

[CONTRIBUTION FROM THE RESEARCH CENTER, HERCULES POWDER CO., WILMINGTON, DEL.]

The Reaction of Cobalt Hydrotetracarbonyl with Olefins

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That cobalt hydrotetracarbonyl adds to olefins to form alkylcobalt tetracarbonyls, as the first step in the hydroformylation reaction, has been demonstrated by isolation of the resulting products as their monotriphenylphosphine adducts. Addition to 1-pentene gives approximately the same isomer distribution at 0° that it does at elevated temperatures, whereas the directions of addition to isobutylene and to methyl acrylate change with temperature. The addition is reversible. An investigation of the effect of CO on the addition reaction, on the subsequent reduction of the adduct, and on olefin isomerization led to the conclusion that these reactions involve coordinately unsaturated species. A unified mechanism is proposed for the hydroformylation reaction and the concurrent olefin isomerization.

Introduction

The addition of cobalt hydrotetracarbonyl to olefins has been postulated, on the basis of spectroscopic evidence, as the first step in the well-known hydroformylation or oxo reaction.¹ It was deemed important to obtain more direct evidence and to investigate the reaction in greater detail.

Very little is known about the reaction of cobalt hydrotetracarbonyl with olefins. If our postulate that this is the first step in the oxo reaction is accepted, most information comes from investigations of the products resulting from hydroformylation of olefins. There is qualitative, but not quantitative, agreement in the literature as to the composition of these products. Thus, according to Keulemans, Kwantes and van Bavel,² the distribution of alcohols derived from 1- and 2-pentene is about the same, 50–55% 1-hexanol, 35–40% 2-methyl-1-pentanol and 10% 2-ethyl-1-butanol. Goldfarb and Orchin³ reported 80% 1-hexanol and 14–18% 2-methyl-1-pentanol from 1-pentene, and 70% 1-hexanol and 26–30% 2-methyl-1-pentanol from 2-pentene; both olefins yielded 2–4% 2-ethyl-1-butanol. According to Hughes and Kirshenbaum⁴ the ratio of linear to branched products is a function of temperature and catalyst concentration, at least with terminal olefins. That some olefin isomerization accompanies hydroformylation has been proved by analysis of the remaining olefins in an interrupted hydroformylation reaction.^{5–6} Isobutylene is reported to yield about 97% 3-methylbutyraldehyde and 3% trimethylacetaldehyde,⁷ whereas according to Adkins and Krsek⁸ methyl acrylate gave exclusively methyl 3-formylpropionate.

Since the conditions used in the oxo reaction are generally rather drastic (100–300 atmospheres pressure of 1:1 CO–H₂ at 100–150°), the possibility exists that the aldehydes isolated do not reflect

the composition of the initial adducts. There is very little in the literature on low temperature reactions. Several workers^{9–11} have shown that 1-olefins react with cobalt hydrotetracarbonyl at room temperature to form aldehydes, but the composition of the products was not determined.

Results and Discussion

It had been demonstrated¹ that cobalt hydrotetracarbonyl reacts with a 1-olefin in the presence of CO to absorb more than 80% of the quantity of CO calculated for the formation of an acylcobalt tetracarbonyl. The solution showed a band at 5.8 μ indicative of an acylcobalt linkage, but the product was too unstable to isolate. When this reaction was carried out with 1-pentene at 0°, the addition of triphenylphosphine to the reaction mixture resulted in CO evolution and the isolation of a stable, crystalline mixture of monotriphenylphosphine adducts, with properties similar to those of other acylcobalt tricarbonyl triphenylphosphine complexes.¹² In the absence of CO, the same products were isolated, but the yield was lower because of subsequent reaction of the alkylcobalt carbonyl (*vide infra*). Cleavage of the crude complex with iodine and methanol yielded a mixture of isomeric methyl hexanoates. The reactions appear to take the course outlined in the diagram. Gas chromatographic analysis of the esters indicated the presence of approximately equimolar amounts of methyl *n*-hexanoate and methyl 2-methylpentanoate.¹³ Thus, it would appear that the addition of cobalt hydrotetracarbonyl to a straight-chain 1-olefin takes essentially the same course at 0° as it does at 120°.

Quite different results were obtained, however, with certain other terminal olefins. Isobutylene was treated with cobalt hydrotetracarbonyl and CO and then with triphenylphosphine as above. The complex was cleaved immediately with iodine and methanol; about a 20% yield of methyl trimethylacetate was obtained, essentially free of 3-methylbutyrate according to gas chromatographic analysis. Thus, the direction of addition at 0° is essentially the reverse of that at elevated temperatures.⁷

(9) I. Wender, H. W. Sternberg and M. Orchin, *ibid.*, **75**, 3041 (1953).

(10) P. Pino, R. Ercoli and F. Calderazzo, *Chim. e ind. (Milan)*, **37**, 783 (1955).

(11) L. Kirch and M. Orchin, *J. Am. Chem. Soc.*, **80**, 4428 (1958); **81**, 3597 (1959).

(12) R. F. Heck and D. S. Breslow, *ibid.*, **82**, 4438 (1960).

(13) Our gas chromatograph was unable to separate the 2-ethylbutyrate from the 2-methylpentanoate at the low concentrations used.

(1) R. F. Heck and D. S. Breslow, *Chemistry & Industry*, 467 (1960); Second International Catalysis Congress, Paris, France, July 4–9, 1960, paper 27.

(2) A. I. M. Keulemans, A. Kwantes and T. van Bavel, *Rec. trav. chim.*, **67**, 298 (1948).

(3) I. J. Goldfarb and M. Orchin, "Advances in Catalysis," Vol. IX, Academic Press, Inc., New York, New York, 1957, p. 609.

(4) V. L. Hughes and I. Kirshenbaum, *Ind. Eng. Chem.*, **49**, 1999 (1957).

(5) G. Natta, R. Ercoli and S. Castellano, *Chim. e ind. (Milan)*, **37**, 6 (1955).

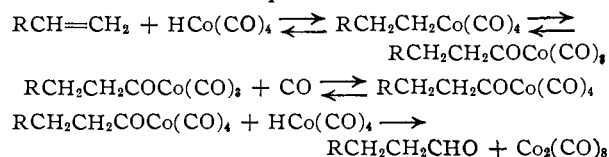
(6) I. Wender, S. Metlin, S. Ergun, H. W. Sternberg and H. Greenfield, *J. Am. Chem. Soc.*, **78**, 5401 (1956).

(7) I. Wender, J. Feldman, S. Metlin, B. H. Gwynn and M. Orchin, *ibid.*, **77**, 5760 (1955).

(8) H. Adkins and G. Krsek, *ibid.*, **71**, 3051 (1949).

of propionaldehyde and 5% of ethane. Propionylcobalt tetracarbonyl reacted similarly. A control experiment showed that the ethylene had not been formed from the triethyloxonium salt during the preparation of the cobalt compound. Irrespective of the fate of the cobalt, it would be converted into cobalt hydrotetracarbonyl under oxo conditions.

Although these reactions have been written as involving tetracarbonyls, evidence is accumulating that they instead involve tricarbonyls. Karapinka and Orchin¹⁷ found that the formation of aldehyde from olefin and cobalt hydrotetracarbonyl is inhibited by CO at 0°, although not at 25°. The reaction may be considered to take the following course,¹ illustrated with only one of the possible isomers. It was not possible to decide from their

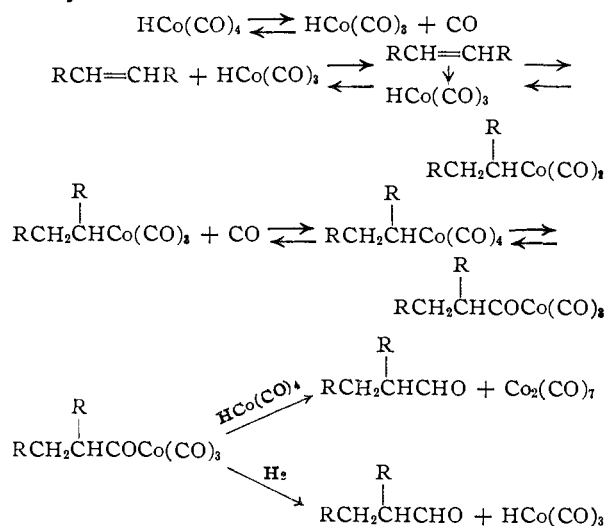


data, however, whether the addition to the olefin or the reduction of the acylcarbonyl by cobalt hydrotetracarbonyl was inhibited by CO.

We, therefore, repeated their experiments under conditions favoring formation of alkylcobalt carbonyls, *i.e.*, using a very large excess of olefin. Two identical experiments were carried out, one under nitrogen and the other under CO. In both, a solution of cobalt hydrotetracarbonyl was added to pure 1-pentene at 0°. After 15 minutes, the unreacted hydrocarbonyl was inactivated by adding excess dicyclohexylethylamine. The products then were analyzed by high resolution infrared spectroscopy, by which means it was possible to distinguish aldehydes, which absorb at 5.77 μ , and alkyl- or acyl-cobalt tetracarbonyls, which absorb at 5.81 μ . In the time allowed, the reaction under CO absorbed about 0.2 mole of gas per mole of hydrocarbonyl. A comparison of the spectra from the two reaction mixtures showed that, in the presence of CO, both the formation of alkyl- and acyl-cobalt carbonyls and their reduction to aldehydes were inhibited, essentially no aldehyde and about 30% less alkyl- or acyl-cobalt carbonyls being produced under one atmosphere of CO than under nitrogen.

The most reasonable explanation of these results is that the addition to olefin involves cobalt hydrotricarbonyl rather than tetracarbonyl. Probably the tetracarbonyl loses carbon monoxide to form tricarbonyl in a reaction which would be inhibited by carbon monoxide. The tricarbonyl then forms a π -complex with the olefin. Although we have no direct evidence for this essentially S_N1-type reaction, numerous reactions of metal carbonyls and their derivatives have been shown to take place by an S_N1 mechanism.¹⁸ The π -complex would then rearrange to an alkylcobalt tricarbonyl.¹ This would react with CO to give an alkylcobalt tetracarbonyl. Previously, we found that alkyl

tetracarbonyls are in equilibrium with acylcobalt tricarbonyls.¹ Reduction of the latter with cobalt hydrotetracarbonyl would yield aldehyde in another reaction inhibited by carbon monoxide; a less likely path would be reduction of acylcobalt tetracarbonyl by cobalt hydrotricarbonyl. Reduction of acylcobalt tricarbonyl by hydrogen rather than by hydrocarbonyl appears to be more likely in the oxo synthesis.¹



The isomerization of olefins by cobalt hydrotetracarbonyl can be explained by this mechanism. Here, too, Karapinka and Orchin¹⁷ found that the reaction was inhibited by carbon monoxide, and we confirmed their findings. It is reasonable to assume, therefore, that the actual isomerization catalyst is cobalt hydrotricarbonyl and that the isomerization takes the course in the formulas below. If certain assumptions are made, this scheme explains all the known facts in the reaction of cobalt carbonyls with olefins. The most important of these is that some complex, which we assume to be the olefin π -complex, must be an intermediate in the isomerization. The equilibrium mixture of 1-pentene and 2-pentene contains only about 5% 1-pentene at 125°. Since the 1-olefin forms aldehyde only 3.5 times faster than 2-olefin does,⁶ it would be impossible to obtain large amounts of *n*-aldehyde from 2-olefin unless a mechanism existed for going from 2-olefin to the products without the intermediate formation of 1-olefin.¹⁹ The observed ratio of aldehydes isolated is explainable if the assumption is made that the π -complex with 1-olefin is the most stable one²⁰ and that its formation is rapid compared with aldehyde formation or with return to olefin and hydrocarbonyl. This hypothesis also serves to explain why we were unable to demonstrate reversibility of addition

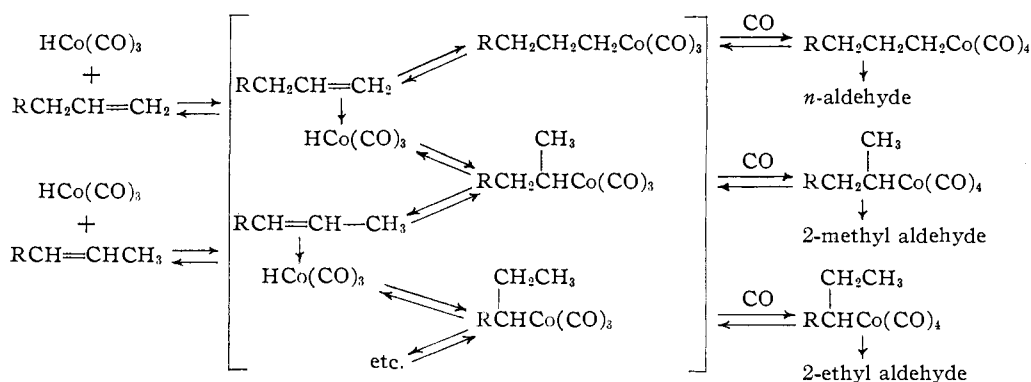
(19) The literature⁶ does not state whether this rate difference is for *cis*- or *trans*-2-olefin. Our results show that *cis*-olefin reacts more rapidly than *trans*, as would be expected if π -complex formation is required for reaction.²⁰ Although this weakens our hypothesis somewhat, Goldfarb and Orchin² have shown that olefin equilibration is far from complete under oxo conditions, and the argument should still be valid.

(20) Equilibrium constants for the reaction of Ag⁺ with butenes are: 1-butene, 119.4; *cis*-2-butene, 62.3; *trans*-2-butene, 29.2.²¹

(21) F. R. Hepner, K. N. Trueblood and H. J. Lucas, *J. Am. Chem. Soc.*, **74**, 1333 (1952).

(17) G. Karapinka and M. Orchin, Abstracts 137th A.C.S. Meeting, Cleveland, Ohio, April 5-14, 1960, p. 92-O.

(18) L. S. Meriwether and M. L. Fiene, *J. Am. Chem. Soc.*, **81**, 4200 (1959); F. Basolo and A. Wojcicki, *ibid.*, **83**, 520, 525 (1961).



at room temperature by treating ethylcobalt tetracarbonyl with an amine, in spite of the fact that cobalt hydrotetracarbonyl isomerizes olefins under these conditions. According to the above mechanism, the olefin would have formed only if the alkylcobalt tetracarbonyl lost CO and it apparently does not do so readily at 25°.

In conclusion, it has been demonstrated that addition of cobalt hydrotetracarbonyl to olefin, olefin isomerization by hydrotetracarbonyl, and reduction of acylcobalt carbonyl to aldehyde both by cobalt hydrotetracarbonyl and by hydrogen¹ are inhibited by CO. Pino has shown the formation of cobalt hydrotetracarbonyl from dicobalt octacarbonyl and hydrogen is also inhibited by CO.¹⁰ It appears that the intermediate formation of coordinately unsaturated species is a rather general phenomenon, and that complex formation may be a necessary prerequisite for reaction.

Experimental

Addition of Cobalt Hydrotetracarbonyl to 1-Pentene.—

In the previously described apparatus²² at 0° was placed 25 ml. of 1-pentene (Phillips Petroleum Co., 99 mole %) under nitrogen saturated with 1-pentene. To it was added, with stirring, 9 ml. of 0.29 *M* cobalt hydrotetracarbonyl in *n*-pentane solution. After 15 minutes 3.0 ml. of 1.0 *M* triphenylphosphine in ether was added. A 2-ml. sample of the solution was removed, treated with 2.0 ml. of 0.2 *M* iodine in methanol and analyzed by vapor phase chromatography. A 1:1 ratio of methyl *n*-hexanoate to methyl 2-methylpentanoate was found. The remainder of the reaction mixture was centrifuged to remove insoluble material, mainly dicobalt hexacarbonyl bis-(triphenylphosphine) formed from any hydrocarbonyl and octacarbonyl present, and evaporated to dryness. The crystalline residue was recrystallized four times from a mixture of ether and pentane at -80° to give 0.1 g. of pale yellow prisms, m.p. 89-93° dec.

Anal. Calcd. for $\text{C}_{27}\text{H}_{50}\text{O}_4\text{PCo}$: C, 64.29; H, 5.20. Found: C, 64.47; H, 5.30.

The infrared spectrum in carbon tetrachloride had absorption at 3.29(w), 3.41(m), 3.51(w), 4.90(m), 5.10(vs), 5.98(s), 6.78(m), 6.90(w), 7.00(m), 7.16(vw), 7.30(vw), 7.55(vw), 7.69(w), 7.83(vw), 8.44(w), 9.03(w), 9.12(m), 9.35(vw), 9.71(w), 10.00(w), 10.90(w), 11.20(w), 11.42(w) μ and in carbon disulfide at 12.00(w), 13.40(m), 14.14(m) and 14.42(s) μ .

When treated with excess 0.2 *M* iodine in methanol, the product gave 70% methyl *n*-hexanoate and 30% methyl 2-methylpentanoate by vapor phase chromatography.

If the same reaction is carried out in the presence of CO (atmospheric pressure) using 60 ml. of 1-pentene and 10.0 ml. of 0.29 *M* cobalt hydrotetracarbonyl in *n*-pentane, 92.5% of the calculated 2.9 millimoles of CO was absorbed in 3 hours. Addition of 3.0 ml. of 1.0 *M* triphenylphosphine

in ether solution led to the evolution of 77.5% of the expected 2.9 millimoles of CO. Isolation of the product as described above gave more than a 50% yield of the same mixture of hexanoylcobalt tricarbonyl triphenylphosphine.

Addition of Cobalt Hydrotetracarbonyl to Isobutylene.—In a 150-ml. capped pressure bottle was placed 20 ml. of isobutylene under 10 p.s.i. of CO pressure. After cooling to 0°, the solution was stirred magnetically and 10 ml. of 0.23 *M* cobalt hydrotetracarbonyl in *n*-pentane was injected, followed after 4 hours at 0° by 3.0 ml. of 1.0 *M* triphenylphosphine in ether. After another 30 minutes, the solution was evaporated to dryness at 0° and, immediately, 15 ml. of 0.2 *M* iodine in methanol was added. The reaction mixture was stirred for 30 minutes at 25° and was then analyzed by vapor phase chromatography. Only 0.41% methyl trimethylacetate and only a trace, if any, of methyl 3-methylbutyrate were found. The yield of methyl trimethylacetate based upon the cobalt hydrotetracarbonyl used was therefore about 23%.

Addition of Cobalt Hydrotetracarbonyl to Methyl Acrylate.—In a gasometric apparatus, which had been flushed with CO at 0°, was placed 15 ml. of methyl acrylate, and 2.0 ml. of 0.46 *M* cobalt hydrotetracarbonyl in pentane was injected with stirring. In 2 hours, 17 ml. of gas was absorbed and the reaction stopped. Addition of 1.5 ml. of 1.0 *M* triphenylphosphine in ether led to the evolution of 20 ml. of gas in 2 hours. The excess methyl acrylate and solvent were evaporated at 0° in vacuum. The residue was extracted several times with ether and centrifuged to remove insoluble material. Evaporation of the ether at 0° left a yellow crystalline residue, which was treated with 10 ml. of 0.2 *M* iodine in methanol. Vapor phase chromatography showed the presence of 0.5% dimethyl methylmalonate and 0.1% dimethyl succinate. These values correspond to about 25% dimethyl methylmalonate and 5% dimethyl succinate based upon the cobalt hydrotetracarbonyl used.

In similar experiments, the crystalline complex obtained after removing the ether was recrystallized several times from ether-pentane; m.p. 83.5-85° dec. The infrared spectrum in carbon tetrachloride contained coordinated carbonyl bands at 4.85(w) and 5.1(vs) μ , an ester carbonyl at 5.75(m) μ , and an acylcobalt carbonyl at 6.0(m) μ .

Anal. Calcd. for $\text{C}_{26}\text{H}_{22}\text{O}_6\text{PCo}$: C, 60.01; H, 4.26. Found: C, 60.18; H, 4.51.

Pyrolysis of Ethylcobalt Tetracarbonyl.—In a small glass tube was placed 0.4 g. of triethyloxonium fluoroborate. The tube was quickly closed, flushed with nitrogen, and cooled to 0°. Then 10 ml. of 0.07 *M* sodium cobalt carbonyl in ether was injected and the tube was shaken for 30 minutes. The infrared spectrum indicated the reaction was complete (absence of the 5.3 μ band of the cobalt carbonyl anion). Injection of the product into the heated inlet of a gas chromatograph at 220° resulted in the formation of 0.23% ethylene, 0.01% ethane, 0.02% propionaldehyde and very small amounts of two unknowns. These values correspond to 80% of the theoretical amount of ethylene, about 5% ethane and about 10% propionaldehyde.

In two control experiments, it was shown that neither the saturated ether solution of triethyloxonium fluoroborate nor the sodium cobalt carbonyl solution in ether yielded ethylene when submitted to the same gas chromatographic procedure. In another experiment, ethylcobalt tetracarbonyl was prepared in the same manner as above. Most of the solvent then was removed in vacuum and replaced with

(22) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 1097 (1961).

fresh solvent to remove any ethylene that might have been formed in the reaction of triethyloxonium fluoroborate with sodium cobalt tetracarbonyl. This solution gave the same analysis as the solution which had not been evaporated.

In a series of similar experiments carried out with a heated inlet at only 170° about 0.14% ethylene was found (about 50% of theor.).

When the same reaction was carried out in the presence of CO and, therefore, formed the propionylcobalt tetracarbonyl, pyrolysis at 170° yielded the same amounts of products as the reaction run under nitrogen at 170°.

Effect of CO upon the Addition of Cobalt Hydrotetracarbonyl to 1-Pentene.—Two experiments were carried out in the same manner except that one was done under CO and the other under nitrogen. In the gasometric apparatus, which had been filled and flushed with the pentane-saturated gas at 0°, was placed 15 ml. of 1-pentene. To this was added 2.0 ml. of 0.46 M cobalt hydrotetracarbonyl in *n*-pentane. After 15 minutes, 0.5 ml. of dicyclohexylethylamine was added and the infrared spectrum was taken on a Beckman IR-7 infrared spectrophotometer. The reaction carried out under CO absorbed about 5 ml. of gas.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO, BOULDER, COLO.]

Mechanisms of Elimination Reactions. XXIII. Phenyllithium-induced Dehydrochlorination of the Isomeric Chlorodiphenylethenes¹

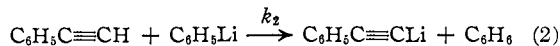
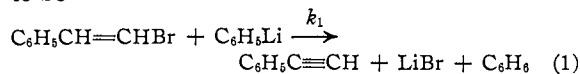
BY STANLEY J. CRISTOL AND ROBERT S. BLY, JR.

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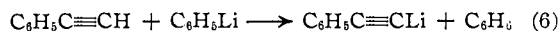
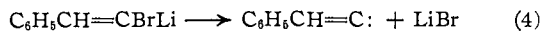
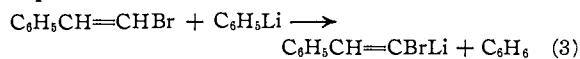
The rates of phenyllithium-induced dehydrochlorination of 2-chloro-1,1-diphenylethene and *cis*- and *trans*-1-chloro-1,2-diphenylethene have been measured in *n*-butyl ether. The reactions are shown to be first order in chloroethene and first order in base; the product in each case is toluene. Under the conditions employed in this study, α -elimination proceeds more readily than *cis*- β -elimination, which is in turn more facile than *trans*- β -elimination. Possible mechanisms for these reactions are considered.

Introduction

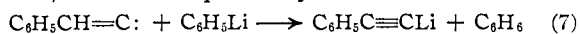
In an earlier paper in this series,^{2a} it was reported that the reaction of excess phenyllithium in *n*-butyl ether with both *cis*- and *trans*-1-bromo-2-phenylethene gives phenylacetylene in each case, is kinetically first order in phenyllithium and first order in 1-bromo-2-phenylethene and that at 2.10°, *cis* elimination is preferred to *trans* elimination by a factor of 5.5. The course of the reaction appears to be



where $k_2 \gg k_1$. When competitive experiments were performed in ethyl ether at 25°, *cis* elimination was preferred over *trans* by a factor of 2. An α elimination mechanism was postulated to explain these results.



It was pointed out that 3 and 4 might be combined and/or 5 and 6 replaced by 7



In support of this mechanism, the relative inertness of 2-bromo-3-phenyl-2-propene, in which the α -hydrogen³ is replaced by a methyl group,^{4a} was

(1) (a) This work was presented in part at the 14th National Organic Symposium at Lafayette, Ind., in June, 1955. (b) Previous paper in this series: S. J. Cristol and F. R. Stermitz, *J. Am. Chem. Soc.*, **82**, 4692 (1960).

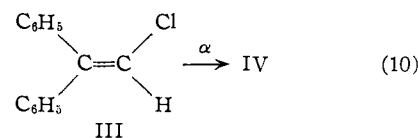
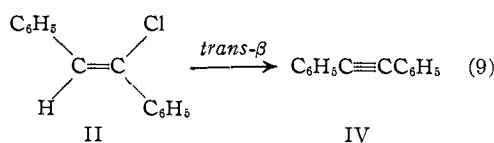
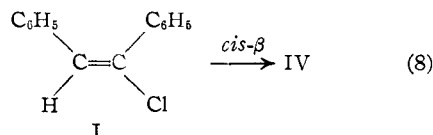
(2) (a) S. J. Cristol and R. F. Helmreich, *ibid.*, **77**, 5034 (1955); (b) R. F. Helmreich, Ph.D. Thesis, Department of Chemistry, University of Colorado, 1953.

(3) The carbon to which the departing halogen is attached will be referred to as the " α carbon" throughout this paper. The expression " β carbon" will be used to designate the adjacent carbon that participates in the formation of the double or triple bond.

pointed out, as was the known propensity for strong bases such as the organolithiums and the alkali amides to initiate α -elimination reactions.^{2a} The discrepancy between the reported third-order kinetics for the reaction of 1-chloro-2-phenylethene with phenyllithium⁴ and the demonstrated second-order kinetics for reactions 1 and 2³ has not yet been clarified.

In order to understand better the relative steric and energetic requirements of α - and β -eliminations, we decided to examine in some detail the phenyllithium-initiated dehydrohalogenation of 1-chloro-*cis*-1,2-diphenylethene (I), 1-chloro-*trans*-1,2-diphenylethene (II) and 2-chloro-1,1-diphenylethene (III).⁵

These three isomeric chlorodiphenylethenes can be easily prepared and distinguished; each can lose the elements of hydrogen chloride in a unique manner; *i.e.*



(4) (a) G. Wittig and G. Harborth, *Ber.*, **77B**, 315 (1944); (b) G. Wittig, *Angew. Chem.*, **62**, 231 (1950); (c) O. Grummitt and J. J. Lucier, Abstracts of Papers presented before the 121st Meeting of the American Chemical Society, Buffalo, N. Y., March, 1952, p. 49-K.

(5) A study of the sodium hydroxide in ethanol-initiated dehydrohalogenations of these compounds will be reported in a later paper.