Highly Branched Carbonic–Phosphoric and Carbonic–Carboxylic Anhydrides. The Nuclear Magnetic Resonance Methyl Splitting in 2,4-Dimethyl-3-pentyl Derivatives[1]

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Highly branched carbonic–carboxylic anhydrides (**1**) have been prepared from 2,4-dimethyl-3-pentanol and 2,3,4-trimethyl-3-pentanol. Both give *p*-nitrobenzanilide with aniline. The corresponding carbonic–phosphoric anhydrides give urethans with amines. Thiolcarbonic–phosphoric anhydrides (**7**) have been prepared from *t*-butyl mercaptan and 2,4-dimethyl-3-pentanethiol (for which a suitable synthesis has been developed); these anhydrides disproportionate at room temperature. With aniline they yield dialkyl thiolcarbonates, N-phenyl alkylthiolurethans, and diphenylurea. Many of the derivatives of the 2,4-dimethyl-3-pentyl system and its 3-methyl homologs show four peaks for the methyl protons of the isopropyl groups, owing to the asymmetry inherent in the molecule.

Earlier papers have described carbonic–carboxylic anhydrides derived from *t*-butyl alcohol[2] (**1**) and *t*-butyl mercaptan (**2**).[3] Carbonic–phosphoric anhydrides (**3**)

ROCOOCOAr **1** RSCOOCOAr **2**

1a, R = *t*-Bu; Ar = $p\text{-O}_2\text{NC}_6\text{H}_4$
1b, 2b, R = $[(\text{CH}_3)_2\text{CH}]_2\text{CH}$; Ar = $p\text{-O}_2\text{NC}_6\text{H}_4$
1c, 2c, R = $[(\text{CH}_3)_2\text{CH}]_2\text{CCH}_3$; Ar = $p\text{-O}_2\text{NC}_6\text{H}_4$

derived from *t*-butyl alcohol have been found[4] to react readily with amines to form *t*-butoxycarbonyl derivatives **4**, and to form *t*-butoxycarbonyl azide **5** when treated with sodium azide.[5] Attack of these nucleophiles takes place only at the carbonate carbonyl group, and not at the phosphorus. The present paper describes anhydrides of types **1** and **3**, in which the *t*-butyl group is replaced by a more highly branched group, such as 2,4-dimethyl-3-pentyl or the 2,3,4-trimethyl-3-pentyl. We have also prepared some thiolcarbonic–phosphoric anhydrides (**7**), to see how their behavior compares with that of the oxygen compounds such as **3**.

ROCOOPO(OEt)_2
3a, R = *t*-Bu
b, R = $[(\text{CH}_3)_2\text{CH}]_2\text{CH}$
c, R = $[(\text{CH}_3)_2\text{CH}]_2\text{CCH}_3$

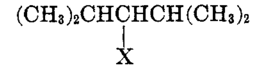
$$\mathbf{3a} + \text{RNH}_2 \longrightarrow \underset{\mathbf{4}}{(\text{CH}_3)_3\text{COCONHR}}$$

$$\underset{\mathbf{5}}{(\text{CH}_3)_3\text{COCON}_3}$$

$$\text{RSH} \xrightarrow[\text{3. ClPO(OEt)}_2]{\text{1. NaH or KO-}t\text{-Bu} \quad \text{2. CO}_2} \text{RSCOOPO(OEt)}_2$$

6a, R = $(\text{CH}_3)_3\text{C}$ **7a**, R = $(\text{CH}_3)_3\text{C}$
b, R = $[(\text{CH}_3)_2\text{CH}]_2\text{CH}$ **b**, R = $[(\text{CH}_3)_2\text{CH}]_2\text{CH}$

The *t*-butylthiolcarbonic–phosphoric anhydride was prepared readily from *t*-butyl mercaptan by carbonation and phosphorylation.[2-4] The preparation of **6b**, 2,4-dimethyl-3-pentanethiol (diisopropylcarbinyl mercaptan), from the corresponding alcohol proved troublesome. It is claimed,[6] without experimental detail, that treatment of 2,4-dimethyl-3-pentanol with hydrogen sulfide over thoria yielded the corresponding thiol (**8b**). 3-Bromo-2,4-dimethylpentane (**8c**) has been obtained[7] in small yield by the von Braun reaction of phosphorus pentabromide on the 3-benzamido compound. Our attempts to prepare the bromide **8c** from the alcohol, **8a**, using hydrogen bromide, or with bromine and triphenylphosphine,[8] yielded mixtures consisting of rearrangement and elimination products. The tosylate **8d** with thiourea gave only the thiourea tosylate salt in high yield. The tosylate group in **8d** was displaced satisfactorily by sodium benzyl mercaptide, to give the benzyl sulfide **8e**, which was converted by sodium–liquid ammonia into the desired thiol **8b**.



$$\underset{\displaystyle \text{X}}{(\text{CH}_3)_2\text{CH}\overset{}{\text{C}}\text{HCH}(\text{CH}_3)_2}$$

8a, X = OH
b, X = SH
c, X = Br
d, X = OTos
e, X = $\text{SCH}_2\text{C}_6\text{H}_5$
f, X = $\text{SCOSCH}[\text{CH}(\text{CH}_3)_2]_2$

The highly branched carbonic–carboxylic anhydrides **1b** and **1c** were prepared from the corresponding alcohols[9] by the carbonation procedure,[2] using sodium hydride in tetrahydrofuran (THF) to produce the alkoxide; **1b** was also obtained by preparation of 2,4-dimethyl-3-pentyl chlorocarbonate,[10] followed by treatment of this with *p*-nitrobenzoic acid. Treatment of both **1b** and **1c** with aniline gave reaction only at the carboxyl carbonyl, to form *p*-nitrobenzanilide.

The action of amines on the corresponding carbonic–phosphoric anhydrides **3b** and **3c** followed the opposite course, found earlier[5] for the *t*-butyl compound **3a**; thus,

$$\text{ROCOOPO(OEt)}_2 + \text{R}'\text{NH}_2 \longrightarrow$$
3b, R = $[(\text{CH}_3)_2\text{CH}]_2\text{CH}$
c, R = $[(\text{CH}_3)_2\text{CH}]_2\text{CCH}_3$

$$\text{ROCONHR}' + \text{HOPO(OEt)}_2$$
9a, R = $[(\text{CH}_3)_2\text{CH}]_2\text{CH}$; R′ = H
b, R = same; R′ = C_6H_5
c, R = same; R′ = CH_2COOEt
d, R = $[(\text{CH}_3)_2\text{CH}]_2\text{CCH}_3$; R′ = C_6H_5

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[1] Aided by Grant GP-7874 from the National Science Foundation.

[2] C. J. Michejda and D. S. Tarbell, *J. Org. Chem.*, **29**, 1168 (1964).

[3] (a) L. Wei and D. S. Tarbell, *ibid.*, **33**, 1884 (1968); (b) D. S. Tarbell and T. Parasaran, *ibid.*, **29**, 2471 (1964).

[4] (a) D. S. Tarbell and M. A. Insalaco, *Proc. Nat. Acad. Sci. U. S.*, **57**, 233 (1967); (b) *cf.* D. L. Griffith and M. Stiles, *J. Amer. Chem. Soc.*, **87**, 3710 (1965); (c) A. A. Shamshurin, *et al.*, *Zh. Obsch. Khim.*, **35**, 1877 (1965) [*Chem. Abstr.*, **64**, 1945 (1966); also English translation].

[5] M. A. Insalaco and D. S. Tarbell, *Org. Syn.*, in press.

[6] A. Mailhe, *Bull. Soc. Chim. Fr.*, [4] **15**, 328 (1914).

[7] N. J. Leonard and E. W. Nommensen, *J. Amer. Chem. Soc.*, **71**, 2812 (1949).

[8] G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *ibid.*, **86**, 964 (1964); G. A. Wiley, B. M. Rein, and R. L. Hershkowitz, *Tetrahedron Lett.*, 2509 (1964).

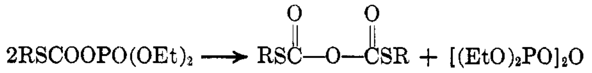
[9] 2,3,4-Trimethyl-3-pentanol was made by the method of F. C. Whitmore and R. S. George, *J. Amer. Chem. Soc.*, **64**, 1241 (1942).

[10] D. S. Tarbell and J. A. Price, *J. Org. Chem.*, **22**, 245 (1957).

the carbonate carbonyl was attacked by the amine, even in the highly branched compounds **3b** and **3c**.

Heating the anhydride **1c** derived from the tertiary alcohol at 60–100° gave an 88% yield of *p*-nitrobenzoic acid.[2]

The thiolcarbonic–phosphoric anhydrides **7a** and **7b** both disproportionated rapidly on standing according to the following reaction to yield the dithiol dicarbonate

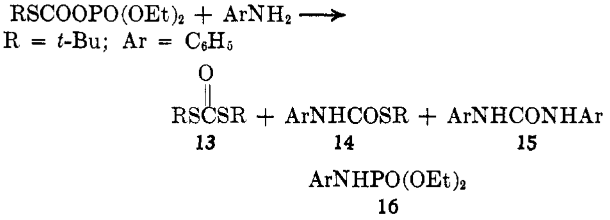


$$\underset{7}{2RSCOOPO(OEt)_2} \longrightarrow \underset{10,\ R\,=\,t\text{-Bu}}{RS\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}SR} + \underset{11}{[(EtO)_2PO]_2O}$$

10 and presumably tetraethyl pyrophosphate **11**. The evidence for the disproportionation reaction is the change in the infrared absorption of **7** from a single band at 1770 cm^{-1} (for **7**) to a spectrum with bands at 1770 and 1710 cm^{-1}; the latter are shown by the dicarbonate **10** obtained by heating the tricarbonate[11] **12** to 75°. Disproportionation of carboxylic–phosphoric anhydrides to pyrophosphates and carboxylic anhydrides has been reported.[12]

$$\underset{12,\ R\,=\,t\text{-Bu}}{RSCOOCOOCOSR} \xrightarrow[-CO_2]{75°} \underset{10}{RSCOOCOSR}$$

Treatment of the *t*-butylthiocarbonic–phosphoric anhydride **7a** with aniline yielded a mixture of di-*t*-butyl dithiolcarbonate (**13**, 6%), N-phenyl-*t*-butylthiolurethan (**14**, 65%), and diphenylurea (**15**, *ca.* 16%). There was obtained about 13% diethyl phenylamidophosphate (**16**), but this may have been formed from aniline and the dicarbonate **10** (formed by disproportionation of **7a**). The origin of the diphenylurea is not certain; it does not result from the action of aniline with the thiolurethan **14**, as shown by a separate experiment. It may be formed by successive reactions of two molecules of aniline with the disproportionation product, the dicarbonate **10**.[13]



$$RSCOOPO(OEt)_2 + ArNH_2 \longrightarrow$$

7a, $R = t\text{-Bu};\ Ar = C_6H_5$

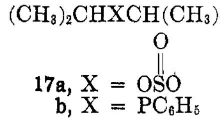
$$\underset{13}{RS\overset{O}{\overset{\|}{C}}SR} + \underset{14}{ArNHCOSR} + \underset{15}{ArNHCONHAr}$$

$$\underset{16}{ArNHPO(OEt)_2}$$

The reaction of aniline with the highly branched thiolcarbonic–phosphoric anhydride **7b** gave results similar to those obtained with the *t*-butyl compound **7a**, except that no amidophosphate **16** was isolated.

Nmr Spectra of 2,4-Dimethyl-3-pentyl and 2,3,4-Trimethyl-3-pentyl Compounds.—Many of these derivatives (*e.g.*, **7b**, **8f**, **1c**, the *p*-nitrobenzoate of 2,3,4-trimethyl-3-pentanol, the phenylurethan of this alcohol, and others) show four peaks for the protons of the methyls of the two isopropyl groups, indicating magnetic nonequivalence of two groups of six protons. Each group is split into a doublet by the adjacent hydrogen, $J = ca.$ 6.5 cps, and the difference in chemical shift in CCl_4 or $CDCl_3$ is about 3.5 cps. For the benzyl sulfide, **8e**, the chemical shift difference is 1 cps.

The magnetic nonequivalence of methylene protons adjacent to an asymmetric center has been extensively documented;[14] cases of nonequivalence of isopropyl protons have been observed occasionally.[15,16] A pertinent example is the quartet from the methyl protons in diisopropyl sulfite[17] (**17a**), and in diisopropylphenylphosphine[17] (**17b**). It was demonstrated for **17b** that the quartet did not collapse to a doublet at 150°, and hence the magnetic nonequivalence of methyl protons is due to inherent asymmetry[18] and not to hindered rotation.



$$(CH_3)_2CHXCH(CH_3)_2$$

17a, $X = O\overset{O}{\overset{\|}{S}}O$
b, $X = PC_6H_5$

The same situation undoubtedly obtains with the compounds studied by us.

Experimental Section[19]

***t*-Butylthiolcarbonic–Diethylphosphoric Anhydride (7a).**—This mixed anhydride was prepared by the carbonation method which has been described earlier;[3a,4a] complete exclusion of oxygen and moisture is necessary for this preparation. (THF is distilled from lithium aluminum hydride immediately before use, and the apparatus is dried by heating in a nitrogen stream with a Bunsen burner.)

To a solution of potassium *t*-butoxide (5.6 g) in 250 ml of THF was added dropwise with stirring *t*-butyl mercaptan (4.5 g) under nitrogen. The mixture was refluxed for 1 hr. The resulting slurry was cooled to −10° and dry carbon dioxide was passed into the flask for 2 hr with vigorous stirring. Diethyl chlorophosphate (8.6 g) in 50 ml of THF was added dropwise, and the mixture was stirred at 0° for 2 hr under nitrogen, then concentrated under vacuum at ambient temperature, and diluted with pentane. The precipitate was removed by centrifuging, suspended in pentane, and recentrifuged to remove further product. The solution was concentrated again and diluted with pentane to precipitate the remaining potassium chloride. The solvent was removed under vacuum at ambient temperature to give *ca.* 10 g of a colorless oil, which showed a carbonyl band at 1770 cm^{-1} (film). Other characteristic bands were at 1290 (P=O), 1155 (POEt), and 1020 cm^{-1} (POC). The nmr spectrum (CCl_4) showed the same signals as diethyl chlorophosphate and an additional singlet at δ 1.50 (*t*-butyl).

Anal. Calcd for $C_9H_{19}O_5PS$: C, 39.99; H, 7.09; P, 11.46; S, 11.86. Found: C, 40.23; H, 7.35; P, 11.39; S, 11.63.

The compound disproportionates very rapidly to the corresponding symmetrical anhydrides as shown by the change of the ir carbonyl absorption.

Instead of potassium *t*-butoxide, also sodium hydride can be used as base. Since the mixed anhydride cannot be purified by distillation, it is necessary to remove the mineral oil completely from the NaH by washing for several times with pentane and

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[11] A. W. Friederang and D. S. Tarbell, *Tetrahedron Lett.*, 5535 (1968).

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[14] References and discussion are available in two excellent reviews: (a) M. van Gorkon and G. E. Hall, *Quart, Rev.*, **22**, 14 (1968); (b) M. L. Martin and G. J. Martin, *Bull. Soc. Chim. Fr.*, 2117 (1966).

[15] N. S. Bowman, D. E. Rice, and B. R. Switzer, *J. Amer. Chem. Soc.*, **87**, 4477 (1965).

[16] C. van der Vlies, *Rec. Trav. Chim. Pays-Bas*, **84**, 1289 (1965).

[17] M. Brink, *Tetrahedron Lett.*, 4653 (1968). W. McFarlane, *Chem. Commun.*, 229 (1968). Also R. Keat, W. Sim, and D. S. Payne, *ibid.*, 191 (1968); A. Vigevani, *et al.*, *Tetrahedron*, **25**, 573 (1969). A similar case involving fluorine atoms in the dodecafluoro derivative of **8a** is reported by W. J. Middleton and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.* **86**, 4948. (1964).

[18] G. M. Whitesides, F. Kaplan, K. Nagarajan, and J. D. Roberts, *Proc. Nat. Acad. Sci. U. S.*, **48**, 1112 (1962).

[19] Ir spectra were recorded on a Beckman IR-10 spectrophotometer. Nmr spectra were recorded on a Varian A-60 instrument with tetramethylsilane as internal standard. *Chemical shifts are given in δ values, $\delta_{TMS} = 0$ ppm.* Vapor phase chromatography (vpc) was run isothermally using F & M Model 720 (thermal conductivity unit) with a 6 ft × 0.25 in. o.d. stainless steel column packed with 10% silicone gum rubber SE-30 (80–100 mesh). Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn. All melting points and boiling points are uncorrected.

finally with anhydrous THF. In this operation, loss of some NaH cannot be avoided and, therefore, it is almost impossible to determine the required amount of the chlorophosphate. In the reaction with aniline (see below), however, difficulties arose when potassium *t*-butoxide was used. For this reaction, the mixed anhydride was prepared using NaH as base. Using acetone as solvent for the above reaction[4c] gave very poor results.

2,4-Dimethyl-3-pentylthiolcarbonic–Diethylphosphoric Anhydride (7b).—Compound **7b** was prepared from 2,4-dimethyl-3-pentanethiol (**8b**) in the same way. The product was a colorless oil, with a carbonyl band at 1725 cm^{-1} (film). This compound also disproportionates to the corresponding symmetrical anhydrides.

Anal. Calcd for $C_{12}H_{25}O_5PS$: C, 46.12; H, 8.10; P, 9.91; S, 10.26. Found: C, 45.93; H, 8.03; P, 10.01; S, 10.02.

3-Tosyloxy-2,4-dimethylpentane (8d).—This compound was prepared from the alcohol **8a**, tosyl chloride, and pyridine at −10–0°. The tosylate precipitated as solid (mp 66–68°) and was recrystallized from pentane to give 255 g (88%) of 3-tosyloxy-2,4-dimethylpentane, mp 67–68° (mmp 37–62° with tosyl chloride). Ir and nmr spectra were consistent with this structure.

Anal. Calcd for $C_{14}H_{22}O_3S$: C, 62.18; H, 8.20; S, 11.86. Found: C, 62.50; H, 8.20; S, 12.00.

Reaction of 3-Tosyloxy-2,4-dimethylpentane with Thiourea.[20]—The tosylate (4.2 g) and 1.18 g of thiourea were refluxed in 20 ml of anhydrous alcohol for 60 min. The clear solution was concentrated under vacuum to give 3.67 g of white crystals. This product, however, showed no signals of an isopropyl group in the nmr spectrum [taken in D_2O or $(CD_3)_2SO$)], but only peaks corresponding to the tosyl group and to HDO or H_2O. It was identified as thiuronium tosylate by the ir spectrum (KBr), which showed bands at *ca.* 3200 (br, NH), 2515 (SH), 1670 ($C{=}N^+$), 1200, 1160, 1030, and 690 cm^{-1} ($ArSO_3^-$), mp 171–175° (lit.[21] mp 173–174°), and elemental analysis.

Anal. Calcd for $C_8H_{12}N_2O_3S_2$: C, 38.69; H, 4.87; N, 11.28; S, 25.82. Found: C, 38.80; H, 4.66; N, 11.21; S, 25.60.

The same product also was obtained when the reaction was carried out at room temperature using dimethylformamide as solvent.

Benzyl 2,4-Dimethyl-3-pentyl Sulfide (8e).—Benzylmercaptan (62.1 g) was added to 24.0 g of 50% sodium hydride suspension in 300 ml of anhydrous THF with stirring under nitrogen. The mixture was refluxed for 45 min. A solution of 145.6 g of 3-tosyloxy-2,4-dimethylpentane in 400 ml of anhydrous THF was added at once, and the resulting solution was refluxed for 6 hr with stirring under nitrogen. After the solution cooled to room temperature, 150 ml of water were added, and the organic layer was separated. The aqueous layer was diluted with saturated sodium chloride solution to separate it into two layers. The combined organic layers were washed with sodium chloride solution, dried, and concentrated. Vacuum distillation of the residue gave 53 g (48%) of a colorless liquid of bp 82–87° (0.35 mm), which gave one peak on vpc and one spot on tlc. The nmr spectrum (CCl_4) showed signals at δ (ppm) 0.90 [d, 12, J = 6.5 Hz, $(CH_3)_2CH$–], *ca.* 1.5–2.0 (m, 3), 3.55 (s, 2, $-SCH_2C_6H_5$), and 7.05 (s, 5, aromatics). Each peak of the isopropyl doublet was shifted into two signals, separated by *ca.* 1 cps.

Anal. Calcd for $C_{14}H_{22}S$: C, 75.61; H, 9.97; S, 14.42. Found: C, 75.56; H, 10.03; S, 14.73.

2,4-Dimethyl-3-pentanethiol (8b).—The above sulfide (77.3 g) in 700 ml of liquid ammonia was reduced by addition of sodium. Solid ammonium chloride was added to discharge the color, the ammonia was largely evaporated by flushing with nitrogen, and *ca.* 300 ml of ether was added. Dilute hydrochloric acid was added dropwise with stirring and cooling; the organic layer was separated and extracted with three portions of dilute hydrochloric acid and three portions of sodium chloride solution, dried, and concentrated. The thiol was separated from toluene by distillation over a 45-cm spinning-band column: yield, 28.6 g (62%); bp 152–153°. The product was homogeneous on tlc (chloroform–hexane, 1:1) and vpc. Characteristic ir bands (film) were at 2560 (SH), 1370, and 1360 cm^{-1} (*gem*-dimethyl). The nmr spectrum (CCl_4) showed a doublet at δ 0.85 [J = 6 cps, $(CH_3)_2$-CH–)] and two multiplets between 1.5 and 2.5.

Anal. Calcd for $C_7H_{16}S$: C, 63.56; H, 12.20; S, 24.24. Found: C, 63.70; H, 12.30; S, 24.26.

Phosphorothionic Acid O,O-Diethyl S-*t*-Butyl Triester.—*t*-Butyl mercaptan (9.0 g) in 100 ml of anhydrous THF was added to 5.0 g of the 50% sodium hydride suspension in 150 ml of anhydrous THF with stirring under nitrogen. After 1-hr refluxing, the mixture was cooled to room temperature, and 17.25 g of diethyl chlorophosphate in 100 ml of anhydrous ether was added. The mixture was stirred under nitrogen for 1 hr and then kept overnight at room temperature. The precipitate was removed by filtration over Celite, the solvent was evaporated, and the residue was distilled to give 10.2 g (45%) of the triester, bp 98–100° (1.5 mm). The product was homogeneous on vpc and tlc (chloroform–hexane, 1:1, and chloroform). The ir spectrum (film) showed bands at 1250 (P=O), 1160 (POEt), and 1010 cm^{-1} (POC). The nmr signal (CCl_4) of the *t*-butyl group was split into a doublet (J = 1.3 cps) by coupling with the phosphorus atom.

Anal. Calcd for $C_8H_{19}O_3PS$: C, 42.46; H, 8.46; P, 13.69; S, 14.17. Found: C, 42.51; H, 8.53; P, 13.46; S, 14.17.

Phosphorothionic Acid O,O-Diethyl S-2,4-Dimethyl-3-pentyl Triester.—This compound was analogously prepared from **8b**: yield, 50%; bp 86–87° (0.05 mm).

Anal. Calcd for $C_{11}H_{25}O_3PS$: C, 49.23; H, 9.39; P, 11.56; S, 11.95. Found: C, 49.42; H, 9.52; P, 11.44; S, 12.13.

N-Phenyl-2,4-dimethyl-3-pentylthiolurethan.—This compound was prepared by the action of phenyl isocyanate on the thiol **8b** in 92% yield, mp 112–113° (benzene–pentane).

Anal. Calcd for $C_{14}H_{21}NOS$: C, 66.90; H, 8.42; N, 5.57; S, 12.76. Found: C, 66.64; H, 8.55; N, 5.77; S, 12.96.

Reaction of *t*-Butylthiolcarbonic–Diethylphosphoric Anhydride (7a) with Aniline.—To a solution of the mixed anhydride in *ca.* 300 ml of anhydrous THF (prepared at −65° from 5.0 g of the 50% sodium hydride suspension, 9.0 g of *t*-butyl mercaptan, carbon dioxide, and 17.2 g of diethyl chlorophosphate) was added at −40° 9.3 g of aniline (distilled from zinc powder) in 50 ml of anhydrous THF. The mixture was stirred at −40° for 45 min, then kept in the refrigerator overnight, diluted with ether, and extracted with three portions of ice-cold diluted hydrochloric acid, three portions of ice-cold sodium carbonate solution, and three portions of ice-cold sodium chloride solution. During the sodium carbonate extraction a white solid precipitated, which was separated, washed with water and ether, and identified as *s*-diphenylurea (1.3 g) by comparison of its ir spectrum (KBr) with that of an authentic sample and by the melting point.

The organic solution was dried and evaporated under vacuum to give 8.3 g of a white solid which was identified as a mixture of di-*t*-butyl dithiolcarbonate (**13**), *s*-diphenylurea (**15**), N-phenyl-*t*-butylthiolurethan (**14**), and diethyl phenylamidophosphate (**16**) by the following data.

A sample was dissolved in $CDCl_3$ and filtered (the residue was *s*-diphenylurea); the nmr spectrum of this solution showed signals at δ 1.25 (m), 1.50 (s), 1.55 (s), *ca.* 4.2 (m), and *ca.* 7.3 (m).

The crude material (770 mg) was chromatographed on 50 g of neutral alumina, activity I, using as eluents petroleum ether (bp 30–75°), petroleum ether–benzene (1:1), benzene, and chloroform. The compounds obtained were characterized by comparison of the ir and nmr spectra with those of authentic samples and, if isolated as pure solids, also by the melting point as di-*t*-butyl dithiolcarbonate (**13**,[3a] *ca.* 6% of the crude product), N-phenyl-*t*-butylthiolurethan[22] (**14**, *ca.* 65%), diphenylurea (**15**, *ca.* 16%), and diethyl phenylamidophosphate (**16**, *ca.* 13%). Di-*t*-butyl dithiolcarbonate (**13**) could not be separated completely from the thiolurethan; the relative amounts were determined by nmr integration.

Reaction of 2,4-Dimethyl-3-pentylthiolcarbonic–Diethylphosphoric Anhydride (7b) with Aniline.—This reaction was carried out in the same way. The products (2.9 g, starting from 2.64 g of the thiol) were separated by column chromatography on alumina and identified by comparison with authentic samples as 2,4-dimethyl-3-pentyl dithiolcarbonate (*ca.* 29% of the crude product), N-phenyl-2,4-dimethyl-3-pentylthiolurethan (*ca.* 35%), and *s*-diphenylurea (*ca.* 36%). No amidophosphate was detected in this reaction.

Reaction of N-Phenyl-*t*-butylthiolurethan (14) with Aniline.—The thiolurethan 14 (0.5 g), aniline (0.5 g), and 1 drop of triethylamine were refluxed in 75 ml of anhydrous THF overnight. The solution was concentrated and diluted with anhydrous ether to precipitate a few milligrams of *s*-diphenylurea, identified

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[20] General procedure of D. Klamann and F. Drahowzal, *Monatsh.*, **83**, 463 (1952).

[21] L. Bauer and L. A. Gardella, Jr., *J. Org. Chem.*, **26**, 82 (1961).

[22] E. Dyer and J. F. Glenn, *J. Amer. Chem. Soc.* **79**, 366 (1957).

by its mp 237–239°. The solution was evaporated, and the remaining solid was starting material.

Bis(2,4-dimethyl-3-pentyl) Dithiolcarbonate.—Phosgene was passed for 30 min into a suspension of the sodium salt of 2,4-dimethyl-3-pentanethiol **8b** (prepared from 6.65 g of the thiol) in 200 ml of anhydrous THF with stirring and cooling. The mixture was stirred at room temperature for 1 hr, flushed with nitrogen to remove the excess of phosgene, concentrated under vacuum, diluted with anhydrous ether, and centrifuged. The solution was evaporated, and the remaining oil was distilled to give 5.9 g (41%) of a colorless oil, bp 106–108° (0.025 mm). The ir spectrum (film) showed bands at 1730, 1680, 1640 (C═O), 1460 (CH_3), 1385 and 1365 (*gem*-dimethyl), 860, and 810 cm^{-1}. Nmr signals (CCl_4) were at δ 0.85 [q, 12, $(CH_3)_2CH$, J = 6.5 cps], 2.95 [sextet, 2, $(CH_3)_2CH$] and 3.40 {t, 1, $[(CH_3)_2CH]_2CH$, J = 6.5 cps}.

Anal. Calcd for $C_{15}H_{30}OS_2$: C, 62.01; H, 10.41; S, 22.07. Found: C, 62.25; H, 10.52; S, 21.92.

2,4-Dimethyl-3-pentylcarbonic–*p*-Nitrobenzoic Anhydride (1b).—This product was obtained in 63% yield by the carbonation procedure using 5 g of 2,4-dimethyl-3-pentanol, 2.2 g of sodium hydride in mineral oil, carbon dioxide for 1.5 hr at Dry Ice temperature, and 8.8 g of *p*-nitrobenzoyl chloride, all in anhydrous THF. *p*-Nitrobenzoic anhydride (1.2 g) was isolated by dissolving the reaction mixture in cyclohexane. The carbonic–*p*-nitrobenzoic anhydride (8.4 g) melted at 77°, after crystallization from cyclohexane. The ir showed bands at 1795 and 1738 cm^{-1} in the carbonyl region. The nmr (in $CDCl_3$) showed the 12 CH_3 protons in four peaks (J = 6.8 cps) and chemical shift between doublets of 1.6 cps.

Anal. Calcd for $C_{15}H_{19}NO_6$: C, 58.25; H, 6.19; N, 4.53. Found: C, 58.22; H, 6.08; N, 4.33.

The same anhydride was obtained in poorer yield using potassium *t*-butoxide and also from 2,4-dimethyl-3-pentyl chlorocarbonate and *p*-nitrobenzoic acid. Treatment of the anhydride with aniline gave an 88% yield of *p*-nitrobenzanilide. Heating the anhydride (200 mg) at 190–200° for 40 min yielded 22 mg (23%) of *p*-nitrobenzoic anhydride and 122 mg (71%) of 2,4-dimethyl-3-pentyl *p*-nitrobenzoate, mp 65–66°. An authentic sample was prepared from the alcohol and *p*-nitrobenzoyl chloride.

2,3,4-Trimethyl-3-pentylcarbonic–*p*-Nitrobenzoic Anhydride (1c).—Compound **1c**, prepared by the procedure above, was obtained in 36% yield after recrystallization from petroleum ether, mp 48°; the ir (CCl_4) showed carbonyl bands at 1800 and 1750 cm^{-1}. *p*-Nitrobenzoic anhydride (30%) and a small amount of *p*-nitrobenzoic acid were also obtained.

Anal. Calcd for $C_{16}H_{21}NO_6$: C, 59.43; H, 6.55; N, 4.33. Found: C, 59.33; H, 6.53; N, 4.50.

The carbonic–carboxylic anhydride gave with aniline a 91% yield of *p*-nitrobenzanilide.

The anhydride began to decompose at 60–70°; 100 mg, heated at 90–100° for 30 min gave 46 mg (88%) of *p*-nitrobenzoic acid. The olefin presumably formed was not isolated.

2,4-Dimethyl-3-pentylcarbonic–Diethylphosphoric Anhydride (3b).—Compound **3b** was prepared from the carbonate derived from 5.0 g of the alcohol and diethyl chlorophosphate; it was obtained as a pale yellow oil. The isopropyl methyl groups showed as in other cases four peaks (J = 7.3 cps) with difference in chemical shift of 2.2 cps.

Treatment with dry ammonia in ether gave the known urethan,[10] mp 125–126°. Aniline gave a 90% yield of known **phenylurethan**[23] **(9b)**, mp 94°.

Reaction with glycine ethyl ester gave 75% of the corresponding urethan **9c**, mp 75–76°.

Anal. Calcd for $C_{12}H_{23}NO_4$: C, 58.75; H, 9.45; N, 5.71. Found: C, 58.60; H, 9.25; N, 5.73.

The same product was obtained from $O{=}C{=}NCH_2COOC_2H_5$ and the alcohol.

Hydrolysis of the urethan from glycine ethyl ester with base in aqueous dioxane gave the corresponding acid, mp 85–86°.

Anal. Calcd for $C_{10}H_{19}NO_4$: C, 58.28; H, 8.81; N, 6.45. Found: C, 55.29; H, 8.86, N, 6.34.

2,3,4-Trimethyl-3-pentylcarbonic–Diethylphosphoric Anhydride (3c).—Compound **3c** was prepared similarly from the corresponding alcohol; treatment with aniline gave the corresponding **urethan 9d** (84%), mp 91°. The isopropyl methyl groups showed four bands (J = 6.7 cps) and a difference of chemical shift of 1.6 cps.

Anal. Calcd for $C_{15}H_{23}NO_2$: C, 72.25; H, 9.30; N, 5.62. Found: C, 71.97; H, 9.39; N, 5.56.

Registry No.—**1b**, 21991-16-2; **1c**, 21991-17-3; **7a**, 21991-18-4; **7b**, 21991-19-5; **8b**, 21991-20-8; **8d**, 21991-21-9; **8e**, 21991-22-0; **9c**, 21991-23-1; **9c** (free acid), 21991-24-2; **9d**, 21991-25-3; phosphorothionic acid O,O-diethyl S-*t*-butyl triester, 7795-74-6; phosphorothionic acid O,O-diethyl S-2,4-dimethyl-3-pentyl triester, 21991-27-5; N-phenyl-2,4-dimethyl-3-pentylthiolurethan, 21991-28-6; bis(2,4-dimethyl-3-pentyl) dithiolcarbonate, 21991-29-7.

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[23] J. B. Conant and A. H. Blatt, *J. Amer. Chem. Soc.*, **51**, 1227 (1929).