tion times). The retention times and peak areas were compared directly with those of authentic deoxybenzoin, *cis*-bromostilbene,[16] and *trans*-bromostilbene.[17] This oil was chromatographed over 150 g of silica gel to give *cis*- and *trans*-bromostilbene, eluted with 5% benzene in hexane, and deoxybenzoin, eluted with 50% benzene in hexane, mp and mmp 56°.

The aqueous fraction was acidified with glacial acetic acid to pH 5 and the solid collected by filtration and recrystallized from ether-petroleum ether (30–60°) to give 1.3 g (26%) of recovered *cis*-α-phenylcinnamic acid, mp 176–178°. Acidification of the filtrate to pH 2 with concentrated hydrochloric acid gave a slightly turbid solution but no significant amount of solid could be isolated.

Addition of Bromine to Sodium *trans*-α-Phenylcinnamate (Ib).—The reaction was carried out in exactly the same manner as with **1a**. The ether extract gave an oil which on analysis by glpc showed there to be 8% **2a**, 61% **3**, and 5% **2b** in order of increasing retention times. Deoxybenzoin (**3**) was crystallized from this crude oil and identified by melting point and mixture melting point (56°). Upon acidification with glacial acetic acid, the aqueous solution gave 11% **1a**. Decreasing the pH of the filtrate gave a slightly turbid solution but no isolable material. The total yield was 85%.

Registry No.—Bromine, 7726-95-6; **1a**, 15352-96-2; **1b**, 15352-97-3.

Acknowledgment.—The authors wish to express their appreciation to Professor F. G. Bordwell for very helpful discussions. We also wish to thank the National Science Foundation for their support.

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Small-Ring Compounds. XVIII. The Formation of a π-Allylic Palladium Chloride Complex from Vinylcyclopropane Derivatives

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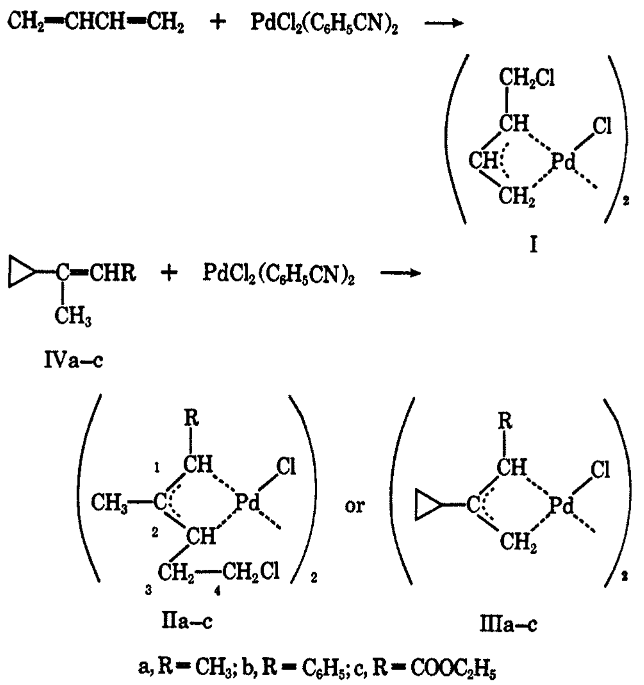
Received August 21, 1967

The possibility of conjugative interaction of a cyclopropane ring with an adjacent unsaturated group has been of interest to many workers. Recent nmr,[1] electron diffraction,[2] and solvolysis studies[3] have strongly suggested the existence of such an interaction. In the present study, we wish to report the formation of a π-allylic palladium chloride complex from vinylcyclopropane derivatives. The formation of a π-palladium complex (I) from butadiene has been reported;[4] thus, if the character of the cyclopropane ring in the vinylcyclopropane derivatives is olefinic, the formation of a similar type of complex, such as II, may be expected as shown in Scheme I.[5] On the other hand, if the cyclopropane ring does not participate in the formation of the complex, complex III may be formed instead of II.[6]

SCHEME I



The reaction of IVa–c, prepared from methyl cyclopropyl ketone by reaction with the corresponding Wittig reagent, with bisbenzonitriledichloropalladium was carried out in benzene at room temperature (IVa,b) or at refluxing temperature (IVc), under an atmosphere of nitrogen, and the product was obtained by pouring the reaction mixture into large excess of petroleum ether (30–70°). The purified complexes are pale yellow and soluble in chloroform and benzene. The elemental analyses, nmr spectra (in C_6D_6), melting points, and molecular weights are shown in Table I. The elemental analyses and molecular weights are in good agreement with the calculated values for the type II complexes and the nmr data indicate that the structure of the complex can be assigned to the type II.[7] A brown amorphous complex was obtained along with the type II complex in every case. These by-products were unstable, and gave elemental analyses which were not in agreement with reasonable structures, although the nmr spectra of them are quite similar to those of the corresponding type II complexes. Further work on

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(2) L. S. Bartell and J. P. Guillory, *J. Chem. Phys.*, **43**, 647 (1965).

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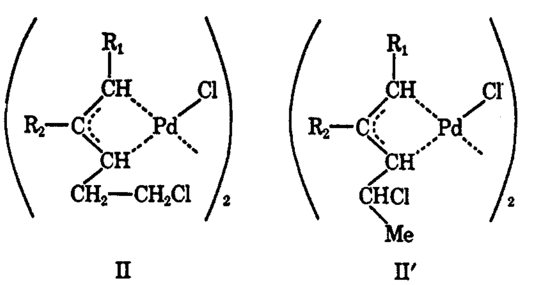
(7) A. D. Ketley and J. A. Braatz have reported that the π-allylic complex obtained from vinylcyclopropane was a mixture consisting of the type II and type II′ complexes ($R_1 = R_2 = H$). The nmr spectra shown in Table I,



II II′

however, exclude the existence of the type II′ complex ($R_2 = CH_3$), as the relative intensity of each absorption is in good agreement with that calculated for the type II complex ($R_2 = CH_3$) and, furthermore, there is no absorption corresponding to the methyl group (Me) of the type II′ complex, which should be observed as a triplet at about τ 9.12.

TABLE I

			Complex											
					Anal., %									
			Mol wt		C		H		Chemical shift (multiplicity[a]) (relative intensity)					
Starting compd	R	Mp, °C	Calcd	Found	Calcd	Found	Calcd	Found	CH_3	τ_1	τ_2	τ_3	τ_4	R
IVa	CH_3	170–173	546.9	536	30.74	30.30	4.42	4.59	8.70 (s) (3.0)	7.20 (q) (1.0)	7.06 (t) (1.0)	8.30 (m) (1.8)	6.65 (q) (2.0)	9.13 (d) (3.0)
IVb	C_6H_5	139–140	671.1	660	42.95	43.20	4.21	4.50	8.48 (s) (3.0)	6.24 (s) (1.0)	6.82 (t) (1.2)	8.30 (m) (2.4)	6.60 (q) (2.0)	
IVc	$COOC_2H_5$	171–173	660.8	658	32.61	32.63	4.26	4.03	8.00 (s) (3.0)	7.23 (s) (1.0)	7.06 (t) (1.0)	8.30 (m) (2.3)	6.70 (q) (2.3)	

[a] Abbreviations used were s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

these by-products was not performed in the present study.[8]

That the complexes IIa,b are formed at room temperature, whereas the formation of the complex IIc from IVc, in which the double bond would be electron deficient, requires a higher temperature would suggest that in the initial step of the formation of the complexes IIa–c an intermediate similar to a cyclopropylcarbinyl cation would be formed by donation of an electron pair from the olefin to the palladium component. Thus, the cyclopropane ring would be opened through the usual cyclopropylcarbinyl–homoallyl rearrangement.

Experimental Section

2-Cyclopropylbutene-2 (IVa).—To an ethereal solution of the Wittig reagent, prepared from 37 g (0.1 mole) of ethyltriphenylphosphonium bromide, was added 8.4 g (0.1 mole) of cyclopropyl methyl ketone at room temperature. A white precipitate was formed immediately. The suspension was refluxed for 10 hr and filtered. The filtrate was washed with water, dried, and distilled to give 4.1 g of IVa, the yield being 48.9%, bp 102°.

Anal. Calcd for C_7H_{12}: C, 87.42; H, 12.58. Found: C, 87.21; H, 12.47.

1-Phenyl-2-Cyclopropylpropene-1 (IVb).—To an ethanolic solution of the Wittig reagent, prepared from 47.5 g (0.123 mole) of benzyl-triphenylphosphonium chloride, was added 10.3 g (0.123 mole) of cyclopropyl methyl ketone at room temperature over a period of 10 min. The reaction mixture was refluxed for 3.5 hr and worked up in usual way. The product, IVb, was obtained in a yield of 31% (6 g), bp 108° (15 mm).

Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.17; H, 8.95.

Ethyl 3-Cyclopropyl-2-butenoate (IVc).—To a suspension of 1.2 g (0.05 mole) of sodium hydride in 100 ml of 1,2-dimethoxyethane was added 11.2 g (0.05 mole) of diethyl carboethoxymethylphosphonate over a period of 50 min. After the reaction mixture was stirred for 2 hr at room temperature, 4.2 g (0.05 mole) of cyclopropyl methyl ketone was added to the mixture over a period of 5 min, and then it was heated at 55° for 19 hr. The reaction mixture was poured into 300 ml of water and the organic layer was extracted with ether. The ethereal solution was distilled to give 5.6 g of IVc, the yield being 73%, bp 82–85° (17 mm).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.88; H, 9.18.

Complexes IIa–c.—An equimolar solution of IVa–c and bisbenzonitriledichloropalladium in benzene was refluxed (IVc) for 60 hr or was allowed to stand at room temperature (IVa,b) for 19 hr and was then poured into a large excess of petroleum ether. The precipitate formed was filtered and the filtrate was concentrated to give the complex which was purified by recrystallization from toluene (IIa,c) or benzene (IIb).

Registry No.—IVa, 5860-30-0; IVb, 15353-03-4; IVc, 825-78-5.

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(8) The type II' complex might exist in the by-products.

The Preparation of 4-Substituted Bicyclo[2.2.1]heptane-1-carboxylic Acids[1]

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In a recent paper, the p*K*'s of several 4-substituted bicyclo[2.2.2]octane- and bicyclo[2.2.1]heptanecarboxylic acids in various solvents were reported.[2] This paper presents the syntheses of the bicycloheptane acids, which were all new compounds. The corresponding bicyclooctane acids were either available from earlier work or were prepared by known literature methods.

The key to the synthesis of the bicycloheptane acids was the conversion of 1,4-dichlorobicyclo[2.2.1]heptane[3] (1) into the 1,4-diacid, 2, since the methods already developed[4] for the synthesis of the bicyclooctane acids could be applied to the heptane diacid. The obvious method for conversion of the dichloride into the diacid was by carbonation of some metallic derivative. Several analogous reactions had been reported for the conversion of 1-chloro compounds into monoacids.[5–8]

Our early experiments in this direction were unsuccessful.[9] The dichloride did not react with lithium or sodium–potassium alloy in cyclohexane or decalin. In tetrahydrofuran or dibutyl ether, a reaction did occur, but apparently the intermediate anion abstracted hydrogens from the solvents since the only product isolated was norbornane. With sodium–potassium alloy in cyclohexane–benzene only benzoic acid was isolated. An attempt to carry out a lithium–halogen exchange on the dichloride with butyllithium in diethyl ether failed as did an attempt to form a transient Grignard reagent in cyclohexane–pyridine mixtures.

In the present work it was confirmed that 1-chlorobicyclo[2.2.1]heptane was readily converted into the

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(1) Based on the Ph.D. Dissertation of C. Leung to be submitted to the Cornell Graduate School, Ithaca, N. Y., Sept 1967. This material was presented in part at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

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(3) C. F. Wilcox, Jr., and J. G. Zajacek, *J. Org. Chem.*, **29**, 2209 (1964).

(4) C. F. Wilcox, Jr., and J. S. McIntyre, *ibid.*, **30**, 777 (1965), and references therein.

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