composition were similar to those used by Peterson as was the uv spectrophotometric procedure for rate determinations.[5] The buffered trifluoroacetolysis rate of neopentyl *p*-toluenesulfonate at 75.0° was 8.5×10^{-5} sec^{-1}. There was some yellowing and decomposition during the solvolysis, but the major, volatile product was *t*-amyl trifluoroacetate.

The significance of these results can be best seen by comparing the solvolyses of ethyl, 2-phenylethyl, and neopentyl *p*-toluenesulfonates in three commonly used solvolysis media and in trifluoroacetic acid.

Table I. Solvolysis Rates (Relative to Neopentyl *p*-Toluenesulfonate in Acetic Acid) as a Function of Solvent at 75°[a]

Reactant	Ethanol	Acetic acid	Formic acid	Trifluoroacetic acid[b]
CH_3CH_2OTs	356	9.2	226	6.4
$C_6H_5CH_2CH_2OTs$	85	3.4	952	10,500
$(CH_3)_3CCH_2OTs$	0.2	1.0	227	1,018

[a] For all rates except trifluoroacetolysis of neopentyl *p*-toluenesulfonate see: S. Winstein and H. Marshall, *J. Amer. Chem. Soc.*, **74**, 1120 (1952); S. Winstein, C. R. Lindegren, H. Marshall, and L. L. Ingraham, *ibid.*, **75**, 147 (1953); and ref 2. [b] Rates in trifluoroacetic acid in buffered solution.

The first point of interest is the striking rate enhancement of neopentyl *p*-toluenesulfonate relative to ethyl *p*-toluenesulfonate, a factor of 159 for the buffered trifluoroacetolysis.[6] Ethyl *p*-toluenesulfonateh as no alkyl group to provide anchimeric assistance to ionization. The solvolysis rate of ethyl *p*-toluenesulfonate is usually enhanced through displacement by solvent; however, trifluoroacetic acid is a solvent of low nucleophilicity and high ionizing power, a combination which accentuates SN1 and diminishes SN2 reactions.[7] It therefore appears that the rate of ionization of neopentyl *p*-toluenesulfonate is significantly enhanced, relative to ethyl *p*-toluenesulfonate, due to methyl participation during ionization with concomitant formation of the tertiary substituted product.[8]

It is also of interest to look at the relative rates of each individual *p*-toluenesulfonate as the solvent changes from trifluoroacetic acid to ethyl alcohol, *i.e.*, as the solvents progress from low nucleophilicity and high ionizing power to high nucleophilicity and low ionizing power. For displacement reactions with ethyl *p*-toluenesulfonate, formic acid offers the most effective combination of ionizing power and nucleophilicity,[2] with ionizing power decreasing on going to acetic acid without a compensating increase in nucleophilicity. The rate of ethyl *p*-toluenesulfonate increases in ethyl alcohol due to the increase in nucleophilicity and decreases in trifluoroacetic acid due to the decrease in nucleophilicity. Thus, the solvolysis rate of ethyl *p*-toluenesulfonate is more sensitive to nucleophilicity than to ionizing power when compared with the other two systems; *i.e.*, SN1 is much less important than SN2. 2-Phenylethyl *p*-toluenesulfonate, on the other hand, can benefit both from an increase in nucleophilicity and in ionizing power since the solvolysis rate can be enhanced by solvent displacement or by phenyl participation and it is reasonable that the rate would be increased, relative to acetic acid, in going either to ethyl alcohol or to formic and trifluoroacetic acids. In neopentyl *p*-toluenesulfonate solvent participation is sterically prohibited, so that solvolysis rate is only a function of the ionizing power of the solvolysis medium; therefore, the rates progressively increase from ethyl alcohol to trifluoroacetic acid.

Turning to the question of the role of alkyl participation during ionization of neopentyl *p*-toluenesulfonate in media other than trifluoroacetic acid, it is anticipated that, as the ionizing power of the solvolysis medium is decreased, the need for assistance in ionization increases. This means that assistance from internal displacement, *i.e.*, methyl participation, should become even more important as one changes solvent from trifluoroacetic acid to formic and acetic acids.[9]

(5) P. E. Peterson, R. E. Kelley, Jr., R. Belloli, and K. A. Sipp, *J. Amer. Chem. Soc.*, 87, 5169 (1965).

(6) A similar enhancement has been reported for solvolysis in concentrated sulfuric acid: P. C. Myhre and K. S. Brown, 155th National Meeting of the American Chemical Society, San Francisco, Calif., March 1968, Abstract P-194.

(7) (a) In 2-phenylethyl *p*-toluenesulfonate, there is no SN2 component in trifluoroacetic acid; however, the extent of SN2 with ethyl *p*-toluenesulfonate in trifluoroacetic acid is uncertain (see ref 2). This implies that the transition-state energy in the neopentyl solvolysis is lowered through methyl participation by at least 2 kcal in trifluoroacetic acid. (b) Inductive effects are amplified in trifluoroacetic acid relative to formic and acetic acids, and this would somewhat reduce the enhancement due solely to methyl participation, *i.e.*, $\rho_I = -15.7$ for trifluoroacetolysis, -7.79 for formolysis, and -5.72 for acetolysis (see ref 2 and 5).

(8) Nordlander has used similar reasoning to show phenyl participation in 2-phenylethyl *p*-toluenesulfonate. See ref 2.

(9) The view has recently been presented that ionization and rearrangement are sequential during the acetolysis of simple neopentyl systems: J. E. Nordlander, S. P. Jindal, P. von R. Schleyer, R. C. Fort, Jr., J. J. Harper, and R. D. Nichols, *J. Amer. Chem. Soc.*, **88**, 4475 (1966). One, of course, might question the validity of comparing adamantylcarbinyl *p*-toluenesulfonate directly with neopentyl *p*-toluenesulfonate: W. G. Dauben, J. L. Chitwood, and K. V. Scherer, Jr., *ibid.*, 90, 1014 (1968).

(10) National Institutes of Health Predoctoral Fellow, 1966–1968.

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Synthesis of Porphyrins. Deoxophylloerythroetioporphyrin[1]

Sir:

Deoxophylloerythroetioporphyrin (DPEP) (I) has been generally accepted as the predominant porphyrin in crude oil; however, mass spectral studies suggest that a number of homologs are also present.[2] The isocyclic ring in DPEP and the resulting steric interactions have made synthesis of such porphyrins related to chlorophylls extremely difficult. Two syntheses of I have been reported;[3,4] both involve condensation of the same dipyrrylmethenes, gave extremely low yields (*ca.* 0.03%), and reported different electronic spectra for the product. A third preparation of DPEP has recently been reported[5] from pheophytin in *ca.* 0.5%

(1) This research was supported in part by Grant AI-04888 from the National Institutes of Health, U. S. Public Health Service.

(2) (a) M. Blumer and G. Omenn, *Geochim. Cosmochim. Acta*, **25**, 81 (1961); (b) E. W. Baker, *J. Am. Chem. Soc.*, **88**, 2311 (1966); (c) E. W. Baker, F. F. Yen, J. P. Dickie, R. E. Rhodes, and L. F. Clark, *ibid.* **89**, 3631 (1967).

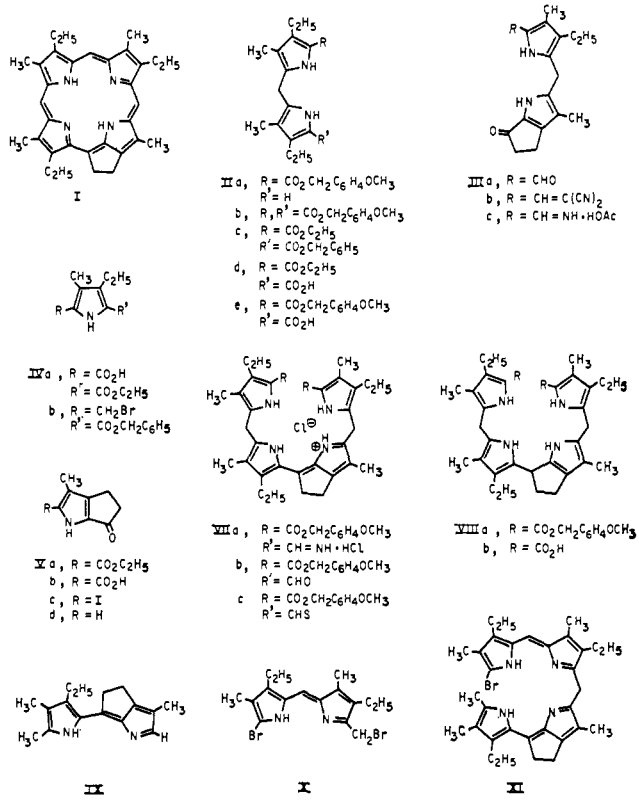
(3) H. Fischer and H. Orth, "Die Chemie des Pyrroles," Vol. 2, Part 2, Akademische Verlagsgesellschaft, Leipzig, 1937, p 206; H. Fischer and H. J. Hoffmann, *Ann.*, **517**, 274 (1935).

(4) J. M. Sugihara and L. R. McGee, *J. Org. Chem.*, **22**, 795 (1957).

(5) E. W. Baker, A. H. Corwin, E. Klesper, and P. E. Wei, *ibid.*, **33**, 3144 (1968).

yield. These illustrate the need for a generally useful synthesis of porphyrins bearing the fused cyclopenteno ring. We now wish to report such a synthesis which is adaptable to the preparation of homologs and the insertion of isotopes.

Our method involves the condensation of two dipyrrylmethanes of general structures II and III, with the R groups of the left dipyrrylmethane, II, such that the synthesis is suitable for fully unsymmetrically porphyrins. To this end the left dipyrrylmethane was blocked at one end with an anisyloxycarbonyl group. This dipyrrylmethane (IIa) might have been prepared *via* a partial hydrogenolysis of the symmetrical 5,5′-diester IIb as in recent syntheses,[6] but such reductions give a mixture of products, and the necessary symmetry would limit the range of applicability of the synthetic method. For these reasons a new route to IIa was



devised. The two pyrroles IVa[7] and IVb[8] were joined as their respective lithium salt and pyridine complex by heating in formamide.[8] The resulting mixed ester IIc [mp 75–77°; λ_{max} 293 nm (ϵ 32,100), 277 (27,100), 248 sh (12,800)][9] was hydrogenolyzed to the half-ester IId [$\lambda_{max}^{CH_3OH}$ 289 nm (ϵ 28,400), 277 sh (24,000), 248 sh (12,500)]. Base-catalyzed transesterification of IId gave an excellent yield of the corresponding anisyl half-ester IIe [mp 159–162° dec; $\lambda_{max}^{CH_3OH}$ 291 nm (ϵ 28,600), 275 (25,600), 227 (18,700)], which was then decarboxylated to IIa by heating at 180° for a few minutes. This sensitive dipyrrylmethane, characterized by nmr, was used immediately.

The right dipyrrylmethane, III, features a unique 6-oxocyclopenteno[*b*]pyrrole moiety.[10] This moiety was formed in 60% yield when 2-carbethoxy-4-(β-carboxyethyl)-3-methylpyrrole[11] was cyclized with polyphosphoric acid. The resulting 2-carbethoxy-3-methyl-6-oxocyclopenteno[*b*]pyrrole [Va, mp 159–160°; λ_{max} 291 nm (ϵ 23,800), 206 sh (23,500), 220 (11,000)] was hydrolyzed to the acid Vb. Decarboxylation to the key intermediate Vd [mp 210° dec; λ_{max} 278 nm (ϵ 18,600), 266 sh (15,400)] was accomplished by treatment of the sodium salt with iodine followed by catalytic hydrogenolysis of the resulting iodo compound Vc. After protecting the formyl group of cryptopyrrole-2-aldehyde[12] by condensation with malononitrile, the 5-methyl group was oxidized with lead tetraacetate to give 2-(2,2-dicyanovinyl)-3-methyl-4-ethyl-5-acetoxymethylpyrrole (VIa) [mp 143–144°; λ_{max} 392 nm (ϵ 71,000), 327 sh (8500)]. Condensation of Vd and VIa in ethanolic hydrochloric acid gave the dipyrrylmethane IIIb [mp 275° dec; λ_{max} 405 nm (ϵ 40,000), 287 (20,000), 267 sh (10,000)], which was then quantitatively converted to IIIa [λ_{max} 315 nm (ϵ 25,000), 288 (20,000), 262 sh] by hydrolysis in 10% sodium hydroxide containing a few drops of ethanol.

To ensure initial condensation of the ketone moiety of IIIa, the formyl group was converted into an aldimine.[13] Thus heating IIIa with ammonium acetate in benzene gave the aldimine IIIc isolated as the acetate salt [λ_{max} 332, 290 nm]. When treated with phosphorus oxychloride in methylene chloride, the aldimine IIIc condensed smoothly with IIa forming the formiminobilene-b dihydrochloride VIIa [λ_{max} 475 nm (ϵ 50,000), 450 sh (30,000), 345 (26,000), 284 (18,500)]. We have found phosphorus oxychloride in methylene chloride to be a superior, mild reagent for methene formation with a variety of pyrrole aldehydes and ketones even in the presence of labile esters.

VIIa underwent rapid and facile conversion to a product with a different visible spectrum [λ_{max} 469 nm (ϵ 35,000), 445 (33,000)], believed to be the formiminobiladiene-ab. Hydrolysis of VIIa by heating with a mixture of benzene and water was quite facile, yielding the formylbilene-b VIIb [λ_{max} 475 nm (ϵ 50,000), 450 (30,000), 286 (20,000), 308 sh (18,000)] plus some of the corresponding formylbiladiene-ab. Treatment of VIIa with alkali followed by hydrogen sulfide rapidly produced the thioformylbilene-b VIIc (as the free base) [$\lambda_{max}^{CHCl_3}$ 476 nm (ϵ 20,000), 400 (50,000); $\lambda_{max}^{H^+}$ 480 nm (ϵ 45,000), 455 sh (40,000), 405 (40,000), 283 (20,000)]. When VIIb or VIIc was subjected to 2.5% hydriodic acid in acetic acid followed by air oxidation, deoxophylloerythroetioporphyrin (I) was formed in 6% yield.

Formation of DPEP in only 6% yield, while a vast improvement over other synthesis,[3–5] is undoubtedly due to steric interactions involving the isocyclic ring. This belief is supported by our results obtained when

(6) (a) A. H. Jackson, G. W. Kenner, G. McGillivray, and G. S. Sach, *J. Chem. Soc.*, 676 (1965); (b) A. H. Jackson, G. W. Kenner, and G. S. Sach, *ibid.*, 2045 (1967).

(7) W. Siedel, *Z. Physiol. Chem.*, **231**, 167 (1935).

(8) J. Ellis, A. H. Jackson, A. C. Jain, and G. W. Kenner, *J. Chem. Soc.*, 1943 (1964).

(9) Satisfactory analyses were obtained for all new compounds. All compounds were characterized by nmr and uv spectra, the latter being determined in 95% ethanol except where otherwise noted.

(10) The only example in the literature of this structural unit is the cyclization product from porphobilinogen lactam [G. H. Cookson and C. Rimington, *Biochem. J.*, **57**, 476 (1954)].

(11) G. Kleinspehn and A. Corwin, *J. Am. Chem. Soc.*, **75**, 5295 (1953).

(12) H. Fischer and H. Orth, "Die Chemie des Pyrroles," Vol. 1, Akademische Verlagsgesellschaft, Leipzig, 1937.

(13) Initial condensations with a free aldehyde group in one of the dipyrrylmethanes always led to bilene-b's (in excellent yield when phosphorus oxychloride was the reagent), but subsequent macrocycle formation *via* the ketone could not be effected.

the recent refinements of the classical dipyrrylmethene condensation[14] were applied to the synthesis of I. The dipyrrylmethane IX hydrobromide and dicryptopyrrylmethene (X)[14b] hydrobromide were readily joined by the action of stannic chloride followed by methanolic hydrobromic acid. The biladiene-ac XI dihydrobromide [$\lambda_{max}^{CHCl_3}$ 363 nm (ϵ 13,500), 450 (31,000), 523 (157,000)], which resulted in 87% yield, gave <3% yield of DPEP (I) when treated with DMSO–pyridine for 3 days. Heating XI in *o*-dichlorobenzene produced only a trace of DPEP.

The electronic spectrum of our synthetic DPEP (I) is identical with that reported for the material obtained in the first synthesis[3] and by degradation from pheophytin.[5] In the nmr it shows absorption (in TFA) at δ 1.98 (t, 9 H), 3.81 (s, 12 H), 4.32 (q, 6 H), 4.50 (m, 2 H), 5.90 (m, 2 H), and 10.89 (s, 3 H), completely consistent with structure I. Further development of these methods and application to other porphyrin syntheses, particularly alkyl derivatives of DPEP, are being pursued.

(14) (a) R. L. N. Harris, A. W. Johnson, and S. F. Kay, *Chem. Commun.*, 232 (1965); (b) R. L. N. Harris, A. W. Johnson, and S. F. Kay, *J. Chem. Soc., C*, 22 (1966); (c) P. Bamfield, R. L. N. Harris, A. W. Johnson, S. F. Kay, and K. W. Shelton, *ibid.*, 1436 (1966).

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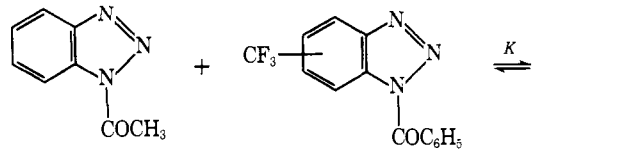
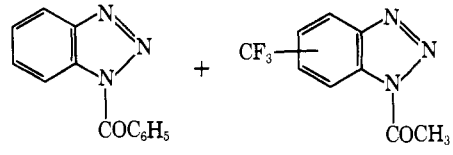
The Thermal Intermolecular Exchange between N-Acylbenzotriazoles

Sir:

We wish to report an example of a thermal intermolecular acyl exchange reaction between N-acylbenzotriazoles. The over-all reaction scheme involves the equilibration of the following N-acylbenzotriazoles.[1]

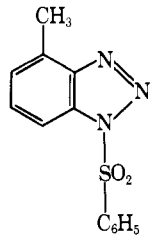


I II

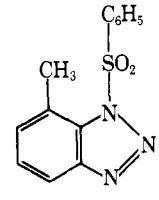


III IV

(1) A possibly related reaction is that of the thermal isomerization of N-benzenesulfonylbenzotriazoles i and ii. However, the question of intermolecular *vs.* intramolecular rearrangement was not investigated: G. T. Morgan and G. E. Schraff, *J. Chem. Soc.*, **105**, 117 (1914).

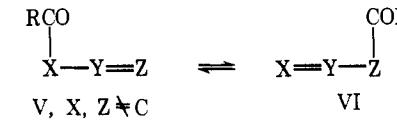


i



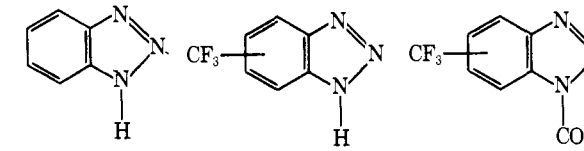
ii

The phenomenon of thermal *intramolecular* acyl migration in acyclic allyloid systems (V and VI) is well documented.[2] To our knowledge the demonstra-



tion of thermal *intermolecular* acyl exchange, on the other hand, has not been reported. The possibility, however, that certain cyclic systems such as sterically constrained isoimides may undergo rearrangement *via* mechanisms other than intramolecular acyl migration has been postulated.[2]

The N-acylbenzotriazoles used in this investigation were prepared by acylation of benzotriazole (VII) or 5- and 6-trifluoromethylbenzotriazoles (VIII) by previously reported methods.[3,4] The benzoylbenzotriazoles II and the acetylbenzotriazoles IV were prepared and in each case characterized as mixtures of the N-1 and N-3 substituted isomers.[5] No analytical problems



VII VIII II, R = C_6H_5
IV, R = CH_3

were encountered in working with II and IV as isomeric mixtures due to the elution of each isomer pair as a single peak by glpc.[6]

The equilibration of compounds I through IV was approached both by starting with I and II and by starting with III and IV. Equilibrations were carried out in refluxing *o*-xylene (bp 144°) under a N_2 atmosphere. In an experiment starting with only III and IV present initially, a sample of II was isolated (by glpc). Similarly, when starting with only I and II, a sample of III was isolated. The uv maxima and melting point values for the isolated samples of II and III were identical with those of standard samples of II and III.

The equilibration of compounds I through IV has also been studied using an nmr method of analysis. In a typical experiment, aliquots of a solution of III (0.180 *M*) and IV (0.180 *M*) in *o*-dichlorobenzene were sealed in nmr tubes and heated at 144° for a total of 12 hr. The acetyl proton singlet peaks for the two N-acetylbenzotriazoles I and IV are sufficiently separated (1.0 cycle using a Varian A-60 nmr spectrometer) at this given concentration in *o*-dichlorobenzene to permit integration of the two respective peaks. Attainment of an equilibrium *K* value of ~1 was reached after 7–8

(2) (a) Curtin and Miller have recently reviewed the subject of 1,3-acyl-migration reactions: D. Y. Curtin and L. L. Miller, *J. Am. Chem. Soc.*, **89**, 637 (1967); (b) E. Hedaya, R. L. Hinman, and S. Theodoropulos, *J. Org. Chem.*, **31**, 1317 (1966).

(3) N. G. Gaylord, *J. Am. Chem. Soc.*, **76**, 285 (1954).

(4) Benzotriazoles have been shown to be tautomeric in solution with respect to hydrogen attached to nitrogen: F. Benson and W. L. Sevell, *Chem. Rev.*, **46**, 1 (1950).

(5) (a) The acylation of substituted benzotriazoles has been shown to lead to a mixture of the isomeric 1- and 3-N-acylbenzotriazoles, but not to the 2-N-acylbenzotriazoles. See ref 4. (b) The isomeric nature of II and IV was supported by their ^{19}F nmr spectra.

(6) (a) All glpc analyses were carried out using a 5% SE-30 on Chromosorb W column. (b) Satisfactory microanalyses were obtained for all new compounds.