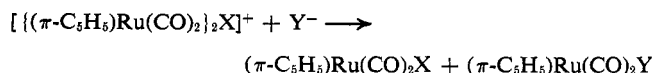


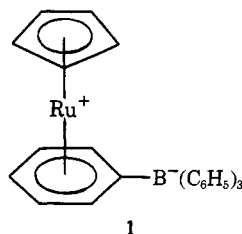
solution. These compounds revert to the yellow species, $[(\pi\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2]_2\text{XPF}_6$ ($\text{X} = \text{Br}$ and Cl) at room temperature in both solution and in the solid state and consequently could not be obtained analytically pure. The infrared spectra of these green complexes correspond with those of the yellow $[(\pi\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2]_2\text{XPF}_6$ ($\text{X} = \text{Br}$ and Cl) and thus these green compounds are proposed to be a second isomeric form of $[(\pi\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2]_2\text{XPF}_6$.

The green and yellow isomers of $[(\pi\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2]_2\text{XPF}_6$ ($\text{X} = \text{Br}$ and Cl) are very susceptible to nucleophilic attack and react readily with a wide range of anions. For instance, treatment of $[(\pi\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2]_2\text{XPF}_6$ ($\text{X} = \text{Br}$ and Cl) in solution with halides and pseudohalides e.g., Cl^- , Br^- , I^- , CN^- , SCN^- , and N_3^- , readily leads to the formation of neutral products according to the scheme



The cations $[(\pi\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2]_2\text{X}^+$ ($\text{X} = \text{Br}$ and Cl) also react readily with the anion, tetraphenylboron, in solution. Fission of a boron-carbon bond in $\text{B}(\text{C}_6\text{H}_5)_4^-$ and transfer of a phenyl group to a ruthenium atom is effected and the products $(\pi\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{X}$ and $(\pi\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{-}\sigma\text{-C}_6\text{H}_5$ obtained. The anion $\text{B}(\text{C}_6\text{H}_5)_4^-$ is attacked in an analogous manner. Although mercury salts are known to cleave boron-carbon bonds, reactions involving the transfer of a phenyl group from boron to a transition metal atom are not well documented. Two isolated examples are the slow formation of *trans*- $\text{Pt}\{\text{P}(\text{C}_2\text{H}_5)_3\}_2(\text{C}_6\text{H}_5)_2$ from *cis*- $\text{Pt}\{\text{P}(\text{C}_2\text{H}_5)_3\}_2\text{Cl}_2$ and $\text{NaB}(\text{C}_6\text{H}_5)_4$ in refluxing tetrahydrofuran³ and the reaction of $[\text{Pt}\{\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5\}_2(\text{CH}_3\text{OH})\text{CH}_3]^+$ with $\text{NaB}(\text{C}_6\text{H}_5)_4$ in solution to give *trans*- $\text{Pt}\{\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5\}_2(\text{C}_6\text{H}_5)_2$.⁴ The cyanide and not a phenyl group is extracted from $\text{B}(\text{C}_6\text{H}_5)_3\text{CN}^-$ on reaction with $[(\pi\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2]_2\text{X}^+$ ($\text{X} = \text{Br}$ and Cl); $(\pi\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{X}$ and $(\pi\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{CN}$ are formed as products.

The reaction of $(\pi\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{Cl}$ with $\text{NaB}(\text{C}_6\text{H}_5)_4$ in ethanol under reflux is also observed to afford the σ -phenyl derivative $(\pi\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{-}\sigma\text{-C}_6\text{H}_5$. The corresponding reaction involving $(\pi\text{-C}_5\text{H}_5)\text{Ru}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2\text{Cl}$ does not afford $(\pi\text{-C}_5\text{H}_5)\text{Ru}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2\text{-}\sigma\text{-C}_6\text{H}_5$, however. A product shown not to contain phosphorus is obtained instead, and this has been characterized as $\text{C}_5\text{H}_5\text{RuB}(\text{C}_6\text{H}_5)_4$. The presence of four strong bands in the $1500\text{--}1350\text{-cm}^{-1}$ region of



the infrared spectrum of this derivative is indicative of one of the phenyl rings of the tetraphenylboron being π bonded to the ruthenium atom.^{5,6} The sandwich structure shown (1) is thus proposed for this zwitterionic species.⁷

(5) M. J. Nolte, G. Gafner, and L. M. Haines, *Chem. Commun.*, 1406 (1969); L. M. Haines, *Inorg. Chem.*, in press.

(6) R. R. Schrock and J. A. Osborn, *ibid.*, 9, 2339 (1970).

(7) Although a number of Rh and Ir derivatives containing a tetraphenylboron anion directly bonded to the metal atom through an arene ring have recently been reported,^{5,6} compounds with sandwich structures which contain this ligand are not known.

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General Approach to the Synthesis of α -Patchoulane Sesquiterpenes. The Intramolecular Lewis Acid Catalyzed Addition of Diazo Ketones to Olefins

Sir:

The presence of a wide variety of sesquiterpenes which possess the α -patchoulane skeleton 1 in patchouli oil,¹ Indian valerian root oil,² and various cyperus oils³ has been reported, but evaluation of the odor and flavor of many of these sesquiterpenes has been limited due to the lack of synthetic means for attaining working quantities of these compounds. Although specific syntheses of individual α -patchoulane type sesquiterpenes⁴⁻⁸ have been recorded, it was the objective of our work to develop a general synthetic approach which would be adaptable to all of the sesquiterpenes in this series. We record here such a general, albeit multistep, approach to the α -patchoulane skeleton using as the target compounds the sesquiterpenes *dl*-

(1) N. Tsubaki, K. Nishimura, and Y. Hirose, *Bull. Chem. Soc. Jap.*, 40, 597 (1967).

(2) C. S. Narayanan, K. S. Kulkarni, A. S. Vaidya, S. Kanthamani, G. Lakshmi Kumari, B. V. Bapat, S. K. Paknikar, S. N. Kulkarni, G. R. Kelkar, and S. C. Bhattacharyya, *Tetrahedron*, 20, 963 (1964).

(3) (a) O. Motl, B. Trivedi, V. Herout, and F. Sorm, *Chem. Ind. (London)*, 1284 (1963); *Collect. Czech. Chem. Commun.*, 29, 1675 (1964); (b) B. Trivedi, O. Motl, J. Smolikova, and F. Sorm, *Tetrahedron Lett.*, 1197 (1964); (c) H. Hikino, K. Aota, and T. Takemoto, *Tetrahedron*, 23, 2169 (1967); (d) H. Hikino, Y. Takeshita, Y. Hikino, and T. Takemoto, *Chem. Pharm. Bull.*, 13, 628 (1965); (e) S. B. Nerali and K. K. Chakravarti, *Tetrahedron Lett.*, 2447 (1967); (f) S. B. Nerali, P. S. Kalsi, K. K. Chakravarti, and S. C. Bhattacharyya, *ibid.*, 4053 (1965); (g) H. Hikino, K. Aota, and T. Takemoto, *Chem. Pharm. Bull.*, 16, 52 (1968).

(4) For example, total syntheses have been recorded for α -patchoulene,⁵ δ -patchoulene,⁶ cyperene,⁶ patchoulene,⁶ and patchouleneol.⁸ Syntheses of patchouli alcohol^{5,7} and β -patchoulene^{5,8} compounds which are easily converted to α -patchoulene have also been effected.

(5) G. Büchi, W. D. MacLeod, Jr., and J. Padilla O., *J. Amer. Chem. Soc.*, 86, 4438 (1964); (b) G. Büchi and W. D. MacLeod, Jr., *ibid.*, 84, 3205 (1962); (c) G. Büchi, R. E. Erickson, and N. Wakabayashi, *ibid.*, 83, 927 (1961).

(6) H. Hikino, K. Ito, K. Aota, and T. Takemoto, *Chem. Pharm. Bull.*, 16, 43 (1968).

(7) S. Danishefsky and D. Dumas, *Chem. Commun.*, 1287 (1968).

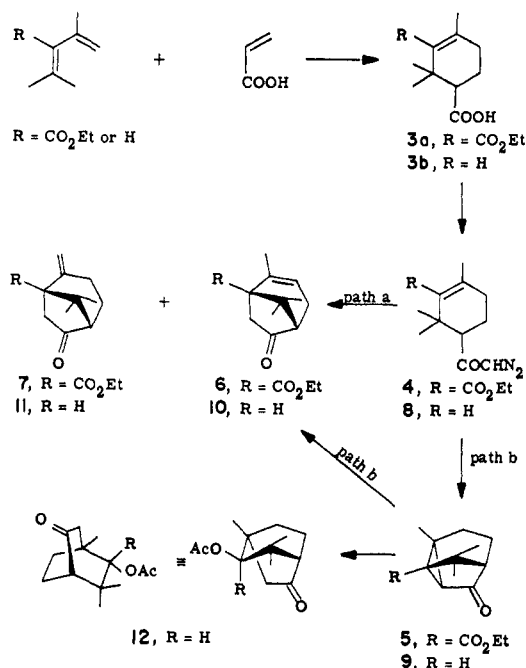
(8) R. B. Bates and R. C. Slagel, *J. Amer. Chem. Soc.*, 84, 1307 (1962).

(3) H. C. Clark and K. R. Dixon, *J. Amer. Chem. Soc.*, 91, 596 (1969).

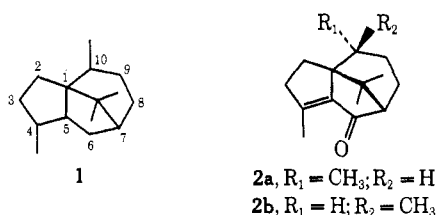
(4) H. C. Clark and J. D. Ruddick, *Inorg. Chem.*, 9, 1226 (1970).

patchoulone (**2a**)⁹ and *dl*-epipatchoulone (**2b**). The key step in this total synthesis is the intramolecular Lewis acid catalyzed cyclization of the diazo ketone **4** to the bicyclo[3.2.1]octenone **6** (Chart I, path a). This

Chart I



reaction, which represents the first reported example of the *acid-catalyzed* addition of a diazo ketone to an olefin,¹⁰ has potential application for the synthesis of bicyclic ketones in general.



Our overall strategy for the synthesis of the α -patchoulane skeleton involved the construction and copper-catalyzed thermal cyclization of the diazo ketone **4** to the cyclopropyl ketone **5** and acid-catalyzed cleavage of the latter ketone to deliver the bicyclic ring system **6** (Chart I, path b). The carboxy group served as an electron-withdrawing substituent to direct ring opening and provided a handle for introducing the fused five-membered ring. Direct Lewis acid catalyzed cyclization of **4** to **6** (Chart I, path a) eventually was found to be superior to the two-step procedure. By judicious choice of the sequence in which steps are performed, one can effect annelation of a five-membered

ring to produce sesquiterpenes in which unsaturation is eliminated from, or retained in, the 9,10 position. In this communication, we describe a sequence in which the double bond is reduced before formation of the ring.

Diels-Alder condensation¹¹ (200°, 16 hr, 2000 psi nitrogen pressure) of ethyl 3-carboxy-2,4-dimethyl-1,3-pentadiene¹² (30 mol equiv) and acrylic acid (10 mol equiv) in the presence of hydroquinone (1 mol equiv) afforded the acid **3a** in 41% yield [methyl ethyl ester, bp 120° (0.9 mm)].¹³ The acid chloride of **3a** (prepared by the action of oxalyl chloride on the sodium salt of **3a**) was converted with ethereal diazomethane to the diazo ketone **4** (yellow crystals from petroleum ether-benzene, mp 47–49°, 72% overall yield from the acid **3a**).

Copper-catalyzed thermal decomposition of **4**¹⁴ produced the cyclopropyl ketone **5** [liquid, evaporative distillation 140° (0.3 mm)] in 16% yield. Relatively drastic conditions (15% boron tribromide in refluxing glacial acetic acid for 15 hr) were required to effect cleavage of **5** to the ketones **6** and **7** (54% yield; ratio **6**:**7** = 96:1). However, when **4** was exposed to boron trifluoride etherate (2% in 1,2-dichloroethane) for a period of only 3 hr at mild temperature (0–27°), the ketone **6** (colorless plates from petroleum ether, mp 74–75°) and the ketone **7** [colorless liquid, evaporative distillation 130–135° (0.4 mm)] were isolated in yields of ca. 30 and 3%, respectively.

The advantages of the direct acid-catalyzed cyclization of diazo ketones, compared to the cleavage of cyclopropyl ketones, for the preparation of bicyclo[3.2.1]octenones is exemplified further by comparative studies of the boron trifluoride catalyzed transformations of the diazo ketone **8** and the cyclopropyl ketone **9**. When ketone **9** [liquid, bp 91–92° (4.75 mm)], in which an ester group is not present to direct ring cleavage, was treated with 10% boron trifluoride etherate in glacial acetic acid (118°, 3 hr), a mixture of the bicyclo[3.2.1]octenones **10** [liquid, bp 112° (5.0 mm); 2,4-dinitrophenylhydrazone, mp 135.5–137° (from ethanol), 51% yield] and **11** [liquid, bp 115° (4.0 mm), <1% yield] and the bicyclo[2.2.2]octanone **12** [colorless crystals from petroleum ether, mp 61–62°, 31%] was obtained.¹⁵ Since **9** was formed in 65% yield by the copper-catalyzed thermal decomposition¹⁴ of diazo ketone **8**,¹⁶ the overall yield of **10** from **8** is 33%. In comparison, the ketone **10** was obtained directly in one step in ca. 56% yield along with a small quantity of **11** (6% yield) by the action of

(11) Cf. Diels-Alder condensation of 2,4-dimethyl-1,3-pentadiene and acrylic acid: W. F. Erman, E. Wenkert, and P. W. Jeffs, *J. Org. Chem.*, **34**, 2196 (1969).

(12) Prepared by a variation in the procedure of I. Alkonyi and D. Szabo, *Chem. Ber.*, **100**, 2773 (1967).

(13) Spectral parameters (nmr, ir, and mass) and elemental analyses were consistent with the structures assigned to all new compounds. Products from all reactions, unless otherwise stated, were isolated by adsorption chromatography on Davison 100–200 mesh silica gel. Final purification of liquids was achieved by preparative gas chromatography and subsequent flash distillation. Yields are based on distilled or recrystallized products.

(14) Cf. H. O. House, S. G. Boots, and V. K. Jones, *J. Org. Chem.*, **30**, 2519 (1965).

(15) Since treatment of **10** or **12** with boron trifluoride etherate under the same conditions gave less than 2% interconversion of these two ketones, the products are those of kinetic, rather than thermodynamic, control.

(16) Prepared in 52% overall yield from 2,2,4-trimethyl-3-cyclohexene-1-carboxylic acid (**3b**)¹¹ by the same sequence described for diazo ketone **4**.

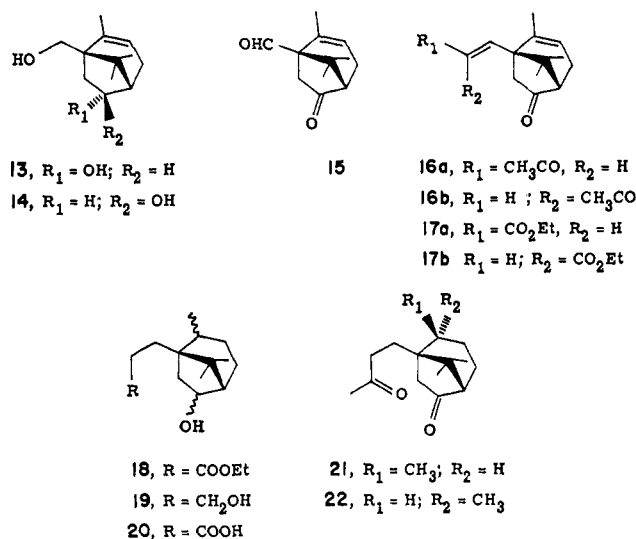
(9) The structure, stereochemistry, and absolute configuration of patchoulone (**2**) from *Cyperus rotundus* L. tuber oil has been established rigorously by chemical degradation, synthesis, and nmr spectroscopy.^{3a,6}

(10) Surprisingly, only one example of the acid-catalyzed addition of a diazo compound to an olefin—i.e., the addition of phenyldiazomethane to tetramethylethylene—has been recorded: G. L. Closs, R. A. Moss, and S. H. Goh, *J. Amer. Chem. Soc.*, **88**, 364 (1966).

boron trifluoride etherate (2% in 1,2-dichloroethane, 85 min)¹⁷ on **8**.

Lithium aluminum hydride reduction of the keto ester **6** in ether solution provided an inseparable mixture of the epimeric alcohols **13** and **14** (82% yield) in a ratio of 55:45¹⁸ (Chart II). Oxidation of this mixture with

Chart II



dipyridinechromium trioxide in methylene chloride¹⁹ rendered the aldehyde **15** as colorless plates, mp 120° (dec) after sublimation (69% yield). Attempts to condense **15** with acetone or with sodium diethylphosphonoacetate over extended periods failed to provide even traces of the desired diketones **16a** or **16b**. However, the condensation of **15** with 1 equiv of sodium triethylphosphonoacetate, using essentially a procedure described by Wadsworth and Emmons²⁰ (benzene solvent, 4-hr reflux) led to a mixture of the *E* and *Z* unsaturated esters **17a** and **17b** (52% yield), which was easily resolved by preparative gas chromatography (ratio **17a**:**17b** = 10:1 to 14:1). A side product was the ketone **9** (2%) which probably was formed by thermal homolytic decarbonylation of **15**. Hydrogenation of an ethanol solution of a 10:1 mixture of **17a** and **17b** in the presence of W-5 Raney nickel²¹ produced a mixture of epimeric hydroxy esters **18** (50–93%)²² and diols **19** (5–40%).²² The free acids **20** were separated readily from the diols **19** after saponification of the esters **18** with 10% methanolic potassium hydroxide. Treatment of **20** with 3 molar equiv of ethereal methyllithium at 26–27° for 16 hr provided a mixture of epimeric ketols which were converted directly to the diketones **21** and **22** (43% yield; ratio **21**:**22** = 9:1) on treatment with standard chromate solution in acetone.²³ The epimer **21** was crystallized

from petroleum ether as colorless plates, mp 62–63.5°, while the epimer **22** was obtained only as an oil by adsorption chromatography on silica gel. The epimer **21** was cyclized to epipatchoulenone (**2b**) in 92% yield by the action of potassium *tert*-butoxide in *tert*-butyl alcohol (26–27°, 30 min). The ketone **2b** was recrystallized from petroleum ether as colorless plates, mp 75.5–77.5° [ir (CCl₄) 1713, 1668 cm⁻¹; nmr (CDCl₃) τ 8.03 (broad s), 8.84 (d, $J = 6.5$ Hz), 8.88 (s); mass spectrum (70 eV) base and parent ion peak, m/e 218].

Similar treatment of **22** with potassium *tert*-butoxide afforded *dl*-patchoulenone (**2a**) (colorless plates, mp 37–38°) in 70% yield. The infrared and nmr spectra of our specimen of *dl*-**2a** were identical in all major respects with the infrared^{24,25} and nmr²⁵ spectra of natural patchoulenone. The high-resolution mass spectrum showed a parent ion peak of m/e 218 and a base peak of m/e 91.

Acknowledgments. We gratefully acknowledge Professor William von E. Doering for his vital suggestion to attempt the acid-catalyzed transformation of **4** to **6** and fruitful discussions with Professors Ernest Wenkert and E. C. Taylor.

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(24) Kindly sent to us by Professor Hiroshi Hikino, Pharmaceutical Institute, School of Medicine, Tohoku University, Sendai, Japan.

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(S-B) 3-(Methylthio)propylborane, a Distillable Monoalkylborane

Sir:

Although a number of disubstituted derivatives of borane are well known, stable uncomplexed monomeric monosubstituted derivatives of borane are almost unknown. The only well-documented example is dimethylstibinoborane.¹ Brown has reported the preparation of monoalkylboranes with bulky alkyl groups, but these are actually dialkyldiboranes even in basic ethers and are not distillable without disproportionation and pyrolysis. He suggested their utility in synthesis, but no application was reported.^{2a} Hawthorne demonstrated that a monoalkylborane complex (trimethylamine-*tert*-butylborane)^{3a} is useful in preparing heterocyclic boron compounds from doubly unsaturated substances such as divinyl ether. However, the preparation of this complex is an involved multistep process,^{3b,4} and elevated temperatures are required for its use in hydroborations. We had previously prepared an internally coordinated alkylborane (3-di-

(17) These and related studies of the addition of diazo ketones to olefins and the mechanism of product formation will be discussed elsewhere.

(18) Determined from the nmr spectrum.

(19) According to the procedure of J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Lett.*, 3363 (1968).

(20) W. S. Wadsworth, Jr., and W. D. Emmons, *Org. Syn.*, **45**, 44 (1965).

(21) H. R. Billica and H. Adkins, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 176.

(22) The relative yields of hydroxy esters and diols varied with the period of storage of the W-5 Raney nickel.

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(2) H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962: (a) Chapter 11; (b) p 64; (c) Chapter 12.

(3) (a) M. F. Hawthorne, *J. Amer. Chem. Soc.*, **83**, 2541 (1961); (b) *ibid.*, **81**, 5836 (1959).

(4) P. M. McCusker, E. C. Ashby, and H. S. Makowski, *ibid.*, **79**, 5179 (1957).