into the bottom of the reaction vessel and allowed to sweep through the entire system. The cooling bath surrounding the biallyl trap now was replaced by a liquid nitrogen bath and sweeping with helium was continued for 7 hr until some 10–15 l. of helium had passed through the system. The biallyl trap was found to contain 0.631 g (7.68 mmoles, 46% yield) of crude biallyl. In the present run the crude biallyl was subjected to ozonization in chloroform solution without prior purification. Half of the ozonide solution was reduced with zinc and aqueous acetic acid and worked up as described above. The dimethone derivative was put through the modified Vorländer procedure for separation of formaldimethone from acetaldimethone but was found to contain only formaldimethone. After three recrystallizations from absolute ethanol, the formaldimethone amounted to 0.371 g of material, mp 190–191.3° (activity 0.0329 ± 0.0003 μcurie/mmole); after another recrystallization from aqueous ethanol the compound had activity of 0.0330 ± 0.0005 μcurie/mmole. The other half of the ozonide solution was worked up according to the procedure of Bailey.[49] Solvent was removed from the ozonide *in vacuo* at room temperature on a rotating evaporator. To the residual thick, syrupy liquid was added 25 ml of 90% formic acid and 12 ml of 30% hydrogen peroxide. The reaction mixture was warmed to initiate reaction; after the initial reaction had ceased the reaction mixture was heated at reflux for 30 min and allowed to stand overnight. The solvent was removed with the aid of a rotating evaporator and the residue of succinic acid was sublimed *in vacuo*. After a second vacuum sublimation, 0.346 g of succinic acid of activity 0.1426 ± 0.0009 μcurie/mmole was obtained. After one recrystallization from water and two more vacuum sublimations the succinic acid had mp 184.2–184.7° and activity of 0.1409 ± 0.0009 μcurie/mmole.

Runs 1 and 2 of Table VII were run similarly except that for these runs the crude biallyl before ozonization was subjected to some purification by vapor phase chromatography on a large preparative column (Perkin-Elmer column E, 3 m long and 25 mm in diameter, operated at 32–34°). In run 4 the sodium amide present was destroyed in the usual manner by addition of ammonium chloride (0.829 g, 15.5 mmoles) 20 min after completion of the addition of sodium. The unreacted allyl chloride was, in the course of the usual sweeping process, collected along with biallyl in the cold trap and then the mixture of biallyl and allyl chloride was separated by vapor phase chromatography at 40° on the preparative column mentioned above (retention time of biallyl, 5.6 min; allyl chloride, 11 min). Ozonization of the recovered allyl chloride was carried out in the usual manner. The sample of allyl-1-$C^{14}$ chloride used in run 4 was subjected to similar vapor phase chromatography before ozonization.

**Assays for Radioactivity.** Organic samples for radioactivity determinations were converted to carbon dioxide by a wet oxidation method with combustion reagents prepared according to the procedure of Van Slyke, *et al.*[50] The procedure and apparatus were similar to that of Neville[51] but a U tube filled with $SnCl_2 \cdot 2H_2O$ crystals and a tube packed with lead dioxide heated at 180° were placed in the combustion line, in the order given, between the combustion flask and the ionization chamber. Two to three combustions were generally run on each of the present samples.

Radioactivities were measured with a vibrating-reed electrometer (Applied Physics Corp., Model 31) by the "rate of drift method" (the time, in the present work ordinarily 200–500 sec, was measured for a condenser to become charged a predetermined amount by the ionization current arising from the radioactivity). Each sample of radioactive carbon dioxide was counted an average of three times. The numbers given in the tables are the average values of the activity. The ± numbers after each value refer usually to the mean deviation of the average value from the individual values for separate combustions or sometimes to the mean deviation in counting the samples of carbon dioxide, whichever is the larger of these two possibilities. The average of the combined activities of propylene and formaldehyde for eight samples of propylene from a common sample of allyl-1-$C^{14}$-trimethylammonium chloride in Tables V and VI is 0.3563 ± 0.0066 μcurie/mmole. These values were determined over a period of 5 months and demonstrate reasonable stability of the instrument used for measuring radioactivity. It is believed that the ratios of the activity of formaldimethone to that of acetaldimethone anhydride may be more accurately compared than the magnitude of the individual activities since for each sample of propylene the corresponding ozonolysis products were ordinarily assayed on the same day and therefore small variations in instrument and cell response from day to day should tend to cancel in comparisons of the ratios of activity. Since no primary standard was always available to calibrate our electrometer, the molar activities are reported in self-consistent units which are only approximately those of microcuries per mmole.

**Acknowledgments.** This work was supported generously by the U. S. Atomic Energy Commission under Contract AT-(40-1)-2453 and in part from institutional grant funds from the National Science Foundation. One of us (E. G.) wishes to acknowledge an informative conversation with Professor B. M. Wepster on related unpublished work in Professor Wepster's laboratory.

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(49) P. S. Bailey, *J. Org. Chem.*, **22**, 1548 (1957).

(50) D. D. Van Slyke, J. Plazin, and J. R. Weisiger, *J. Biol. Chem.*, **191**, 299 (1951).

(51) O. K. Neville, *J. Am. Chem. Soc.*, **70**, 3499 (1948).

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# Organic Syntheses by Means of Noble Metal Compounds. XXII.[1]
# Palladium-Catalyzed Carbonylation of Diphenylacetylene

**Jiro Tsuji and Tatsuo Nogi**

*Contribution from the Basic Research Laboratories, Toyo Rayon Co., Ltd., Kamakura, Japan. Received November 19, 1965*

**Abstract:** Diphenylacetylene and carbon monoxide react in ethanol in the presence of palladium chloride and hydrogen chloride to form α,β-diphenyl-γ-crotonolactone. The structure of the lactone was confirmed by several chemical transformations. No carbonylation was observed in the reaction carried out in benzene.

The interaction of palladium chloride with diphenylacetylene to form the tetraphenylcyclobutadiene–palladium chloride complex and related products has been a subject of extensive studies.[2] It is apparent from these studies that palladium chloride and diphenyl-

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[1] Part XXI: J. Tsuji and K. Ohno, *Tetrahedron Letters*, 3969 (1965).

[2] L. Malatesta, G. Santarella, L. M. Vallarino, and F. Zingales, *Angew. Chem.*, **72**, 34 (1960); A. T. Blomquist and P. M. Maitlis, *J. Am. Chem. Soc.*, **84**, 2329 (1962); P. M. Maitlis and M. L. Games, *Can. J.*

**Table I.** Carbonylation of Diphenylacetylene[a]

| Diphenylacetylene, g | Catalyst, g | Solvent, ml | Lactone (I), g (%) | Other products, g (%) |
|---|---|---|---|---|
| 10 | $PdCl_2$, 3 | HCl (10%)/EtOH, 45 | 8.7 (66) | Diester (II), 4.7 (26) |
| 10 | $PdCl_2$, 2 | EtOH, 50 | 2.7 (20) | 2,3-Diphenylacrylate[b] |
| 5 | 10% Pd–C, 2 | HCl (10%)/EtOH, 50 | 2.3 (35) | 2,3-Diphenylacrylate[b] |
| 3.5 | $PdCl_2$, 2 | HCl (10%)/MeOH, 50 | 2.8 (60) | Diester (II), 2 (34) |
| 5 | $PdCl_2$, 2 | HCl (10%)/benzyl alcohol, 30 | 3.8 (58) | Benzyl ether, 3 |

[a] Reaction temperature 100°, CO pressure 100 kg/cm²; reaction time 15 hr. [b] Only small amount, and yield was not determined.

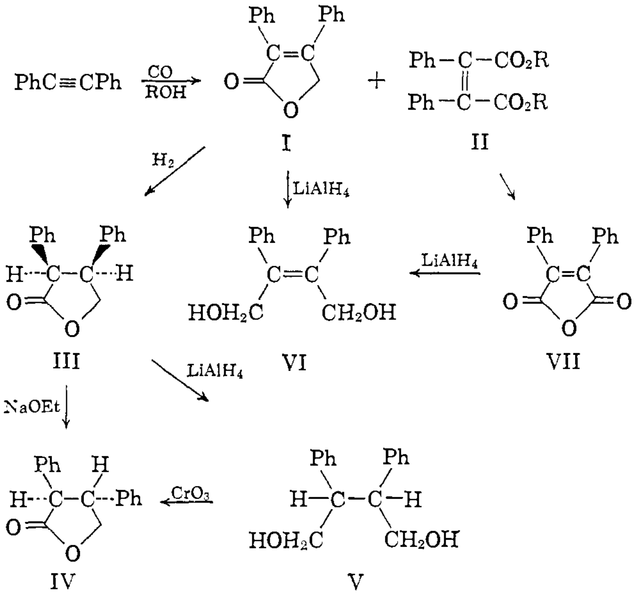
acetylene react very easily. Furthermore, chemical properties of these complexes have been studied as well as carbonylation of the tetraphenylcyclobutadiene complex to form 2,3,4,5-tetraphenyl-2-cyclopentenone and small amount of tetraphenylcyclopentadienone.[3] However no studies on the direct carbonylation of diphenylacetylene catalyzed by palladium chloride have been reported. On the other hand, carbonylation of diphenylacetylene was studied using nickel carbonyl as catalyst in various solvents;[4] ethyl 2,3-diphenylacrylate was obtained in a mixture of benzene and ethanol, and 2,3,4,5-tetraphenylcyclopentenone was obtained as the main product in a mixture of dioxane and ethanol.

We have studied the catalytic carbonylation of various olefinic compounds using palladium as catalyst.[5] The carbonylation of acetylene gave rise to maleyl and muconyl chloride in benzene,[6] and acrylate, maleate, and fumarate were obtained in ethanol.[7] The carbonylation of diphenylacetylene was attempted under various conditions and an unexpected product was obtained. The results are described in this paper.

## Results and Discussion

We have reported before that hydrogen chloride and metallic palladium were essential for the catalytic carbonylation of various olefinic compounds. Therefore, the carbonylation of diphenylacetylene was attempted in ethanol, containing hydrogen chloride, under a carbon monoxide pressure of 100 kg/cm.[2] Under these conditions, carbonylated products were obtained in high yield. It was found that the concentration of hydrogen chloride had a vital influence on the product of carbonylation. Thus in a 10% solution, the main product was an unsaturated lactone, accompanied by a small amount of ethyl diphenylmaleate. No 2,3,4,5-tetraphenylcyclopentenone was obtained. The results of the carbonylation under different conditions are given in Table I. Thus unlike the reaction catalyzed by nickel carbonyl, palladium-catalyzed carbonylation of diphenylacetylene gave dicarbonylation products in the presence of hydrogen chloride and the extent of monocarbonylation was very small. At a lower concentration of hydrogen chloride, yield of the dicarbonylation products decreased drastically and a small amount of ethyl 2,3-diphenylacrylate was detected as shown in the table. The dramatic increasing effect of hydrogen chloride on the extent of dicarbonylation was also observed with other acetylenic compounds.[7a]

The structure of the lactone was determined as the previously unknown α,β-diphenyl-γ-crotonolactone in the following reaction sequences.



Infrared bands at 1750 and 1640 cm⁻¹ showed the presence of an unsaturated γ-lactone. An nmr spectrum showed only two peaks at τ 2.71 (aromatic ring protons) and 4.95 (singlet). An ultraviolet absorption maximum at 283 mμ (ε 23,500) supports the structure of the α,β-unsaturated γ-lactone. Hydrogenation over palladium on carbon formed *cis*-diphenyl-γ-butyrolactone (III; infrared 1760 cm⁻¹). By the treatment of the *cis* lactone III with sodium ethoxide, the less hindered *trans* lactone (IV) was obtained, which showed an infrared band at 1775 cm⁻¹. The reduction of the saturated lactone (III) with lithium aluminum hydride gave *meso*-2,3-diphenyl-1,4-butanediol (V), which is a known compound.[8] An attempt to oxidize the diol V to known diphenylsuccinic acid with chromic anhydride in pyridine was not successful and the saturated *trans* lactone IV was formed instead. The reduction of the unsaturated lactone with lithium aluminum hydride gave rise to *cis*-2,3-diphenyl-2-butene-1,4-diol (VI). On the other hand, ethyl diphenylmaleate which is a

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*Chem.*, **42**, 183 (1964); P. M. Maitlis, A. Efraty, and M. L. Games, *J. Am. Chem. Soc.*, **87**, 719 (1965); R. Huttel and H. J. Neugebauer, *Tetrahedron Letters*, 3541 (1964).

(3) (a) L. M. Vallerino and G. Santarella, *Gazz. Chim. Ital.*, **94**, 252 (1964); (b) R. C. Cookson and D. W. Jones, *J. Chem. Soc.*, 1881 (1965).

(4) G. P. Mueller and F. L. MacArtor, *J. Am. Chem. Soc.*, **76**, 4621 (1954).

(5) J. Tsuji, J. Kiji, S. Imamura, and M. Morikawa, *ibid.*, **86**, 4350 (1964), and the literature cited therein.

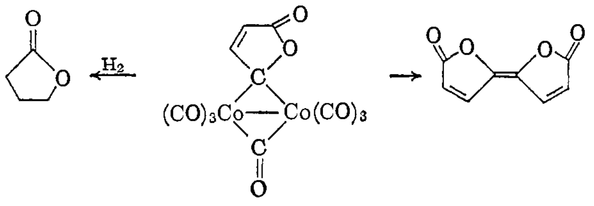
(6) J. Tsuji, M. Morikawa, and N. Iwamoto, *ibid.*, **86**, 2095 (1964).

(7) (a) J. Tsuji, M. Morikawa, and T. Nogi, unpublished work; (b) G. Jacobsen and H. Spathe, German Patent 1,138,760 (1962); *Chem. Abstr.*, **58**, 6699 (1963).

(8) (a) A. G. Brook, H. L. Cohen, and G. F. Wright, *J. Org. Chem.*, **18**, 447 (1953); (b) F. F. Blicke, P. E. Wright, and W. A. Gould, *ibid.*, **26**, 2114 (1961); (c) G. Fraenkel and P. D. Bartlett, *J. Am. Chem. Soc.*, **81**, 5589 (1959).

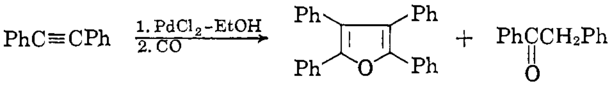
minor product of the carbonylation, was hydrolyzed to a free acid with base, but the acid was converted into the known diphenylmaleic anhydride (VII) when the hydrolyzed solution was acidified. The reduction of diphenylmaleic anhydride with lithium aluminum hydride gave rise to the diol VI which was identified as the diol obtained from the lactone I. These physical and chemical properties clearly support the structure of the lactone I.

Concerning the reaction mechanism of the formation of the lactone I, it is reasonable to assume that the lactone was formed *via* the *cis* addition of 2 moles of carbon monoxide to the triple bond. Then the diester (II) or anhydride (VII) should be the reaction products of the carbon monoxide addition. Therefore, the first thing to consider is reduction of one of the carbonyl groups to form a lactone. There is one case of a lactone formation in the literature by the carbonylation of acetylene with cobalt carbonyl and the following complex was assumed to be the intermediate of the reaction.[9] This complex was converted to the dimeric lactone. It was also reported that the complex gave rise to γ-butyrolactone by hydrogenation.[10] Although no complex was isolated in the present carbonylation of diphenylacetylene, a similar intermediate complex of palladium seems to be reasonable for the formation of the lactone (I). Hydrogenolysis of the palladium–carbon bond in the complex should give the lactone. But no definite mechanism can be given without further evidence.



The true catalyst of this carbonylation is metallic palladium and hydrogen chloride. For example, palladium on carbon in the presence of hydrogen chloride was found to be an active catalyst for the formation of the lactone. The concentration of hydrogen chloride seems to affect the yield of the products as shown in the table.

When the reaction was carried out in benzene saturated with hydrogen chloride, no carbonylation was observed and the product was hexaphenylbenzene. As reported by several workers,[2] diphenylacetylene and palladium chloride react easily to form the tetraphenylcyclobutadiene complex. It seems likely that the presence of carbon monoxide plays an important role when palladium chloride comes in contact with diphenylacetylene. From this consideration, the following experiment was carried out. Diphenylacetylene was treated with equivalent amount of palladium chloride in ethanol, containing hydrogen chloride, in an autoclave for 1 hr at 50°, and then carbon monoxide was introduced. In this case, no lactone was formed and the products were tetraphenylfuran (VIII) and desoxybenzoin (IX). The formation of the former from the tetraphenylcyclobutadiene complex is known.[3b] Desoxybenzoin was formed by acid-catalyzed addition of ethanol to the triple bond. This fact shows that the presence of carbon monoxide before complex formation is essential for the lactone formation. Probably, palladium chloride is reduced to metallic palladium by the action of carbon monoxide and ethanol, and the reduced palladium acts as catalyst of the carbonylation.



VIII IX

## Experimental Section

The nmr spectra were determined with Varian high-resolution spectrometers, Models DP 60 and HR 100 using tetramethylsilane as an internal standard. The molecular weights were determined in benzene using a Mechrolab vapor pressure osmometer.

**Materials.** Commercially available anhydrous palladium chloride was used without further purification. Carbon monoxide was also a commercial product (99.5% pure).

**Carbonylation of Diphenylacetylene. 1. Carbonylation in Ethanol (Experiment 1).** Diphenylacetylene (10 g) and 45 ml of ethanol, containing hydrogen chloride (10%) and palladium chloride (3 g), were mixed in a glass vessel equipped with a gas inlet capillary. The vessel was set in a 300-ml stainless steel autoclave, and carbon monoxide was introduced (100 kg/cm²). The reaction was carried out at 100° for 15 hr with constant shaking. After cooling, the formation of some crystalline material was observed in the glass vessel. The crystals were dissolved by adding warm alcohol and the solution was separated from metallic palladium by filtration. The alcoholic solution was concentrated until crystals began to deposit. The crystals were collected by filtration and recrystallized from ethanol to give 8.7 g (66%) of pure α,β-diphenyl-γ-crotonolactone, mp 115–116°.

*Anal.* Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12; mol wt, 236. Found: C, 81.46; H, 5.11; mol wt, 232.

The filtrate was confirmed as ethyl diphenylmaleate, yield 4.7 g (26%), which showed the following infrared and nmr spectra: 1725 and 1620 cm$^{-1}$; $\tau$ 2.95 (ring protons), 5.84, and 8.80 (ethyl protons). When ethanol was used without adding hydrogen chloride (experiment 2), the formation of ethyl 2,3-diphenylacrylate was detected by gas chromatography. But no attempt was made to determine the yield.

**2. Attempted Carbonylation in Benzene.** Diphenylacetylene (4 g), benzene (50 ml), and palladium chloride (4 g) were mixed and treated with carbon monoxide (100 kg/cm²) in the same way as described above. After the reaction, different types of crystals formed two layers in the glass vessel. They were separated mechanically. The lower brownish ones were recrystallized from diphenyl ether repeatedly and hexaphenylbenzene was obtained. The infrared spectrum of hexaphenylbenzene was identical with that of an authentic sample. The reddish brown upper layer, which was the minor product, was insoluble in ordinary solvents and seemed to be a new palladium complex. Owing to the lack of solubility, the complex was washed with chloroform. It decomposed at about 170°. No further elucidation of the complex was carried out. Infrared bands at 1980 and 1795 cm$^{-1}$ were observed.

**3. Reaction of Diphenylacetylene and Palladium Chloride, Followed by Carbonylation.** Palladium chloride (4 g), diphenylacetylene (4 g), and ethanol, containing hydrogen chloride (10%), were placed in the glass vessel and the mixture was shaken at 50° for 1 hr in the autoclave. Then carbon monoxide was introduced (100 kg/cm²). The reaction was carried out at 100° for 15 hr with shaking. After the reaction, palladium was filtered off, and the filtrate was evaporated to dryness. The residue was separated into two products with ether. The ether-insoluble part was recrystallized from an ethanol–acetic acid mixture and 2.1 g of tetraphenylfuran was obtained (mp 169–171°; lit[3b] mp 170°). The ether-soluble fraction was recrystallized from methanol and 1.2 g of desoxybenzoin was obtained (mp 58–59°). Both were identified by infrared spectra.

**Structural Determination of α,β-Diphenyl-γ-crotonolactone. Hydrogenation of the Lactone.** The lactone (2 g) was hydrogenated in

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(9) H. W. Sternberg, J. G. Shukys, C. D. Donne, R. Markby, R. A. Friendel, and I. Wender, *J. Am. Chem. Soc.*, **81**, 2339 (1959).

(10) S. Sato, R. Morishima, and H. Wakamatsu, Abstracts of the Papers presented at 18th Annual Meeting of the Chemical Society of Japan, Osaka, April 1965.

ethanol in the presence of 10% palladium on carbon (0.5 g) for 5 hr. The catalyst was removed and the filtrate was evaporated to dryness. The residue was recrystallized from ethanol to give *cis*-$\alpha,\beta$-diphenylbutyrolactone (1.5 g), mp 128–129°. The lactone showed an infrared band at 1760 $cm^{-1}$.

*Anal.* Calcd for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92; mol wt, 228. Found: C, 80.41; H, 5.88; mol wt, 227.

**Conversion of the *cis* Lactone to the *trans* Lactone (IV).** The *cis* lactone (1 g) was dissolved in 10 ml of ethanol, and the solution was added to a sodium ethoxide prepared from 0.5 g of sodium and 10 ml of ethanol. The mixed solution was stirred at room temperature for 3 hr. After acidification of the solution with hydrochloric acid, the solution was extracted with ether. The ethereal solution was washed with water and dried. The ether was removed and the residue was recrystallized from ethanol to give the *trans* lactone (IV), mp 94–95°.

*Anal.* Found: C, 80.46; H, 5.90; mol wt, 225.

An infrared spectrum showed a carbonyl band at 1775 $cm^{-1}$.

**Reduction of the Lactone (I).** Lithium aluminum hydride (0.5 g) was added to ether (80 ml). To the solution was added dropwise over a period of 20 min an ethereal solution of the lactone (I, 1.2 g in 180 ml). The solution was stirred for 2 hr at room temperature. After the usual work-up, the residue was recrystallized from carbon tetrachloride to give needles of 2,3-diphenyl-2-butene-1,4-diol, mp 86.5–87.5°. The diol showed the following nmr peaks: $\tau$ 3.07 (ring protons), 5.60 (singlet, $CH_2$), 6.20 (OH).

*Anal.* Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71; mol wt, 226. Found: C, 79.79; H, 6.69; mol wt, 225.

**Reduction of Diphenylbutyrolactone.** Lithium aluminum hydride (0.5 g) was dissolved in 80 ml of ether and an ethereal solution of the butyrolactone (III, 1.2 g in 180 ml) was added. After the usual work-up, *meso*-2,3-diphenyl-1,4-butanediol was obtained, mp 143–144° (different melting points had been reported for this compound, 137–138°,[8a] 143–144°,[8b] and 153–154°[8c]).

*Anal.* Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49; mol wt, 226. Found: C, 78.98; H, 7.35; mol wt, 224.

**Formation of Diphenylmaleic Anhydride.** Ethyl diphenylmaleate (1 g) was added to a solution of ethanolic sodium hydroxide (3 g) and the solution was refluxed for 25 hr. The solution was acidified and then extracted with ether. Evaporation of ether gave diphenylmaleic anhydride which was recrystallized from ethanol, mp 155–156° (lit.[11] mp 158°).

**Reduction of Diphenylmaleic Anhydride.** The anhydride (VII, 1 g) was reduced with 0.5 g of lithium aluminum hydride in ether (250 ml) at room temperature. After the usual work-up, 2,3-diphenyl-2-butene-1,4-diol was obtained and identified with the diol obtained above by mixture melting point determination and infrared spectra.

**Chromic Anhydride Oxidation of the Diol (V).** A pyridine solution of chromic anhydride (1.7 g) was prepared by the known method. To the solution was added a solution of the diol (1 g) in pyridine (12 ml) and the mixture was stirred at room temperature for 2 hr, and left overnight. The reaction mixture was poured into water and extracted with ether. After the usual work-up, the residue was recrystallized from ethanol, and *trans*-diphenylbutyrolactone (IV) was obtained and identified with the one obtained above.

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[11] W. Metlescis and H. Zeiss, *J. Am. Chem. Soc.*, **81**, 4117 (1959).

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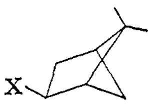
# Highly Strained Bicyclic Systems. XI. Synthesis of 2-Bicyclo[2.1.1]hexanol and Tricyclo[2.2.0.$0^{2,6}$]hexane-1-carboxylic Acid[1,2]

**J. Meinwald and J. K. Crandall**[3]

*Contribution from the Department of Chemistry, Cornell University, Ithaca, New York.* *Received October 1, 1965*

**Abstract:** A convenient synthetic route from bicyclo[2.2.1]heptadiene (**3**) to nortricyclanone (**7**) and then to a number of simple, bifunctional bicyclo[2.1.1]hexanes is described. Decarboxylation of the readily available 2-acetoxybicyclo[2.1.1]hexane-5-carboxylic acids (**12** and **13**) leads to the preparation of bicyclo[2.1.1]hexan-2-ol (**23**). Base treatment of the tosyloxy ester **26** yields **28**, the first representative of the tricyclo[2.2.0.$0^{2,6}$]hexane ring system; a discussion of the nomenclature problems posed by polycyclic molecules of this type is presented in the Appendix. Hydrogenolytic and base-catalyzed cleavages of this tricyclic nucleus are described.

Earlier papers of this series have been concerned with the synthesis of a number of substituted bicyclo[2.1.1]hexanes and an exploration of the chemistry of these highly strained compounds.[4] Of particular concern is the behavior of the various cations derived from this carbon skeleton. The homologous bicyclo[2.2.1]heptanes have enjoyed extensive investigation for a number of years, and this work has produced a host of highly interesting and important results of practical and theoretical significance.[5] It appeared worthwhile to extend these investigations to smaller ring, bridged, bicyclic systems. In this connection, the solvolysis of 5,5-dimethylbicyclo[2.1.1]hex-2$\beta$-yl tosylate (**1**, X = OTs) and the nitrous acid deamination of the corresponding amine (**1**, $X = NH_2$) have been discussed in prior publications.[6,7] To permit similar studies on the *parent* ring system, free of methyl substituents, simple bicyclo[2.1.1]hex-2-yl derivatives were required. Synthetic work leading to this objective is



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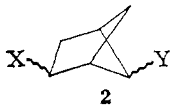

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[1] Presented in part at the 18th National Organic Chemistry Symposium, Columbus, Ohio, June 16–20, 1963, Abstracts, pp 37–44.

[2] The partial support of this research by National Science Foundation Research Grant G-22,541 is acknowledged with pleasure.

[3] National Institutes of Health Predoctoral Fellow, 1960–1963.

[4] For the previous paper in this series see J. Meinwald, C. B. Jensen, A. Lewis, and C. Swithenbank, *J. Org. Chem.*, **29**, 3469 (1964).

[5] J. A. Berson in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963.

[6] J. Meinwald and P. G. Gassman, *J. Am. Chem. Soc.*, **85**, 57 (1963).

[7] J. Meinwald and P. G. Gassman, and J. J. Hurst, *ibid.*, **84**, 3722 (1962).