

TABLE I
 ACYLATION OF TRIPHENYLAMINE WITH HEXANOYL CHLORIDE IN THE PRESENCE OF ZINC CHLORIDE

Experiment	Ratio of reactants ^a	Solvent	Time, hr. (temp., °C.)	Yield, mole % of <i>p</i> -hexanoylated triphenylamine	Found, %			Mol. wt.	
					C	H	N	Calcd.	Found
A	1:1:1	Nitrobenzene	4 (25)	50, mono-	83.5	7.0	4.2		
B	1:2:2	Nitrobenzene	4 (25)	58, mono-	83.5	7.0	4.2		
C	1:1:1	Dichloromethane	48 (25)	50, mono-	83.5	7.0	4.2	343	340 ±17
D	1:2:2	Dichloromethane	6 (25)	75, mono-	83.6	7.1	3.9	343	337 ±17
E	1:3:3	Dichloromethane	6 (25)	75, mono-			3.8	343	354 ±18
F	1:3:3	Dichloromethane	20 (40)	<1, mono- 27.5, di- 22.5, tri- 37, polymer			3.4 3.0 9.7	441 539	431 581 ±29 1220

^a Triphenylamine-hexanoyl chloride-zinc chloride.

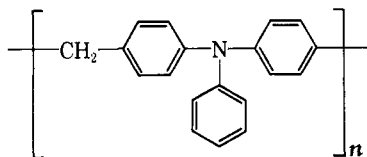
decomposition. Under these conditions, 27 and 36% yields of the mono- and trisubstituted products were obtained, respectively. There was no evidence of the disubstituted product, *p,p'*-dihexanoyltriphenylamine, in contrast to the results obtained using zinc chloride.

At room temperature decomposition of the triphenylamine was avoided by first allowing the aluminum chloride to complex with an excess of hexanoyl chloride as solvent and then adding triphenylamine. When an excess of hexanoyl chloride was used, the only product isolated was *p,p',p''*-trihexanoyltriphenylamine (61% yield).

Dodecanoyl chloride reacted with triphenylamine in the presence of zinc chloride to give a 62% yield of *p*-dodecanoyltriphenylamine when the reaction was allowed to proceed for 3 hr. at room temperature and the reactants were in a 1:1:1 ratio. This result was analogous to that obtained with hexanoyl chloride, and a higher yield of acylated product was obtained than when acetyl chloride was used.

Although acylation with aliphatic acid chlorides was successful in the presence of zinc chloride, less reactive acid chloride, such as benzoyl chloride and furanoyl chloride, failed to react. However, triphenylamine was readily benzoylated in the presence of aluminum chloride. When the reaction was carried out with an excess of benzoyl chloride as solvent, the only product isolated was *p,p',p''*-tribenzoyltriphenylamine (64% yield).

When dichloromethane was used as a solvent in the presence of aluminum chloride at 5°, it reacted with triphenylamine. Both chlorines were displaced and a low-molecular-weight polymer was formed. This was



avoided by the use of an inert solvent such as carbon disulfide. Alkylation failed to occur in the presence of zinc chloride even when a more reactive molecule such as an alkyl bromide was used. Alkyl-substituted triphenylamines were readily obtained by hydrogenation

of the corresponding acylated product. Thus, *p*-hexanoyl- and *p*-lauroyltriphenylamine gave *p*-hexyl- and *p*-dodecyltriphenylamine, respectively.

The identities of the various substituted products were established by elemental analyses, molecular-weight determinations, and by infrared absorption spectra. In addition to strong carbonyl absorption at 1670 cm^{-1} , the mono- and dihexanoyl derivatives showed absorption at 825 cm^{-1} characteristic of *para* disubstitution and at 755 and 695 cm^{-1} characteristic of monosubstituted aromatic compounds. The trisubstituted product, *p,p',p''*-trihexanoyltriphenylamine, showed absorption only at 825 cm^{-1} , as expected for disubstituted aromatic rings.

Experimental

Acetylation of Triphenylamine in the Presence of Zinc Chloride.—A solution of 39.2 g. (0.50 mole) of acetyl chloride in 100 ml. of dichloromethane was added at room temperature, during 5 min., to a slurry of 68.0 g. (0.50 mole) of zinc chloride suspended in a solution of 123.0 g. (0.50 mole) of triphenylamine in 1 l. of dichloromethane. The initial reaction was slightly exothermic. After the addition was completed, the mixture was heated under reflux for 20 hr. The reaction mixture was then poured into cold, dilute hydrochloric acid. The organic layer was separated, washed with water until the wash water was neutral, and then dried over anhydrous magnesium sulfate. The dichloromethane was removed by distillation and the residue was crystallized from 95% ethanol to give 95 g. (0.33 mole, 66% yield) of crude 4-acetyltriphenylamine. Further recrystallization from absolute alcohol resulted in 73 g. of product (m.p. 136–139°), and an additional recrystallization step gave 49 g. of product (m.p. 142–143°, b.p. 230–235° at 0.5 mm.).

Anal. Calcd. for $\text{C}_{20}\text{H}_{17}\text{NO}$: C, 83.7; H, 5.9; N, 4.9. Found: C, 83.9; H, 5.8; N, 4.8.

Unreacted triphenylamine (20 g., 0.082 mole) was recovered from the mother liquor after separation of the crude product.

When an identical mixture was heated under reflux for only 1 hr. after the addition was completed, the yield was only 30%. If the mixture was simply stirred at room temperature for 3 hr. after the addition, only unreacted triphenylamine was recovered.

Alternatively, acetic anhydride may be used in place of acetyl chloride.

Acylation of Triphenylamine with Hexanoyl Chloride in the Presence of Zinc Chloride.—To a suspension of 13.6 g. (0.10 mole) of zinc chloride in a solution containing 12.3 g. (0.050 mole) of triphenylamine in 100 ml. of nitrobenzene there was added 13.4 g. (0.10 mole) of hexanoyl chloride. The resulting mixture was stirred at room temperature for 4 hr. and then poured onto a mixture of 100 g. of ice and 10 ml. of concentrated hydrochloric

acid. The organic layer was washed successively with water, 5% sodium hydroxide, water, and saturated sodium chloride, and finally dried over anhydrous magnesium sulfate. Distillation under reduced pressure resulted in 10 g. (0.029 mole, 58% yield) of an iridescent, viscous liquid, b.p. 230–235° at 0.5 mm., n_D^{25} 1.6421.

Anal. Calcd. for $C_{24}H_{25}NO$: C, 83.9; H, 7.3; N, 4.1. Found: C, 83.5; H, 7.0; N, 4.2.

The infrared spectrum exhibited absorption at 1670, 825, 755, and 695 cm^{-1} , and the ultraviolet spectrum in methanol exhibited λ_{max} 232, 290, and 350 $m\mu$ (ϵ 1.14×10^4 , 1.1×10^4 , and 2.35×10^4 , respectively). Unreacted triphenylamine, b.p. 190–230° at 0.5 mm. (5 g., 0.02 mole), was recovered as a forecut of the distillation. Methylene chloride was used as the solvent in subsequent reactions to avoid the difficulty of removing nitrobenzene from the product.

In a series of experiments, the ratio of triphenylamine–hexanoyl chloride–zinc chloride was increased from 1:1:1 to 1:3:3. These results are summarized in Table I. The experimental conditions and the procedure for treating the products were as already described unless indicated otherwise. In experiment F the fractions were separated by distillation at 13–14 μ , with a pot temperature of 220–264°. In addition to the acylated products, a 37% yield of polymeric material (molecular weight, 1220, 9.7% N) was obtained.

Acylation of Triphenylamine with Hexanoyl Chloride in the Presence of Aluminum Chloride.—A solution of 37.7 g. (0.154 mole) of triphenylamine in 150 ml. of carbon disulfide was added dropwise, with rapid stirring, to a slurry of 60.9 g. (0.46 mole) of aluminum chloride and 62.2 g. (0.46 mole) of hexanoyl chloride at 4–5°. After the resulting brown mixture had been stirred at 4–5° for 5 hr., it was hydrolyzed with 250 ml. of water. One hundred milliliters of carbon disulfide was added and the organic layer was washed once with 200 ml. of 5% aqueous sodium hydroxide and three times with water. The solvent was removed at reduced pressure and the residual light brown oil (55.0 g.) was distilled to give 14.2 g. (0.041 mole, 27% yield) of monohexanoyltriphenylamine, b.p. 230° at 1 μ .

Anal. Calcd. for $C_{24}H_{25}NO$: C, 83.9; H, 7.3; N, 4.1; mol. wt., 343. Found: C, 83.3; H, 7.3; N, 4.0; mol. wt., 36 ± 17 .

Trihexanoyltriphenylamine, 29.9 g. (0.055 mole, 36% yield), b.p. 280° at 3 μ , was also recovered.

Anal. Calcd. for $C_{36}H_{45}NO_3$: C, 80.1; H, 8.4; N, 2.6; mol. wt., 539. Found: C, 80.5; H, 8.3; N, 2.8; mol. wt., 549 ± 27 .

This latter fraction was collected as an oil that solidified on long standing, to give an oily solid. An infrared spectrum of the former product showed absorption at 1670, 825, 755, and 695 cm^{-1} . The spectrum of the latter fraction also showed absorption at 1670 and 825 cm^{-1} , but there were no bands at 755 and 695 cm^{-1} .

In another experiment, 12.2 g. (0.050 mole) of triphenylamine was added to a slurry of 26.5 g. (0.20 mole) of aluminum chloride in 40.0 g. (0.30 mole) of hexanoyl chloride at 4–5°. The temperature was allowed to reach 25° gradually, and the mixture was stirred for 21 hr. The reaction mixture was then hydrolyzed with 150 ml. of water and the organic material was dissolved in 100 ml. of methylene chloride. The isolation was as described for the previous experiment. Distillation yielded 16.5 g. (0.0306 mole, 61.2% yield) of trihexanoyltriphenylamine, b.p. 258° at 3 μ .

Anal. Found: C, 79.8; H, 8.5; N, 2.6; mol. wt., 528 ± 21 .

Hydrogenation of *p*-Hexanoyltriphenylamine.—A solution of 34 g. (0.10 mole) of hexanoyltriphenylamine in 120 ml. of dioxane was hydrogenated during 17 hr. in the presence of 10 g. of copper chromite catalyst. The initial and final pressures were 2900 and 1700 p.s.i.g. at 25°. The maximum temperature of 250° resulted in a pressure of 4100 p.s.i.g.

The catalyst was removed by filtration. Distillation resulted in 27 g. (0.082 mole, 82 mole % yield) of *p*-hexyltriphenylamine, b.p. 195–200° at 0.5 mm.

Anal. Calcd. for $C_{24}H_{27}N$: C, 87.6; H, 8.2; N, 4.3. Found: C, 87.3; H, 8.2; N, 4.5.

The infrared spectrum did not exhibit carbonyl absorption and the ultraviolet spectrum in methanol exhibited λ_{max} 299 $m\mu$ (ϵ 1.95×10^4).

Acylation of Triphenylamine with Dodecanoyl Chloride in the Presence of Zinc Chloride.—Dodecanoyltriphenylamine was prepared in 62 mole % yield by the procedure described for hexanoyltriphenylamine except that dodecanoyl chloride was used. The product was a viscous liquid, b.p. 280–290° at 0.5 mm., which crystallized on chilling, m.p. 35°.

Anal. Calcd. for $C_{30}H_{37}NO$: C, 84.3; H, 8.7; N, 3.3. Found: C, 84.2; H, 8.6; N, 3.4.

The absorption spectra were identical with those described for hexanoyltriphenylamine. Triphenylamine (20.2 mole %) was recovered as a forecut from the distillation.

Hydrogenation of *p*-Dodecanoyltriphenylamine.—Hydrogenation of dodecanoyltriphenylamine was carried out as described for hexanoyltriphenylamine. *p*-Dodecyltriphenylamine, b.p. 244–250° at 0.2 mm., was obtained in 53 mole % yield, n_D^{25} 1.5473.

Anal. Calcd. for $C_{30}H_{39}N$: C, 87.2; H, 9.4; N, 3.4. Found: C, 87.2; H, 9.9; N, 3.5.

The absorption spectra were identical with those just described for hexyltriphenylamine.

Acylation of Triphenylamine with Benzoyl Chloride in the Presence of Aluminum Chloride.—To a rapidly stirred slurry of 79.5 g. (0.60 mole) of aluminum chloride in 182.4 g. (1.20 moles) of benzoyl chloride at 25° was added 49 g. (0.20 mole) of triphenylamine. It was necessary to use an ice bath to keep the temperature at 25°. The resulting dark brown homogeneous mass was stirred for an additional 23.5 hr. at room temperature, cooled in dry ice–acetone, and treated with 4 *M* sodium hydroxide. The resulting mixture was refluxed for 1 hr. and cooled; then 500 ml. of methylene chloride was added to dissolve the solid material. The organic layer was washed with 4 *M* sodium hydroxide to remove residual benzoic acid and then washed continuously with water until the wash water was neutral. The emulsion which formed was separated from the organic layer and the latter was poured into ligroin. The precipitate was filtered and dried to give 70.9 g. (64% yield) of *p,p',p''*-tribenzoyltriphenylamine, m.p. 173.5–175.5°. The product was recrystallized from a mixture of chloroform and isopropyl alcohol. An infrared spectrum showed absorption at 1660 and 825 cm^{-1} and the ultraviolet spectrum in chloroform exhibited λ_{max} 248, 382 $m\mu$ (ϵ 3.9×10^4 , 4.4×10^4).

Anal. Calcd. for $C_{39}H_{27}NO_3$: C, 83.9; H, 4.9; N, 2.5; mol. wt., 557. Found: C, 83.5; H, 5.4; N, 2.5; mol. wt., 585 ± 29 .

Unreacted triphenylamine was recovered from the ligroin after the precipitation.