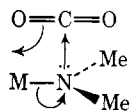


tion state of the type shown below for which electronic and steric factors will be important. A consideration



of the structures of $W(NMe_2)_6$ ⁵ and **1** leads us to believe that steric factors are not the sole controlling factors in the formation of **1**. We suggest that insertion is limited by the nucleophilicity of the NMe_2 ligands. Six dimethylamino ligands, Me_2N^- , offer tungsten a total of 24 electrons although the available metal valence orbitals can accommodate only 18 electrons. Thus for $W(NMe_2)_6$ ligand to metal π -bonding may lead to a maximum W–N bond order of 1.5. However, in $W(NMe_2)_3(O_2CNMe_2)_3$ replacement of three NMe_2 ligands by weaker π -donating oxygen ligands leads to greater N to W π bonding as evidenced by the very short W–N bond length of 1.922 (7) Å; cf. W–N 2.032 (25) Å in $W(NMe_2)_6$.⁵ The *fac*- WN_3O_3 geometry of **1** allows for maximum W–N π bonding. The nucleophilic character of the dimethylamido lone pairs is thus diminished and further insertion of CO_2 is not favored. Insertion of CO_2 into metal–nitrogen covalent bonds may thus parallel the insertion of CO_2 into metal–alkyl bonds for which the importance of the carbanionic character of the alkyl group has recently been emphasized.⁷

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Supplementary Material Available. A listing of data and structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$6.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-6214.

(7) T. Tsuda, K. Veda, and T. Saegusa, *J. Chem. Soc., Chem. Commun.*, 380 (1974).

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Photochemistry of Aromatic Compounds.

Photorearrangement of 3,5-Dimethoxybenzyl Acetate

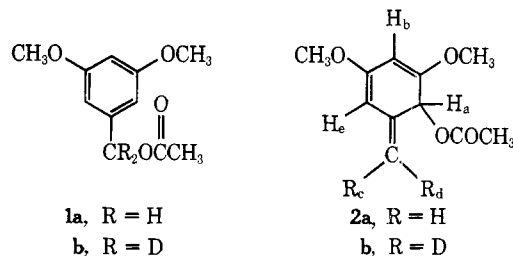
Sir:

The photochemical reaction pathway of a carboxylic acid ester is dependent on structure and on reaction conditions.¹ Reactions involving either stepwise or concerted homolytic processes usually predominate,

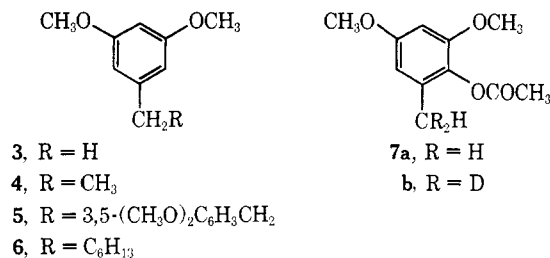
(1) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, pp 434–441.

including, for example, photodecarboxylation,² photodecarbonylation,^{20,3} Norrish type II analogs,⁴ and the photo-Fries rearrangement.⁵ Several reactions involving heterolytic processes have also been observed, for example, photosolvolysis of substituted benzyl acetates⁶ and photohydrolysis of aryl benzoates.⁷ We wish to report the novel photochemical rearrangement of a substituted benzyl acetate to a relatively stable non-aromatic isomer.⁸

Irradiation⁹ of a 0.006 *M* hexane solution of acetate **1a**⁶ gave a mixture of **1a** (3.6%),¹⁰ 1,3-dimethoxy-5-methylene-6-acetoxycyclohexa-1,3-diene (**2a**, 17.2%),



3¹¹ (5.6%), **4**¹² (46.8%), **5** (9.5%), mp 106–107° (lit.¹³ 102°), and **6**¹⁴ (17.2%) obtained as a mixture.¹⁵ Column



chromatography on silica gel with ether–hexane allowed

(2) (a) B. Matuszewski, R. S. Givens, and C. Neywick, *J. Amer. Chem. Soc.*, **95**, 595 (1973); (b) T. O. Meiggs, L. I. Grossweiner, and S. I. Miller, *ibid.*, **94**, 7986 (1972); (c) T. O. Meiggs and S. I. Miller, *ibid.*, **94**, 1989 (1972); (d) R. S. Givens and W. F. Oettle, *J. Org. Chem.*, **37**, 4325 (1972); (e) L. J. Mittal, J. P. Mittal, and E. Hayon, *J. Phys. Chem.*, **77**, 2267 (1973), and references therein.

(3) (a) P. Ausloos, *J. Amer. Chem. Soc.*, **80**, 1310 (1958); (b) M. H. J. Wijnen, *ibid.*, **82**, 3034 (1960), and references therein.

(4) (a) M. L. Yarchak, J. C. Dalton, and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **95**, 5224, 5228 (1973); (b) Y. Ogata, K. Takagi, and Y. Takayanagi, *J. Chem. Soc. Perkin Trans. 1*, 1244 (1973); (c) J. A. Bartrop and J. D. Coyle, *J. Chem. Soc. B*, 251 (1971); (d) J. G. Pacifici and J. A. Hyatt, *Mol. Photochem.*, **3**, 267, 271 (1971).

(5) (a) C. E. Kalmus and D. M. Hercules, *J. Amer. Chem. Soc.*, **96**, 449 (1974); (b) W. Adam, J. A. DeSanabia, and H. Fischer, *J. Org. Chem.*, **38**, 2571 (1973); (c) D. Belluš, *Advan. Photochem.*, **8**, 109 (1971), and references therein.

(6) H. E. Zimmerman and V. R. Sandel, *J. Amer. Chem. Soc.*, **85**, 915 (1963).

(7) J. G. Pacifici, J. S. Zannucci, G. R. Lappin, J. C. Ownby, and C. A. Kelley, *Mol. Photochem.*, **3**, 349 (1972), and references therein.

(8) Photochemical rearrangement of benzyl benzoates to benzylbenzoic acids has been reported, M. Afzal, *Chem. Ind. (London)*, 37 (1974).

(9) For each run 250 ml of solution was degassed with purified nitrogen for 40 min prior to and during irradiation for 30 min with a 450-W Hanovia lamp through a Corex filter.

(10) Yields were determined by pmr analysis of product after rotary evaporation of hexane. Essentially all resonances could be assigned to indicated compounds.

(11) S. Ludwinowsky and J. Tambor, *Chem. Ber.*, **39**, 4037 (1906).

(12) J. P. Brown, N. J. Cartwright, A. Robertson, and W. B. Whalley, *J. Chem. Soc.*, 859 (1949).

(13) T. Petržilka, W. Haefliger, and C. Sikemeier, *Helv. Chim. Acta*, **52**, 1102 (1969).

(14) The pmr, ir, and mass spectra were consistent with the structural assignment, and carbon and hydrogen analyses were within 0.3% of theory.

(15) H. E. Zimmerman and V. R. Sandel found⁶ that in 50% (v/v) aqueous dioxane **1a** undergoes photosolvolysis to yield 3,5-dimethoxybenzyl alcohol; **2a** is not formed.

partial separation of the product mixture. Elution of **2a** as an oil overlapped with that of **1a** and **7a** which is formed by rearrangement of **2a**. The identity of **7a** was confirmed by independent synthesis. Hydroxylation of **3** with *m*-chloroperoxybenzoic acid in CH_2Cl_2 at 0° yielded 2,4-dimethoxy-6-methylphenol (**8**),¹⁶ which was converted to **7a**,¹⁴ mp $56\text{--}57^\circ$.

The ir spectrum (neat) of **2a**¹⁷ displayed bands at 2830 (CH_3O), 1740 ($\text{C}=\text{C}$), and 1615 cm^{-1} ($\text{C}=\text{C}$); the uv spectrum (hexane) λ_{max} 316 nm ($\log \epsilon \sim 2.6$); and the pmr spectrum (100 MHz, CDCl_3) a singlet at δ 2.01 (3 H, OCOCH_3), a triplet at δ 5.58 for H_e , $J_{ee} = 2.0$ and $J_{de} = 2.5$ Hz, a triplet at δ 5.16 for H_c , $J_{ee} = 2.0$, $J_{ac} = 2.0$, and $J_{cd} \sim 0$ Hz, a doublet of doublets at δ 5.07 for H_d , $J_{de} = 2.5$ and $J_{ad} = 1.4$ Hz, a doublet at δ 4.65 for H_b , $J_{ab} = 1.4$ Hz, a singlet at δ 3.62 (3 H, CH_3O) overlapping with a multiplet for H_a at δ 3.58, and a singlet at δ 3.24 (3 H, CH_3O). The pmr assignments were confirmed by the spectrum of **2b**, prepared by photolysis of **1b**,¹⁸ in which H_c and H_d were absent and H_a and H_e appeared as doublet, $J_{ab} = 1.4$ Hz, and singlet, respectively. All other resonances were unaltered with respect to the spectrum of **2a**. Further confirmation of the structural assignment was obtained by spin decoupling. With irradiation of H_a , H_e was unaltered, H_b appeared as a singlet, and H_c and H_d appeared as doublets, $J_{ee} = 2.0$ and $J_{de} = 2.5$ Hz, respectively.

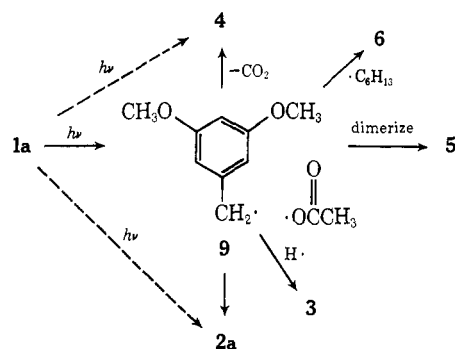
When a 0.017 *M* benzene solution of **2a**¹⁷ was stirred at 55° for 3 hr, **2a** was converted in $\sim 90\%$ yield to **7a**. Analogously, **2b** yielded **7b** (eq 1). The rearrangements



of **2a** and **2b** to **7a** and **7b**, respectively, support the structural assignment of **2**.^{20,21} It is interesting to note that **2** rearranges to **7** in an apparently thermal process by a symmetry-forbidden²² [1,3]-hydrogen shift and not to **1** by symmetry-allowed²² [1,3]- or [3,3]-acetoxy shifts.

The formation of **3**, **4**, **5**, and **6** is consistent with initial photoinduced cleavage of **1a** to give 3,5-dimethoxybenzyl (**9**) and acetoxy free radicals, Scheme I.

Scheme I



(16) E. Späth, M. Pailer, and G. Gregely, *Chem. Ber.*, **73**, 795 (1940).

(17) This material was contaminated with 7.9% **1a** and 3.4% **7a**.

(18) Lithium aluminum deuteride reduction of methyl 3,5-dimethoxybenzoate¹⁹ yielded 3,5-dimethoxybenzyl-1,1-*d*₂ alcohol, which was converted to **1b**.

(19) C. Bülow and G. Riess, *Chem. Ber.*, **35**, 3900 (1902).

(20) The parent hydrocarbon, 5-methylene-1,3-cyclohexadiene, has been prepared; W. J. Bailey and R. A. Baylouny, *J. Org. Chem.*, **27**, 3476 (1962).

(21) Attempts to form a Diels-Alder adduct with dimethyl acetylenedicarboxylate and with tetracyanoethylene were unsuccessful.

(22) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, pp 114-119.

Hydrogen abstraction by and dimerization of **9** yield **3** and **5**, respectively. Decarboxylation of acetoxy radical followed by combination of resultant methyl radical and **9** yields **4**, which could also result from a concerted photoinduced expulsion of CO_2 from **1a**. Hydrogen abstraction from solvent by **9**, acetoxy, or methyl radical would yield hexyl radical, which combines with **9** to yield **6**. Formation of **2a** can proceed by recombination of **9** and acetoxy radical or by a concerted process from **1a**. For the latter route photochemical [1,3]- and [3,3]-acetoxy shifts are symmetry allowed and forbidden,^{22,23} respectively. For a thermally excited ground state both shifts should be symmetry allowed.²² We plan to investigate the mechanism of the **1** to **2** transformation.

Acknowledgment is made to the Donors of The Petroleum Research Fund, administered by the American Chemical Society, and to the University of Wyoming, Division of Basic Research, for support of this research.

(23) A referee has suggested that use of *n* electrons on the carbonyl oxygen could allow a photochemical [3,3] process.

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Frontier Control Nucleophilic Reactivity and Photoelectron Spectroscopy Data within the Klopman Equation. The Thiocarbonyl Group

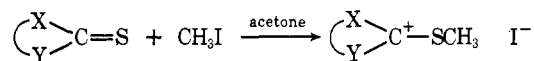
Sir:

Many equations correlating the rate of reaction between various nucleophiles and electrophiles with physicochemical parameters have been established.¹⁻⁶ The approach of Hudson and Klopman^{5,6} illustrates the relative importance of the control of reactivity by charges and by frontier orbitals.

Unfortunately this approach has been difficult to check experimentally because of the lack of a tool capable of measuring the effective energies of orbitals involved in reactivity. Photoelectron spectroscopy (pes) now fills this gap.

We wish to report the results arising from a comparison of kinetic measurements⁷ and the ionization potentials of some heterocyclic thiocarbonyl compounds.

The kinetics of the reaction have been studied by a



conductometric method previously described.^{8,9} The

(1) J. O. Edwards, *J. Amer. Chem. Soc.*, **76**, 1540 (1954).

(2) J. O. Edwards and R. G. Pearson, *J. Amer. Chem. Soc.*, **84**, 16 (1962).

(3) R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3571 (1963); *Chem. Eng. News*, **43**, 90 (1965); *Chem. Brit.*, **3**, 103 (1967); *J. Chem. Educ.*, **45**, 581 (1968).

(4) R. S. Drago and B. B. Wayland, *J. Amer. Chem. Soc.*, **87**, 3571 (1965).

(5) G. Klopman and R. F. Hudson, *Theor. Chim. Acta*, **8**, 165 (1965).

(6) G. Klopman, *J. Amer. Chem. Soc.*, **90**, 223 (1968).

(7) M. Arbelot, R. Gallo, M. Chanon, and J. Metzger, *Int. J. Sulfur Chem.*, in press.

(8) R. Cottet, R. Gallo, J. Metzger, and J. M. Surzur, *Bull. Soc. Chim. Fr.*, **12**, 4502 (1967).

(9) M. Chanon, R. Gallo, J. M. Surzur, and J. Metzger, *Bull. Soc. Chim. Fr.*, **7**, 2881 (1968).