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 [$\lambda_{\max}^{\mathrm{CHCl_3}}$ 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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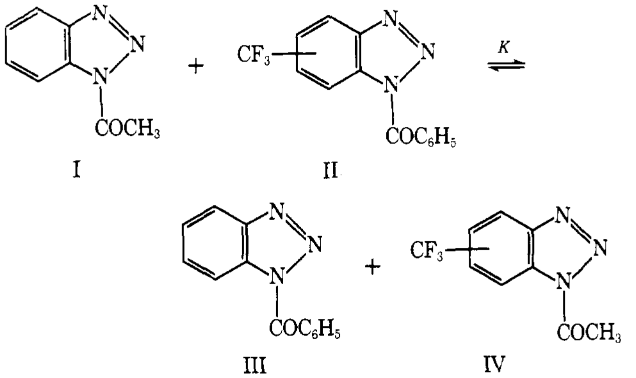
The Thermal Intermolecular Exchange between N-Acylbenzotriazoles

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]

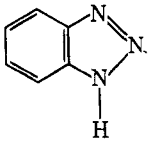


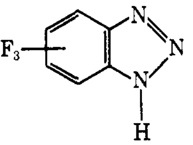
The phenomenon of thermal *intramolecular* acyl migration in acyclic allyloid systems (V and VI) is well documented.[2] To our knowledge the demonstration of thermal *intermolecular* acyl exchange, on the other hand, has not been reported. The possibility, however, that certain cyclic systems such as sterically constrained isoimides may undergo rearrangement *via* mechanisms other than intramolecular acyl migration has been postulated.[2]

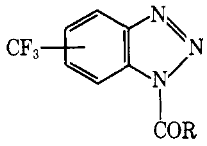
$$\overset{\mathrm{RCO}}{\mathrm{X}}\text{—Y=Z} \rightleftharpoons \mathrm{X{=}Y}\text{—}\overset{\mathrm{COR}}{\mathrm{Z}}$$

V, X, Z$\neq$C VI

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 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]


VII


VIII


II, R = C$_6$H$_5$
IV, R = CH$_3$

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

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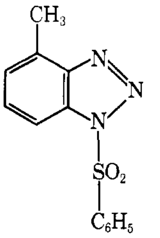
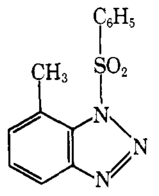
(1) A possibly related reaction is that of the thermal isomerization of N-benzenesulfonylbenzotriazoles i and ii. However, the question of intermolecular *vs.* intramolecular rearrangement was not investigated: G. T. Morgan and G. E. Schraff, *J. Chem. Soc.*, **105**, 117 (1914).


i


ii

(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).

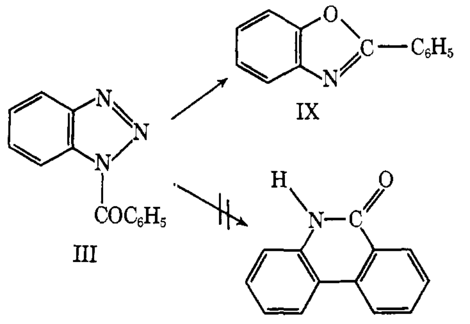
(4) Benzotriazoles have been shown to be tautomeric in solution with respect to hydrogen attached to nitrogen: F. Benson and W. L. Sevell, *Chem. Rev.*, **46**, 1 (1950).

(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.

hr. After 12 hr no decrease in the total concentrations of I and IV was detected by comparison of the nmr integral for an unheated sample of starting soluton of III and IV. Thus, no significant yield losses to side reactions has occurred. Finally, the possibility of catalysis of the *trans*-acylation reaction by trace acylating agent in III or IV was examined.[7] A portion of the *o*-dichlorobenzene solution containing III (0.180 *M*) and IV (0.180 *M*) was treated with benzoyl chloride (0.005 g/ml), sealed in an nmr tube, and heated and analyzed as described above. The rate of *trans* acylation was found to be measurably retarded rather than being enhanced. The same result was found using *o*-xylene as solvent, thus indicating that the *trans*-acylation reaction does not result from catalysis by trace acylating agent.

The possibility that the thermal decomposition of N-acylbenzotriazoles might be of some preparative value was briefly examined. It was anticipated that benzoxazole (IX) and/or phenanthridone (X) might be formed from decomposition of III.[8] The decomposition of III was carried out either with samples in the melt in sealed tubes (350–400°) or in diphenyl ether solution (250°). In a typical experiment (0.1 *M* in diphenyl ether), an 11% yield of benzoxazole (IX) was isolated after 6 hr by means of liquid chromatography using Florisil.[9] No phenanthridone was detected (<1% by glpc) in the reaction mixture. A number of minor products whose presence was indicated were not isolated.



III

IX

X

A more detailed investigation of the *trans*-acylation reaction discussed above is currently being made.

Acknowledgment. The assistance of Mr. R. S. Sudol and Mrs. J. H. Taylor in obtaining nmr spectra is appreciated.

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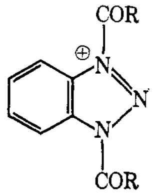
(7) A referee has suggested that trace acid chloride could cause *trans* acylation *via* an intermediate such as iii.



iii

(8) The thermal decomposition of N-phenylbenzotriazole provides a convenient synthesis of carbazole: C. D. Hurd, "Pyrolysis of Carbon Compounds," American Chemical Society Monograph Series, J. J. Little and Ives Co., New York, N. Y., 1929, p 639.

(9) (a) Identification of IX was made by comparison of spectroscopic data with those of authentic IX prepared by standard methods: F. F. Stephens and J. D. Bomer, *J. Chem. Soc.*, 2971 (1949). (b) The half-life for decomposition of III was approximately 2.5 hr at 250° in diphenyl ether.

Evidence for a Covalent Organolanthanide. Tris(indenyl)samarium–Tetrahydrofuran[1]

Sir:

The only organolanthanides reported previous to our current investigation have been those containing the cyclopentadienide group. All of the trivalent derivatives of the type $\mathrm{Ln(C_5H_5)_3}$[2] have been prepared with the exception of that of radioactive promethium. In addition, mixed derivatives of the types $\mathrm{LnCl(C_5H_5)_2}$[3] and $\mathrm{LnCl_2(C_5H_5)\cdot 3THF}$[4] have also been isolated for several of the lanthanides.

The divalent compounds $\mathrm{Eu(C_5H_5)_2}$ and $\mathrm{Yb(C_5H_5)_2}$[2c] have also been reported. For all of these compounds an "ionic" bonding mode of the $\mathrm{C_5H_5}$ group to the rare earth metal has been postulated on the basis of their chemical reactivity and their magnetic moments which are essentially those of the corresponding "free" ion.[5] However, recent electronic spectral studies have provided evidence for some f orbital interaction in the cases of $\mathrm{Yb(C_5H_5)_3}$[6] and $\mathrm{Tm(C_5H_5)_3}$.[7] This observation is of great theoretical significance in view of the generally held theory that the 4f orbitals are effectively shielded from interaction with external forces by the outer $5s^25p^6$ orbitals and that the bonding of the lanthanides is essentially ionic.[8]

Here we wish to report the preparation of the indenyl (In) derivatives of the trivalent rare earths and in particular evidence for a covalent bonding mode in the samarium compound, $\mathrm{SmIn_3\cdot THF}$.

The reaction of 1 equiv of $\mathrm{SmCl_3}$ and 3 equiv of NaIn in THF media at room temperature under inert conditions resulted in the formation of a wine red solution. Removal of the NaCl formed by centrifugation and subsequent concentration of the red solution led to the isolation of an orange-red solid which was purified by recrystallization from tetrahydrofuran. This air- and moisture-sensitive compound, mp 185–200° (turned to black at 165–170°), has been formulated as $\mathrm{Sm(C_9H_7)_3\cdot}$

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(1) Supported by the Petroleum Research Fund, administered by the American Chemical Society.

(2) (a) J. M. Birmingham and G. Wilkinson, *J. Amer. Chem. Soc.*, **78**, 42 (1956); (b) S. Manastyrskyj and M. Dubeck, *Inorg. Chem.*, **3**, 1647 (1964); (c) E. O. Fischer and H. Fischer, *J. Organometal. Chem.*, **3**, 181, (1965); (d) A. F. Reid and P. C. Wailes, *Inorg. Chem.*, **5**, 1213 (1966); (e) M. Tsutsui, T. Takino, and D. Lorentz, *Z. Naturforsch.*, *B*, **21**, 1 (1966).

(3) R. E. Maginn, S. Manastyrskyj, and M. Dubeck, *J. Amer. Chem. Soc.*, **85**, 672 (1963).

(4) S. Manastyrskyj, R. E. Maginn, and M. Dubeck, *Inorg. Chem.*, **2**, 904 (1963).

(5) T. Moeller, "The Chemistry of the Lanthanides," Reinhold Publishing Corp., New York, N. Y., 1963, p 27.

(6) R. D. Fischer and H. Fischer, *J. Organometal. Chem.*, **4**, 412 (1965).

(7) R. D. Fischer and H. Fischer, *ibid.*, **8**, 155 (1967).

(8) (a) T. Moeller, D. F. Martin, L. C. Thompson, R. Ferrus, G. R. Feistel, and W. J. Randall, *Chem. Rev.*, **65**, 1 (1965); (b) J. L. Burmeister, S. D. Patterson, and H. J. Gysling, Proceedings of the 10th International Conference on Coordination Chemistry, Tokyo, Japan, Sept 1967 p 356.