DL-3-Benzoyloxy-1-hexyne[12] (3). A. From DL-3-Tolysulfonyloxy-1-hexyne (2).—A stirred mixture of DL-3-*p*-tolysulfonyloxy-1-hexyne (2, 2.00 g) and sodium benzoate (7.5 g) in dry *N,N*-dimethylformamide (300 ml) was heated for 5 hr at 120–130°. The solution was poured into ice and water (800 ml) and the mixture was extracted with three 100-ml portions of chloroform. The extract was washed with three 100-ml portions of water and dried (magnesium sulfate) and the solvent was evaporated at 60° (3–4 torr) to yield a yellow chromatographically homogeneous, mobile oil. Distillation gave 894 mg (56%) of pure **3**: bp 96–98° (0.7 torr); R_f 0.9; λ_{max}^{film} 3.12 (C≡CH), 4.77 (C≡C), 5.80 μm (C=O); nmr (chloroform-*d*), τ 1.89, 2.53 (multiplets, five protons, aryl), 4.32 (one-proton triplet of narrow doublets, $J_{3,4}$ = 6.5 Hz, H-3), 7.52 (one-proton doublet $J_{1,3}$ = 2 Hz, H-1), 8.32, 9.02 (multiplets, seven protons, propyl).

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.23; H, 6.95.

B. From DL-1-Hexyn-3-ol (1).—To a solution of 1 (2 g) in dry pyridine (20 ml) at 0° was added benzoyl chloride (2.7 ml, ~1.1 mole equiv) dropwise with shaking. The solution was kept for 1 hr at 0° and a further 3 hr at room temperature. A few drops of water were then added and after 10 min the mixture was poured into aqueous sodium hydrogen carbonate (400 ml). The product was extracted with three 50-ml portions of chloroform, and the extract was washed with two 50-ml portions of water, dried (magnesium sulfate), and concentrated. Pyridine was removed by coevaporation with toluene, and the product was distilled to give 2.2 g (53%) of **3**, bp 80–82° (0.1 torr), identical with the product prepared by method A, by tlc and by comparative ir and nmr spectra.

Nmr Data for DL-1-Hexyn-3-ol (1) and Its Acetate.—Substance 1 (R_f 0.5 in 9:1 benzene–ether) gave the following data (carbon tetrachloride): τ 5.69 (one-proton triplet of narrow doublets, $J_{3,4}$ = 6 Hz, $J_{1,3}$ = 2 Hz, H-3), 6.65 (one-proton singlet, OH), 7.65 (one-proton doublet, H-1), 8.40, 9.05 (multiplets, seven protons, propyl).

Acetylation of 1 with acetic anhydride and pyridine gave chromatographically homogeneous DL-3-acetoxy-1-hexyne: bp 155–165° (760 torr) (lit.[10] bp 74° (30 torr)); R_f 0.9 (9:1 benzene–ether); λ_{max}^{film} 3.05 (C≡CH), 4.73 (C≡C), 5.75 μm (OAc), OH absent; nmr (carbon tetrachloride), τ 4.69 (one-proton triplet of narrow doublets, $J_{3,4}$ = 6 Hz, $J_{1,3}$ = 2 Hz, H-3), 7.65 (one-proton doublet, H-1), 7.99 (three-proton triplet, OAc), 8.39, 9.03 (multiplets, seven protons, propyl). In chloroform-*d* the spectrum was closely similar, except that the H-1 signal was observed at τ 7.54 and the acetoxy group signal was observed at 7.93.

Registry—1, 15352-98-4; 1 acetate, 15352-99-5; 2, 15353-00-1; 3, 15353-01-2.

(13) M. Koulkes and I. Marszak, *Bull. Soc. Chim. France*, 556 (1952).

Reaction of Bromine with α-Phenylcinnamic Acid

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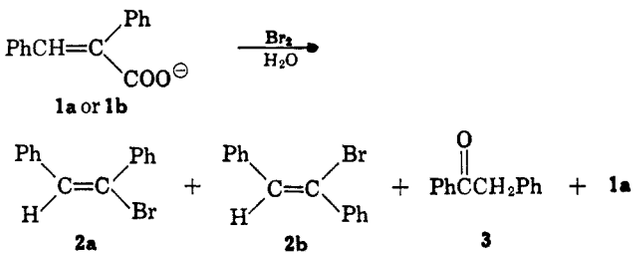
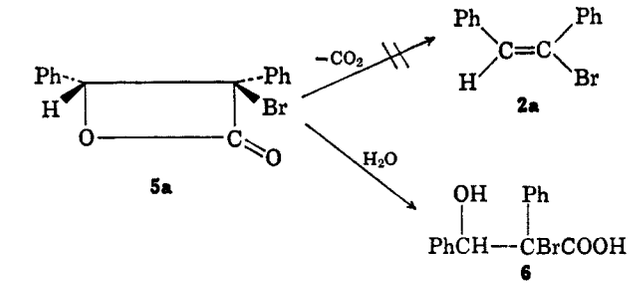
In connection with other studies we wished to obtain samples of *cis*- and *trans*-bromostilbene. An attractive synthesis appeared to be that reported by Berman and Price[2] in which the sodium salts of α-phenylcinnamic acids gave these bromostilbenes upon treatment with bromine in water. The reaction was reported as going in a stereospecific manner with retention; *i.e.*, sodium *cis*-α-phenylcinnamate (**1a**) gave *cis*-bromostilbene (**2a**) and sodium *trans*-α-phenylcinnamate (**1b**) gave *trans*-bromostilbene (**2b**).[3] In our hands, under similar conditions, these sodium salts of α-phenylcinnamic acid gave α-bromostilbenes with little stereoselectivity. In addition to the α-bromostilbenes obtained, deoxybenzoin (**3**) was also a major product and, in fact, in the reaction of bromine with **1b**, **3** proved to be the major product.

Adding 1 equiv of Br_2 to a solution of **1a** in slightly basic aqueous solution at 55° gave **2a**, **2b**, and **3** (in the ratio of 21:16:11, respectively) along with recovered **1a**. This same reaction with **1b** gave **2a**, **2b**, **3** (in the ratio of 8:5:61), and **1a** with no observable amount of **1b** recovered.



Varying the temperature from 40 to 70° had little effect on the course of the reaction. Increasing the base concentration gave lower yields, presumably owing to the consumption of bromine by hydroxide ion, but did not significantly affect the relative amounts of reaction product.

The stereoselectivity of these reactions of **1a** and **1b** with bromine as observed by Berman and Price[2] was explained by invoking a bromonium ion intermediate (**4**) which lost carbon dioxide before equilibration could take place through an open carbonium ion. They ruled out the formation of the lactone **5** since this should not lose carbon dioxide to give bromostilbene[4] but should undergo hydrolysis in protic solvent to give β-hydroxy acid (**6**).[5,6] In contrast, Tarbell and Bartlett[7] observed the formation of lactones in the bromination of α,β-unsaturated carboxylic acids. These lactones opened to the corresponding β-hydroxy acids upon hydrolysis.



The fact that we observe little or no stereoselectivity in this reaction strongly suggests that the intermediate bromonium ion goes to or equilibrates with an open-chain carbonium ion (**7**) thus inducing loss of stereochemistry. Such a species as **4** or **7** can lose carbon dioxide and give bromostilbene, or ring close to give

(1) To whom inquiries should be sent: Department of Chemistry, University of Maryland, College Park, Md.

(2) J. D. Berman and C. C. Price, *J. Am. Chem. Soc.*, **79**, 5474 (1957).

(3) Berman and Price[2] report isolating a 20% yield of diphenylacetylene from this latter reaction. We observe at the most only trace amounts of diphenylacetylene.

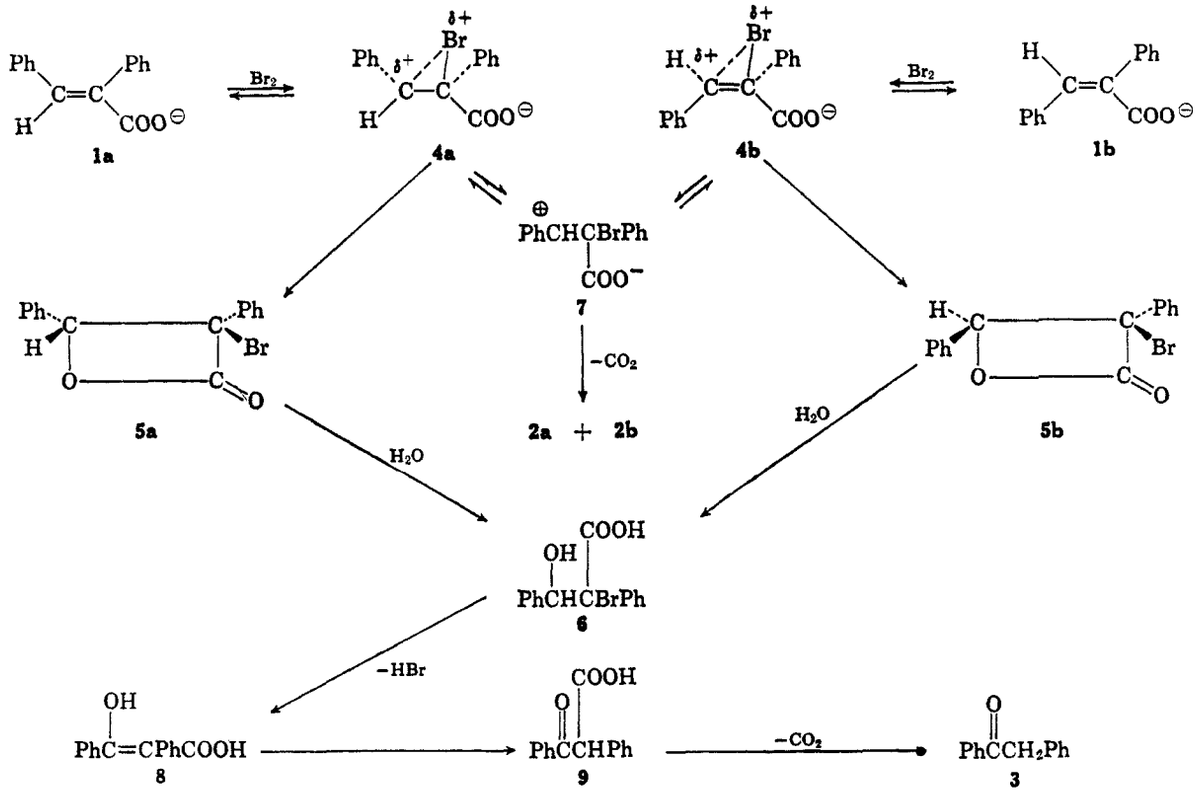
(4) A. Basler, *Ber.*, **16**, 3001 (1883).

(5) H. Staudinger, *ibid.*, **41**, 1355 (1908).

(6) H. Solkowski, *J. Prakt. Chem.*, **106**, 253 (1923).

(7) D. S. Tarbell and P. D. Bartlett, *J. Am. Chem. Soc.*, **59**, 407 (1937).

SCHEME I



the lactone **5**. One might have anticipated the formation of the open carbonium ion **7** in analogy to that observed in the bromination of the stilbenes.[8] In polar solvent both *cis*- and *trans*-stilbene reacted with bromine to give the same mixture of stilbene dibromides. Furthermore, after partial reaction, *cis*-stilbene was found to have partially isomerized to *trans*-stilbene.[8] These data seem well accounted for by assuming an equilibration between the bromonium ion and the open carbonium ion. Note that we too observe isomerization of the less stable isomer to the more stable isomer (**1b** → **1a**) under the influence of bromine.[9]

Our view of the reaction of bromine with **1** is shown in Scheme I.

The fact that **1b** gives rise to larger amounts of deoxybenzoin (**3**) than does **1a** is due probably to the reluctance of **4a** to cyclize to **5a** compared with **4b** going to **5b**. The phenyl rings are forced into one another in going from **4a** to **5a** while in going from **4b** to **5b** there is a sterically smaller phenyl–bromine eclipsing. The ratio of **2a** to **2b** in both reactions is similar enough to propose that a significant percentage of both reactions leading to the bromostilbenes goes through **7**.[10] From these data, it appears that the majority of the lactone must come from **4a** (or **4b**) for, if **7** gave rise to the lactones as well as to the bromostilbenes, the ratio of **2** to **3** would be the same starting with either **1a** or **1b**. Hydrolysis of the lactone **5** should be rapid to give **6** which could easily lose hydrogen bromide to give **8**[11] and then tautomerize to **9**. Under the reaction conditions, **9** would decarboxylate to **3**.[12–13]

(8) R. E. Buckles, J. M. Badar, and R. J. Thurmaier, *J. Org. Chem.*, **27**, 4523 (1962).

(9) The equilibrium mixture of α-phenylcinnamic acid is reported to be 81% *cis*- and 19% *trans*-α-phenylcinnamic acid: H. E. Zimmerman and L. Abramjian, *J. Am. Chem. Soc.*, **81**, 2086 (1959).

(10) The fact that we observe the less stable *cis*-bromostilbene (**2a**) predominating over the more stable *trans*-bromostilbene (**2b**) in both reactions is somewhat surprising. No explanation for this can be offered at the present. This as well as other facets of these reactions are being studied further.

Experimental Section[14]

Addition of Bromine to Sodium *cis*-α-Phenylcinnamate (1a).—*cis*-α-Phenylcinnamic acid[15] (5 g, 23 mmoles) was added to 15 ml of water at 55°. A 10% sodium hydroxide solution was added slowly until the acid was dissolved. The pH of the resulting solution was *ca.* 8–9. To this solution was added with stirring 3.7 g (23 mmoles) of bromine (dropwise). After all the bromine had been added, the reaction mixture was allowed to stir for an additional 10 min at 55°. This mixture was then washed with ether into a separatory funnel containing 50 ml of 2% sodium hydroxide solution. The resulting solution was extracted well with ether, and the ether layers combined and washed once with 50 ml of 2% sodium hydroxide solution. The aqueous washings were combined and saved. The ethereal fraction was dried with anhydrous magnesium sulfate. The ether was removed *in vacuo* and the resulting oil was analyzed by glpc (F & M 5750 with 0.25-in. (OD) column, 6 ft in length, with 10% silicon gum rubber (SE-30) on diaport P; temperature at 180°). The analysis showed there to be three major peaks: *cis*-bromostilbene, 4.8 mmoles (21%); deoxybenzoin, 2.6 mmoles (11%); and *trans*-bromostilbene, 3.7 mmoles (16%) (in order of increasing reten-

(11) Loss of hydrogen bromide from **6** in a 1,3 manner would give 2,3-diphenylglycidic acid which might also have lost carbon dioxide to give **3**. However, 2,3-diphenylglycidic acid is apparently stable under these conditions and should be isolable: H. E. Zimmerman, L. Singer, and B. S. Thyagarajan, *J. Am. Chem. Soc.*, **81**, 108 (1959). None was found.

(12) (a) S. D. Work, D. R. Bryand, and C. R. Hauser, *J. Org. Chem.*, **29**, 722 (1964); (b) D. Ivanov and N. J. Nicolov, *Bull. Soc. Chim. France*, **51**, 1331 (1932).

(13) NOTE ADDED IN PROOF.—In a private communication Professor Price has confirmed that the previous results in this system[2] were not reproducible. Furthermore, evidence has been found for the intermediacy of a β-lactone in the reaction of the silver salts of **1** with bromine: H. Blunt, Ph.D. Thesis, University of Pennsylvania, 1965.

(14) Melting points were determined on a Fisher-Johns apparatus and are uncorrected.

(15) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 3rd ed, 1957, p 182.

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.

(16) J. Wislicenos and F. Seeler, *Ber.*, **28**, 2692 (1895).
(17) G. Drefahl and C. Zimmer, *Chem. Ber.*, **93**, 505 (1960).

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

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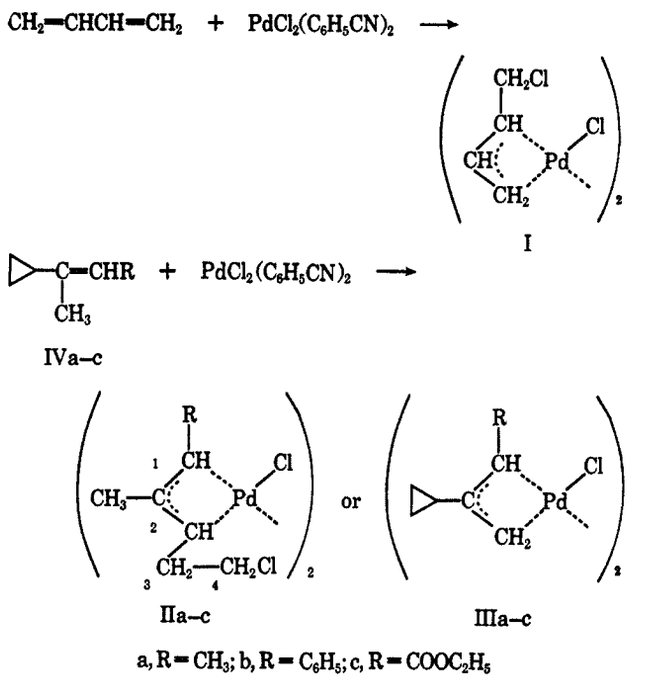
The possibility of conjugative interaction of a cyclopropane ring with an adjacent unsaturated group has been of interest to many workers. Recent nmr,[1] electron diffraction,[2] and solvolysis studies[3] have strongly suggested the existence of such an interaction. In the present study, we wish to report 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

(1) G. L. Closs and H. B. Klinger, *J. Am. Chem. Soc.*, **87**, 3265 (1965).
(2) L. S. Bartell and J. P. Guillory, *J. Chem. Phys.*, **43**, 647 (1965).
(3) H. C. Brown and J. D. Cleveland, *J. Am. Chem. Soc.*, **88**, 2051 (1966).
(4) J. Tsuji and S. Hosaka, *ibid.*, **87**, 4075 (1965).
(5) Our attention has been called to the fact that the formation of type II complex from vinylcyclopropane was reported by A. D. Ketley and J. A. Braatz [*J. Organometal. Chem.* (Amsterdam), **9**, 5 (1967)].
(6) J. Tsuji, S. Imamura, and J. Kiji, *J. Am. Chem. Soc.*, **86**, 4491 (1964).

(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, 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.