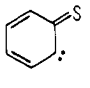
(11) In this case, the intermediate may be the thio-keto carbene **20** rather than the diradical **11**. In our case, thio-keto carbene intermediate can be a priori ruled out because of structural demands.


20

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Addition of Complexed Amino Radicals to Conjugated Alkenes[1]

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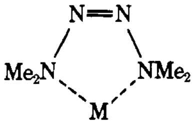
Abstract: Dimethylamino radicals, complexed by zinc chloride, added to styrene, α- and β-methylstyrenes, and indene to give the corresponding bis(dimethylamino) adducts in fair to good yields. The radicals were generated by the thermal (60 °C) decomposition of the tetramethyl-2-tetrazene:zinc chloride complex. The addition of the two dimethylamino groups is shown to be a stepwise process, rather than concerted, as suggested previously by us. The relative rates of addition of the zinc chloride complexed amino radicals to substituted α-methylstyrenes were well correlated by the Hammett equation with a ρ value of -0.98 ± 0.04. In contrast, the ρ value for the addition of uncomplexed radicals was found to be $+0.69 \pm 0.03$. The addition of dimethylamino radicals coordinated by $ZnBr_2$, $HgCl_2$, and $CdCl_2$ to α-methylstyrene was also observed, but no addition was obtained with $ZnSO_4$, $Zn(OAc)_2$, $Zn(C_6H_5)_2$, or $Zn(C_6F_5)_2$.

Tetramethyl-2-tetrazene (TMT) forms 1:1 complexes with a variety of Lewis acids, such as zinc halides, zinc alkyls and aryls,[3] mercuric, aluminum, and cadmium halides,[4] and aluminum alkyls.[5] The structure of these complexes was assumed to be the cis structure **1**. This structure was shown to be incorrect by the single crystal X-ray structure determination of bis(perfluorophenyl)tetramethyltetrazenezinc(II), **2**.[6]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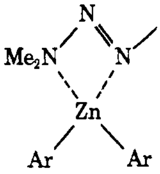
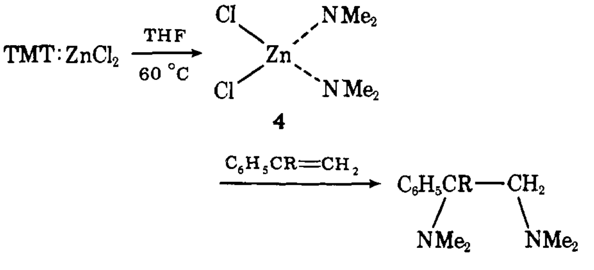

2, Ar = C_6F_5

The TMT:$ZnCl_2$ complex was shown to lose nitrogen at low temperatures.[3] We showed that, when this complex was decomposed in the presence of styrene or α-methylstyrene, 30-40% yields of the diamino adducts, **3**, were obtained.[7] This initial study was carried out before the correct structure of the complex was known. As a consequence of this, we assumed that the complex decomposed to the biradical intermediate, **4**, which was then captured by the olefin.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(1)

3, R = H, Me

The purpose of this paper is to show that this initial assumption was incorrect, to suggest a more correct mechanism for the addition, and to discuss the reactivity of the zinc chloride complexed amino radical and to contrast it with the reactivity of the neutral, uncomplexed radical.

Experimental Section

All melting and boiling points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 237 spectrophotometer; NMR spectra were recorded on Varian A60D and XL100 instruments (chemical shifts reported in this paper are in ppm at 60 MHz); the mass spectra were obtained on a Perkin-Elmer Hitachi RMU-6D spectrometer. GLPC was carried out on a Varian Aerograph 1520 instrument, equipped with both thermal conductivity and flame ionization detectors and a Disc integrator. HPLC analyses were carried out on a Waters ALC-201 instrument using a 13 ft × 0.25 in. i.d. column packed with Porasil A. Benzene, containing 5% methanol, was the eluting solvent with a flow rate of 3 mL per min. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill.

Materials. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ under a nitrogen atmosphere. It was then stored over 4-Å molecular sieves under a nitrogen atmosphere.

Anhydrous zinc chloride was prepared from the hydrate by fusion in a crucible until water evolution ceased. This material was then cooled in a dry nitrogen atmosphere, broken up into a powder, and stored as a saturated solution in dry THF under nitrogen in a glove box. Anhydrous zinc bromide was prepared in an analogous manner.

Cadmium chloride was dried over P_2O_5 in a vacuum desiccator for 1 week. Reagent grade mercuric chloride was used without treatment.

Bis(perfluorophenyl)tetramethyltetrazenezinc(II) was prepared by the method of Noltes and van den Hurk.[3] The Grignard reagent, prepared from pentafluorobromobenzene, was treated with anhydrous $ZnCl_2$ to give bis(pentafluorophenyl)zinc, which, when treated with TMT, gave almost quantitative yields of the complex. The compound crystallized from pentane is well defined: white needles, mp 144-146 °C (lit.[3] 136-137 °C); NMR spectrum (benzene-d_6) 2.41 ppm (s). Anal. Calcd for $C_{16}H_{12}F_{10}N_4Zn$: C, 37.27; H, 2.35; N, 10.87. Found: C, 36.94; H, 2.34; N, 10.81.

Diphenyl(tetramethyltetrazene)zinc(II) was prepared in the same manner as the fluorinated analogue. This material, although formed in high yield from diphenylzinc and TMT, was more difficult to purify, mp 70-77 °C (lit.[3] 73-75 °C).

Dichloro(tetramethyltetrazene)zinc(II) was best prepared by adding TMT to a saturated solution of anhydrous zinc chloride in ether. Crystals of this complex formed immediately. These could be dried under nitrogen, but always retained a trace of ether. This ether could be removed by repeated washing with dry pentane. The crystals

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were stored under nitrogen and appeared to be stable at room temperature, in contrast to the reported behavior.[3]

Dibromo(tetramethyltetrazene)zinc(II) was prepared by adding TMT to a dry ethereal solution of anhydrous zinc bromide. The crystals precipitated from solution and were washed repeatedly with dry pentane to remove traces of ether.

Tetramethyl-2-tetrazene (TMT) was prepared by modification of the method of McBride and Kruse.[8] A 1-L three-necked flask, fitted with a mechanical stirrer and two dropping funnels, was charged with 40 g (0.67 mol) of 1,1-dimethylhydrazine. The flask was cooled to −10 °C with an ice-salt bath. The dropping funnels were filled with 127 g (1 mol) of iodine in 250 mL of saturated KI solution and the other with 45 g (1.12 mol) of sodium hydroxide in 250 mL of water. These materials were added dropwise to the well-stirred hydrazine over a period of 1-1.5 h. The aqueous reaction mixture was then extracted with ether by using a circulating ether extractor for 2 days. The ether extract was dried ($MgSO_4$), and the ether was removed in vacuo. The residue was distilled twice from KOH pellets under aspirator pressure: yield, 10-15 g of TMT (30-50% yield, based on iodine), bp 40-42 °C (20 mm) (lit.[9] 44 °C (30 mm)). The procedure of Watson,[9] utilizing the yellow mercuric oxide oxidation of 1,1-dimethylhydrazine, was also used, but the advantages of the procedure above are the somewhat cheaper reagents and safer reaction conditions.

Tetramethyl-2-tetrazene-d_{12} (TMT-d_{12}) was made by the mercuric oxide oxidation[9] of 1,1-dimethylhydrazine-d_6. The latter was obtained from the reduction of dimethylnitrosamine-d_6, prepared by the method of Keefer and Fodor.[10] To 6.2 g (0.084 mol) of dimethylnitrosamine (DMN) contained in a 100-mL round-bottomed flask was added 10 g of D_2O which was approximately 0.5 N in NaOD. The solution was heated at a mild reflux for 1 h and was then extracted with ether. The extracts were dried ($MgSO_4$) and the ether was removed in vacuo. The partially deuterated DMN was again treated with the NaOD/D_2O solution and the cycle was repeated. Four cycles of deuteration were carried out in this manner. The final DMN showed 48.1% d_6, 36.7% d_5, 11.3% d_4, and 1.8% d_3, by mass spectral analysis. The crude, deuterated DMN was reduced with $LiAlH_4$. The nitrosamine was dissolved in 20 mL of dry ether and this solution was added dropwise, over 1 hr, to a stirred solution of 5 g of $LiAlH_4$ in 150 mL of ether. The excess $LiAlH_4$ was destroyed with water, followed by 6 N NaOH. The solution was separated and the aqueous layer was extracted with 50 × 3 mL of ether. The combined ether extracts were then treated with solid mercuric oxide, added a little at a time over a 15-min period. The addition was stopped when no further reaction was observed. The solution was filtered and the ether was removed in vacuo. The crude tetrazene (2 g) was purified by GLPC, by using a Polysorb-J-treated Carbowax 20 M column (10 ft) operated at 75 °C. The final tetrazene showed 24.2% d_{12}, 35.7% d_{11}, 24.4% d_{10}, 10.1% d_9, and 2.5% d_8, by mass spectrometric analysis.

***cis*-β-Methylstyrene** was prepared by low-pressure hydrogenation of 1-phenyl-1-propyne over Raney nickel catalyst, by using the procedure of Campbell and O'Connor.[11] The reduction of 25 g (0.22 mol) of propyne yielded, after fractional distillation, 10.8 g (0.092 mol) of *cis*-β-methylstyrene, bp 163-165 °C (1 atm) [lit.[11] 166.7 °C (746 mm)]. The 60-MHz NMR ($CDCl_3$) showed 1.73 (doublet of doublets, 3 H, CH_3 group), 5.65 (doublet of quartets, 1 H, olefinic CH), 6.35 (multiplet, 1 H, olefinic C-H), 7.18 ppm (5 H, aromatic protons).

Substituted α-Methylstyrenes. Most were prepared from the corresponding acetophenones by using a variation of the method of Seymour and Wolfstirn.[12] A 500-mL three-necked flask was fitted with a mechanical stirrer, dropping funnel, and a reflux condenser. A nitrogen atmosphere was maintained throughout the reaction. Methylmagnesium bromide (ca. 0.25 mol) in 100 mL of ether was added to the flask. To this was added 0.2 mol of the acetophenone in 200 mL of ether during 30 min. The resulting mixture was heated at reflux for 10-14 h, with continuous stirring. The reaction mixture was then treated with about 5 g of ammonium chloride, followed by slow addition of ice-water. After the separation and drying of the ether layer, the crude carbinol was obtained by the removal of the ether in vacuo. This material was treated with *p*-toluenesulfonic acid and was distilled at aspirator pressure. The distillate consisted of the corresponding α-methylstyrene.

***p*-Cyano-α-methylstyrene** was obtained in 12.9 g (44.5%) yield from *p*-cyanoacetophenone. Distillation of the styrene, bp 131-136 °C (20 mm), resulted in a product contaminated by the acetophenone. The material used in the subsequent experiments was purified by LC (high pressure liquid chromatography). NMR spectrum ($CDCl_3$): 2.18 (m, 3 H, α-CH_3), 5.18 (m, 1H, olefinic CH), 5.43 (m, 1H, olefinic CH), 7.65 (s, 4H, aromatic).

***p*-Methoxy-α-methylstyrene** was made in 62% yield from 34.2 g (0.23 mol) of *p*-methoxyacetophenone. The initially formed material was purified by LC and then recrystallized from pentane, mp 33-34 °C (lit.[12] 34 °C). NMR spectrum ($CDCl_3$): 2.09 (m, 3 H, α-CH_3), 3.66, (s, 3 H, methoxyl), 4.96 (m, 1 H, olefinic CH), 5.30 (m, 1 H, olefinic CH), 7.08 (A_2B_2, 4 H, aromatic).

***p*-Bromo-α-methylstyrene** was made in 77% yield from *p*-bromoacetophenone. The styrene was collected at 140-142 °C (20 mm) [lit.[13] 102 °C (11 mm)]. The distillate was purified by LC. NMR spectrum ($CDCl_3$): 2.06 (m, 3 H, α-CH_3), 5.05 (m, 1 H, olefinic CH), 5.33 (m, 1 H, olefinic CH), 7.33 (A_2B_2, 4 H, aromatic).

***p*-Fluoro-α-methylstyrene** was prepared in 69% yield from *p*-fluoroacetophenone. The product was distilled at atmospheric pressure, bp 182-183 °C [lit.[12] 98-101 °C (45 mm)]. NMR spectrum ($CDCl_3$): 2.08 (m, 3 H, α-CH_3), 5.03 (m, 1 H, olefinic CH), 5.28 (m, 1 H, olefinic CH), 7.19 (m, 4 H, aromatic).

***p*-α-Dimethylstyrene** was made from *p*-methylacetophenone in 71% yield. The material had bp 82-83 °C (20 mm) [lit.[13] 69 °C (10 mm)] and was pure by GLPC and NMR standards. NMR spectrum ($CDCl_3$): 2.05 (m, 3 H, α-CH_3), 2.25 (s, 3 H, *p*-CH_3), 5.00 (m, 1 H, olefinic CH), 5.33 (m, 1 H, olefinic CH), 7.15 (A_2B_2, 4 H, aromatic).

***p*-Chlorostyrene** was prepared by the Wittig reaction.[14] A 500-mL three-necked flask was filled with a mechanical stirrer, a reflux condenser, and a nitrogen inlet. The flask was flushed with nitrogen throughout the course of the reaction. The flask was charged with 45 mL of a 15% solution of *n*-butyllithium in ether (0.11 mol) and 200 mL of additional ether. Triphenylmethylphosphonium bromide (35.7 g, 0.1 mol) was added to the flask slowly over a 10-min period. Stirring was contined for 3 h, whereupon 15.5 g (0.11 mol) of *p*-chlorobenzaldehyde in 100 mL of ether was added dropwise. The solution was heated at reflux overnight. The ether solution was then washed three times with 100-mL portions of water and dried over anhydrous calcium chloride, and the ether was removed in vacuo. The product distilled at 75-77 °C (20 mm). NMR spectrum ($CDCl_3$): 5.06 (doublet of doublets, 1 H, olefinic CH), 5.48 (doublet of doublets, 1 H, olefinic CH), 6.47 (doublet of doublets, 1 H, olefinic CH), 7.08 (s, 4 H, aromatic).

Preparation of 1,2-Bis(dimethylamino)alkanes. In most cases, solutions of TMT in the neat alkene (0.1 to 0.5 M) were mixed with equal volumes of zinc chloride saturated THF. These solutions were placed in Pyrex tubes equipped with 10/30 inner joints for attachment to a vacuum line. The air was removed by three freeze-pump-thaw cycles and the tubes were sealed. A precipitate formed in the solutions initially but redissolved with shaking. The tubes were then immersed in an oil bath heated to 70-120 °C for a period of time. Usually the solutions became cloudy within 5-15 min as a precipitate started to form. This precipitate settled out of the reaction mixture after 30-60 min. The solutions were pale yellow to bright red, depending on the olefin used. The reactions were worked up by breaking the seals and mixing the contents with 50 mL of 6 N HCl to destroy the complex and to dissolve the amines in the aqueous layer. The acid aqueous solution was extracted twice with ether to remove the excess olefin. The water layer was then made basic with 100 mL of 6 N NaOH and extracted several times with ether. The combined ether extracts were dried over magnesium sulfate and the ether was removed under reduced pressure. The residue was subjected to GLPC analysis. In preparative runs, the diamine could be purified by precipitation from an ethereal solution of zinc chloride. The precipitate was washed with cold methanol. The pure diamine was then isolated from the zinc chloride complex by treatment with aqueous base and extraction with ether.

1,2-Bis(dimethylamino)-1-phenylethane was made from 0.46 g (4 mmol) TMT and 3.0 g (20 mmol) of styrene. The product formed in 23.2% yield. NMR spectrum ($CDCl_3$): 2.18 (s, 6 H, N-CH_3), 2.23 (s, 6 H, NCH_3), 2.70 (octet, 2 H, CH_2), 3.55 (t, 1 H, CH), 7.28 (m, 5 H, aromatic). Anal. Calcd for $C_{12}H_{20}N_2$: C, 74.95; H, 10.48; N, 14.57. Found: C, 74.68; H, 10.28; N, 14.72.

***trans*-1,2-Bis(dimethylamino)indane** was made from 0.70 g (6 mmol) of TMT and 2.25 g (19.4 mmol) of indene. The crude amine (0.16 g, 13% yield) could not be precipitated by zinc chloride and was purified by GLPC. This compound was made independently by the method of Wyss and Schindler.[15] A solution of 6.96 g (0.094 mol) of dimethylnitrosamine, 50.97 g (0.44 mol) of freshly distilled indene,

Table I. Para-Substituted 1,2-Bis(dimethylamino)-2-phenylpropanes

para substituent	yield %	NMR spectrum ($CDCl_3$), ppm	empirical formula		anal., % C	H	N
H	28.4	1.36 (s, 3 H, CH_3), 1.92 (s, 6 H, NCH_3) 2.17 (s, 6 H, N-CH_3), 2.58 (s, 2 H, CH_2) 7.38 (m, 5 H, arom)	$C_{13}H_{22}N_2$	C[a] F[b]	75.68 75.52	10.75 10.71	13.58 13.91
CH_3	31	1.21 (s, 3 H, CH_3), 1.81 (s, 6 H, N-CH_3) 2.05 (s, 6 H, N-CH_3), 2.19 (s, 3 H, p-CH_3) 2.43 (s, 2 H, CH_2), 7.15 (A_2B_2, 4 H, arom)	$C_{14}H_{24}N_2$	C F	76.31 76.32	10.98 11.25	12.71 12.46
F	31.2	1.32 (s, 3 H, CH_3), 1.92 (s, 6 H, N-CH_3) 2.16 (s, 6 H, N-CH_3), 2.53 (s, 2 H, CH_2) 7.26 (m, 4 H, arom)	$C_{13}H_{21}N_2F$	C F	69.61 69.94	9,44 9.84	12.59 12.52
CN	17.5	1.24 (s, 3 H, CH_3), 1.80 (s, 6 H, N-CH_3) 2.06 (s, 6 H, N-CH_3), 2.43 (s, 2 H, CH_2) 7.55 (s, 4 H, arom)	$C_{14}H_{21}N_3$	C F	72.68 73.01	9.15 9.14	18.16 18.13
OCH_3	33.4	1.31 (s, 3 H, CH_3), 1.92 (s, 6 H, N-CH_3) 2.15 (s, 6 H, N-CH_3), 2.52 (s, 2 H, CH_2) 3.73 (s, 3 H, OCH_3), 7.12 (A_2B_2, 4 H, arom)	$C_{14}H_{24}N_2O$	C F	71.14 71.22	10.23 10.46	11.85 11.76
Cl	26.2	1.32 (s, 3 H, CH_3), 1.43 (s, 6 H, N-CH_3) 2.16 (s, 6 H, N-CH_3), 2.53 (s, 2 H, CH_2) 7.39 (A_2B_2, 4 H, arom)	$C_{13}H_{21}N_2Cl$	C F	64.85 64.86	8.79 8.72	11.63 11.24
Br	31.3	1.30 (s, 3 H, CH_3), 1.93 (s, 6 H, N-CH_3) 2.15 (s, 6 H, N-CH_3), 2.52 (s, 2 H, CH_2) 7.43 (s, 4 H, arom)	$C_{13}H_{21}N_2Br$	C F	54.74 54.88	7.42 7.66	9.82 9.75

[a] Calculated. [b] Found.

and 9 mL of concentrated hydrochloric acid in 460 mL of methanol was irradiated for 7 h under a nitrogen atmosphere by using a 450-W, medium-pressure, mercury arc in a water-cooled, immersion well. The solvent was then removed in vacuo and the residue was treated with 100 mL of 2 N HCl and extracted with ether. The aqueous layer was made basic with ammonium hydroxide and again extracted with ether. The ether solution was dried and the solvent removed in vacuo. The crude aminooxime was recrystallized from hexane (yield 2.3 g, 13% yield). This was dissolved in ether (250 mL) and was added dropwise to a solution of 1.5 g (0.156 mol) of $LiAlH_4$ in 100 mL of ether. The reaction was heated at reflux overnight, the excess $LiAlH_4$ was destroyed by careful addition of water, and the aqueous layer was extracted with ether. The combined extracts were dried and concentrated. The concentrate was treated with an excess of formaldehyde and formic acid for 2 h at reflux. Extraction of this reaction mixture led to the product which was a mixture of the monomethylated (minor) and the dimethylated product. These were separated by GLPC. The dimethylated material was in every way identical with the compound prepared above. NMR spectrum ($CDCl_3$): 2.24 (s, 6 H, NCH_3), 2.32 (s, 6 H, NCH_3), 2.91 (d, 2 H, CH_3), 3.40 (m, 1 H, CH), 4.20 (d, 1 H, CH), 7.22 (m, 4 H, aromatic). Anal. Calcd for $C_{13}H_{20}N_2$: C, 76.42; H, 9.87; N, 13.71. Found: C, 76.22; H, 9.92; N, 13.55.

1,2-Bis(dimethylamino)-1-phenylpropanes were prepared from *cis*- and *trans*-β-methylstyrenes. *trans*-β-Methylstyrene (7.64 g, 64.75 mmol) and TMT (1.39 g, 11.0 mmol) were reacted together in presence of zinc chloride as described above. The reaction was heated at 90 °C for 2 h. The crude, nonvolatile amines (0.45 g) consisted almost exclusively of *erythro*- and *threo*-diamine adducts, in the ratio of 3:1, respectively. The neutral extracts contained only *trans*-β-methylstyrene—no cis isomer was found. *cis*-β-Methylstyrene (7.76 g, 65.76 mmol) and TMT (1.35 g, 11.6 mmol) were reacted under identical conditions as the trans isomer. The crude, nonvolatile amine extract (0.45 g) consisted of exactly the same distribution of product as in the trans case. The recovered *cis*-β-methylstyrene showed no trace of the trans isomer.

Attempts to separate the erythro and threo isomers by GLPC were only partially successful. The erythro isomer was isolated in the pure form, but the threo was always contaminated by traces of the erythro. The two were finally separated by LC. The *erythro*-1,2-bis(dimethylamino)-1-phenylpropane, mp 51-52 °C, had the NMR spectrum ($CDCl_3$): 1.10 (d, 3 H, CH_3), 2.07 (s, 6 H, NCH_3's), 2.10 (s, 6 H, NCH_3's), 3.28 (m, 2 H, CH's), 7.26 (m, 5 H, aromatic). Anal. Calcd for $C_{13}H_{22}N_2$: C, 75.68; H, 10.75; N, 13.58. Found: C, 75.58; H, 10.76; N, 13.36.

***threo*-1,2-Bis(dimethylamino)-1-phenylpropane,** mp 43-44 °C, had the NMR spectrum ($CDCl_3$): 0.63 (d, 3 H, CH_3), 2.14 (s, 6 H, N-CH_3's), 2.33 (s, 6 H, N-CH_3's), 3.30 (m, 2 H, CH's), 7.29 (m, 5 H, aromatic). Anal. Calcd for $C_{13}H_{22}N_2$: C, 75.68; H, 10.75; N, 13.58. Found: C, 75.92; H, 10.96; N, 13.54. The mass spectra of the two isomers were very similar, and completely consistent with the structures.

Preparation of Para-Substituted 1,2-Bis(dimethylamino)-2-phenylpropanes. These compounds were prepared according to the general procedure described above. The various pertinent characteristics are listed in Table I.

Relative Rate of Reaction of Para-Substituted α-Methylstyrenes with TMT:$ZnCl_2$. Solutions were prepared in THF which were 0.08 M in TMT and 2 M in each of two styrenes. A volume (2-3 mL) of these solutions were placed into a Pyrex tube equipped with a 10/30 inner joint for attachment to a vacuum line. To these solutions were mixed equal volumes of saturated $ZnCl_2$ in THF solutions. The tubes were degassed by three freeze-pump-thaw cycles and were sealed under vacuum. The tubes were then heated at 85 °C for 2 h and worked up in the usual way to give the crude amine products. A small amount of biphenyl was weighed into the crude product. The mixture was dissolved in ether. This ether solution was analyzed by GLPC using a 20 ft × 0.25 in. glass column packed with 5% Carbowax and 0.5% Polysorb J on acid-washed Chromosorb W at an oven temperature of 175 °C. The areas corresponding to the two diamino products and the biphenyl were determined by a Disc Integrator, each sample being injected two to four times. The sensitivity factor for each product was determined against biphenyl by measuring at least three different known concentrations of the product vs. the standard. The sensitivity factor, Z, was evaluated by the equation

$$i_s/i_u = ZM_s/M_u$$

where i_s is the integrated value for the standard biphenyl, i_u is the value for the diamino product, and M_s and M_u are the known molarities of the diamine and the biphenyl, respectively. The relative rates of addition to substituted styrenes were calculated from the equation[13]

$$k/k_\alpha = (A^*/B^*)(Y/X)$$

where the Y and X are the concentrations of diamino products from the substituted styrene and α-methylstyrene, respectively, and A^* and B^* are the concentrations of the unreacted α-methylstyrene and the substituted styrene ($A^* = A_0 - X$ and $B^* = B_0 - Y$, where A_0 and B_0 are the initial concentrations). Sometimes, when either the relative rates were too disparate, or when difficulties were encountered in

Table II. Yields of 1,2-Bis(dimethylamino) Adducts

olefin	% yield[a]	log (k/k_O)[b]	σ
styrene	23		
indene	15[c]		
stilbene	5[c]		
acenaphthene	10[c]		
trans-β-methylstyrene	20[d]		
cis-β-methylstyrene	20[d]		
α-methylstyrene	28	0.0	0.0
p-methoxy-α-methylstyrene	33	0.376 ± 0.030	−0.268
p-methyl-α-methylstyrene	31	0.256 ± 0.020	−0.170
p-fluoro-α-methylstyrene	31	0.009 ± 0.002	0.062
p-chloro-α-methylstyrene	26	-0.210 ± 0.017	0.232
p-bromo-α-methylstyrene	31	-0.175 ± 0.014	0.227
p-cyano-α-methylstyrene	18	-0.540 ± 0.043	0.660
p-nitro-α-methylstyrene	15		

[a] Based on stoichiometry: TMT + C=C → $Me_2N—C—C—NMe_2$. [b] Relative rates obtained from competition experiments as described in the text. Errors evaluated from integration errors and duplicate runs. [c] Estimated, usually by direct isolation. [d] Mixture of erythro and threo isomers.

chromatographic separations, a secondary standard was used instead of α-methylstyrene. The relative rates were then evaluated by the equation

$$k/k_\alpha = (k/k_O)(k_O/k_\alpha)$$

where k_O/k_α was the rate ratio of the secondary standard substituted styrene and α-methylstyrene and k/k_O was the ratio of rates of the unknown substituted styrene and the secondary standard. The styrenes used for the competition runs were, α-methylstyrene, *p*,α-dimethylstyrene, *p*-bromo-α-methylstyrene, *p*-chloro-α-methylstyrene, *p*-fluoro-α-methylstyrene, *p*-methoxy-α-methylstyrene, and *p*-cyano-α-methylstyrene.

Relative Rates of Addition of Neutral Dimethylamino Radicals to Styrenes. Photolysis of TMT in presence of substituted α-methylstyrenes was carried out by using a Hanovia 450-W, medium-pressure, mercury lamp. The lamp was inserted in a water-cooled quartz well. The Pyrex tubes containing the photolysis solutions were attached directly to the well and the whole assembly was immersed in a large water bath cooled by tap water running through a copper coil. The temperature of the photolysis was approximately 25 °C. The photolysis solutions were 0.14 M in TMT and 2 M in each of two styrenes in cyclohexane. The solutions (4 mL) were placed in Pyrex tubes and were degassed and sealed as described above. Photolysis was carried out for 12 h. After the usual extraction of the basic product, the relative yields of the addition products were obtained by GLPC, as described above. The relative rates were obtained from the yields of the 1,2-bis(dimethylamino)-2-arylpropanes, as described above. The styrenes used in this experiment were, α-methylstyrene, *p*,α-dimethylstyrene, *p*-chloro-α-methylstyrene, *p*-fluoro-α-methylstyrene, *p*-methoxy-α-methylstyrene, and *p*-cyano-α-methylstyrene. *p*-Bromo-α-methylstyrene was also used, but apparently either the product or the parent styrene was not stable under the photolysis conditions and erratic values were obtained.

Catalysis of TMT Addition to α-Methylstyrene by Metal Salts Other than $ZnCl_2$. Mixtures of TMT, α-methylstyrene, and the metal salt, all in THF were treated under the same conditions as the $ZnCl_2$ reactions. Thus dry $ZnBr_2$ behaved in the same manner as $ZnCl_2$, 25% of the bis(dimethylamino) adduct was isolated. The mixing of a saturated solution of $HgCl_2$ in ether with TMT caused the precipitation of the complex,[3] which, when mixed with an excess of α-methylstyrene in benzene at reflux for 1 h, gave after the usual workup about a 6% yield of the adduct. The reaction of TMT, a slight excess of $CdCl_2$, and a large excess of α-methylstyrene in THF at 75 °C for 23 h gave, after workup, only a trace of the adduct. Attempts to catalyze the reaction of TMT with α-methylstyrene by $ZnSO_4$ were frustrated by the insolubility of the salt in all of the solvents tried (THF, acetone, acetonitrile). Diphenyl(tetramethyltetrazene)zinc(II) and bis(perfluorophenyl)tetramethyltetrazenezinc(II) did not catalyze the breakdown of TMT, even at elevated temperatures (142 °C for 1 h), and no adducts were obtained.

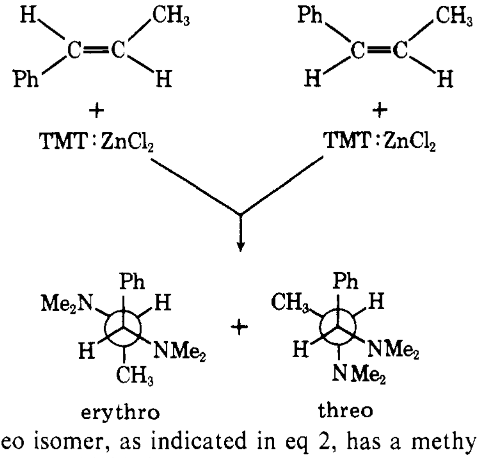
Reaction of *N*,*N*′-azobishomopiperidine with α-methylstyrene catalyzed by $ZnCl_2$ was carried out by heating at reflux for 2 h 10 mL of saturated $ZnCl_2$ in THF together with 6.93 g (58.73 mmol) of α-methylstyrene and 1.60 g (8.16 mmol) of *N*,*N*′-azobishomopiperidine. After the usual workup, GLPC analysis indicated a small amount of the hydrazine, dihomopiperidine, and about a 10% yield of the monoadduct, 3-(1-homopiperidino)-2-phenylpropene.

Results and Discussion

Decomposition of the tetramethyl-2-tetrazene (TMT): zinc chloride complex at 40 °C leads to the loss of nitrogen and the formation of a solid material whose empirical formula is $C_4H_{12}N_2ZnCl_2$.[3] When TMT is mixed with an excess of zinc chloride and an excess of a conjugated alkene in absence of oxygen, addition of two dimethylamino radicals to the double bond occurs. Table II lists the alkenes used and the yields of the adduct obtained. The yields in the table are averaged over several runs, in most cases.

In our earlier report on this addition reaction, we suggested that it proceeded via the biradical intermediate as indicated in eq 1. The data presented herein will show that this mechanism is incorrect and will suggest that the mechanism of the reaction involves stepwise addition of amino radicals to the double bond.

We have already shown that the structure of the TMT: $ZnCl_2$ complex is most likely related to **2** rather than **1**. In view of this, it is difficult to reconcile the formation of the biradical **4** from its precursor. The primary evidence for the stepwise addition rests on the following two experiments. Reaction of the TMT: $ZnCl_2$ complex with both *cis*- and *trans*-β-methylstyrene resulted in the formation, in 20% yield, of the *same* mixture of erythro and threo adducts (approximately a 50:50 mixture). The identifications of the two isomers were made from the NMR spectra.[16]



(2)

The threo isomer, as indicated in eq 2, has a methyl group which is more shielded by the phenyl than the erythro isomer.

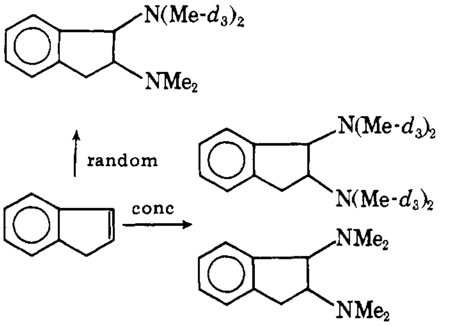
Table III. Distribution of Deuterium Label Assuming Randomization

mass[a]	starting material[b]	product exp[b]	product theory[c]
M	54.5	27.4	28.7
M + 1	3.3	4.8	4.4
M + 2		0.6	0.3
M + 3		1.4	0.8
M + 4		5.0	5.0
M + 5		16.5	16.4
M + 6		22.1	22.8
M + 7		3.4	3.3
M + 8	1.1	0.8	0.6
M + 9	4.3	1.7	1.7
M + 10	10.4	4.4	4.1
M + 11	15.3	6.4	6.2
M + 12	10.3	4.7	4.5
M + 13	0.6	0.7	0.7

[a] M = 116 for starting material and 204 for product. [b] Percent of total parent ion from mass spectral peak heights. [c] Calculated from the statistical analysis (see Appendix).

As a consequence of this, the doublet corresponding to the methyl of the threo isomer appears at 0.63 ppm, while the doublet corresponding to the methyl of the erythro isomer appears at 1.10 ppm. Isolation of the unreacted *cis*- and *trans*-β-methylstyrenes from the reaction mixtures indicated that no isomerization of the double bonds had occurred during the reaction. These data indicate that both the cis and the trans olefins react through a common intermediate, which precludes a concerted reaction such as eq 1.

Reaction of the TMT:$ZnCl_2$ complex with indene produces a 15% yield of the adduct, which is exclusively the *trans*-1,2-bis(dimethylaminoindane). The structure of this substance was confirmed by two independent syntheses (see Experimental Section). The NMR spectrum is also consistent with the trans compound[17] as is the fact that this substance does not precipitate from the reaction mixture as a complex with $ZnCl_2$, in contrast to other diamino adducts where a cisoid conformation of the amine groups is possible. The indene adduct shows a strong parent ion in its mass spectrum, again in contrast to the acyclic adducts. This allowed the following experiment to be carried out. A mixture of deuterated TMT (see Experimental Section) and undeuterated TMT was treated with an excess of $ZnCl_2$ and indene. Equation 3 indicates the possibilities of the distribution of deuterium.



(3)

If the reaction were a concerted one, the product would either have the same label distribution as TMT-d_{12} or would not be labeled at all. If, on the other hand, the reaction were not concerted, the label would become randomized. By using a statistical calculation based on a binomial expansion (see Appendix), it is possible to calculate the distribution of the label assuming randomization of the dimethylamino groups. The results of the calculation, together with the experimental numbers, are shown in Table III. These data show, without any doubt, that the dimethylamino groups do become randomized and that the product formation must be a stepwise process.

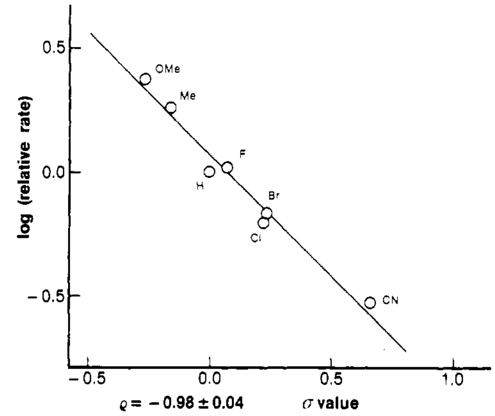
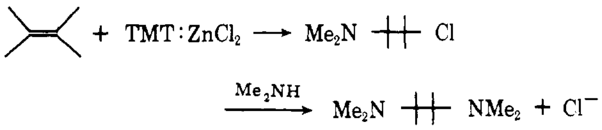


Figure 1. Hammett plot of the relative rate data for the addition of zinc chloride complexed dimethylamino radicals to substituted α-methylstyrenes.

The formation of the diamines, in principle, could occur by the intermediate formation of β-chloroamines, as indicated in eq. 4.

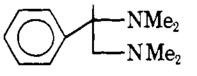


(4)

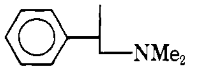
When the reaction was carried out in the presence of a large excess of diethylamine or when the diethylamine was added to the reaction mixture immediately after the completion of the reaction, no trace of the mixed product was detected, the sole product being the bis(dimethylamino) adduct.

The role of the zinc chloride in the reaction is twofold. The TMT:$ZnCl_2$ complex decomposes smoothly at 65 °C, a temperature at which TMT alone is completely stable.[18] Thus the zinc salt effectively catalyzes the decomposition. The other role is that apparently dimethylamino radicals are coordinated by zinc chloride. This was demonstrated most effectively by considering the relative rates of addition to substituted α-methylstyrenes and comparing the resulting Hammett equation plot with that obtained from the addition of the uncomplexed radical to the same styrenes.[19] The procedure used for the relative rate data is described in the Experimental Section. The relative rates were plotted against the Hammett σ values, and the resulting curve is shown in Figure 1. The slope of the line in Figure 1 yields the ρ value for the reaction, which is -0.98 ± 0.04. Clearly, the zinc chloride complexed amino radical is an electrophilic species; i.e., electron-donating substituents favor the reaction.

The reactivity of the uncomplexed radical was more difficult to measure. Photochemical decomposition (25 °C) of TMT in the presence of α-methylstyrene in cyclohexane as the solvent leads to three products which contain the olefin moiety, **4**, **5**, and **6**. The diadduct **4** was formed in approximately 10% yield, while **5** and **6** were formed in yields of 2–5%. The bulk of the dimethylamino groups was accounted for in the formation of tetramethylhydrazine and dimethylamine. Several other, unidentified basic products were also formed in trace amounts (<1%). Attempts to use products **5** and **6** as a measure of the rate of reaction were unsatisfactory, because they were formed in low yields and it was difficult to get clean separations of them in the gas chromatographic analysis. The diadduct **4** was suitable, however, because it was formed in higher yield



4



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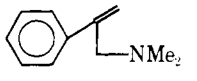

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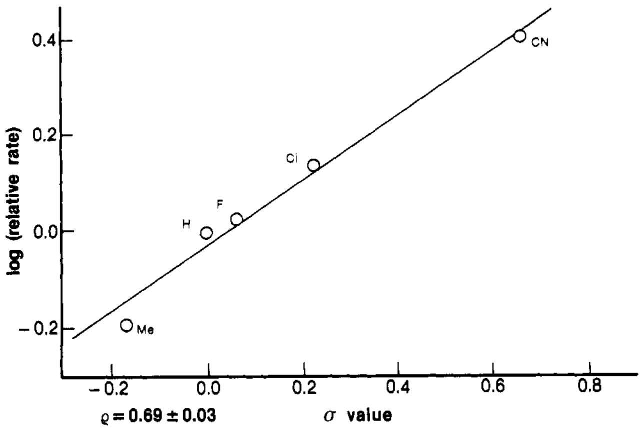


Figure 2. Hammett plot of the relative rate data for the addition of neutral dimethylamino radicals to substituted α-methylstyrenes.

Table IV. Relative Rates of Addition of Dimethylamino Radicals to α-Methylstyrene[a]

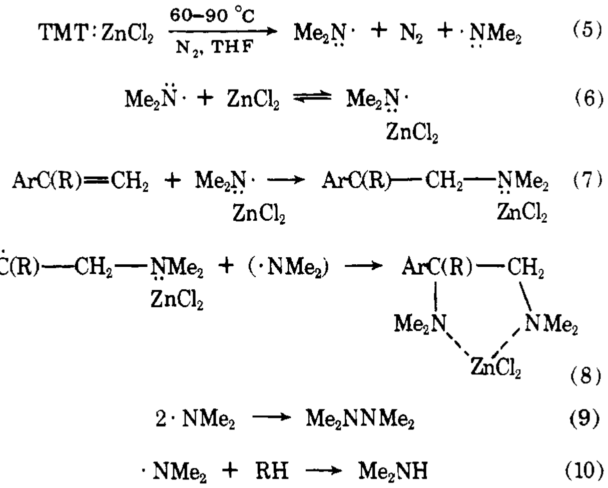
α-methylstyrene	$\log (k/k_0)$[b]	σ
p-OCH$_3$	-0.217 ± 0.2	-0.268
p-CH$_3$	-0.196 ± 0.035	-0.170
p-H	0.0	0.0
p-F	0.028 ± 0.013	0.062
p-Cl	0.139 ± 0.063	0.227
p-CN	0.408 ± 0.031	0.660

[a] The relative rates were obtained from competition experiments, as described in the text. [b] The error limits were evaluated from GC integration errors, and from duplicate experiments. The value for p-methoxy-α-methylstyrene was excluded from the calculation of the ρ value because the relative rate was very concentration dependent, presumably due to secondary reactions of the bis(dimethylamino) product and/or the starting styrene.

and its GLPC peak was well separated from all interfering components. The results of the relative rate study, using the formation of diadduct **4** as the measure of the reaction, are presented in Table IV and plotted in Figure 2. It was found that p-bromo-α-methylstyrene gave erratic values, probably because of photolability of either the olefin or the product. There was also a problem with p-methoxy-α-methylstyrene. The product, the bis(dimethylamino) adducts, apparently reacted with the dimethylamino radicals. This reaction probably occurred at the O-methyl group. It is interesting to note that this complication did not exist with the zinc chloride complexed radicals. The reaction was also negligible with the p-methyl-α-methylstyrene. Because of these complications, the points for p-bromo-α-methylstyrene and p-methoxy-α-methylstyrene were deleted from Figure 2. The slope of the line in Figure 2 is +0.69 ± 0.03, and hence the uncomplexed radical is *nucleophilic* in the addition reaction. This behavior contrasts with that observed for the same radical in abstraction of a hydrogen atom from substituted toluenes, where the ρ value was found to be -1.08.[18] These results clearly indicate that the radicals formed from the TMT:ZnCl$_2$ complex are not simple dimethylamino radicals and are probably complexed by zinc chloride.

The question of validity of the use of a small yield reaction to measure reactivity is important. In the present case, we found the data to be highly reproducible and other, more circumstantial, pieces of evidence also point to the overall conclusion. Thus, p-chlorostyrene reacts with the dimethylamino radical about 1.5 times faster than styrene. While adducts **5** and **6** could not be measured with the required precision to be useful in measuring relative rates, it was clear that they were formed more rapidly when the phenyl ring had a para-electron-attracting substituent than when it was substituted by an electron-donating group. These data do not constitute a proof of the validity of our procedure, but they do support the qualitative conclusion that the dimethylamino radical is nucleophilic in addition reactions.

Scheme I



$$\mathrm{TMT{:}ZnCl_2} \xrightarrow[\mathrm{N_2,\ THF}]{60\text{-}90\ ^\circ\mathrm{C}} \mathrm{Me_2\ddot{N}\cdot} + \mathrm{N_2} + \cdot\mathrm{\ddot{N}Me_2} \tag{5}$$

$$\mathrm{Me_2\ddot{N}\cdot} + \mathrm{ZnCl_2} \rightleftharpoons \underset{\mathrm{ZnCl_2}}{\mathrm{Me_2\ddot{N}\cdot}} \tag{6}$$

$$\mathrm{ArC(R){=}CH_2} + \underset{\mathrm{ZnCl_2}}{\mathrm{Me_2\ddot{N}\cdot}} \longrightarrow \mathrm{Ar\dot{C}(R){-}CH_2{-}}\underset{\mathrm{ZnCl_2}}{\mathrm{\ddot{N}Me_2}} \tag{7}$$

$$\mathrm{Ar\dot{C}(R){-}CH_2{-}}\underset{\mathrm{ZnCl_2}}{\mathrm{\ddot{N}Me_2}} + (\cdot\mathrm{NMe_2}) \longrightarrow \begin{array}{ccc} \mathrm{ArC(R)} & - & \mathrm{CH_2} \\ | & & \backslash \\ \mathrm{Me_2N} & & \mathrm{NMe_2} \\ & \mathrm{ZnCl_2} & \end{array} \tag{8}$$

$$2\cdot\mathrm{NMe_2} \longrightarrow \mathrm{Me_2NNMe_2} \tag{9}$$

$$\cdot\mathrm{NMe_2} + \mathrm{RH} \longrightarrow \mathrm{Me_2NH} \tag{10}$$

The foregoing data can be incorporated into a mechanism for the addition reaction, as shown in Scheme I.

There is no direct evidence that the complexation of free amino radicals by zinc chloride (reaction 6) actually occurs, but, considering the fact that the reaction was carried out in excess of zinc chloride, it would be surprising if it did not. The nature of the (·NMe$_2$) in eq 8 is unknown. Perhaps the radical is coordinated with zinc chloride. A systematic variation of the concentrations of the three reactants (α-methylstyrene, TMT, zinc chloride) indicated that the reaction is favored by high zinc chloride and styrene concentration, but low TMT concentration. There was absolutely no evidence for polymerization of the α-methylstyrene, either in the absence of zinc chloride (i.e., photolysis of TMT in presence of α-methylstyrene) or in its presence. Likewise, there appeared to be little or no effect of temperature on the yield of the diamino adduct. Thus, variation of temperature from 60 to 120 °C gave essentially the same yield of the product. These data appear to indicate that the product-forming step(s) has negligible activation energy. There was also no significant variation in the product yield when the solvent was THF, acetonitrile, or acetone. The high olefin concentration, coupled with the low TMT concentration, favors addition, presumably because those conditions minimize competition from the accompanying radical-radical reactions. The high zinc chloride concentration required for maximum yield of the adduct suggests the importance of coordination of the radicals by the Lewis acid.

As was stated in the introductory section, TMT is known to form complexes with a variety of Lewis acids. These complexes, however, do not all catalyze the addition reaction described in this paper. Thus, the zinc bromide complex is a little more stable than the one from zinc chloride, but it decomposes readily at 70 °C in presence of α-methylstyrene to give the diamino adduct in about 30% yield. The mercuric chloride complex gives some adduct (~5%), but the reaction was complicated by poor solubility of the complex, and hence the yield is probably not a reflection of the reactivity of mercuric chloride complexed radicals. The reaction of the cadmium chloride complex at 75 °C in THF resulted in a small yield of adduct, but again there were difficulties with solubility. Reactions of TMT in presence of α-methylstyrene catalyzed by zinc acetate and zinc sulfate were unsuccessful at temperatures below 120 °C. Likewise, the complexes of TMT and diphenylzinc and bis(perfluorophenyl)zinc were stable at higher temperature and failed to catalyze the addition reaction. The latter case is particularily surprising because the perfluorophenyl group is reported to be about as electron attracting as the bromine atom.[3] Our previous work[5] suggests, however, that there is an equilibrium between the free TMT and bis(perfluorophenyl)zinc in solution, which may not be very favorable for the complex at higher temperatures. The reaction was not carried out with an excess of the diarylzinc and consequently the reactions actually observed were those of essentially uncomplexed TMT.

Appendix

Product Labeling Pattern in the Reaction of Indene with Deuterated and Undeuterated TMT, Assuming Random Redistribution. The equation used for the calculation of the theoretical values for the isotopic distribution in 1,2-bis(dimethylamino)indane is based on a binomial distribution. Thus, the value for the fraction of a given isotopic peak, $P(M)$, in the molecular ion of the diaminoindane is given by:

$$P(M) = 0.859D_n{}^2 + 2D_xD_y + 0.131D_{n-1}{}^2 + 2D_kD_l + 0.008D_{n-2}{}^2 + 2D_iD_j$$

D = relative isotopic abundances in the dimethylamino groups, assuming randomization. The subscripts, are integers, which range from 0 to 6

$$x + y = n; l + k = n - 1; i + j = n - 2$$

The coefficients were evaluated from the known isotopic composition of carbon and nitrogen and the fact that the molecule being examined has 13C and 2N, 85.9% of the ions in a given isotopic peak of the parent cluster have 13^{12}C and 2^{14}N, 13.1% have either one ^{13}C or one ^{15}N, and 0.8% have two mass units contributed by the heavier isotopes.

A given D is evaluated independently from the isotopic distribution of the parent dimethylnitrosamine-d_6, using the equation

$$D_z = (N_z - 0.028N_{z-1}) + 0.028N_z$$

Where N's are the intensities of a given peak in the parent ion of the nitrosamine, and 0.028 is the correction factor for ^{13}C and ^{15}N.

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE 76-24095). We are grateful to Mr. Joseph Mahaffy for pointing out how to do the statistical analysis of the deuterium label randomization.

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Petroporphyrins. 1. Preliminary Characterization of the Porphyrins of Gilsonite

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Abstract: Eight predominantly single carbon number porphyrin fractions were isolated chromatographically from a bitumen, gilsonite (Eocene, Uinta Basin, Utah). Each alkyl porphyrin fraction was analyzed by ^{1}H NMR, mass spectrometry, and LC. The seven etioporphyrins isolated ranged from C_{29} to C_{32} and contained only methyl, ethyl, and hydrogen substituents, but no meso (bridge) alkyl groups. One of the two C_{29} etioporphyrin fractions was unambiguously assigned as 2-ethyl-3,7,8,12,13,17,18-heptamethylporphine. The presence of an isocyclic ring was confirmed in the C_{31} DPEP porphyrin fraction. One of the two C_{32} DPEP porphyrins isolated cochromatographed on LC with standard deoxophylloerythroetioporphyrin. The combined spectrometric and chromatographic data indicate that the porphyrins are derived from chlorophyll *a*.

Introduction

Alkyl porphyrins in geological samples (petroporphyrins) occur as complex mixtures of two major series: the deoxophylloerythroetio (DPEP) and etio types (**1** and **2**, respectively).[1-4] It has been suggested that they are derived from defunctionalization of naturally occurring chlorophylls,[5-7] with additional carbon atoms in the higher members ($>C_{32}$) arising from either diagenetic transalkylation or chlorobium chlorophylls.[8] Evidence for these hypotheses was provided only by visible absorption and mass spectrometric data from total petroporphyrin mixtures. It is essential to isolate single carbon number species and elucidate their structures to investigate

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