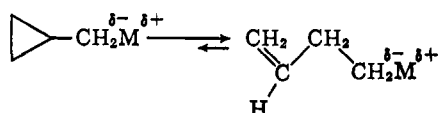


The above results provide positive evidence for the existence of cyclopropylcarbinyllithium at low temperatures but clearly reveal the facile isomerization of this species to allylcarbinyllithium. This was dramatically illustrated when rapid removal of some of an exchange mixture, which had been kept at -70° for 5 min., by a hypodermic syringe already containing an uncooled ethereal solution of benzaldehyde in the barrel resulted in a ratio of III/II of ca. 20! This observation shows that conditions must be controlled carefully in order to get reproducible data and explains any apparent anomalies in product ratios reported above. Our experiments are in accord with the results of Roberts, *et al.*,² who showed that the cyclopropylcarbinyl Grignard reagent is an unstable intermediate in the equilibration of C₁- and C₂-labeled allylcarbinylmagnesium bromide at room temperature.



The present work demonstrates that cyclopropylcarbinyllithium is definitely accessible under appropriate conditions and makes this reagent available for synthetic work.

Further studies on the generation and properties of cyclopropylcarbinyllithium are underway and will be reported at a later date.

Acknowledgment.—We are grateful to the U. S. Army Research Office (Durham) for generous support of this work.

(10) National Aniline Research Fellow, 1962–1963.

DEPARTMENT OF CHEMISTRY PETER T. LANSBURY
STATE UNIVERSITY OF NEW YORK AT BUFFALO
BUFFALO 14, NEW YORK VICTOR A. PATTISON¹⁰

RECEIVED APRIL 11, 1963

A General Synthesis of Tetraphenylcyclobutadiene–Metal Complexes by Ligand-Transfer

Sir:

Although a number of cyclobutadiene–metal complexes, particularly those of tetraphenylcyclobutadiene^{1–4}, have now been synthesized, all the syntheses are unique for the particular compounds prepared and are not readily extended to others. We report here a synthesis of tetraphenylcyclobutadiene–metal complexes which appears to have general applicability to transition metals which form carbonyls. Thus, reaction of tetraphenylcyclobutadiene palladium bromide⁵ (I, M = PdBr₂) with iron pentacarbonyl or nickel tetracarbonyl gives tetraphenylcyclobutadiene iron tricarbonyl [I, M = Fe(CO)₃] and tetraphenylcyclobutadiene nickel bromide (I, M = NiBr₂), respectively. This is the first example of the conversion of one hydrocarbon–transition metal complex into another by direct ligand transfer and also of a reaction involving cyclobutadienes in which the cyclobutadiene group remains intact.

Tetraphenylcyclobutadiene palladium bromide (1.6 mmoles) and a large excess (25 mmoles) of iron penta-

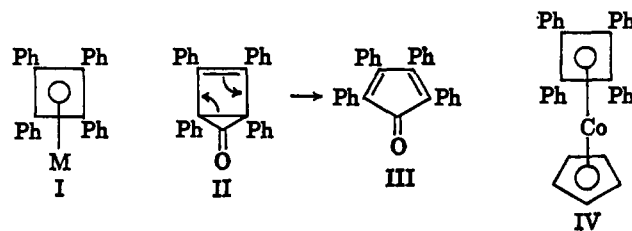
(1) R. Criegee and G. Schröder, *Ann.*, **623**, 1 (1959); R. Criegee, *Angew. Chem. Intern. Ed. English*, **1**, 519 (1962).

(2) H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2194, 2195 (1961).

(3) W. Hübel, E. H. Braye, A. Clauss, E. Weiss, U. Krueker, D. A. Brown, G. S. D. King and C. Hoogzand, *J. Inorg. Nucl. Chem.*, **9**, 205 (1959); cf. R. P. Dodge and V. Schomaker, *Nature*, **186**, 798 (1960).

(4) A. T. Blomquist and P. M. Maitlis, *J. Am. Chem. Soc.*, **84**, 2329 (1962).

(5) Synthesized by an analogous route to that for the chloride⁴; preliminary results, however, suggest that there is little difference in the reactivities of the different halides.



carbonyl were refluxed in xylene until evolution of carbon monoxide had nearly ceased (20 min.). Filtration from the insoluble material gave a yellow solution which yielded 88% of tetraphenylcyclobutadiene iron tricarbonyl [I, M = Fe(CO)₃],³ m.p. after crystallization from cyclohexane 232° (uncorr.), identical with an authentic sample⁶ (mixture melting point and infrared spectrum).

Tetraphenylcyclobutadiene palladium bromide (1.6 mmoles) was treated with 11 mmoles of nickel carbonyl in benzene under nitrogen. Reaction began slowly at room temperature and was complete after 2.5 hr. of refluxing. Filtration gave a purple solution which yielded 17% tetraphenylcyclopentadienone (III).⁷ Extraction of the benzene-insoluble residue with boiling chloroform gave a 47% yield of tetraphenylcyclobutadiene nickel bromide (I, M = NiBr₂).⁸

These reactions are not unexpected since it has been shown previously that the halogens attached to palladium in tetraphenylcyclobutadiene palladium chloride (I, M = PdCl₂) are not strongly bound and that thermal decomposition, for example, gave 1,4-dichloro-1,2,3,4-tetraphenylbutadiene. It has also been shown that a highly colored and paramagnetic species, probably tetraphenylcyclobutadiene, is obtained transiently in decomposition reactions of tetraphenylcyclobutadiene palladium complexes⁹ and related systems² in solution. Since metal carbonyls are known to react with some covalently-bound halogens¹⁰ the first step in the first reaction must be formation of iron tetracarbonyl bromide.¹¹ Removal of the bromine from the palladium complex causes total decomposition and releases the tetraphenylcyclobutadiene which then reacts with excess iron pentacarbonyl present by ligand displacement to give I [M = Fe(CO)₃] in the usual manner for reactions of metal carbonyls and polyolefins.¹³ The nickel reaction is more complex and the nature of the product is probably determined by the greater stability of the nickel bromide complex I (M = NiBr₂) compared with that of the unknown carbonyl I [M = Ni(CO)₂]. In neither of these reactions was any of the tetraphenylcyclobutadiene dimer (octaphenylcubane⁹) or tolan detected.

These reactions are very solvent-sensitive and only proceed in aromatic hydrocarbons; no product was obtained using saturated hydrocarbons such as cyclohexane or decalin or ethers such as diglyme. This is

(6) Kindly supplied by Dr. W. Hübel.

(7) Tetraphenylcyclopentadienone (III) is not an unreasonable product from this reaction and is probably formed by insertion of carbon monoxide into a cyclobutadiene ring via an intermediate (II).

(8) Identified by comparison with an authentic sample kindly supplied by Dr. H. H. Freedman; the infrared and visible spectra were identical and both samples showed a fairly sharp decomposition point (dark green to light brown) at 316° (uncorr.) in an evacuated tube. Both I [M = Fe(CO)₃] and I (M = NiBr₂) gave satisfactory analyses.

(9) P. M. Maitlis and F. G. A. Stone, *Proc. Chem. Soc.*, 330 (1962); H. H. Freedman and D. R. Petersen, *J. Am. Chem. Soc.*, **84**, 3837 (1962).

(10) U. S. Patent 2524833 (1950) [Chem. Abstr., **45**, 1618a (1951)]; E. Coffey, *J. Am. Chem. Soc.*, **83**, 1623 (1961); E. O. Fischer and G. Bürger, *Z. Naturforsch.*, **16b**, 77 (1961).

(11) The xylene-insoluble residue from this reaction contained palladium and a compound similar in character and infrared spectrum to that obtained by heating iron tetracarbonyl bromide¹² in xylene for 30 min.

(12) W. Hieber and G. Bader, *Ber.*, **61**, 1717 (1928).

(13) E. O. Fischer and H. Werner, *Angew. Chem. Intern. Ed. English*, **2**, 85 (1963).

probably due to the insolubility of an intermediate in the saturated hydrocarbons; complexing solvents are themselves known to decompose I ($M = \text{PdBr}_2$).

It was also found that in favored cases the tetraphenylcyclobutadiene group could replace a cyclopentadienyl group. Thus cobaltocene (another compound which readily abstracts covalently-bound halogens¹⁴) reacted with I ($M = \text{PdBr}_2$) in refluxing xylene to give a 12% yield of (π -cyclopentadienyl)-(π -tetraphenylcyclobutadiene)-cobalt (IV). This was identical with a sample prepared from cobaltocene and diphenylacetylene,¹⁵ and this ligand transfer reaction provides additional confirmation for the structure of IV.¹⁶

The extension of this work to other systems and reactions in which cyclopentadienyl groups can also be transferred from one metal to another will be reported later.

Acknowledgment.—We thank the National Research Council of Canada and the Research Corporation of New York for supporting this work.

(14) S. Katz, J. F. Weiher and A. F. Voight, *J. Am. Chem. Soc.*, **80**, 6459 (1958).

(15) A. K. Nakamura and N. Hagihara, *Bull. Chem. Soc. Japan*, **34**, 452 (1961); J. L. Boston, D. W. A. Sharp and G. Wilkinson, *J. Chem. Soc.*, 3488 (1962).

(16) It is conceivable at least that this reaction too may go *via* primary dissociation of tetraphenylcyclobutadiene into two diphenylacetylenes which then react with the cobaltocene. However, as there is as yet no definite evidence for this process occurring we prefer to regard this too as a direct ligand replacement reaction.

DEPARTMENT OF CHEMISTRY
McMASTER UNIVERSITY
HAMILTON, ONTARIO, CANADA

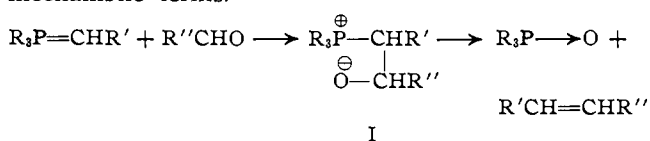
P. M. MAITLIS
M. L. GAMES

RECEIVED APRIL 29, 1963

Reaction of Phosphorus Compounds. VI. Kinetics and Mechanism of the Wittig Reaction

Sir:

Our recent work on the Wittig reaction of resonance-stabilized α -halomethylenephosphoranes¹ has prompted a thorough examination of the mechanism of this reaction. The Wittig reaction, represented by the following sequence, has been qualitatively described in mechanistic terms.^{1b,2-4}



Four mechanistic possibilities were considered at the outset of this study: (a) irreversible formation of betaine (I) with subsequent slow decomposition of the betaine, either *via* a four-membered ring intermediate or synchronously, to phosphine oxide and olefin; (b) rate-determining, irreversible formation of the betaine and rapid decomposition of betaine to products; (c) rapid, reversible formation of betaine with subsequent rate-controlling formation of products; (d) slow, reversible formation of betaine and rapid decomposition of betaine to phosphine oxide and olefin.

We have studied the kinetics of the reaction of carbomethoxymethylenetriphenylphosphorane with several aldehydes in benzene at 25°. The reaction was found to be second-order over-all; first-order in each of aldehyde and ylid. These data are reported in Table I.

The observed rate constant for olefin formation in the reaction of the above ylid with *p*-methoxybenzaldehyde

- (1) A. J. Speziale and K. W. Ratts, *J. Org. Chem.*, **28**, 465 (1963);
(2) A. J. Speziale and K. W. Ratts; to be published.
(3) H. O. House and G. H. Rasmusson, *J. Org. Chem.*, **26**, 1278 (1961).
(4) H. J. Bestmann and O. Kratzer, *Ber.*, **95**, 1894 (1962).
(5) G. Wittig, H. Weizmann and M. Schlosser, *ibid.*, **94**, 676 (1961).

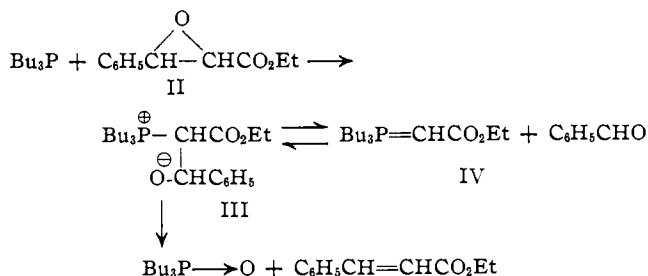
TABLE I

Aldehyde	$k_{\text{obs.}}$ (l./mole-sec.)
<i>p</i> -Methoxybenzaldehyde	$7.10 \pm 0.00 \times 10^{-5}$
<i>p</i> -Methylbenzaldehyde	$2.15 \pm 0.03 \times 10^{-4}$
Benzaldehyde	$9.62 \pm 0.02 \times 10^{-4}$
<i>m</i> -Chlorobenzaldehyde	$1.20 \pm 0.04 \times 10^{-2}$
<i>p</i> -Nitrobenzaldehyde	$1.07 \pm 0.00 \times 10^{-1}$

was $7.00 \pm 0.13 \times 10^{-5}$ l./mole-sec. Within experimental error the rate of disappearance of ylid is the same as the rate of formation of olefin.

The enhanced rate with electron-withdrawing substituents can be interpreted in terms of any of the previously mentioned mechanisms. The rate expression for mechanism (a), however, demands different rates of disappearance of ylid and of formation of olefin. Since we have observed these to be identical, mechanism (a) may be eliminated. These quantitative results are in accord with the qualitative observations of Johnson and LaCount,⁵ who were unable to isolate a betaine intermediate in the reactions of stable ylids. If mechanism (a) were operative, as it most likely is in the reactions of unstable ylids,⁴ the betaine intermediate should be isolable.

It is not possible to choose among the three remaining mechanistic possibilities on the basis of kinetic data alone. Consequently, the demonstration of reversibility or irreversibility of betaine formation becomes very important in the elucidation of the mechanism of the Wittig reaction. The ring opening of *trans*-ethyl phenylglycidate (II) with tributylphosphine was studied in order to arrive at the betaine (III) *via* a different route. Boskin and Denny⁶ have shown that the attack of tributylphosphine on *cis*- and *trans*-2-butene oxide occurs mainly at carbon. Further, it has been shown that nucleophilic attack in the ring opening of ethyl phenylglycidate occurs at the α carbon atom.⁷



If betaine formation in the Wittig reaction is reversible, evidence for reversibility may be obtained by trapping the ylid (IV) with an aldehyde more reactive than benzaldehyde.

Tributylphosphine was allowed to react with *trans*-ethyl phenylglycidate in the presence of a three-molar excess of *m*-chlorobenzaldehyde in refluxing ethanol. Under these conditions the reaction was essentially complete in 20 hr. V.p.c. analysis of the products of the reaction showed the presence of *m*-chlorobenzaldehyde, benzaldehyde, ethyl cinnamate and ethyl *m*-chlorocinnamate in the following area proportions: benzaldehyde, 1.0; *m*-chlorobenzaldehyde, 6.5; ethyl cinnamate, 1.3; ethyl *m*-chlorocinnamate, 1.1. Each of the products was isolated with preparative v.p.c. The aldehydes were oxidized to the corresponding benzoic acids and

- (5) A. W. Johnson and R. B. LaCount, *Tetrahedron*, **9**, 130 (1960).
(6) M. J. Boskin and D. B. Denney, *Chem. Ind.*, 330 (1959).
(7) R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959).