In addition to the five aromatic hydrogens at low field, single peaks are observed at 5.61 τ (1C$_\beta$–H) and 7.55 τ (1N–CH$_3$). Rather surprisingly, the C$_\alpha$-*gem*-dimethyls appear nearly equivalent with a peak at 8.74 τ. The n.m.r. spectrum of the crude reaction product further indicates that Ia is obtained in excess of 95% yield. Although Ia is stable for months when stored in a tightly stoppered flask, it decomposes upon contact with water to give α-formylisobutyranilide (II) in 93% yield,[5] m.p. 57–60° (ether–petroleum ether), (*Anal.* Calcd. for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32. Found: C, 68.69; H, 7.10; N, 7.18; infrared: CHO, 5.83 μ; CONH, 5.95 μ). The n.m.r. spectrum of II is consistent with the structure shown.

The mode of decomposition of Ia, rupture of the C$_\beta$ to amide-N bond with formation of the transient dimethylimine cation of II, suggests that delocalization of the free electron pair on the amino nitrogen would stabilize the ring system. This was, in fact, realized by replacing one of the N-methyls in Ia by a phenyl group.

Phenyl isocyanate and N-methyl-N-phenylisobutenylamine[6] do not react at room temperature, but after 48 hours at 80° the reaction mixture is free of phenyl isocyanate absorption in the infrared region, and shows the desired 5.71 μ β-lactam band. The resulting dark oil crystallizes upon standing. Recrystallization of the product from ether–petroleum ether affords the white solid, Ib [1-phenyl-3,3-dimethyl-4-(N-methylanilino)-2-azetidinone], m.p. 113–115°[7] [*Anal.* Calcd. for $C_{18}H_{20}N_2O$: C, 77.11; H, 7.19; N, 9.99. Found: C, 77.33; H, 7.31; N, 10.11; λ_{max}^{EtOH} 248 (28,000): with added acid λ_{max}^{EtOH} 243 (14,200)]. In addition to the ten low field aromatic protons detectable in the n.m.r. spectrum of Ib, peaks occur at 4.71 τ (1C$_\beta$–H), 7.12 τ (N–CH$_3$) and at 8.49 τ and 8.83 τ (1 >C–CH$_3$ each). The increased stability of Ib *vs.* Ia is demonstrated by the fact that an ethereal solution of the compound not only survives washings with water, but also *N* acid and *N* base. Upon several days of exposure to moist air, however, Ib also decomposes to II.

Since previously reported[8,9] reactions of enamines and isocyanates have given, after hydrolysis, β-carbonylcarboxamides analogous to II, it seemed necessary to consider the possibility that labile β-lactams, although present, had been overlooked by previous workers before hydrolysis of their reaction products. We therefore studied the reaction of phenyl isocyanate and N,N-dimethyl-1-butenylamine.[9] In order to moderate the very exothermic reaction and minimize decomposition of any potential β-lactam intermediate, the enamine is stirred in an ice bath and phenyl isocyanate is added dropwise so as to keep the temperature of the mixture below 30°. Immediately upon completion of the addition (5–10 minutes), a sample withdrawn for infrared studies shows no isocyanate or β-lactam absorption. Amide carbonyl and N–H absorption is quite strong, however, and subsequent hydrolysis of the product gives α-formyl-*n*-butyranilide as reported by Hünig, *et al.*[9,10]

Continuing work on this enamine reaction indicates that structural requirements are very specific. Details of this work and of some further products derived from Ia will be published in the near future.

Acknowledgment.—The authors wish to acknowledge the assistance of Mr. Paul Landis in obtaining and discussing the n.m.r. spectra.

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[5] This instability of Ia to traces of moisture and to the common methods of purification did not allow the preparation of an analytical sample.

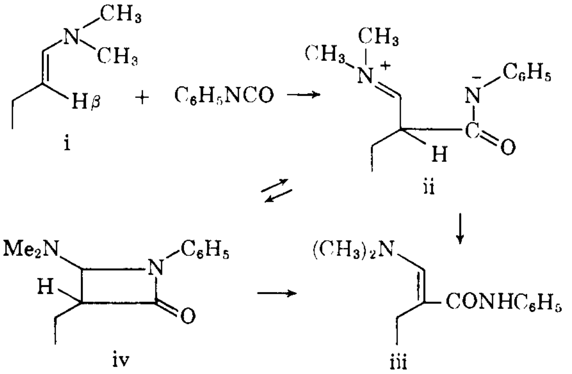
[6] E. Benzing, *Angew. Chem.*, **71**, 521 (1959).

[7] The yields of Ib vary from 65–90% depending upon the purity of the reactants and the care taken to exclude moisture and air from the reaction vessel.

[8] S. Hünig, *Angew. Chem.*, **71**, 312 (1959). D. Clemens and W. Emmons, *J. Org. Chem.*, **26**, 767 (1961). G. Berchtold, *ibid.*, **26**, 3043 (1961).

[9] S. Hünig, K. Hübner and E. Benzing, *Ber.*, **95**, 926 (1962).

[10] The enamines of previous workers[8,9] have in common the presence of a β–H (*e.g.*, i). Thus, the intermediate ii can alternatively be



stabilized by cyclization to β-lactam iv or by abstraction of the β–H to yield iii as suggested by infrared. Although we prefer the direct route (i → ii → iii), the possibility cannot be excluded, of course, that the initial reaction product is iv which rapidly decomposes to iii by abstraction of the C$_\beta$–H, or reverts to ii by participation of the amino nitrogen's free pair of electrons. If iv does, in fact, ever exist, decomposition *via* ii seems most likely. By selecting an enamine possessing no β–H, (*e.g.*, N,N-dimethylisobutenylamine) one obtains an intermediate (similar to ii) incapable of stabilization by a route other than lactam formation. In addition, the mode of decomposition of the lactam is restricted to the reverse reaction (analogous to iv → ii, but excluding iv → iii).

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ON THE ORIGIN OF HYDROGEN IN METAL HYDRIDE COMPLEXES FORMED BY REACTION WITH ALCOHOLS

Sir:

We wish to report some observations on the origin of hydrogen in transition metal hydride complexes obtained from the system of metal halide, triphenylphosphine, and an alcohol (or related solvents). Of the several reactions we have investigated,[1] the one leading to an iridium monohydride complex, $[IrHCl_2(Ph_3P)_3]$ (I)[2] (Table I), emerged as most intriguing in view of the mild conditions (25°) under which it can be obtained.[2]

In order to determine the source of hydrogen giving rise to a metal–hydrogen bond in (I), we have carried out comparative experiments with deuterated aqueous[3] ethanols which gave these results.

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[1] L. Vaska, *Chem. and Ind.*, 1402 (1961), references quoted therein, and unpublished data.

[2] L. Vaska, *J. Am. Chem. Soc.*, **83**, 756 (1962).

[3] Water was required to dissolve K_2IrCl_6.

$$K_2Ir^{IV}Cl_6 + Ph_3P \left\{ \begin{array}{ll} + CH_3CH_2OH + H_2O \longrightarrow & \\ \qquad [Ir^{III}HCl_2(Ph_3P)_3]\ (I)^4 & (1) \\ + CH_3CH_2OH + \mathit{D_2O} \longrightarrow \text{Hydride (I)} & (2) \\ + CH_3CH_2O\mathit{D} + \mathit{D_2O} \longrightarrow \text{Hydride (I)} & (3) \\ + CH_3C\mathit{D_2}OH + H_2O \longrightarrow & \\ \qquad \textit{Deuteride}\text{ (I) (Table I)} & (4) \end{array} \right.$$

The experimental conditions ($Ir/Ph_3P = {}^1/_4$, water/alcohol = $^1/_2$, refluxing for several hours under nitrogen) were such that the primary product (I) precipitated upon its formation, which largely eliminated H–D exchange in the complex, and its further reactions with the alcohol (*cf.* ref. 2).[5]

TABLE I

Compound (P = Ph_3P)	Type	Color	Infrared spectrum (cm.$^{-1}$)[a] $\nu_{IrH,D}$	$\delta_{IrH,D}$		Dipole μ,D
[$IrHCl_2P_3$]	I	Yellow	2197	840	804	5.5
[$IrDCl_2P_3$]	I	Yellow	1562[b]	606[b]	575[b]	..
[$IrHCl_2P_3$]	II	White	2049	835	820	..
[$IrHCl_2P_3$]	III	White	2243	806		8.1

[a] 2300–1500, halocarbon mull, CaF_2 optics, ±2 cm.$^{-1}$; 900–800, Nujol mull, NaCl optics, ±3 cm.$^{-1}$; 600–500, Nujol mull, CsBr optics, ±3 cm.$^{-1}$. [b] $\nu_{IrH}/\nu_{IrD} = 1.406$, $\delta_{IrD}/\delta_{IrD} = 1.39, 1.40$; calcd., 1.41.

Reaction (4) shows that the hydrogen in the complex (I) originates from the α-carbon atom of the alcohol, eliminating those of the β-carbon, phenyl hydrogens of Ph_3P (used in excess), and hydroxylic hydrogens of the alcohol and water. The latter conclusion is confirmed by reactions (2) and (3). Acetaldehyde and hydrochloric acid (*cf.* ref. 2) have been found to be the principal by-products, indicating the fate of ethanol in the over-all reaction.

$$CH_3CH_2OH \longrightarrow CH_3CHO + H^+ + [H^-]\ (I) \qquad (5)$$

These results agree with those reported by Chatt and Shaw[6] for a related system, and confirm their suggestion[7] for the source of hydride in the metal complex formed by reaction with ethanol.

In addition to primary alcohols, the monohydride (I) has been obtained also by reaction with secondary alcohols (*e.g.*, 2-propanol), ethers (*e.g.*, 1,2-dimethoxyethane), and formic acid,[8] all of which possess hydrogen attached to the carbon atom having a functional group (*cf.* equation 4).

The hydrogen of the α-carbon atom of ethanol is not, however, the only type of species required to obtain metal hydrides from these systems. Iridium chloride, Ph_3P, and refluxing aqueous *tertiary* butanol also yield a pure monohydride complex. The same product results when methanol or acetic acid[8] is used as a reacting solvent. This compound (II) (see Table I) is apparently a stereoisomer of (I). The two complexes show identical elemental analysis, but exhibit different Ir–H vibrations (Table I) and X-ray diffraction patterns. (There are three octahedral stereoisomers possible for [$IrHCl_2(Ph_3P)_3$]. The third one, given in Table I, is obtained in pure form by reaction of [$IrH_2Cl(Ph_3P)_3$][2] with HCl. The assignment of structures for these compounds will be discussed elsewhere.)

The reactions leading to monohydride (II) have not been studied by isotopic methods, but they appear to involve a $-CH_3$ group (*tert*-$(CH_3)_3COH$, CH_3OH, CH_3COOH), demonstrating a strong tendency of iridium to extract covalently bonded hydrogen.

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[4] It is considered that Ir(IV) is reduced to Ir(III) by Ph_3P used in excess.

[5] These optimum conditions (giving also good yields) were determined by independent experiments.

[6] J. Chatt and B. L. Shaw, *Chem., and Ind.*, 931 (1960).

[7] J. Chatt and B. L. Shaw, *ibid.*, 290 (1961).

[8] Experiment carried out by Dr. S. S. Bath.

THE ELECTRON PARAMAGNETIC RESONANCE OF PHENYLMETHYLENE AND BIPHENYLENEMETHYLENE; A LUMINESCENT REACTION ASSOCIATED WITH A GROUND STATE TRIPLET MOLECULE

Sir:

Recently we reported the electron paramagnetic resonance (e.p.r.) of diphenylmethylene, which demonstrated that it is a ground state triplet molecule.[1,2] Skell[4] has assigned a triplet state for diphenylmethylene on the basis of its chemical reactivity. However, the chemistry of phenylcarbene (I) (or phenylmethylene[5]), C_6H_5CH, and biphenylenemethylene (II) has provided no definite evidence regarding their ground state.[6] We now have observed the e.p.r. of I and II and conclude that they are ground state triplet molecules.

The experimental technique has been described previously.[1] A dilute solution (*ca.* $10^{-3}M$) of phenyldiazomethane[7] in Fluorolube[8] was cooled to 77°K. to form a rigid glass. After irradiation of the glass with a Hanovia 140-w. mercury arc with Pyrex filter, e.p.r. absorptions were found at 2346, 4815, and 5830 gauss (free spin at 3240). No line attrib-

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[1] R. W. Murray, A. M. Trozzolo, E. Wasserman and W. A. Yager, *J. Am. Chem. Soc.*, **84**, 3214 (1962).

[2] A line corresponding to that at 1978 gauss[1] was absent in the results of the single crystal study by Brandon, Closs and Hutchison.[3] When a rigid glass of diphenyldiazomethane was photolyzed using a Pyrex filter, the line at 1978 gauss was absent, showing that its origin is different from that of the other five absorption lines. Continued filtered irradiation yielded no additional lines. We assume that since the absorption lines can be fitted to a Hamiltonian, they are associated with diphenylmethylene, the most likely ground state triplet to arise in this system.

[3] R. W. Brandon, G. L. Closs and C. A. Hutchison, Jr., *J. Chem. Phys.*, **37**, 1878 (1962). We wish to thank Professor Hutchison for communicating his results in advance of publication and for several interesting discussions. We are particularly indebted to him for indicating the difficulties associated with the presence of a line at 1978 gauss.

[4] R. M. Etter, H. S. Skovronek and P. S. Skell, *J. Am. Chem. Soc.*, **81**, 1008 (1959).

[5] We believe that the suggestion made by Skell[4] regarding the naming of divalent carbon species (carbene for singlet states and methylene for triplet states) should be re-examined. Since the electronic state of the reactive divalent carbon species depends greatly on the reaction conditions [see *e.g.*, F. A. L. Anet, R. F. W. Bader and A. Van der Auwera, *ibid.*, **82**, 3217 (1960)], we feel that confusion may result by giving two different names to two different electronic states of the same species. We suggest that the distinction in names be based on the ground state of the divalent carbon species with the name methylene being assigned to those species having triplet ground states. The name assignment would be retained in all contexts. Thus, the divalent carbon species described in this paper always would be referred to as methylenes.

[6] For a general discussion of this point, see C. D. Gutsche, G. L. Bachman and R. S. Coffey, *Tetrahedron*, **18**, 617 (1962).

[7] Prepared by the method of P. Yates and B. L. Shapiro, *J. Org. Chem.*, **23**, 759 (1958). The authors wish to thank Dr. Edwin A. Chandross of these laboratories for a generous supply of azibenzil.

[8] Obtained from the Hooker Chemical Company.