Table I. Comparison of Formation Constants for p-FC_6H_4OH–Base Complexes Obtained by F Nmr, Infrared, and Calorimetric Methods in CCl_4 at 25.0°

Base	F nmr method[a]		Infrared method[b]		Calorimetric method[c]	
	Base range, M	K_f, M^{-1}	Base range, M	K_f, M^{-1}	Base range, M	K_f, M^{-1}
THF[d]	0.0241–0.201	19.1 ± 0.9	0.0221–0.0933	17.7 ± 0.5	0.00705–0.0211	19.4 ± 1.0
Pyridine	0.00690–0.0509	76.7 ± 2	0.00467–0.0240	76.2 ± 0.9	0.00344–0.0186	74.0 ± 5
DMF[e]	0.00665–0.0205	121 ± 2	0.00660–0.0427	116 ± 3	0.00361–0.0203	122 ± 9

[a] Obtained by best fit of δ_{obsd} values to fixed values of K_f and Δ (*cf.* footnote 4); p-FC_6H_4OH = 0.0093–0.013 M. [b] Obtained as indicated in text, with p-$FC_6H_4OH \leq 0.004$ M. [c] Obtained as indicated in ref 5. [d] Tetrahydrofuran. [e] N,N-Dimethylformamide.

Table II. F Nmr Shifts of p-FC_6H_4OH–Base Complexes

Base	Δ values,[a,d] ppm		Apparent % proton transfer[a]
	Titration curve (30–80% complexing)	Directly observed (97–99% complexing)	
THF	2.03 ± 0.03[b]	. . .	14
Pyridine	2.48 ± 0.03[b]	2.53 ± 0.02 (0.698)[c]	18
DMF	2.71 ± 0.02[b]	2.73 ± 0.02 (0.457)[c]	20

[a] *Cf.* text. [b] Standard error of Δ from 6–12 points on "titration" curve calculated using K_f from the infrared method. [c] Base concentration employed. [d] Preliminary experiments[9b] carried out with 0.1 M p-FC_6H_4OH 'and relatively high base concentrations gave: $\Delta_{THF} = 2.10 \pm 0.15$, $\Delta_{pyr} = 2.55 \pm 0.05$, $\Delta_{DMF} \doteq 2.75 \pm 0.05$.

condition 1 is met. However, the analysis and assumptions are confirmed by the further conditions: (2) agreement of the value of K_f obtained by the F nmr method with those obtained by two reliable independent methods (*cf.* Table I), and (3) agreement of the value of Δ obtained in the analysis with a directly measured value (for 97–99% complex formation which is corrected to 100%).

Tables I and II summarize the confirmatory results obtained for the three typical bases.[6] In Table I the values of K_f obtained by the three independent methods are given together with the conditions of the measurements. In Table II are given the directly observed values of Δ and those calculated from the observed shifts, δ, for solutions in which 30–80% complex formation occurs ($\Delta = (\delta/[\text{complex}])[\text{acid}]_s$, where [complex] = equilibrium concentration of complex and $[\text{acid}]_s$ = stoichiometric concentration of p-FC_6H_4OH). The third confirmatory condition (above) is limited to bases for which $K_f >$ *ca.* 50 because of medium effects in the F nmr method (*i.e.*, at base concentrations > *ca.* 0.5 M). For bases with $K_f <$ *ca.* 50, only condition 2 may be applied as illustrated by the results for THF.

The infrared formation constants given in Table I have been obtained (L. J. and P. von R. S.) using a Perkin-Elmer 421 double-beam grating spectrophotometer to measure the transmittance of the fundamental OH stretching vibration (3610 cm^{-1}) of the uncomplexed p-fluorophenol in equilibrium with the complex. No reproducible systematic variation of K_f with base concentration beyond the precision measure was found.

Values of Δ are directly proportional to (at least approximately) the change in π-electron charge density at the p-carbon atom,[7] and, probably, of the oxygen atom,[8] of p-fluorophenol which occurs on complex formation. The Δ value for complete proton transfer as obtained from the shielding effects of p-FC_6H_4OH in CCl_4 and p-fluorophenoxide ion in dimethyl sulfoxide solution is approximately 14 ppm.[9,10] Consequently, the F nmr of the p-fluorophenyl label provides a *novel measure of the extent of proton transfer in the H-bonded complex, i.e.*, the apparent % proton transfer = 100Δ/14 (*cf.* results listed in Table II). The apparent per cent proton transfer is of particular concern in linear free-energy relationships between log K_f and pK_A of the base. The order of both Δ and log K_f values is THF < pyridine < DMF, whereas $-\Delta H_f$ values[5] give THF < DMF < pyridine. These matters will be examined in detail for wide structural variation in the base in a subsequent publication.

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(6) Immediately before use, reagent-grade CCl_4, DMF, and pyridine were distilled from CaH_2, p-FC_6H_4OH was sublimed, and THF was distilled from Na-benzophenone.

(7) R. W. Taft, F. Prosser, L. Goodman, and G. T. Davis, *J. Chem. Phys.*, **38**, 380 (1963).

(8) F. Prosser, Ph.D. Thesis, The Pennsylvania State University, Aug 1961.

(9) (a) Unpublished results of Dr. George Allen; (b) Ph.D. Thesis of M. G. Schwartz, The Pennsylvania State University, Dec 1965.

(10) The complementary shift for complete protonation of p-FC_6H_4-OH is not available. However, the coordination of oxygen with BCl_3 is expected to give rise to a similar value.[3c] The Δ value for complexation of p-fluoroanisole with BCl_3 in CH_2Cl_2 solutions is −12.6 ppm (unpublished results of Mr. J. W. Carten). This figure may be taken as support for the direct relationship assumed between shift and extent of protonation.

(11) National Institutes of Health Predoctoral Fellow, Princeton University, 1967; Ph.D. Thesis, Princeton University, 1967.

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The Photochemical Decomposition of Geminal Diazides. I. Dimethyl Diazidomalonate

Sir:

Photolysis of alkyl azides proceeds with loss of molecular nitrogen to yield products which may derive from a nitrene intermediate.[1] Photochemical decomposition of a geminal diazide could proceed analogously with loss of one, two, or three molecules of nitrogen.[2] The respective intermediates would be

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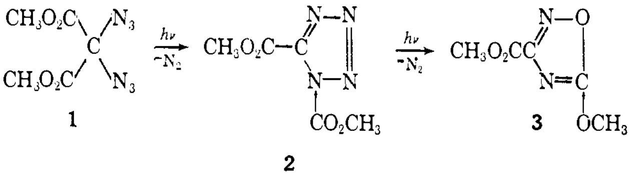
(1) R. M. Moriarty and M. Rahman, *Tetrahedron*, **21**, 2877 (1965); D. H. R. Barton and A. N. Starratt, *J. Chem. Soc.*, 2444 (1965). For reviews, see L. Horner and A. Christmann, *Angew. Chem. Intern. Ed. Engl.*, **2**, 599 (1963); R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, **64**, 149 (1964).

(2) L. Barash, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, reported that irradiation of benzophenone diazide in several matrices at 77°K yielded an epr spectrum identical with that of diphenylmethylene obtained by photolysis of diphenyldiazomethane. In the accompanying communication, we report on the photolysis of benzophenone diazide. See also L. Barash, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc*, **89**, 3931 (1967).

an azidonitrene, a dinitrene, or ultimately a carbene. The first two processes could produce either tetrazoles or diazirines. In view of these manifold possibilities, and also the unusual nature of the starting material[3] and some of the intermediates, we undertook a study of the photolytic reaction.

Irradiation of a 1% benzene solution of dimethyl diazidomalonate (**1**) for 7 hr caused the loss of 1 molar equiv of nitrogen.[4] Disappearance of the azido stretching frequency in the infrared paralleled this change. A small amount of carbon dioxide was also evolved. Continued irradiation led to evolution of a second molar equivalent of nitrogen.

The implication of an initial formation of a product which subsequently loses nitrogen in a second step was confirmed. Interruption of the photolysis after evolution of 1 molar equiv of nitrogen afforded 48% of dimethyl tetrazole-1,5-dicarboxylate (**2**): mp 77–80°; ν_{CCl_4} (cm^{-1}) 1750 (C–CO), 1813 (NCO); δ_{CDCl_3} 4.13, 4.37. The microanalysis and Rast molecular weight determination were correct for $C_5H_6N_4O_4$. The mass spectrum showed no parent molecular ion at *m/e* 186; however, an intense P − 28 peak appeared at *m/e* 158. The behavior is typical of 1,5-disubstituted tetrazoles.[5] Treatment of **2** with 15% sodium hydroxide at 100° for 12 hr yielded tetrazole.[6]

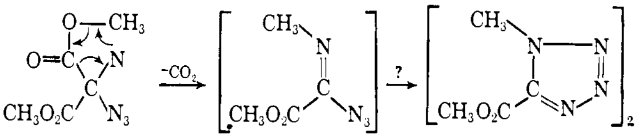


Prolonged irradiation of **1** or separate irradiation of **2** yielded 32% of compound **3**: mp 83–84°; ν_{CCl_4} (cm^{-1}) 1600 (C=N), 1750 (C=O); λ_{max}^{EtOH} 233 mμ (ϵ 6303); δ_{CDCl_3} 4.00, 4.16. The microanalysis and Rast molecular weight corresponded to $C_5H_6N_2O_4$. The high-resolution mass spectrum showed a parent molecular ion at *m/e* 158.0328; $C_5H_6N_2O_4$ requires 158.0328. The presence of the C–OCH$_3$ group was supported by observation of a peak at *m/e* 128.0248. Loss of CH_2O from $C_5H_6N_2O_4$ requires 128.0222; further a metastable transition at *m/e* 103.7 supports the change 158 → 128 + 30. The isomeric diazirine structure for **3** is unlikely in view of the substantial thermal stability of this compound. Only heating to 150° for 1 hr caused decomposition.

Transformation **1** → **2** requires formal migration of a carbomethoxy group from carbon to nitrogen, a change which is without precedent in photochemistry.

Photochemically induced rearrangement of an N-carboalkoxytetrazole to an oxadiazole, such as **2** → **3**, is unknown; however, a somewhat analogous thermal rearrangement is reported in the formation of 5-acetamido-2-methyl-1,3,4-oxadiazole upon prolonged boiling of 5-aminotetrazole with acetic anhydride.[7,8]

Finally, the observed evolution of small amounts of carbon dioxide in the photolysis prompted us to search for a product which might derive from such a process. A third product was isolated in only 5–7% yield and had mp 110–111°; ν_{CCl_4} (cm^{-1}) 1745; δ_{CDCl_3} 4.04, 4.49 (singlets of equal intensity). The microanalysis and Rast molecular weight agreed with the formula $C_4H_6N_4O_2$ (142). The mass spectrum, however, showed no peak at *m/e* 142, but it did have intense peaks at *m/e* 256 and 225. These data may be accommodated by postulation of loss of both nitrogen and carbon dioxide from **1** to yield an N-methylimino azide which dimerizes, possibly through the tetrazole. The dimer would have the mass spectrum in which one might observe a P − 28 peak as the highest mass fragment if the dimer possesses the azo grouping. The molecular weight determined by the Rast method is an apparent molecular weight due to dissociation of the dimer. Available evidence does not permit formulation of the structure of the dimer, which is still under investigation. It may derive from methyl group migration to yield an N-methylimino azide which may dimerize *via* the tetrazole. Such a rearrangement has some analogy in the photochemical decomposition of α-azidocarboxylic acids and esters.[9]



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[3] Handling of such diazides might appear hazardously adventuresome. Dimethyl diazidomalonate is quite stable to shock, and it can be distilled at reduced pressure. This compound is unexpectedly stable to heat. The synthesis of dimethyl diazidomalonate is interesting and is based upon the method of H. Bretschneider and N. Karpitschka, *Monatsh.*, **84**, 1091 (1953). Reaction of dimethyl monobromomalonate and 1 equiv of sodium azide in methanol yields dimethyl diazidomalonate and dimethyl malonate, but no dimethyl monoazidomalonate. One may envision initial formation of

$$(CH_3O_2C)_2CH{-}N_3 \xrightarrow{CH_3OH} (CH_3O_2C)_2\bar{C}{-}N_3$$

which could yield the diazido compound by *trans* bromination followed by displacement by azide anion.

[4] A Hanau high-pressure (Q81, 0.5 w at 2800 A) immersion lamp surrounded by a quartz water-cooled heat exchanger was placed directly into the solution. Progress of the reaction was followed either by manometric measurement of the volume of nitrogen evolved or by loss of azide absorption at 2095 and 2120 cm^{-1} in the infrared.

[5] Analogous behavior was observed in the mass spectrum of 1,5-diphenyltetrazole.

[6] O. Dimroth and G. Fester, *Ber.*, **34**, 2219 (1910).

[7] R. Stolle, *ibid.*, **62**, 1119 (1929).

[8] It should be noted that N-carboalkoxytetrazoles are unknown.

[9] R. M. Moriarty and M. Rahman, *J. Am. Chem. Soc.*, 87, 2519 (1965).

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The Photochemical Decomposition of Geminal Diazides. II. The Solution Photolysis of Benzophenone Diazide

Sir:

In the preceding communication, a reaction sequence was offered for the photochemical decomposition of a geminal diazide.[1] Assuming the identity of the inter-

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[1] R. M. Moriarty, J. M. Kliegman, and C. Shovlin, *J. Am. Chem. Soc.*, **89**, 5958 (1967).