Triamides Prepared by the Diacylation of Amides[1]

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Nine new aliphatic and α,β-unsaturated triamides were prepared from acyl chlorides and amides in the presence of pyridine or α-substituted pyridines. Factors which affect the extent of amide acylation are (1) the sequence of reactant and pyridine mixing; (2) temperature; and (3) substitution at the α positions of both acyl chloride and the pyridine.

Triamides[2] have received little more than passing attention. Their preparation is encountered in Titherley's 1904 listing[3] of methods for acylating amides. Preparation of triamides is also treated in a 1964 summary[4] of more recent contributions dealing with amide acylation.

The reported procedures for preparing triamides are not only few but also lack generality. The work reported here was undertaken initially to provide a method of preparing α,β-unsaturated triamides, but then was extended to include aliphatic triamides as well.

The procedure developed during this investigation was based on the report[5] by Thompson, who observed that an aroyl chloride–pyridine mixture, at an optimum temperature of $-60°$, aroylated amides directly to triamides. This procedure was effective in the preparation of 25 triamides. However, in the aliphatic series, the procedure afforded diamides but no triamides.

Through modification of the Thompson method, triacetamide (**1**) has been prepared conveniently in 80–90% yield. The procedure consisted in treating a cooled, anhydrous methylene chloride solution of 2 equiv of acetyl chloride with slightly more than 2 equiv of 2,6-dimethylpyridine. One equivalent of acetamide was added and the resulting mixture was warmed to *ca.* 10° over a period of 18 hr. This sequence of adding base and then amide to the solution of the acid chloride is referred to as the "normal" mixing sequence in Table I and elsewhere in this paper. Reversing the sequence of mixing by adding the base to a methylene chloride solution of acetyl chloride and acetamide resulted in no substantial change in the yield of **1**. However, a decrease in the yield of tripropionamide (**2**) was observed by reversing the mixing sequence, and the inferior yield of the α,β-unsaturated triamide, **9**, very likely can be attributed to its preparation by the "reversed" rather than the "normal" mixing sequence. When acetamide was acetylated using the same base but at 25° rather than $-40°$, a decrease in the yield of triacetamide resulted. This result is consistent with Thompson's earlier finding[5] of inferior yields obtained at higher initial reaction temperatures.

Triacetamide (**1**) also has been synthesized[6] by the acid-catalyzed acetylation of diacetamide with ketene.

TABLE I

TRIAMIDES PREPARED BY DIACYLATION OF AMIDES

$$2RCOCl + RCONH_2 \longrightarrow (RCO)_3N + 2HCl$$

No.	Triamide	Mixing sequence[a]	Initial temp, °C	Base[b]	Yield,[c] %
1	$(CH_3CO)_3N$	Normal	−40	2,6-DMP	82
		Reverse	25	2,6-DMP	55[d]
		Reverse	−40	2,6-DMP	89
2	$(CH_3CH_2CO)_3N$	Normal	−35	2,6-DMP	81
		Reverse	−35	2,6-DMP	Low[d]
3	$[(CH_3)_2CHCO]_3N$	Normal	−35	2,6-DMP	75
		Normal	−35	Pyr	0
4	$[(CH_3)_3CCO]_3N$	Normal	−35	2,6-DMP	0
		Normal	−35	Pyr	0
5[e]	$[CH_2{=}C(CH_3)CO]_3N$	Normal	−20	Pyr	51
6	$(CH_2{=}CHCO)_3N$	Normal	−30	2,6-DMP	52
		Normal	−20	Pyr	0
7	$[(CH_3)CH{=}CHCO]_3N$	Normal	−40	2-MP	61
		Normal	−20	Pyr	0
8	$[(CH_3)_2C{=}CHCO]_3N$	Normal	−35	2,6-DMP	53
9	$[(CH_3)CH{=}C[CH_3)CO]_3N$	Reverse	−20	Pyr	8
10	$[CH_2(CH_2)_2CH{=}CCO]_3N$	Normal	−35	Pyr	58
11	$[CH_2(CH_2)_3CH{=}CCO]_3N$	Normal	−40	Pyr	84

[a] "Normal" mode of addition involves adding the amide to a solution of acid chloride and base in methylene chloride. "Reverse" mode of addition involves adding the base to a solution of acid chloride and amide in methylene chloride. [b] 2,6-DMP, 2,6-dimethylpyridine; 2-MP, 2-methylpyridine; Pyr, pyridine. [c] Reported yield is based on the weight of purified product unless otherwise indicated. [d] Reported yield is based on the weight of crude product or spectral analysis. [e] R. T. LaLonde and R. I. Aksentijevich, *Tetrahedron Lett.*, 23 (1965).

The melting point of our triacetamide corresponds with that reported.[6] The spectral properties (Experimental Section) are also consistent with the properties expected. In addition, the structure was substantiated by chemical means. Reduction of **1** with excess lithium aluminum hydride afforded triethylamine as the major nitrogeneous product. Earlier a report had been made[7] that the preparation of triacetamide had been achieved from the action of acetyl chloride on sodium diacetamide. However, the reported melting point (77°) is not the same as that found for our triacetamide. Presumably, the material isolated in this earlier attempted synthesis was diacetamide (mp 78°).

The influence of the base employed is large. When pyridine was substituted for 2,6-dimethyl- or 2-methylpyridine, neither the triamide **3** nor any of the α,β-

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(2) Previously, the general names triacylamide and tertiary amide have been applied to $(RCO)_3N$ by various workers. We now prefer the general name triamide on the basis that these compounds are N-acylated derivatives of diamides (RCONHCOR), the latter name being derived from the particular name diacetamide used by *Chemical Abstracts* for $CH_3CONHCOCH_3$.

(3) A. W. Titherley, *J. Chem. Soc.*, **85**, 1684 (1904).

(4) E. S. Rothman, S. Serota, and D. Swern, *J. Org. Chem.*, **29**, 646 (1964).

(5) Q. B. Thompson, *J. Amer. Chem. Soc.*, **73**, 5841 (1951).

(6) N. V. Smirnova, A. P. Skoldinov, and K. A. Kocheshkov, *Dokl. Akad. Nauk, SSSR*, **84**, 737 (1952).

(7) J. N. Rakshit, *J. Chem. Soc.*, **103**, 1561 (1913).

unsaturated triamides **6** or **7** were produced. In these cases anhydrides and diamides were formed. This result is in keeping with the earlier observation[5] that acylation of aliphatic amides by aliphatic acid chlorides in the presence of pyridine gives diamides and not triamides. However, the use of pyridine is satisfactory in the preparation of α,β-unsaturated triamides substituted at the α position, *i.e.*, triamides **5**, **10**, and **11**.

The standard procedure, which evolved during the course of this investigation, allowed for a gradual increase of temperature during the course of the reaction. This warm-up procedure was employed in both normal and reverse mixing experiments. The importance of the warm-up procedure was apparent in attempts to prepare tri(1-cyclopentene-1-carbonyl)amide (**10**). In one attempt, the reagents were mixed at −35° in the "normal" sequence. During the first 30 min of the reaction, a white solid formed, but most of this dissolved over the course of 20 hr when the reaction mixture was warmed gradually to 10°. Subsequent recooling of the mixture did not reprecipitate solid. After having been warmed again to room temperature, the reaction mixture was processed in the customary manner and a 58% yield of **10** was obtained. However, when the reaction mixture was allowed to stand at −20° for 4 hr after initial formation of the solid at −35°, no triamide was obtained.

Attempts to prepare tripivalamide using both pyridine and 2,6-dimethylpyridine in the normal mixing sequence gave pivalic anhydride. Water necessary for the formation of pivalic anhydride presumably is that introduced during the work-up procedure and reacts either with an intermediate, one which was incapable of further acylation because of steric crowding, or an extremely labile tripivalamide.

Experimental Section

General Procedures.—Spectra were determined as follows: nmr, $CDCl_3$ solution, 1% TMS, Varian A-60A; ir $CHCl_3$ solution in 0.05-mm cells, Perkin-Elmer 137 and 621; uv, in solution as indicated, Cary 11; mass, Perkin-Elmer Hitachi RMU6, direct inlet, operating at 70 eV. Vapor phase chromatograms were obtained on a Varian Aerograph 200 equipped with a thermal conductivity detector. Melting points were determined on a Köfler micro hot stage and are uncorrected. Elemental analyses were performed by the analytical laboratory at the State University College of Forestry, Syracuse, N. Y., and Galbraith Laboratories, Knoxville, Tenn.

Preparation of Reagents and Solvents.—Anhydrous methylene chloride was prepared by stirring technical-grade methylene chloride with calcium hydride for at least 1 day and then distilling. The anhydrous solvent was stored over calcium hydride. Anhydrous pyridine, 2-methylpyridine, and 2,6-dimethylpyridine were prepared by refluxing with anhydrous barium oxide for at least 12 hr and then distilling. These anhydrous bases were stored over barium oxide.

Reagent grade acetyl chloride was used as obtained from the supplier. The higher saturated acyl chlorides were prepared from the corresponding carboxylic acid and phosphorous trichloride. Acrylyl chloride was prepared from acrylic acid and benzoyl chloride. Other α,β-unsaturated acyl chlorides were prepared from the corresponding carboxylic acid and thionyl chloride.

Description of the Acylating Apparatus.—Amide acylations were conducted in a long-neck, 500-ml, round-bottom flask resting on the bottom of a 4-l. dewar flask. The neck of the flask extended above the top of the dewar flask in order to minimize contamination of the reaction mixture with condensed water. The reaction mixture in the flask was stirred magnetically. Dry Ice was added to *ca.* 500 ml of 2-propanol in the dewar flask to establish an initial reaction temperature of *ca.* −40°. This cooling mixture would warm to *ca.* 10° during the course of a typical acylation reaction.

Triacetamide (1).—The following detailed description of the synthesis of **1** is typical of the procedure employed to prepare the triamides by the "normal" order of reagent mixing.

A 15.6-g sample (0.20 mol) of acetyl chloride was dissolved in 200 ml of methylene chloride and the mixture was cooled to −40°. A deep amber-colored[8] solution resulted when 26 ml (0.22 mol) of 2,6-dimethylpyridine was added rapidly with vigorous stirring.

Immediately thereafter, 5.9 g (0.10 mol) of acetamide was added in one portion and the color of the solution diminished greatly in intensity. With continued stirring, the reaction mixture was allowed to warm to 10° over the next 18-hr period.

The heterogeneous mixture was rapidly washed with 50 ml of 1 *N* hydrochloric acid, 5% aqueous sodium bicarbonate, and water, and then dried over anhydrous magnesium sulfate. Removal of the solvent on a rotary evaporator gave a liquid product, whose nmr exhibited only a methyl singlet at τ 7.65. Distillation through a short-path apparatus afforded 11.8 g (82%) of analytically pure **1**: bp 44–46° (0.01 mm); $n^{20}D$ 1.4468; mp 10–12° (lit.[6] mp 8–10°); ir 1740 cm^{-1}; uv max (MeOH) 243 nm (ϵ 490); mass spectrum *m/e* 143 (M^+).

Anal. Calcd for $C_6H_9NO_3$: C, 50.36; H, 6.33; N, 9.79. Found: C, 50.29; H, 6.45; N, 9.55.

The detailed procedure described immediately below for the preparation of **1** is typical of that employed in all other "reverse" order of mixing experiments.

A 15.6-g sample (0.20 mol) of acetyl chloride and 5.9 g (0.10 mol) of anhydrous acetamide were dissolved in 200 ml of methylene chloride and the mixture was cooled to −40°. With vigorous stirring, 26 ml (0.22 mol) of 2,6-dimethylpyridine was added dropwise over a 45-min period. With continued stirring, the reaction was warmed to 10° over the next 20-hr period.

The product from this reaction was isolated in a manner identical with that used in the previously described experiment. Removal of the solvent on the rotary evaporator afforded 14.0 g of crude product, which by comparison (nmr and ir) was identical with **1**.

Attempted Synthesis of Triacetamide (1).—A 15.6-g sample (0.02 mol) of reagent grade acetyl chloride and 5.9 g (0.10 mol) of anhydrous acetamide were dissolved in 200 ml of anhydrous methylene chloride at room temperature. With vigorous stirring, 26 ml (0.22 mol) of anhydrous 2,6-dimethylpyridine was added dropwise over a 40-min period.

The product from this reaction was isolated in a manner identical with that used in the two preceding syntheses. Removal of the solvent on the rotary evaporator afforded 8 g of crude product found to be 55% **1** from the integration of the τ 7.65 methyl singlet in the nmr. The appearance of resonance signals at τ 7.79 and 7.70 indicated the presence of acetic anhydride and diacetamide, respectively. No attempt was made to isolate pure products from this reaction.

Reduction of Triacetamide (1).—A 5.7-g sample (0.04 mol) of **1** was dissolved in 50 ml of anhydrous ether and the resulting solution was added dropwise to a slurry of 7.0 g (0.18 mol) of lithium aluminum hydride in 200 ml of anhydrous ether. During the addition of the triacetamide, a large amount of yellow solid formed. This disappeared on heating the reaction mixture to reflux overnight.

The excess lithium aluminum hydride was destroyed by the dropwise addition of water and the resulting inorganic salts were removed by filtration. The ether filtrate was concentrated by slowly distilling off the ether through a 40-cm, porcelain, saddle-packed, fractionating column. The crude product (1.6 g) was chromatographically analyzed on a 20-ft, 5% SF-96 silicone on Fluropak column (temperature 75°, helium flow rate 60 ml/min). Peaks were found at 0.4 (*ca.* 10%), 2.2 (*ca.* 30%), 3.6 (*ca.* 20%), and 8.8 min (*ca.* 40%). These retention times correspond to ethylamine, ethanol, diethylamine, and triethylamine, respectively. Separation of triethylamine by vpc gave pure triethylamine, picrate mp 172–175°.

Tripropionamide (2).—A 37-g sample (0.40 mol) of propionyl chloride, 300 ml of methylene chloride at −35°, 51 ml (0.44 mol) of 2,6-dimethylpyridine, and 14.5 g (0.20 mol) of propionamide were combined in the normal mixing sequence.

(8) The color of the solution obtained on mixing the acyl chloride and the pyridine varied with the pyridine and the acyl chloride used.

After 1 hr at *ca.* −35°, the reaction mixture produced a heavy precipitate. The heterogeneous system was warmed to *ca.* 10° over the next 20-hr period, during which time most of the solid present at the lower temperature dissolved.

Processing the reaction mixture in the customary manner afforded 33 g of crude, crystalline product. One recrystallization from pentane gave 30 g (81%) of off-white crystals. Sublimation at room temperature, at vacuum-pump pressure, yielded analytically pure, white, crystalline **2**: mp 30–31°; nmr τ 8.83 (t, 9, J = 7 Hz) and 7.34 (q, 6, J = 7 Hz); ir 1730, 1780, and 1170 cm^{-1}.

Anal. Calcd for $C_9H_{15}NO_3$: C, 58.37; H, 8.16; N, 7.56. Found: C, 58.44; H, 8.20; N, 7.56.

A 18.5-g sample (0.20 mol) of propionyl chloride, 26 ml (0.22 mol) of 2,6-dimethylpyridine in methylene chloride at −35°, and 7.2 g (0.10 mol) of propionamide were combined in the reverse mixing sequence. The reaction mixture was warmed to 10° over the course of 20 hr and thereafter was processed in the customary manner. Comparison (ir and nmr) of the 11 g of crude product revealed the presence of not only **2** but also substantial amounts of propionic anhydride, ir 1835 cm^{-1}, and some dipropionamide, nmr τ 1.17. No attempt was made to isolate pure compounds from this mixture.

Trisobutyramide (3).—A 21.2-g sample (0.20 mol) of isobutyryl chloride, 200 ml of methylene chloride at −35°, 25.5 ml (0.22 mol) of dimethylpyridine, and 8.7 g (0.10 mol) of isobutyramide were combined in the normal mixing sequence. The heterogeneous system was warmed to *ca.* 10° over the next 18-hr period.

Processing the reaction mixture in the customary manner afforded 21 g of crude product which was a mixture of a crystalline solid and a liquid. These were separated by filtration. The liquid (17 g, 75%) was distilled twice under reduced pressure to yield analytically pure **3**: bp 65–67° (0.05 mm); nmr τ 8.75 (d, 18, J = 7 Hz) and 6.90 (sp, 3, J = 7 Hz); ir 1715, 1175, and 1090 cm^{-1}.

Anal. Calcd for $C_{12}H_{21}NO_3$: C, 63.41; H, 9.24; N, 6.16. Found: C, 63.63; H, 9.21; N, 5.93.

During distillation of **3**, some diisobutyramide, mp 170°, collected in the condenser.

The solid was recrystallized once from hexane–cyclohexane and sublimed at 70° (<0.01 mm) to give 2.0 g (13%) of diisobutyramide: mp 175° subl; ir 3400, 1700, 1730, 1160, and 1190 cm^{-1}; nmr τ 8.84 (d, 12, J = 7 Hz), 6.92 (sp, 2, J = 7 Hz), and 1.3 (s, 1).

Anal. Calcd for $C_8H_{15}NO_2$: C, 61.12; H, 9.62; N, 8.91. Found: C, 61.28; H, 9.76; N, 8.89.

A pure sample of **3** stored in a sealed ampoule for 2 months at room temperature afforded diisobutyramide, mp 170°.

In another attempt to prepare **3**, 20 ml (0.22 mol) of pyridine was used instead of 2,6-dimethylpyridine. Otherwise, precisely the same reaction conditions as those described above were used. Processing the reaction mixture in the customary manner gave 12 g of crude product, whose nmr revealed, by the presence of the τ 1.3 signal (integrated intensity *ca.* 0.5 H) and one of two sets of methyl doublets, that *ca.* one-half was diisobutyramide. The other half of the crude reaction mixture appeared to be isobutyric anhydride based on the chemical shift of methinyl, τ 7.32 (sp), and methyl, τ 8.77 (d), signals. No attempt was made to isolate pure compounds from this mixture.

Attempted Synthesis of Tripivalamide (4).—A 13.0-g sample (0.11 mol) of pivalyl chloride in 100 ml of methylene chloride was cooled to −35°. A 14-ml sample (0.23 mol) of 2,6-dimethylpyridine was added rapidly with stirring to give a colorless, homogeneous solution which was held at this temperature for 2 hr with no evidence of coloration. A 5.45-g sample (0.054 mol) of pivalamide was then added in one portion and the heterogeneous mixture was warmed to *ca.* 10° during a 20-hr period. This mixture was then cooled again to *ca.* −40° and the hygroscopic solid present (about 17 g) was filtered off and, by an examination of its nmr spectrum, identified as 2,6-dimethylpyridine hydrochloride. An ir of the filtrate (CH_2Cl_2) displayed bands at 2080, 1980, 1810, 1770, 1740, and 1680 cm^{-1}. This filtrate was washed rapidly with 50 ml of 1 *N* hydrochloric acid, 5% aqueous sodium bicarbonate, and water, and then dried over anhydrous magnesium sulfate. Removal of the solvent at the rotary evaporator gave 9.5 g (93%) of a liquid product identified as pivalic anhydride by comparison infrared spectra. In another attempt to prepare **4**, 9.0 ml (0.11 mol) of pyridine was used instead of 2,6-dimethylpyridine. Otherwise the reaction conditions were the same as those described above. Processing the reaction mixture in the customary manner gave 10 g of pivalic anhydride identified by comparative ir spectra.

Triacrylamide (6).—A 23.8-ml sample (0.30 mol) of acrylyl chloride in 300 ml of methylene chloride was cooled to −30°. A 38-ml sample (0.33 mol) of 2,6-dimethylpyridine was added with stirring, over a period of 20 min. A colorless, homogeneous solution resulted. A 7.1-g sample (0.10 mol) of anhydrous acrylamide was added in one portion and the heterogeneous mixture was held at −30° for 1 hr. During this time a heavy precipitate formed, which made stirring impossible. The reaction was then removed from the dewar flask and left at room temperature overnight. On warming to room temperature most of the precipitate dissolved. Processing the reaction mixture in the customary manner afforded 17 g of crude, crystalline product. One recrystallization from cyclohexane gave a product, mp 65–70°. Prolonged heating in recrystallization solvent resulted in the formation of additional insoluble material, presumably polymer. Sublimation at 40° (<0.01 mm) of the once-crystallized product afforded 9.0 g (52%) of analytically pure **6**: mp 70–71°; nmr τ 3.5 (m) and 4.1 (m); ir 1720, 1630, and 1160 cm^{-1}; uv max (EtOH) 222 nm (ϵ 34,000).

Anal. Calcd for $C_9H_9NO_3$: C, 60.33; H, 5.06; N, 7.81. Found: C, 59.42; H, 5.20; N, 7.59.

When stored in a tightly sealed bottle at room temperature for 4 months the triacrylamide was converted into a material, presumably polymeric, which did not melt but decomposed at 250–300°.

In another attempt to prepare **6**, 84 g (0.92 mol) of acrylyl chloride in 3.0 l. of chloroform was cooled to −20° in a constant-temperature bath. On the dropwise addition of 90 ml (1.1 mol) of pyridine, an insoluble, red-brown oil formed. A 32-g sample (0.45 mol) of anhydrous acrylamide was added in one portion and the mixture was stirred at −20° overnight. Water was added and the resulting mixture was warmed to room temperature. The red-brown oil was insoluble in chloroform at room temperature and was separated from it. Washing the chloroform solution with 1 *N* hydrochloric acid, 5% aqueous sodium bicarbonate, and water (four 200-ml portions of each) followed by drying over anhydrous calcium chloride and evaporation of the solvent under vacuum gave an intractable, red-brown oil which was found to be insoluble in all common organic solvents and which did not crystallize on standing at reduced pressure.

Tricrotonamide (7).—A 21.8-g sample (0.21 mol) of crotonyl chloride in 200 ml of methylene chloride was cooled to −40°. A 23-ml sample (0.23 mol) of 2-methylpyridine was then added over a period of 10 min. An 8.5-g sample (0.10 mol) of anhydrous crotonamide was added in one portion and the heterogeneous mixture was warmed to room temperature during the course of the reaction.

Processing the mixture in the customary manner afforded 18 g of crude product. Two recrystallizations from cyclohexane afforded 13.3 g of analytically pure **7**: mp 104–105°; nmr 8.09 (q, 9, J = 6.5 and 1.5 Hz), 3.88 (d of q, 3, J = 15 and 1.5 Hz), 3.0 (d, of q, 3, J = 15 and 7 Hz); ir 1720, 1710, 1700, 1650, and 1190 cm^{-1}; uv max (95% EtOH) 235 nm (ϵ 41,000).

Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.15; H, 6.90; N, 6.33. Found: C, 64.90; H, 6.94; N, 6.12.

In another attempt to prepare **7**, 6.17 g (0.059 mol) of crotonyl chloride in 200 ml of methylene chloride was cooled to −20°. A 4.8-ml sample (0.06 mol of pyridine was added rapidly and immediately 2.49 g (0.028 mol) of crotonamide was introduced. The resulting mixture was held at −20° for 14 hr and thereafter processed in the customary manner to obtain 1.9 g of crude product identified as largely crotonic anhydride by comparative nmr, τ 3.10 ($CH_3CH{=}CH$), and ir, 1730, 1790, and 1660 cm^{-1}. No attempt was made at separation.

Tri-β,β-dimethylacrylamide (8).—An 11.9-g sample (0.10 mol) of β,β-dimethylacrylyl chloride in 100 ml of anhydrous methylene chloride was cooled to −35°. A 13-ml sample (0.11 mol) of 2,6-dimethylpyridine was rapidly added with vigorous stirring. A 4.8-sample (0.05 mol) of β,β-dimethylacrylamide was added immediately and the resulting heterogeneous mixture was warmed to 10° over the next 18-hr period. Stirring was continued during this period. Processing in the customary manner afforded 11 g of crude crystals. One recrystallization from hexane–cyclohexane yielded 7.0 g (53%) of a slightly colored product. Sublimation of the once recrystallized product under high vacuum at 50° afforded 1.69 g of analytically pure **8**: mp 102–103°; nmr τ 8.05 (d, 9, J = 1 Hz), 7.77 (d, 9, J = 1 Hz),

and 4.02 (m, 3); ir 1685, 1626, 1200, and 1160 cm^{-1}; uv max (MeOH) 250 nm (ϵ 34,000).

Anal. Calcd for $C_{15}H_{21}NO_3$: C, 68.42; H, 8.04; N, 5.32. Found: C, 68.59; H, 8.07; N, 5.31.

Tritiglamide (9).—A solution of 2.57 g (0.02 mol) of tiglyl chloride, bp 63–66° (10 mm), and 1.0 g (0.01 mol) of tiglamide, mp 76–78°, in 40 ml of methylene chloride was cooled to −20°. A 1.6-ml sample (0.02 mol) of pyridine was added slowly with shaking and the resulting homogeneous solution was warmed to −5° over a 12-hr period and then allowed to remain at room temperature for 1 day. Processing this solution in the customary manner afforded 1.8 g of a crude, liquid product. Crystallization from cyclohexane produced 300 mg of a solid which melted over a wide range. A thin layer chromatogram, developed with 2% methanol in chloroform, revealed that the solid consisted of two components (R_f 0.3 and 0.6 on silica gel GF-254). Column chromatography employing 20 g of 100 mesh activated silica gel eluted with 200 ml of chloroform afforded first 166 mg of **9** exhibiting only a single spot on tlc and showing physical properties as follows: mp 80–83°; nmr τ 8.2 (m, 18) and 3.5 (m, 3); ir 1700, 1660, and 1250 cm^{-1}.

Anal. Calcd for $C_{15}H_{21}NO_3$: C, 68.42; H, 8.04; N, 5.32. Found: C, 68.44; H, 8.10; N, 5.21.

The second compound eluted appeared to be ditiglamide: mp 88–94°; ir 3510, 1750, 1710, 1680, and 1650 cm^{-1}; nmr τ 8.2 (m, 12), 3.5 (m, 2), and 1.5 (s, 1, NH).

Tri(1-cyclopentene-1-carbonyl)amide (10).—1-Cyclopentene-1-carboxylic acid was prepared from cyclopentanone by the method of Cook and Linstead[11] and converted with thionyl chloride into 1-cyclopentenylcarboxylyl chloride, bp 57° (13 mm). To 5.22 g (0.040 mol) of the acid chloride in 50 ml of methylene chloride cooled to −35° was added from a syringe 3.5 ml (0.043 mol) of anhydrous pyridine. Immediately 2.22 g (0.02 mol) of 1-cyclopentene-1-carboxamide, mp 210° subl, was stirred into the solution. After 30 min at −35° a white solid formed which prevented effective stirring. The heterogeneous mixture was warmed to 10° during a 20-hr period. During this time most of the solid present at −35° had dissolved and did not reprecipitate on cooling to −35°. The mixture again was warmed to room temperature and was processed in the customary manner. In this way was obtained 5.0 g of crude crystals, which by comparative spectra contained 19% anhydride: nmr 7.94 (m, 6), 7.38 (m, 12), and 3.03 (t, 3); ir 1730 and 1780 cm^{-1}. Two recrystallizations of crude solid from cyclohexane afforded 3.5 g of analytically pure **10**: mp 126–131°; nmr τ 8.00 (m, 6), 7.45 (m, 12), and 3.39 (m, 3); ir 1748, 1710, 1692, and 1640 cm^{-1}; uv max (MeOH) 239 mμ (ϵ 28,000); mass spectrum *m/e* 299 (M^+) and 95 (100).

Anal. Calcd for $C_{18}H_{21}NO_3$: C, 72.22; H, 7.07; N, 4.68. Found: C, 72.09; H, 7.20; N, 4.62.

Tri(1-cyclohexene-1-carbonyl)amide (11).—Cyclohexene-1-carboxylic acid, mp 30°, was prepared from cyclohexanone *via* the intermediate cyanohydrin by a procedure analogous to that reported by Cook and Linstead[9] for the synthesis of cyclopentene-1-carboxylic acid.

A 28.8-g sample (0.20 mol) of cyclohexene-1-carboxylyl chloride, bp 95° (17 mm), in 200 ml of methylene chloride was cooled to −40°. An 18-ml portion (0.22 mol) of pyridine was added with vigorous stirring over a period of 5 min. Immediately 12.5 g (0.10 mol) of cyclohexene-1-carboxamide, mp 130–133°, was added and the heterogeneous mixture was then warmed to 12° during the next 20 hr. Work-up in the customary manner gave 33 g of off-white crystals, mp 100–110°. Recrystallization once from hexane–cyclohexane gave 29 g, mp 112–120°. Analytically pure material was obtained by column chromatography of a 5.0-g sample.

The column (90 g of 100 mesh activated silica gel) was eluted with benzene and then 3% anhydrous ethyl acetate in benzene to give 2.4 g of **11**: mp 119–121°; nmr τ 8.37 (m, 12), 7.75 (m, 3), and 3.35 (m, 3); ir 1730, 1680, 1670, and 1220 cm^{-1}; uv max (EtOH) 236 nm (ϵ 21,000); mass spectrum *m/e* 341 (M^+) and 109 (100).

Anal. Calcd for $C_{21}H_{27}NO_3$: C, 73.90; H, 7.87; N, 4.10. Found: C, 73.62; H, 8.04; N, 3.85.

Registry No.—**1**, 641-06-5; **2**, 22950-76-1; **3**, 22950-77-2; **6**, 22950-79-4; **7**, 22950-80-7; **8**, 22950-81-8; **9**, 22950-90-9; **10**, 22950-82-9; **11**, 22950-83-0; diisobutyramide, 3668-74-4; ditiglamide, 22950-91-0;

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Bistriphenylsilyl Chromate. Oxidation of Olefins and Use in Ethylene Polymerization

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Bistriphenylsilyl chromate oxidatively cleaves olefins, giving the corresponding aldehydes and ketones along with reduced organochromium species. The reaction appears to be concerted. The silyl chromate also polymerizes ethylene at high pressure without any added cocatalysts. The active polymerization initiator is believed to be a low-valence organochromium compound.

There is increasing interest in highly specific reactions of organic derivatives of transition metals. Illustrative are olefin polymerization,[1] hydrogenation,[2] oxidation,[3] hydroformylation,[4] etc. Generally, these reactions involve a low-valence compound of the metal, and this fact stimulated the present interest in the mechanism of oxidation–reduction interactions of organic derivatives of transition metals.

Bistriphenylsilyl chromate[5] is a red crystalline solid, containing hexavalent chromium. It is easily prepared from triphenylsilanol and chromium trioxide. It is a

$$2(C_6H_5)_3SiOH + CrO_3 \xrightarrow{MgSO_4} (C_6H_5)_3SiO\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr}}OSi(C_6H_5)_3 + H_2O \quad (1)$$

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powerful oxidizing agent which enters into a number of complex reactions.

Results and Discussion

Treatment of a heptane or carbon tetrachloride solution of bistriphenylsilyl chromate with pentene-1,

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