was added 4.0 mL (3.3 g, 53 mmol) of dimethyl sulfide. On completion of the addition the yellow color disappeared. After being stirred for 10 min, a solution of 2.66 g (20 mmol) of tetrahydroquinoline (1) and 2.02 g (20 mmol) of triethylamine in 6 mL of dry methylene chloride was added dropwise. The reaction mixture was stirred for 4 h at −70 °C, and an additional 20 mL of triethylamine was added to the reaction mixture. After being stirred at −70 °C for 1 h, the reaction mixture was allowed to warm to room temperature (23 °C) over a 10-h period. The reaction mixture was washed with dilute sodium hydroxide solution, dried over anhydrous sodium carbonate, filtered, and concentrated to yield an oil. Chromatography of this material on a Waters Prep 500 liquid chromatograph using a silica gel column with 10% ethyl acetate–90% hexane gave 1.76 g (46%) of **2**. Distillation of this material gave 1.50 g (39%) of **2**: bp 95–98 °C (0.1 mm); IR (neat) 3350 (mw), 3040 (vw), 3010 (vw), 2910 (m), 2830 (mw), 1595 (m), 1495 (ms), 1470 (ms), 1440 (m), 1430 (m), 1355 (mw), 1330 (w), 1310 (ms), 1270 (ms), 1225 (w), 1190 (w), 1175 (w), 1150 (vw), 1105 (mw) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.72–2.15 (m, 2 H), 1.92 (s, 3 H), 2.60–2.90 (m, 2 H), 3.18–3.46 (m, 2 H), 3.55 (s, 2 H), 4.35 (s, 1 H), 6.32–7.02 (cm, 3 H); ^{13}C NMR ($CDCl_3$) δ 14.43 (q), 21.68 (t), 27.18 (t), 35.28 (t), 41.88 (t), 115.84 (d), 119.85 (s), 121.99 (s), 128.29 (d), 128.64 (d), 142.98 (s); exact mass m/e 193.0935 (calcd for $C_{11}H_{15}NS$ 193.0924).

Anal. Calcd for $C_{11}H_{15}NS$: C, 68.35; H, 7.82; N, 7.25. Found: C, 68.25; H, 7.87; N, 7.31.

1-(Methylthio)-1,2,5,6-tetrahydro-4*H*-pyrrolo[3,2,1-*ij*]-quinolin-2-one (5). Chlorine (2.0 mL, 44 mmol) was condensed into a dry ice–acetone-cooled addition funnel at −78 °C. The chlorine was added dropwise to 100 mL of dry methylene chloride at −78 °C. To the resultant pale yellow solution, under a static nitrogen pressure, was added 6.5 g (48.5 mmol) of ethyl methylthioacetate in 15 mL of dry methylene chloride. The mixture was stirred at −78 °C for 25 min, and 11.72 g (88 mmol) of tetrahydroquinoline in 15 mL of dry methylene chloride was added dropwise. The reaction mixture was stirred for 4 h at −78 °C, followed by the addition of 20 mL of triethylamine. After being stirred for 1 h at −78 °C, the reaction mixture was allowed to warm to ambient temperature. To the reaction mixture was added 50 mL of 6 *N* hydrochloric acid, and the reaction mixture was stirred for 10 h. The organic layer was separated, dried over anhydrous sodium carbonate, filtered, and concentrated to give an oil, which was chromatographed on a Waters Prep 500 liquid chromatograph using a silica gel column with 20% ethyl acetate–80% hexane to yield 6.6 g (68%) of a solid, which was recrystallized from ether–hexane to give 5.1 g (53%) of **5**: mp 71.5–73.5 °C; IR ($CDCl_3$) 3060 (vw), 2490 (w), 2880 (w), 2840 (vw), 1635 (s), 1625 (m), 1600 (m), 1480 (m), 1435 (vw), 1380 (w) 1350 (ms), 1330 (w), 1295 (w), 1240 (w), 1195 (w), 1170 (w), 1155 (w), cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.80–2.20 (m, 2 H), 2.01 (s, 3 H), 2.60–2.90 (m, 2 H), 3.55–3.86 (m, 2 H), 4.17 (s, 1 H), 6.85–7.27 (cm, 3 H); ^{13}C NMR ($CDCl_3$) δ 11.99 (q), 20.73 (t), 23.92 (t), 38.50 (t), 46.31 (d), 119.70 (s), 121.34 (d), 122.16 (d), 123.83 (s), 127.30 (d), 139.48 (s) 173.44 (s); exact mass m/e 219.0713 (calcd for $C_{12}H_{13}NOS$ 219.0716).

Anal. Calcd for $C_{12}H_{13}NOS$: C, 65.72; H, 5.97; N, 6.39. Found: C, 65.79; H, 6.05; N, 6.41.

1-(Methylthio)-2-methyl-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline (7). Chlorine (2.0 mL, 44 mmol) was condensed into a dry ice–acetone-cooled additional funnel at −78 °C and then added dropwise to 150 mL of dry methylene chloride at −78 °C under a static nitrogen atmosphere. To this pale yellow solution was added 5.0 g (48 mmol) of 1-(methylthio)propan-2-one in 15 mL of dry methylene chloride. An off-white precipitate formed. After the reaction mixture had been stirred for 35 min, a solution of 11.72 g (88 mmol) of tetrahydroquinoline in 12 mL of dry methylene chloride was added dropwise. The reaction mixture was stirred for 2 h at −70 °C, followed by the addition of 25 mL of triethylamine. After being stirred for an additional hour at −70 °C, the reaction mixture was allowed to warm to ambient temperature over a 10-h period. The reaction mixture was extracted with dilute aqueous sodium hydroxide solution, dried over anhydrous sodium carbonate, filtered, and concentrated to give an oil. Chromatography of this oil on a Waters Prep 500 liquid chromatograph using a silica gel column with 5% ethyl acetate–95% hexane yielded 3.70 g (39%) of **7**. Recrystallization of **7** from hexane gave 3.10 g (32%) of analytically pure material: mp 91.5–93.5 °C; IR ($CDCl_3$) 3060 (w), 2940 (m), 2920 (m), 2860 (w), 2840 (vw), 1615 (vw), 1515 (w), 1490 (w), 1440 (m), 1395 (ms), 1375 (w), 1355 (w), 1330 (m), 1255 (m), 1180 (w), 1170 (m), 1050 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.0–2.40 (m, 2 H), 2.19 (s, 3 H), 2.42 (s, 3 H), 2.91 (t, 2 H), 3.94 (t, 2 H), 6.59–7.59 (cm, 3 H); ^{13}C NMR ($CDCl_3$) δ 9.82 (q), 19.97 (q), 22.56 (t), 24.42 (t), 41.78 (t), 102.29 (s), 115.67 (d), 118.19 (d), 119.75 (d), 121.09 (s), 127.32 (s), 133.68 (s), 139.00 (s); exact mass m/e 217.0926 (calcd for $C_{13}H_{15}NS$ 217.0924).

Anal. Calcd for $C_{13}H_{15}NS$: C, 71.84; N, 6.96; N, 6.44. Found: C, 71.76; H, 6.97; N, 6.35.

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Registry No. **1**, 635-46-1; **2**, 88426-28-2; **3**, 50450-25-4; **4**, 88426-29-3; **5**, 88426-30-6; **6**, 50450-24-3; **7**, 88426-31-7; dimethylchlorosulfonium chloride, 23372-58-9; chlorine, 7782-50-5; ethyl methylthioacetate, 4455-13-4; 1-(methylthio)propan-2-one, 14109-72-9; dimethyl sulfide, 75-18-3.

Friedel–Crafts Chemistry: A New Synthetic Route for Polynuclear Compounds

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Friedel–Crafts reaction is one of the most useful reactions in organic chemistry. It has widely been used for the preparation of diverse types of products by alkylation, acylation, cycliacylation, and other miscellaneous types of reactions.[2] Although literature is scanty, haloacylation of organic compounds in Friedel–Crafts conditions has also been described.[2-4] Diacylaton of naphthalene derivatives by the use of excess of Friedel–Crafts reagents has been reported by Gore et al.[5-7] Haloacylation of anisole (1) and phenetole (2) (Chart I) using dichloroacetyl chloride has been reported long ago,[8] and as expected dichloroacylation took place in the para-position with respect to the ether group. In our efforts to prepare polynuclear derivatives by newer synthetic techniques, it was observed that Friedel–Crafts conditions may conveniently be adopted for preparation of such compounds by varying the temperature and proportions of the substrate and the catalyst. Aromatic ethers, e.g., anisole (1) and phenetole (2) were used as model substrates, dichloroacetyl chloride as the reactant, and the versatile anhydrous $AlCl_3$ as the catalyst. The products that were obtained are reported in this paper.

Results and Discussion

It is well-known that when substrates are employed in unimolar proportions in Friedel–Crafts reaction normal

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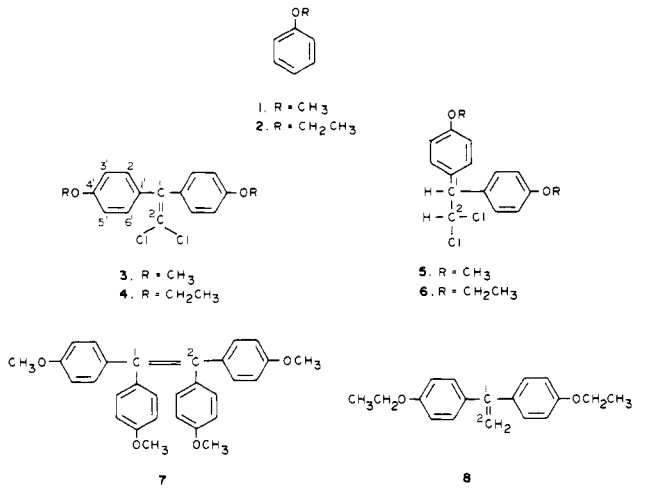
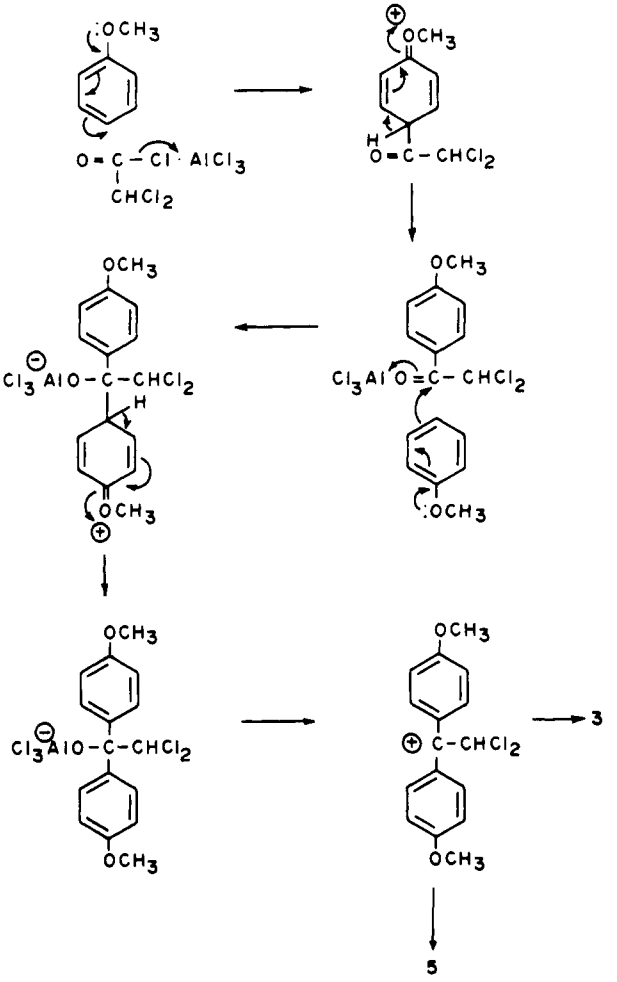
Chart I



products are obtained and their mechanism of formation is well understood. As mentioned earlier, employment of excess of Friedel–Crafts reagents leads to diacylation of naphthalene derivatives. In our contemplation we presumed that if the substrate is used in higher proportion, the normal reaction product that would be obtained might further act with the substrate, giving rise to polynuclear compounds. Thus, in our experiments 1 mol of dichloroacetyl chloride was reacted with varying amounts of **1** and **2** in the presence of 1.5–2 mol of anhydrous $AlCl_3$. No solvent was used as both **1** and **2** are liquids, and the reactions were carried out at ambient temperature (25 °C). When 2 mol of **1** and **2** were used in the reaction, products 2,2-dichloro-1,1-di-4-methoxyphenyl ethylene (**3**) and 2,2-dichloro-1,1-bis(4-ethoxyphenyl)ethylene (**4**), respectively, were formed in good yields and normal dichloroacylation products were not obtained. Employment of 3.8 mol of **1** and **2** led to the formation of 1,1,2,2-tetrakis(4-methoxyphenyl)ethylene (**7**) and **4**, respectively. Interestingly, although tetrameric product **7** was produced on raising the molar proportion of **1**, the corresponding product from **2** could not be obtained and instead the product **4** was isolated, which was also formed when 2 mol of phenetole was used. Enhancement of the molar quantities of **1** and **2** to 4.5 mol, i.e., greater than 4 mol, led to the generation of the products 2,2-dichloro-1,1-bis(4-methoxyphenyl)ethane (**5**) and **7** in case of the former and 2,2-dichloro-1,1-bis(4-ethoxyphenyl)ethane (**6**) and 1,1-bis(4-ethoxyphenyl)ethylene (**8**) in case of the latter. All the reaction products were characterized by their mass spectral, ^1H NMR and ^{13}C NMR data and also by comparison of their melting points with those of literature values. The assignments of the ^{13}C signals were made from their chemical shifts, off-resonance studies, and comparison of the shift data with those of similar compounds.[9] The mechanism of formations of **3** and **5** from **1** is envisaged as shown in Scheme I. When the reaction mixture was processed after 2 and 4 h from the start of the reaction, the formation of normal dichloroacylation compounds was clearly demonstrated by their actual isolation, although these normal dichloroacylation products were not obtained at the end of the reaction, i.e., after 24 h from the start of the reaction. This observation supports the presumption that the normal dichloroacylation compound is initially formed, which reacts further with the substrate to give rise to other products. While the formation of the dichloro diaryl ethylene **3** is unexceptional, that of the corresponding dihydro derivative **5** has a precedent in the reported[10] reaction of α-phenylisobutyryl chloride with $AlCl_3$ in benzene to give isopropyl benzene as one of the products. Formation of **7** necessitates employment of at least about four molar quantities of **1** and may be presumed to have arisen via stepwise or simultaneous alkylation of 2 mol of **1** by **3**. While formation of **4** and **6** from **2** is evidently similar to those of **3** and **5** from **1**, the generation of **8** from **2** is somewhat obscure. However, this difference in behavior may be ascribed to the difference in reactivities of **1** and **2**, the latter being less reactive so far as alkylation by **3** or **4** is concerned. The process of hydrogenolysis may be involved in the formation of **8** from **4**, which surpasses the process of alkylation, rendering the condition unfavorable for the generation of the tetrameric product **7**.

Scheme I



It may be mentioned that the compound 1,1,2-tris(4-methoxyphenyl)but-1-ene, which closely resembles **7**, has been reported to have significant tumor inhibiting properties.[11] We are pursuing our studies to evaluate the biological activities of the compounds.

Experimental Section

Melting points are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a JEOL FT-100 NMR spectrometer

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operating at 100 and 25.15 MHz, respectively. All ^1H and ^{13}C shifts are reported relative to Me_4Si. Mass spectra were obtained on Hitachi Model RMU-6L and MS 50-A.E.I. mass spectrometers at 70 eV by the direct insertion method.

General Procedure. Appropriate amounts (2, 3.8, and 4.5 mol) of anisole (1) and phenetole (2) were condensed with a fixed (1 mol) amount of dichloroacetyl chloride at room temperature in the presence of 1.5–2 mol of anhydrous $AlCl_3$. The acid chloride was added in portions with continuous shaking to a mixture of anhydrous $AlCl_3$ and either 1 or 2, and the reaction mixture was left for 24 h. The product was decomposed with an ice–HCl mixture and then taken up with ether. The ether solution was washed free from acid and dried under reduced pressure, and the residue was subjected to column chromatography over silica gel followed by crystallization. Thus, 2 mol of 1 and 2 gave rise to 3 and 4, respectively, while 3.8 mol of 1 and 2 led to the formation of 7 and 4, respectively. When 4.5 mol of 1 was employed a mixture of 5 and 7 was liberated whereas a mixture of 6 and 8 was isolated when the same molar quantity of 2 was used.

2,2-Dichloro-1,1-bis(4-methoxyphenyl)ethylene (3). This was eluted with petroleum ether–benzene (95:5), yield 1.7 g from 5.4 g of 1, and crystallized from MeOH: mp 107–108 °C (lit.[12] mp 109 °C); MS, m/z (relative intensity) 310 (M + 2, 64), 308 (M^+, 100), 273 (9), 238 (58), 223 (19), 195 (17), 151 (19); ^1H NMR δ 3.86 (s, 6 H, C4′-OCH_3), 6.89 (d, J = 8 Hz, 4 H, C3′-H, C5′-H), 7.25 (d, J = 8 Hz, 4 H, C2′-H, C6′-H); ^{13}C NMR δ 55.1 (t, C4′-OCH_3), 113.5 (d, C3′, C5′), 130.7 (d, C2′, C6′), 132.0 (s, C1′), 139.7 (s, C1, C2), 159.1 (s, C4′).

2,2-Dichloro-1,1-bis(4-ethoxyphenyl)ethylene (4). In column chromatography it was eluted with petroleum ether, yield 1.8 g from 6.1 g of 2: mp 102–103 °C (MeOH) (lit.[12] mp 105 °C); MS, m/z (relative inensity) 338 (M + 2, 29), 336 (M^+, 47), 310 (5), 308 (9), 282 (15), 280 (23), 210 (79), 181 (88), 152 (100); ^1H NMR δ 1.42 (t, J = 7 Hz, 6 H, C4′-OCH_2CH_3), 4.05 (q, J = 7 Hz, 4 H, C4′-OCH_2CH_3), 6.84 (d, J = 8 Hz, 4 H, C3′-H, C5′-H), 7.22 (d, J = 8 Hz, 4 H, C2′-H, C6′-H); ^{13} C NMR δ 14.8 (q, C4′-OCH_2CH_3), 63.4 (t, C4′-OCH_2CH_3), 114.0 (d C3′, C5′), 130.7 (d, C2′, C6′), 131.9 (s, C1′), 139.8 (s, C1, C2).

2,2-Dichloro-1,1-bis(4-methoxyphenyl)ethane (5). It was eluted with petroleum ether–benzene (85:15), yield 1.9 g from 13.5 g of 1: mp 116–117 °C (MeOH) (lit.[13] mp 114 °C); MS, m/z (relative intensity) 312 (M + 2,4), 310 (M^+, 8), 240 (3), 228 (24), 227 (100), 212 (6), 169 (6), 165 (5), 153 (7), 152 (7), 141 (6), 113 (6); ^1H NMR δ 3.81 (s, 6 H, C4′-OCH_3), 4.52 (d, J = 8 Hz, 1 H, C1-H), 6.34 (d, J = 8 Hz, 1 H, C2-H), 6.89 (d, J = 8 Hz, 4 H, C3′-H, C5′-H), 7.30 (d, J = 8 Hz, 4 H, C2′-H, C6′-H); ^{13}C NMR δ 55.1 (q, C4-OCH_3), 68.9 (d, C1), 75.3 (d, C2), 114.0 (d, C3′, C5′), 129.4 (d, C2′, C6′), 132.1 (s, C1′), 158.8 (s, C4′).

2,2-Dichloro-1,1-bis(4-ethoxyphenyl)ethane (6). Elution with petroleum ether–benzene (90:10) afforded 6, yield 1.5 g from 15 g of 2: mp 72–73 °C (MeOH) (lit.[13] mp 73 °C); MS, m/z (relative intensity) 340 (M + 2, 12), 338 (M^+, 18), 303 (56), 268 (5), 255 (100), 226 (5), 197 (6); ^1H NMR δ 1.42 (t, J = 7 Hz, 6 H, C4′-OCH_2CH_3), 4.02 (q, J = 7 Hz, 4 H, C4′-OCH_2CH_3), 4.48 (d, J = 8 Hz, 1 H, C1-H), 6.25 (d, J = 8 Hz, 1 H, C2-H), 6.85 (d, J = 8 Hz, 4 H, C3′-H, C5′-H), 7.24 (d, J = 8 Hz, 4 H, C2′-H, C6′-H); ^{13}C NMR δ 14.9 (q, C4′-OCH_2CH_3), 63.3 (t, C4′-OCH_2CH_3), 69.0 (d, C1-H), 75.3 (d, C2-H), 114.1 (d, C3′, C5′), 129.4 (d, C2′, C6′), 132.1 (s, C1′), 158.7 (s, C4′).

1,1,2,2-Tetrakis(4-methoxyphenyl)ethylene (7). Petroleum ether–benzene (85:15) eluted 7, yield 2 g from 10 g of 1 (crystallized from MeOH): mp 182–183 °C (lit.[14] mp 183–184 °C); MS, m/z (relative intensity) 452 (M^+, 100), 437 ($M^+ - CH_3$, 25), 301 (28), 238 (63), 226 (61), 223 (33), 199 (60); ^1H NMR δ 3.80 (s, 12 H, C4′-OCH_3), 6.68 (d, J = 8 Hz, 8 H, C3′-H, C5′-H), 6.98 (d, J = 8 Hz, 8 H, C2′-H, C6′-H); ^{13}C NMR δ 55.0 (q, C4′-OCH_3), 113.0 (d, C3′, C5′), 132.5 (d, C2′, C6′), 136.8 (s, C1′), 138.3 (s, C1, C2), 157.8 (s, C4′).

1,1-Bis(4-ethoxyphenyl)ethylene (8). It was eluted with petroleum ether, yield 2.6 g from 15 g of 2: mp 140 °C (MeOH) (lit.[12] mp 138 °C); MS, m/z (relative intensity) 268 (M^+, 90), 253 ($M^+ - CH_3$, 12), 240 (25), 239 (32), 211 (75), 197 (85), 182 (45), 180 (65), 164 (100), 152 (71), 151 (75), 138 (50), 114 (61); ^1H NMR δ 1.46 (t, J = 7 Hz, 6 H, C4′-OCH_2CH_3), 4.04 (q, J = 7 Hz, 4 H, C4′-OCH_2CH_3), 5.28 (s, 2 H, C2-H), 6.85 (d, J = 8 Hz, 4 H, C3′-H, C5′-H), 7.24 (d, J = 8 Hz, 4 H, C2′-H, C6′-H); ^{13}C NMR δ 14.9 (q, C4′-OCH_2CH_3), 63.4 (t, C4′-OCH_2CH_3), 111.4 (t, C2), 114.0 (d, C3′, C5′), 129.3 (d, C2′, C6′), 134,2 (s, C1′), 149.0 (s, C1), 158.6 (s, C4).

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Registry No. 1, 100-66-3; 2, 103-73-1; 3, 2132-70-9; 4, 2132-71-0; 5, 7388-31-0; 6, 7388-32-1; 7, 10019-24-6; 8, 5031-92-5; dichloroacetyl chloride, 79-36-7.

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Kinetics and Mechanism of the Reaction between Phenyl Isocyanate and Alcohols in Benzene Medium

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The reactions between an isocyanate (RNCO) and a variety of alcohols, producing industrially useful urethans, have been studied from the kinetic and the mechanistic points of view by a number of workers.[1-5] For instance, Davis and Farnum[1] found that the order of reactivity of primary, secondary, and tertiary alcohols with phenyl isocynate was approximately 1.0, 0.3, and 0.003–0.007, respectively. Baker and co-workers[2-4] observed this reaction to be base catalyzed. They also observed catalysis by alcohol itself.[2] The title investigation has been undertaken in order to find out if a correlation exists between the structure of alcohols and the kinetic parameters.

Experimental Section

AnalaR benzene, phenyl isocyanate (bp 66–68 °C (25 mm)), and alcohols were purified by standard methods and fractionally distilled, collecting the middle cuts for kinetic measurements.

Kinetic measurements were carried out in a benzene medium at 20, 30, and 40 ± 0.1 °C. Depending upon the reaction rate, [alcohol] was always kept higher (1.5 to 4 times) than [phenylisocyanate]. Kinetics was followed by mixing thermally equilibrated solutions of phenyl isocyanate and alcohol in benzene. Aliquots from the reaction mixture were withdrawn at regular time intervals and poured into a known excess of n-butylamine, and the amine was back-titrated against standard sulfuric acid to methyl red end point.[6] Over the periods normally required for the actual runs, the phenyl isocyanate solutions in benzene were quite stable. The reactions were followed up to 50–70% conversion.

Results and Discussion

The reaction of phenyl isocyanate with various alcohols studied followed second-order kinetics, in accord with the rate expression (1).

$$\frac{-d[C_6H_5NCO]}{dt} = k_2\,[\text{alcohol}][C_6H_5NCO] \qquad (1)$$

Plots of log $[b(a-x)/a(b-x)]$ against t were linear and

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