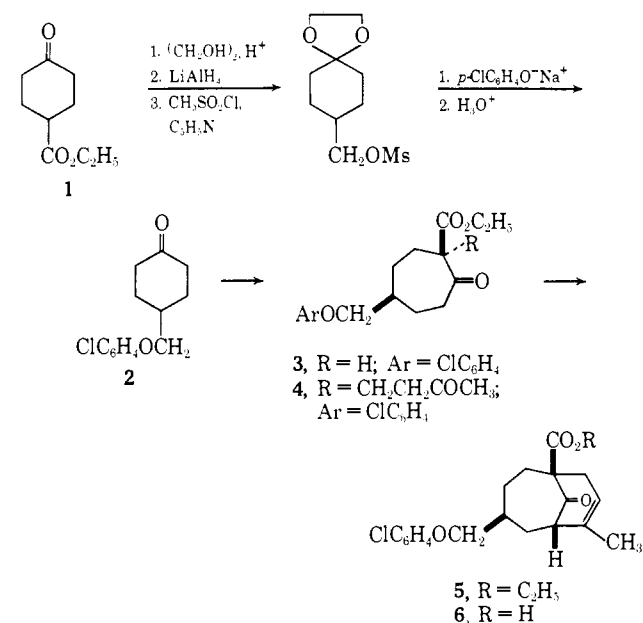
The formidable stereochemical problems associated with the simple bicyclic guaiazulenic sesquiterpenes¹

(1) T. Nozoe and S. Itô in "Fortschritte der Chemie Organischer Naturstoffe," L. Zechmeister Ed., Springer-Verlag, Vienna, 1961, pp

have long thwarted attempts at complete structure elucidation and stereoselective total synthesis.² Thus, for example, the currently accepted structure for bulnesol (18), a hydroazulene with but three asymmetric centers, could be deduced only after extensive degradative studies by numerous workers.³ In this report we describe a stereoselective total synthesis of bulnesol which fully supports the assigned structure and indicates possible solutions to some of the difficult synthesis problems associated with this class of compounds.

Keto ester 1⁴ was converted according to the scheme outlined in Chart I to 4-(*p*-chlorophenoxyethyl)-cyclohexanone (2) [mp $64\text{--}65^\circ$, $\lambda_{\text{max}}^{\text{KBr}}$ 5.82 (CO), 6.23, 6.30 (aromatic C=C), 6.69, 6.79, 8.52, 9.62, 12.02, and 14.95 μ ; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 6.97 (aromatic C-H, A_2B_2 , $J_{AB} = 9\text{ Hz}$, $\Delta\nu_{AB} = 24.5\text{ Hz}$), and 3.81 ppm (OCH_2CH doublet, $J = 6\text{ Hz}$)]. Ring enlargement with ethyl diazoacetate-boron trifluoride etherate⁵ afforded the β -keto ester 3 which readily condensed with methyl vinyl ke-

Chart I



tone in the presence of dilute ethanolic sodium ethoxide. The resulting diketo ester 4 cyclized upon treatment with sulfuric acid-acetic acid (4:1)⁶ giving the bicyclo[4.3.1]decenone ester 5, which was purified *via* saponification to the keto acid 6 [mp $183\text{--}185^\circ$, $\lambda_{\text{max}}^{\text{KBr}}$ 2.92-3.90 (acid OH), 5.83 (CO), 6.24, 6.31 (C=C), 6.69, 6.80, 7.78, 8.02, 12.08, and 14.95 μ ; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 9.13

53-61; R. C. Slagel, "The Conversion of Bulnesol to other Sesquiterpenoids," Ph.D. Dissertation, University of Illinois, 1962.

(2) Notable achievements in the synthesis of tricyclic guaiazulenic sesquiterpenes have recently been recorded: G. Büchi, W. D. MacLeod, and J. Padilla O., *J. Am. Chem. Soc.*, 86, 4438 (1964); G. Büchi, J. M. Kauffman, and H. J. E. Loewenthal; *ibid.*, 88, 3403 (1966); G. Büchi, W. Hofheinz, and J. V. Paukstelis, *ibid.*, 88, 4113 (1966).

(3) T. Sato, H. Minato, H. Shiro, and H. Koyama, *Chem. Commun.*, 363 (1966); H. Minato, *Tetrahedron Letters*, No. 8, 280 (1961); K. Takeda and H. Minato, *ibid.*, No. 22, 33 (1960); L. Dolejš, A. Mironov, and F. Šorm, *ibid.*, No. 11, 18 (1960); E. J. Eisenbraun, T. George, B. Riniker, and C. Djerassi, *J. Am. Chem. Soc.*, 82, 3648 (1960); L. Dolejš, A. Mironov, and F. Šorm, *Collection Czech. Chem. Commun.*, 26, 1015 (1961); J. Simonsen and D. H. R. Barton, "The Terpenes," Vol. III, Cambridge University Press, London, 1952, p 190.

(4) R. A. Finnegan and P. L. Bachman, *J. Org. Chem.*, 30, 4145 (1965).

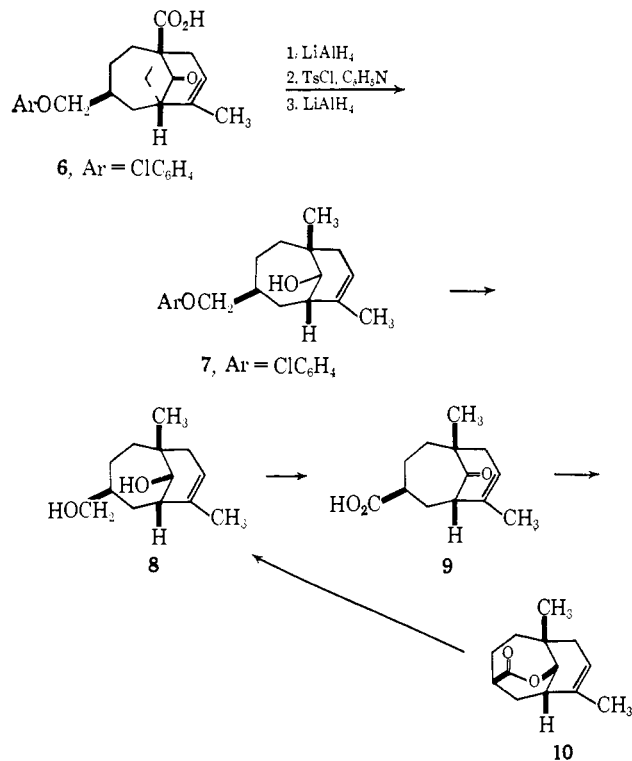
(5) Cf. W. T. Tai and E. W. Warnhoff, *Can. J. Chem.*, 42, 1333 (1964).

(6) Cf. V. Prelog, P. Barman, and M. Zimmerman, *Helv. Chim. Acta*, 32, 1284 (1949).

(OH), 7.01 (aromatic C-H, A_2B_2 , $J_{AB} = 9$ Hz, $\Delta\nu_{AB} = 25$ Hz), 5.60 (olefinic C-H, broad), 3.72 (OCH_2CH doublet, $J = 5.5$ Hz), and 1.77 ppm (vinylic CH_3)].⁷

Keto acid **6** was converted to the alcohol **7** via the routine sequence outlined in Chart II. Removal of the

Chart II



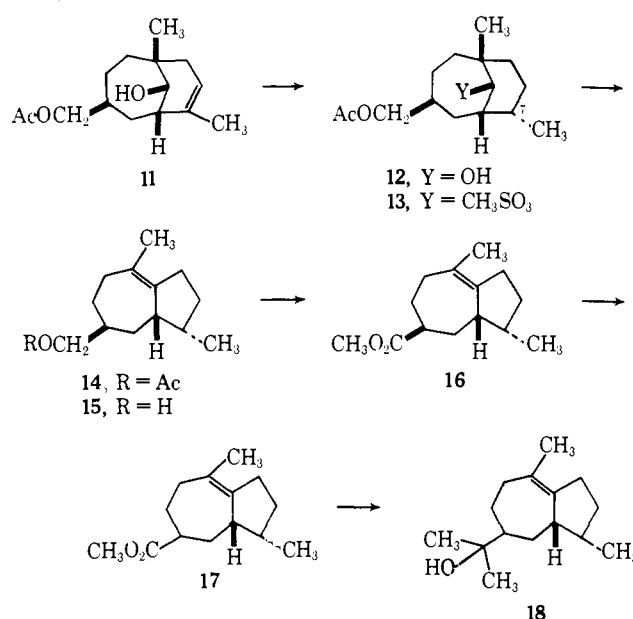
p-chlorophenyl group was readily effected with lithium in ammonia-ethanol followed by acid-catalyzed hydrolysis of the resulting enol ether. The stereochemistry of diol **8** was ascertained through oxidation with Jones reagent⁸ at 0° and treatment of the keto acid **9** with aqueous sodium borohydride whereupon lactone **10** [mp 76–77°, λ_{\max}^{KBr} 5.78 (CO), 7.96, 8.41, 9.32, 9.72, and 10.08 μ ; $\delta_{TMS}^{CCl_4}$ 5.22 (olefinic C-H, broad), 4.09 ($OCHCH$ doublet, $J = 5$ Hz), 1.71 (vinylic CH_3), and 1.07 ppm (quaternary CH_3)] was secured in high yield after acidification. Reduction with lithium aluminum hydride regenerated diol **8** [mp 113–114°, λ_{\max}^{KBr} 2.98 (OH), 7.68, 9.40, 9.51, 10.02, and 12.60 μ].

Diol **8** yielded the monoacetate **11** (Chart III) upon treatment with acetic anhydride in pyridine. Hydrogenation over platinum afforded essentially a single dihydro isomer. Molecular models show that the 1,3-diaxial arrangement required of the four carbon bridge of acetate **11** effectively blocks the bottom face of the cyclohexene double bond, thereby favoring adsorption on the relatively more accessible top face. This analysis and the observed 5.5-Hz coupling constant of the C-7 methyl grouping, indicative of an equatorial methylcyclohexane,⁹ support the stereochemistry de-

(7) We initially chose the phenyl ether as the methylol protecting group. However, even this relatively rugged group failed to survive the concentrated sulfuric acid-acetate acid mixture required to cyclize the diketone ester **4** (Ar = C₆H₅); extensive material losses occurred, presumably owing to sulfonation of the aromatic ring. We therefore turned to the corresponding *p*-chlorophenyl ether on the assumption that ring sulfonation would take place less readily.

(8) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

Chart III



icted in formula **12** for the hydrogenation product.

The methanesulfonate derivative **13**, in refluxing acetic acid containing sodium acetate, rearranged to the bicyclo[5.3.0]decenyl derivative **14**⁹ [λ_{\max}^{film} 5.74 (CO), 7.30, 8.08, 9.50, and 9.65 μ ; $\delta_{TMS}^{CCl_4}$ 3.88 (OCH_2CH doublet, $J = 7$ Hz), 1.97 (CH_3CO_2), 1.60 (vinylic CH_3), and 0.78 ppm (CH_3CH doublet, $J = 7$ Hz)]. Cleavage ($LiAlH_4$) to the alcohol **15** followed by oxidation (Jones reagent⁸) and esterification (CH_2N_2) afforded the methyl ester **16** [λ_{\max}^{film} 5.75 (CO), 8.30, and 8.52 μ ; $\delta_{\max}^{CCl_4}$ 3.61 (CO_2CH_3), 1.60 (vinylic CH_3), and 0.79 ppm (CH_3CH doublet, $J = 7$ Hz)]. This ester epimerized upon treatment with refluxing methanolic sodium methoxide to give a 70:30 mixture of epimers, predominantly ester **17**, which could be purified by gas chromatography. Addition of methyl lithium to this more stable epimer gave racemic bulnesol (**18**) {mp 77–79°, λ_{\max}^{KBr} 3.01 (OH), 8.19, 8.49, 8.77, and 11.10 μ ; $\delta_{\max}^{CDCl_3}$ 1.67 (vinylic CH_3), 1.32 (OH), 1.17 [$(CH_3)_2COH$], and 0.91 ppm (CH_3CH doublet, $J = 6.5$ Hz)} which was identified through comparison of its infrared and nmr spectra with those of the natural material. The two substances also exhibited identical gas chromatographic retention times.

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(9) For a close analogy, see J. A. Marshall and J. J. Partridge, *Tetrahedron Letters*, 2545 (1966).

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