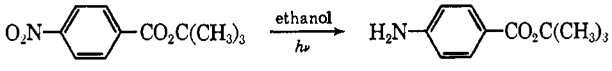
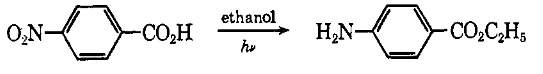
column chromatography, and distillation, allowed the isolation of pure **3** in 32% yield. The only other product characterized was an orange crystalline solid, mp 140–142°, obtained in minute amount and whose spectral properties suggested that it was the known 4,4′-dicarbethoxyazobenzene (lit.[6] mp 143°).

When a solution of **1** in *t*-butyl alcohol was irradiated for 14.5 hr no reduction products could be detected, and although phenol was the major product, only a slight amount of *t*-butyl 4-nitrobenzoate was observed. No ester interchange occurred during irradiation of **2** in a mixed solvent of *t*-butyl–ethyl alcohols (mole ratio 15:1), **3** being the only product detected (37% conversion after 23-hr irradiation). Similarly, no exchange products were found when an ethanol solution of *t*-butyl 4-nitrobenzoate (**4**) was photolyzed. After 6 hr the gas chromatogram of this reaction mixture showed the disappearance of the starting material and the presence of only a single product, *t*-butyl 4-aminobenzoate (**5**) (eq 2), which was isolated by distillation and recrystallization in 52% yield, mp 109–110° (lit.[7] mp 109.5°).



4 **5** (2)

The light-catalyzed ethanolysis of phenyl benzoate has been reported as a minor side reaction during the photo-Fries rearrangement;[3,4] however it appears that the nitro substituent, which is known to depress the photo-Fries[2,4] and related[8] rearrangements, greatly enhances the solvolysis reaction in the case of the phenyl ester.[9] Finally, in this connection we wish to report an example of photochemical esterification, a reaction apparently without precedent. When an ethanol solution of 4-nitrobenzoic acid was irradiated for 23 hr there was obtained, after the appropriate work-up, a 26% yield of ethyl 4-aminobenzoate (eq 3)![11]



(3)

Insofar as the reduction process is concerned, it is very likely that ethanol serves as the reducing agent. Although we have made no attempt to detect solvent oxidation products, Stenberg and Holter[12] have determined acetaldehyde formation in a light-catalyzed reductive condensation reaction of trinitrobenzene in ethanol solution, and Hurley and Testa[13] have detected the presence of acetone after photoreduction of nitrobenzene (to phenylhydroxylamine) in 2-propanol solution.

Additional examples of this new reduction pathway, that is, simple aniline formation in the photolysis of nitroaromatics, are summarized in eq 4–6.[14] In each case ethanol was used as solvent and the percentage yield refers to isolated and purified material and therefore represents a minimum value.

$$\text{ethyl 3-nitrobenzoate} \longrightarrow \text{ethyl 3-aminobenzoate (24\% yield)} \quad (4)$$

$$\text{4-nitroacetophenone} \longrightarrow \text{4-aminoacetophenone (16\% yield)} \quad (5)$$

$$\text{nitrobenzene} \longrightarrow \text{aniline (13\% yield)} \quad (6)$$

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[6] F. Meyer and K. Dahlem, *Ann.*, **326**, 331 (1903).

[7] R. Adams, E. K. Rideal, W. B. Burnett, R. L. Jenkens, and E. E. Dreger, *J. Am. Chem. Soc.*, 48, 1758 (1926).

[8] J. Hill, *Chem. Commun.*, 260 (1966).

[9] The formation in high yield of ethyl 3-(*o*-hydroxyphenyl)propanoate on irradiation of 2,3-dihydrocoumarin in ethanol solution[3] has been found not to be a solvolysis product of the starting lactone but rather the result of solvent addition to an intermediate *o*-hydroxybenzylketene.[10]

[10] E. D. A. Plank, Ph.D. Thesis, Purdue University, 1966; *Dissertation Abstr.*, **B27**, 415 (1966).

[11] In a dark reaction no ester could be detected by infrared examination of the product recovered after 4-nitrobenzoic acid was heated in ethanol solution for 25 hr at 55°.

[12] V. I. Stenberg and D. J. Holter, *J. Org. Chem.*, **29**, 3421 (1964).

[13] R. Hurley and A. C. Testa, *J. Am. Chem. Soc.*, 88, 4330 (1966); **89**, 6917 (1967).

[14] After submission of this communication, two additional examples have come to our attention. In one case,[15] irradiation of nitrobenzene in diethylamine solution produced a 48% yield of aniline, and in the other,[16] 1-nitronaphthalene was reduced to the corresponding amine (70%) by irradiation in hydrochloric acid–2-propanol solution containing disodium anthraquinone-2,6-disulfonate.

[15] J. A. Bartrop, N. J. Bunce, and A. Thomson, *J. Chem. Soc., Sect. C*, 1142 (1967).

[16] S. Hashimoto, H. Fujii, and J. Sunamoto, *Kogyo Kagaku Zasshi*, 70, 316 (1967); *Chem. Abstr.*, **67**, 81675g (1967).

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Reactions of Triplet Methylene with Oxygen. Formation of Molecular Hydrogen, Carbon Monoxide, and Carbon Dioxide

Sir:

Some observations of minor radioactive products from tracer experiments with the photolysis of ketene[1–4] (CHT=CO) have led us to perform additional tracer experiments using doubly tritiated (CT_2=CO) and C^{14}-labeled ($C^{14}H_2$=CO) ketene. In the presence of O_2 and various hydrocarbon substrates, we have observed the over-all reactions summarized in eq 1–3. In each case, the listed product can account for as much as 10% of the total ketene photolyzed.

$$CT_2{=}CO \text{ (with } CH_2{=}CO) \xrightarrow{h\nu,\, O_2} T_2 + \ldots \quad (1)$$

$$C^{14}H_2{=}CO \xrightarrow{h\nu,\, O_2} C^{14}O_2 \ldots \quad (2)$$

$$C^{14}H_2{=}CO \xrightarrow{h\nu,\, O_2} C^{14}O \ldots \quad (3)$$

We conclude that the three reactions are all the consequence of the reaction of triplet methylene with O_2, on

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[1] C. McKnight and F. S. Rowland, *J. Am. Chem. Soc.*, 88, 3179 (1966).

[2] C. McKnight, E. K. C. Lee, and F. S. Rowland, *ibid.*, **89**, 469 (1967).

[3] F. S. Rowland, C. McKnight, and E. K. C. Lee, Proceedings of the International Photochemistry Conference, Munich, Germany, Sept 1967.

[4] C. McKnight, P. S. T. Lee, and F. S. Rowland, *J. Am. Chem. Soc.*, **89**, 6802 (1967).

the basis of [1-9] (a) the insensitivity of the reaction yields to O_2 concentration; (b) the apparently unimpeded progress of the characteristic reactions of singlet methylene; and (c) the observation of the reactions at wavelengths for which the quantum yield is unity for CH_2 formation in CH_2CO photolysis.[10]

Typical experimental data are summarized in Table I. The intramolecular nature of the molecular hydrogen elimination is demonstrated through the observation of T_2:HT ratios of $\sim 10^{-3}$ from the photolysis of ketene-*t* containing T:H in a ratio of about 1:40,000, but with a ratio of $CT_2{=}CO:CHT{=}CO \sim 10^{-3}$.[11] Photolysis of $C^{14}H_2{=}CO$ in C_2H_4 and O_2 showed substantial yields of both $C^{14}O$ and $C^{14}O_2$, as well as the characteristic products of singlet methylene. The sum of $C^{14}O$ and $C^{14}O_2$ is very near the values given for per cent triplet methylene in this system[2,3,12] and suggests that the oxides of carbon account for essentially all of the methylenic carbon under these conditions.

Table I. Radioactive Products Observed from the Reactions of Labeled Methylene

A. Experiments with CHT=CO plus CT_2=CO

Parent molecule	Pressure, cm[a] Parent	O_2	Relative radioactivity yields[b] HT	CH_3T	C_2-*t*	·*t*	·*t*
None	0	206	1.82	0.06	0.03	0.00	0.00
c-C_4H_8	18.2	0	0.01	0.62	8.56	2.10	0
c-C_4H_8	17.6	2.0	2.35	0.14	2.74	1.87	0
c-C_4H_8	17.6	1.8	HT:DT:T_2 = 0.998:0.000:0.002				
c-C_4D_8	17.6	2.0	HT:DT:T_2 = 0.882:0.116:0.002				
C_2H_4	196	0	0.00	0.01	0.08	3.24	4.60
C_2H_4	196	0	0.00	0.01	0.10	3.48	4.89
C_2H_4	196	8	0.45	0.01	0.22	3.09	2.14
C_2H_4	196	28	0.48	0.01	0.19	3.05	2.10
C_2D_4	190	19	HT:DT:T_2 = 0.996:0.002:0.002				
C_3D_8	17.6	1.4	HT:DT:T_2 = 0.892:0.106:0.002				

B. Experiments with $C^{14}H_2$=CO

Parent[c] molecule	Per cent yields of C^{14}-labeled products[d] $C^{14}O$	$C^{14}O_2$	=					
C_2H_4	17	13	9	59	0	0	2	0
C_3H_8	21	14	9	0	17	40	0	0
c-C_4H_8	16	15	8	9	0	0	0	52
				ΣC_4	ΣC_5			
c-C_3H_6[e]	18	16	0.8	61	4			

[a] Pressure of ketene-*t* = 2.0 cm; all irradiations at 3130 Å under equivalent exposure conditions with reproducibility as indicated with C_2H_4. [b] Observed count rates for various products normalized to equal aliquot size, but not for quantum yield. Quantitative comparisons should be restricted to substrates at comparable pressures. [c] Samples (except *c*-C_3H_6) contained 20 cm total pressure of RH:O_2:$C^{14}H_2CO$ in ratio 10:1:1; irradiated at 3130 Å. [d] Per cent total observed volatile activity. [e] *c*-C_3H_6:*cis*-$H_3CCH{=}CHCH_3$:O_2:$C^{14}H_2CO$ in ratios 400:12:1:2; total pressure 230 cm; wavelength 3130 Å.

$$^3CH_2 + O_2 \longrightarrow \text{intermediate(s)} \longrightarrow H_2 + CO_2 \qquad (4)$$

$$\longrightarrow H_2 + CO + O \qquad (5)$$

$$\longrightarrow H + CO + OH \qquad (6)$$

The reaction of $^3CH_2$ with O_2 is highly exothermic toward many possible reactions, including those written as eq 4–6, and involves the reaction with one another of two triplet species. Our observations do not provide any compelling information about the nature of the intermediate(s) involved in these reactions, nor do they establish whether CO or CO_2 is the complementary product to molecular hydrogen. The reaction itself is isoelectronic with the postulated reaction of oxygen atoms with oxygen molecules, as in (7),[13,14] and the

$$O(^3P) + O_2(^3\Sigma_g^-) \longrightarrow O_3 \qquad (7)$$

rapid isotopic exchange of oxygen atoms from decomposition of the ozone so formed would have an exothermic counterpart in the substitution of CH_2 for O with the formation of excited CH_2O. Excited formaldehyde could, in turn, decompose to CO and molecular hydrogen;[15] an excited form of CH_2O_2 may also be involved as an intermediate in the oxidation mechanism. The presence of atomic hydrogen and/or hydroxyl radical has not been established in this system. However, the observation of DT from ketene-*t* photolysis in the presence of *c*-C_4D_8 plus O_2 implies a small yield from some bimolecular process, perhaps one involving atomic hydrogen (including tritium) atoms.

The occurrence of both CO_2 and additional CO (beyond that corresponding to the carbonyl group) during ketene photolysis in the presence of O_2 has been noted by other investigators, without sufficient information for identification of its mechanistic origin.[8,12,16,17] Molecular hydrogen has occasionally been reported, usually in the absence of O_2, and also without identification of its origin.

Further studies with $C^{14}H_2{=}CO$ should prove fruitful in investigation of the mechanism of $^3CH_2$ reaction with *trans*-2-butene and other olefins, especially if the conversion of C^{14} to $C^{14}O$ and $C^{14}O_2$ should be con-

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(5) H. M. Frey, *Progr. Reaction Kinetics*, 2, 131 (1964).

(6) W. B. DeMore and S. W. Benson, *Advan. Photochem.*, 2, 219 (1964).

(7) H. M. Frey in "Carbene Chemistry," W. Kirmse, Ed., Academic Press Inc., New York, N. Y., 1964, p 217.

(8) A. N. Strachan and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, 76, 3258 (1954).

(9) G. A. Taylor and G. B. Porter, *J. Chem. Phys.*, 36, 1353 (1962).

(10) The conclusion that $^3CH_2$ can oxidize to CO or CO_2 does not, of course, preclude the possibility that reactions in the vicinity of 3600 Å involve the oxidation of other species, *e.g.*, $^3CH_2{=}CO$; see G. B. Porter, *J. Am. Chem. Soc.*, 79, 1878 (1957), and ref 9.

(11) Our ketene-*t* is synthesized by the pyrolysis of acetic anhydride-*t*. The latter is manufactured at high specific activity and is then normally diluted prior to sale. Ours was further diluted with inactive material to reduce the specific activity to T:H = 1:40,000. However, the amount of $CT_2{=}CO$ is characteristic of the specific activity during the original synthesis, since isotopic equilibrium of the hydrogen isotopes is never attained afterward during the dilution or pyrolytic procedures. The measured activities were approximately 1:500, or 1:1000 in ratio of T_2:HT molecules.

(12) B. A. DeGraff and G. B. Kistiakowsky, *J. Phys. Chem.*, 71, 3984 (1967).

(13) W. DeMore and O. F. Raper, *J. Chem. Phys.*, 37, 2048 (1962); 44, 1780 (1966).

(14) J. R. McNesby and H. Okabe, *Advan. Photochem.*, 3, 157, (1964).

(15) B. A. DeGraff and J. G. Calvert, quoted in J. G. Calvert and J. N. Pitts, "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 371.

(16) R. A. Holroyd and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, 78 4831 (1956).

(17) R. W. Carr, Jr., and G. B. Kistiakowsky, *J. Phys. Chem.*, 70, 118 (1966).

firmed as nearly quantitative under a variety of conditions. In conjunction with our earlier work with CHT=CO, such experiments should clarify the extent to which O_2 interrupts $^3CH_2$ reactions with 2-butene at the $^3CH_2$ or $^3C_5H_{10}$ stages. The possible contributions of reactions involved in these experiments should also be considered for such diverse other systems as those of recoil C^{11} in H_2 (the yield of $C^{11}O_2$ is enhanced by the introduction of O_2),[18] the photooxidation of acetone,[19] and the reactions of atomic O with C_2H_2 and O_2 mixtures, from which CO_2 has been observed.[20]

[18] C. MacKay, J. Nicholas, and R. Wolfgang, *J. Am. Chem. Soc.*, **89**, 5758 (1967).

[19] See, for example, D. E. Hoare and G. S. Pearson, *Advan. Photochem.*, **3**, 83 (1964).

[20] C. A. Arrington, W. Brennen, G. P. Glass, J. V. Michael, and H. Niki, *J. Chem. Phys.*, **43**, 525 (1965).

[21] This research was supported by AEC Contract No. AT-(11-1)-34, Agreement No. 126.

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The Mechanism of Isomerization of an Olefin and Its Possible Relation to the Mechanism of the Catalytic Hydrogenation with Tris(triphenylphosphine)rhodium Chloride

Sir:

The dihydride $RhH_2Cl(PPh_3)_2$ derived from tris(triphenylphosphine)rhodium chloride is a versatile and useful reagent for the selective reduction of mono- and disubstituted double bonds in homogeneous media.[1] The mechanism of the hydrogenation of olefins with $RhCl(PPh_3)_2$ has been studied by Wilkinson and coworkers.[1a] The hydrogenation is stereochemically a *cis* process, and kinetic studies indicate the following steps

$$\mathrm{RhCl(PPh_3)_2 + H_2 \rightleftharpoons RhH_2Cl(PPh_3)_2}$$

$$\mathrm{RhH_2Cl(PPh_3)_2 + olefin \longrightarrow RhH_2Cl(olefin)(PPh_3)_2}$$

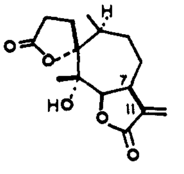
$$\downarrow$$

$$\mathrm{RhCl(PPh_3)_2 + paraffin}$$

The rate-determining step appears to be the formation of olefin-$RhH_2Cl(PPh_3)_2$ complex.[1a] A simultaneous transfer of both hydrogens has been proposed.[1a]

In this communication, we wish to present evidence for an alkyl-rhodium complex as an intermediate in the hydrogenation and, as a corollary, the stepwise transfer of hydrogen from rhodium to the olefin.

The methylene groups in psilostachyine (**1**) and confertiflorin (**3**) are smoothly reduced with $RhH_2Cl(PPh_3)_2$ to yield the dihydro derivatives **2** and **4**, respectively.[2,3] In contrast, however, the main reaction of $RhH_2Cl(PPh_3)_2$ with damsin (**5**) is not hydrogenation, but rather isomerization to isodamsin (**6**).



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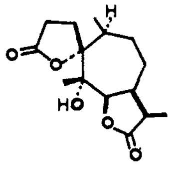

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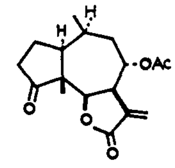

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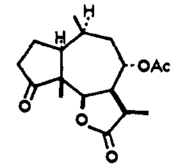

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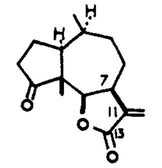

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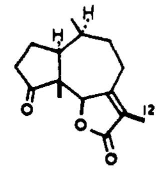
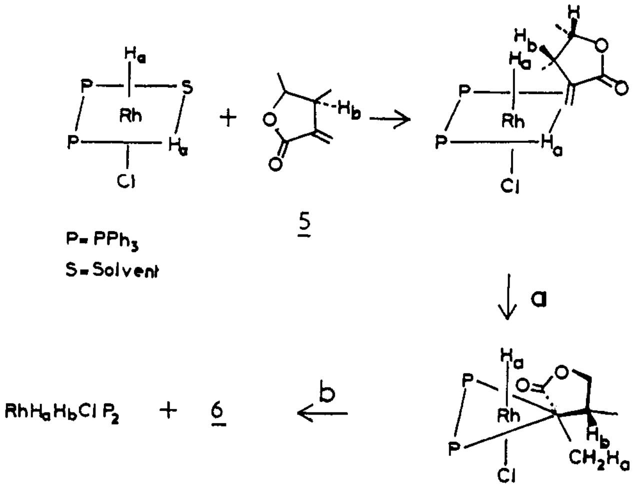


6

While the reason for this difference in behavior is not understood, it was felt that some connection might exist between the mechanism of reduction and the mechanism of this isomerization.

The following observations have been made regarding the isomerization of **5**: (a) no isomerization of **5** to **6** occurs with $RhCl(PPh_3)_2$ alone; addition of hydrogen causes the reaction **5** → **6**; (b) in the presence of EtOD, no incorporation of deuterium atom takes place in the isomerization; (c) the system $RhD_2Cl(PPh_3)_2$ and damsin (**5**) in equivalent amounts leads to a 58% incorporation of one deuterium atom in **6** and 0% of two deuterium atoms in the presence of a catalytic amount of $RhCl(PPh_3)_2$, 70% of **6** contains no deuterium atom, 30% one, and 0% two deuterium atoms.[4] These facts may be accommodated by Scheme I.

Scheme I



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[1] (a) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.*, *A*, 1711 (1966); F. H. Jardine, J. A. Osborn, and G. Wilkinson, *ibid.*, 1574 (1967); (b) J. F. Biellmann and H. Liesenfelt, *C. R. Acad. Sci., Paris, Ser. C*, **263**, 251 (1966); A. J. Birch and K. A. M. Walker, *Tetrahedron Lett.*, 4939 (1966); J. F. Biellmann and H. Liesenfelt, *Bull. Soc. Chim. Fr.*, 4029 (1966); C. Djerassi and J. Gutzwiller, *J. Amer. Chem. Soc.*, 88, 4537 (1966); F. H. Jardine and G. Wilkinson, *J. Chem. Soc.*, *C*, 270 (1967); A. J. Birch and K. A. M. Walker, *ibid.*, 1894 (1966); *Tetrahedron Lett.*, 1935 (1967).

[2] T. J. Mabry, H. E. Miller, H. B. Kagan, and W. Renold, *Tetrahedron*, **22**, 1139 (1966); N. H. Fischer and T. J. Mabry, *ibid.*, **23**, 2529 (1967).

[3] For the synthetic viewpoint it is interesting to note that 1 and 2 are mainly isomerized under conditions of heterogeneous conditions.[2] We wish to thank Dr. Kagan for calling our attention to this problem and Professor Mabry for very kindly supplying the compounds.

[4] Determined by mass spectrometry measurements with MS-9 (Gif-sur-Yvette and National Institutes of Health at Bethesda, Md.) and THN 208 spectrometers (Thomson-Houston) (Strasbourg).