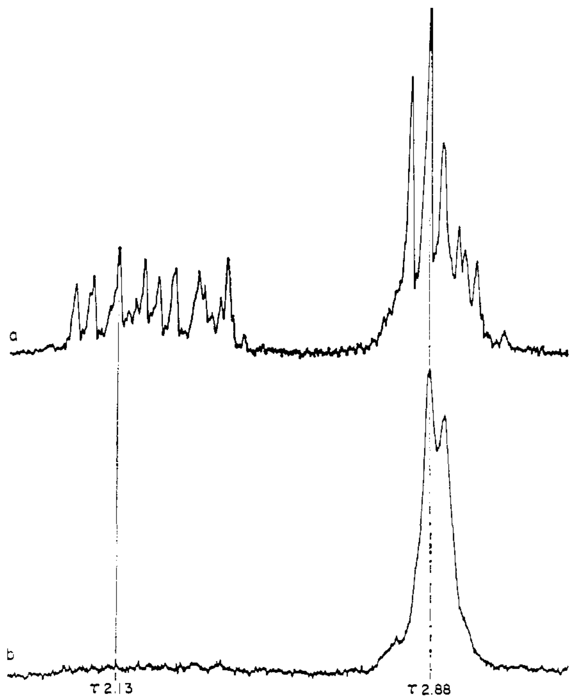
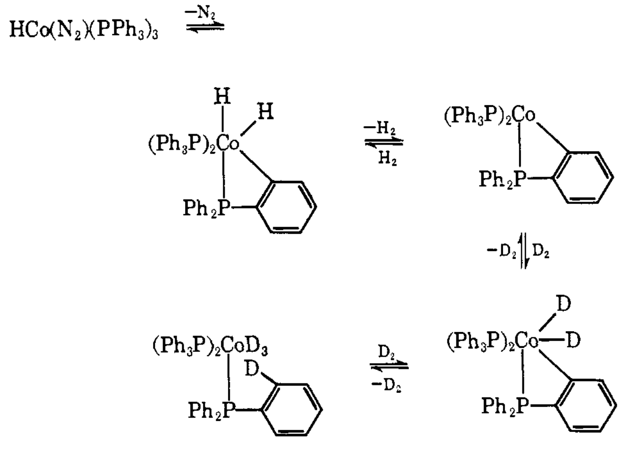


Figure 1. Proton nmr spectra of normal (a) and deuterated (b) triphenylphosphine oxide at 60 MHz in C_6D_6 solution with $(CH_3)_4Si$ internal standard.

The final gas composition was 12% H_2, 43% HD, and 45% D_2 *vs.* a calculated random composition of 10% H_2, 43% HD, and 47% D_2. The complex was decomposed with 30% H_2O_2, and the spectrum of the recovered triphenylphosphine oxide was recorded in C_6D_6 solution in which the *ortho*-proton signal is well separated from those of the *meta* and *para* protons (Figure 1a). The *ortho*-proton signal is almost eliminated in this spectrum (Figure 1b) and the *meta* + *para* signal is collapsed because coupling with the *ortho* protons does not occur. Hence, it appears that most, if not all, of the deuterium introduced into the triphenylphosphine ligands is in the positions *ortho* to the phosphorus atoms.

The most likely explanation for this result is that a rapid equilibrium occurs in which the *ortho* C–H bonds add to a "coordinately unsaturated" cobalt complex (Scheme I). The final complex shown in this series of equilibria is an *o*-deuterioaryl analog of $(Ph_3P)_3CoD_3$ reported by Sacco and Rossi.[3] The irreversible addition of an *ortho* proton of an aryl ligand in a square-planar d^8 complex, $(Ph_3P)_3IrCl$, has been reported by Bennett and Milner.[7] An equilibrium involving addition of a methyl CH of a methylphosphine ligand has been shown by Chatt and Davidson.[8]

Scheme I



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[7] M. A. Bennett and D. L. Milner, *Chem. Commun.*, 581 (1967).

[8] J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 843 (1965).

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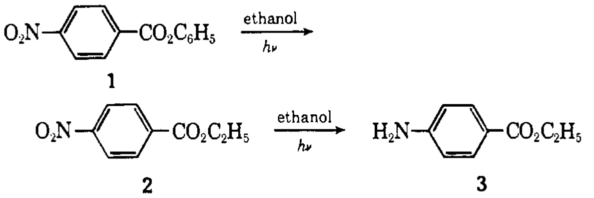
Received January 29, 1968

Photochemistry of Nitrobenzoate Esters and Related Nitroaromatic Compounds. Some Novel Reduction and Esterification Reactions[1]

Sir:

During studies to assess qualitatively the influence of solvent and substituents on the course of the photo-Fries reaction,[1b,2-4] we irradiated[5] an ethanol solution of phenyl 4-nitrobenzoate (**1**) and found that, rather than a Fries rearrangement, a relatively rapid transesterification, followed by reduction of the nitro group to an amino group, comprised the major reaction pathway (eq 1). That the observed solvolysis step was indeed light mediated was indicated by noting that a solution of **1** in ethanol after being heated at 50–55° for 21.5 hr provided **2** in only 2.3% conversion, while during irradiation approximately one-third of **1** was converted to a mixture of **2** and **3** in only 2 hr. After 11.5-hr irradiation, the starting material was completely consumed and the major product consisted of a mixture of phenol, **2**, and **3** in the molar ratio 2.26:1:1.39. The yield of phenol was approximately 60%; a number of minor products have not yet been characterized. The reduction step in eq 1 was realized separately by the irradiation of ethanol solutions of **2**. In less than 1 hr about 25% of **2** had been converted to **3**, and after 12 hr the yield of **3** was greater than 60% as determined gas chromatographically. Work-up of the reaction mixture, which involved acid treatment of the crude product, regeneration of basic material, silica gel



(1)

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[1] (a) Photochemical Studies. VI. (b) For part V, see, R. A. Finnegan and D. Knutson, *J. Am. Chem. Soc.*, **89**, 1970 (1967). (c) This work was supported by Grant GP-5785 from the National Science Foundation.

[2] H. Kobsa, *J. Org. Chem.*, 27, 2393 (1962).

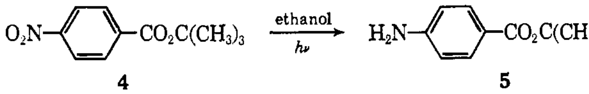
[3] J. C. Anderson and C. B. Reese, *J. Chem. Soc.*, 1781 (1963).

[4] R. A. Finnegan and J. J. Mattice, *Tetrahedron*, 21, 1015 (1965).

[5] In all cases, solutions approximately 1% (w/v) were irradiated with a 450-W, medium-pressure mercury lamp (Hanovia 79A36) housed in a double-walled quartz immersion well. Progress of reaction was followed by infrared and gas chromatographic analysis of aliquots.

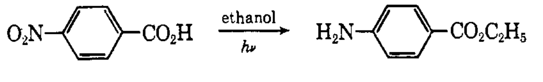
column chromatography, and distillation, allowed the isolation of pure **3** in 32% yield. The only other product characterized was an orange crystalline solid, mp 140–142°, obtained in minute amount and whose spectral properties suggested that it was the known 4,4′-dicarbethoxyazobenzene (lit.[6] mp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

ethyl 3-nitrobenzoate ⟶ ethyl 3-aminobenzoate (24% yield) (4)

4-nitroacetophenone ⟶ 4-aminoacetophenone (16% yield) (5)

nitrobenzene ⟶ aniline (13% yield) (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**, 81675*g* (1967).

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Received October 14, 1967

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.

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

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

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

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).