the solvation shell to stabilize the transition state is of primary importance.

Experimental Section

All boiling points are uncorrected for stem exposure. Purity of all distilled chemicals was established by gas chromatography.

Benzoate Esters.—Methyl benzoate, bp 48° (0.4 mm), *n*-propyl benzoate, bp 63–64° (0.4 mm), isopropyl benzoate, bp 48° (0.2 mm), and isobutyl benzoate, bp 69–70° (0.4 mm), were commercial samples fractionally distilled prior to use. *t*-Butyl benzoate, bp 61–62° (0.2 mm) [lit.[18] bp 67–68° (1 mm)], and neopentyl benzoate, bp 70° (0.4 mm) [lit.[19] bp 110–111° (10 mm)], were prepared from their respective alcohols and benzoyl chloride in the presence of pyridine. 2-Ethylbutyl benzoate, bp 34° (0.5 mm), was prepared in a similar manner.

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.59; H, 8.90.

Purification of Solvent.—Dimethyl sulfoxide was purified by distillation from calcium hydride and was stored over 4A molecular sieves.

Rate Measurements.—The technique and method used were those reported in previous investigations.[1,2]

Treatment of Kinetic Data.—The simple and multiple regression analyses (IBM program 6.0.003) were executed by an IBM 1620 computer.

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Amination of Aldehydes and Ketones by Tris(dimethylamino)arsine and Tetrakis(dimethylamino)titanium

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Received June 20, 1966

Aldehydes and ketones are converted by $As[N(CH_3)_2]_3$ and $Ti[N(CH_3)_2]_4$ into *gem*-diamines and enamines. A number of highly hindered enamines were prepared by this method.

Recently the authors reported the novel amination of carboxylic acid derivatives using tetrakis(dimethylamino)titanium.[1,2] The subject of the present paper is the closely related amination of aldehydes and ketones using tris(dimethylamino)arsine as well as tetrakis(dimethylamino)titanium to yield *gem*-diamines and enamines.

Our results indicate the reactions studied with the arsenic and titanium derivatives are of the same type reported by Nelson and Pelter[3] for the corresponding boron derivatives. In contrast to the arsenic, titanium, and boron derivatives which aminate carbonyl compounds the phosphorous analog has been reported by Mark[4] to give 1:1 adducts and epoxides on reaction with benzaldehydes.

Results and Discussion

Acetaldehyde and benzaldehyde were readily converted into *gem*-diamines by tris(dimethylamino)arsine. The metal is converted in near-quantitative yield to oxide (identified by XRD) in all cases described in this paper. While the benzylidinebisdimethylamine, $C_6H_5CH[N(CH_3)_2]_2$, has been previously reported[5] the ethylidinebisdimethylamine, $CH_3CH[N(CH_3)_2]_2$, appears to be a new compound and is unique among our products being the only *gem*-diamine isolated with a carbon–hydrogen bond in the β-position. All other systems containing a β-hydrogen yielded enamines.

Relatively unhindered ketones react readily with $As[N(CH_3)_2]_3$ to yield enamines. Cyclohexanone for example is converted rapidly to cyclohexenyl-1-dimethylamine. More sterically hindered ketones, however, react only sluggishly with $As[N(CH_3)_2]_3$ and it is necessary to use the much more reactive $Ti[N(CH_3)_2]_4$ to conveniently effect their conversion to enamines.

Thus 3-methyl-2-butanone is converted smoothly by $Ti[N(CH_3)_2]_4$ to N,N-dimethyl(2-methyl-2-methylenepropyl)amine, $CH_2{=}C[N(CH_3)_2]CH(CH_3)_2$, which on prolonged heating is converted to a 50:50 mixture of isomers including the above and the N,N-dimethyl-(1,2-dimethylpropenyl)amine, $(CH_3)_2C{=}C[N(CH_3)_2]CH_3$, as determined by nmr analysis. The latter isomer was not isolated. Isobutyrophenone is converted cleanly into N,N-dimethyl(2-methyl-1-phenylpropenyl)amine, $(CH_3)_2C{=}C[N(CH_3)_2]C_6H_5$. The highly hindered diisopropyl ketone is also converted by $Ti[N(CH_3)_2]_4$ into N,N-dimethyl(1-isopropyl)-2-methylpropenyl)amine, $(CH_3)_2C{=}C[N(CH_3)_2]CH(CH_3)_2$.

Nelson and Pelter[3] suggested that due to concomitant self-condensation pinacolone could not be converted to its enamines by $B[N(CH_3)_2]_3$. Self-condensation occurs in the reaction of pinacolone with $Ti[N(CH_3)_2]_4$ as well, but the high reactivity of the titanium derivative allowed us to choose reaction parameters minimizing the side reaction. Pinacolone is thus converted to N,N-dimethyl(2,2-dimethyl-1-methylenepropyl)amine, $CH_2{=}C[N(CH_3)_2]C(CH_3)_3$, in moderate yield.

The sterically hindered N,N-dimethylenamines described above are, to our knowledge, reported here for the first time.

The ability of titanium, arsenic, and boron amides to engage in this reaction arises from the combination of acid and base functionality in the same molecule as well as the great tendency of the reagents to form oxides. Their approximate order of reactivity appears to be Ti $\gg$ As $>$ B. A plausible mechanistic sequence is described in Scheme I. When R''' is anything but hydrogen the formation of *gem*-diamine is apparently unfavorable probably owing to steric crowd-

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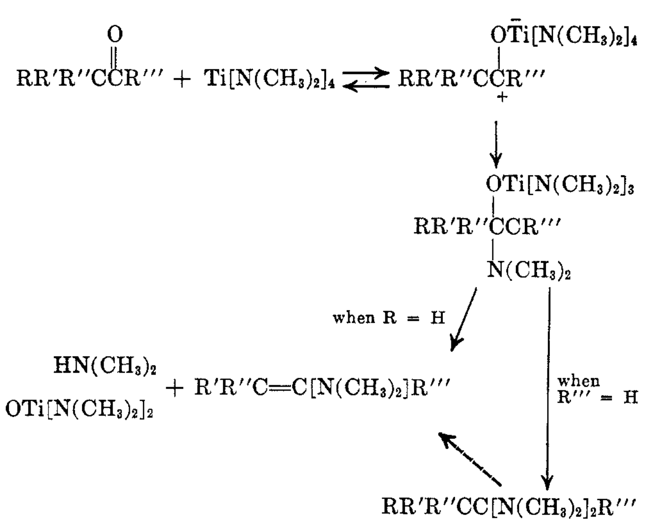
SCHEME I



ing. The *gem*-diamine may, of course, also be precursor to olefin. The $OTi[N(CH_3)_2]_2$ or arsenic analog probably has no discrete existence but is incorporated into $\overset{|}{\underset{|}{Ti}}O\overset{|}{\underset{|}{Ti}}O$ type rings or polymers.

In summary the reactions described in this paper provide a rapid and convenient method for the preparation of *gem*-diamines and enamines. Of particular interest is the preparation of highly hindered enamines not readily obtainable by other routes. Also noteworthy is the incorporation of dimethylamino groups which, due to the volatility of dimethylamine, is difficult to accomplish by other methods.

Experimental Section

Proton nmr spectra were obtained from a Varian Model A-60 spectrometer at a frequency of 60.000 Mc. The tetrakis(dimethylamio)titanium was prepared by the method of Bradley and Thomas.[6] The tris(dimethylamino)arsine was a gift of Dr. Kurt Moedritzer,[7] Monsanto Co. The solvents, benzene, toluene, and ethyl ether, were purified by distillation from $LiAlH_4$. The aldehydes and ketones used were the best commercial grades available and were purified where necessary until they gave sharp, unambiguous nmr and vpc spectra.

Preparation of Ethylidenebisdimethylamine.—To a solution of 4.14 g (0.0200 mole) of $As[N(CH_3)_2]_3$ in 10 ml of ethyl ether was added slowly a chilled solution of 1.32 g (0.0300 mole) of acetaldehyde also in 10 ml of ether. A precipitate of As_2O_3 formed immediately. The reaction mixture was allowed to stand at room temperature for 1 hr, then filtered, and the solvent was removed. The residual oil was distilled, bp ~45° (80 mm).[8] The nmr spectrum [neat liquid, tetramethylsilane (TMS) internal standard] exhibited a quartet at τ 7.31, a singlet at 7.77, and a doublet at 9.03 in the expected ratio of 1:12:3, respectively.

Preparation of Benzylidinebisdimethylamine.—To a solution 4.14 g (0.0200 mole) of $As[N(CH_3)_2]_3$ in 10 ml of toluene was added slowly a solution of 3.18 g (0.0300 mole) of benzaldehyde also in 10 ml of toluene. The reaction was exothermic and a white precipitate was formed immediately. After standing for 1 hr the precipitate was filtered and the solvent was removed. The residue was distilled at reduced pressure yielding 4.4 g (86%) of benzylidinebisdimethylamine,[5] bp 93° (10 mm). The nmr spectrum (neat liquid, TMS internal standard) exhibited three singlets at τ 2.82, 6.64, and 7.95 in the expected ratio of 5:1:12, respectively.

Preparation of Cyclohexenyl-1-dimethylamine.—To a solution of 4.14 g (0.0200 mole) of $As[N(CH_3)_2]_3$ in 10 ml of ethyl ether was slowly added a solution of 2.94 g (0.0300 mole) of cyclohexanone also in 10 ml of ether. A white precipitate was formed after several minutes and the reaction mixture was allowed to stand for 1 hr. The reaction mixture was filtered and the solvent was removed from the filtrate. The residue was distilled yielding 3.3 g (90%) of cyclohexenyl-1-dimethylamine, bp 173° (747 mm) [lit.[9] 81° (35 mm)]. The nmr spectrum (benzene solvent, TMS internal standard) exhibited a triplet at τ 5.46, a singlet at 7.59, and two complex multiplets at 7.90 and 8.42 in the expected ratio of 1:6:4:4, respectively.

Preparation of N,N-Dimethyl(2-methyl-1-methylenepropyl)-amine.—To a solution of 3.00 g (0.0134 mole) of tetrakis(dimethylamino)titanium in 40 ml of ethyl ether was added, dropwise with stirring, a solution of 2.31 g (0.0269 mole) of 3-methyl-2-butanone in 5 ml of ethyl ether. A white precipitate was formed immediately. The mixture stood for 2 hr. The precipitate was filtered and washed with ether; the ether solvent was removed from the filtrate by distillation. Upon distillation the remaining oil yielded 1.61 g (53%) of N,N-dimethyl(2-methyl-1-methylenepropyl)amine, bp 57° (82 mm), $n^{25}D$ 1.4403; the nmr spectrum exhibited singlets at τ 5.95, 6.13, and 7.58, a heptet centered at 7.63, and a doublet at 8.90 in the expected ratio of 1:1:6:1:6 (benzene solvent, TMS internal standard).

Anal. Calcd for $C_7H_{15}N$: C, 74.3; H, 13.3; N, 12.4; mol wt, 113. Found: C, 74.4; H, 13.1; N, 12.8; mol wt, 113 (mass spectrum).

Preparation of N,N-Dimethyl(2-methyl-1-phenylpropenyl)-amine.—To a solution of 3.21 g (0.0143 mole) of tetrakis(dimethylamino)titanium in 40 ml of ethyl ether was added, dropwise with stirring, a solution of 4.23 g (0.0286 mole) if isobutyrophenone in 5 ml of ethyl ether. A white precipitate formed on standing for 2 days. The precipitate was filtered and washed with dry ether; the solvent was removed from the filtrate by distillation. Upon distillation the remaining oil yielded 3.91 g (78%) of N,N-dimethyl(2-methyl-1-phenylpropenyl)amine, bp 67° (3 mm), $n^{25}D$ 1.5234; the nmr spectrum exhibited singlets at τ 7.60, 8.04, and 8.46 in the expected ratio of 2:1:1 (benzene solvent, TMS internal standard).

Anal. Calcd for $C_{12}H_{17}N$: C, 82.3; H, 9.7; N, 8.0; mol wt, 175. Found: C, 82.6; H, 10.0; N, 7.5; mol wt, 175 (mass spectrum).

Preparation of N,N-Dimethyl(1-isopropyl-2-methylpropenyl)-amine.—To a 10-ml round-bottom flask fitted with an air condenser and a nitrogen bleed line were added 4.13 g (0.0184 mole) of tetrakis(dimethylamino)titanium and 3.84 g (0.0337 mole) of diisopropyl ketone. The flask was placed in an oil bath, heated to 70°; the mixture reacted for 65.5 hr. The product was rapidly distilled from the reaction mixture at 1 mm into a Dry Ice trap. This water white distillate was fractionally distilled yielding 2.06 g (43.3%) of N,N-dimethyl(1-isopropyl-2-methylpropenyl)-amine, bp 80° (85 mm), $n^{25}D$ 1.4397; the nmr exhibited a singlet at τ 7.46, 8.32, and 8.40, a doublet at 8.91, and a heptet centered at 7.28 in the expected ratio of 6:3:3:6:1 (benzene solvent, TMS internal standard).

Anal. Calcd for $C_9H_{19}N$: C,76.6; H, 13.5; N, 9.9; mol wt, 141. Found: C, 76.9; H, 13.1; N, 10.1; mol wt, 141. (mass spectrum).

Preparation of N,N-Dimethyl(2,2-dimethyl-1-methylenepropyl)-amine.—To a refluxing solution of tetrakis(dimethylamino)-titanium, 5.0 g (0.022 mole) in 100 ml of ethyl ether, was added dropwise over 0.75 hr a solution of pinacolone 4.4 g (0.044 mole) in 20 ml of ether. The reaction mixture was refluxed 16 hr, then the solvent was removed, and the volatile portion of the residual oil was distilled rapidly at 1 mm into a Dry Ice trap. This water-white distillate was fractionally distilled yielding 1.2 g (21%) of N,N-dimethyl(2,2-dimethyl-1-methylenepropyl)-amine, bp 57° (71 mm), $n^{25}D$ 1.4294; the nmr spectrum exhibited sharp singlets at τ 5.31, 5.57, 7.57, and 8.82 in the expected ratio (1:1:6:9) (benzene solvent, TMS internal standard).

Anal. Calcd for $C_8H_{17}N$: C, 75.5; H, 13.5; N, 11.0; mol wt, 127. Found: C, 75.9; H, 13.1; N, 10.7; mol wt, 127 (mass spectrum).

Acknowledgment.—The authors wish to thank Professor Nelson J. Leonard for his valuable suggestions.

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(8) The product appeared to decompose slightly on distillation preventing our obtaining an analytically pure sample and an accurate boiling point. However, the proton nmr is quite distinctive.

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