protons appeared as a broad multiplet and the ratio of aromatic-aliphatic protons was found to be 4.56 (theoretical, 4.5).

10,11-Dihydro-5,5-diphenyldibenzo[*b,f*]silepin.[4]—To a stirred solution of 4.5 g. (0.026 mole) of 2,2'-dibromodibenzyl in 40 ml. of ether was added 38 ml. of an ethereal solution containing 0.52 mole of *n*-butyllithium,[7] while cooling with an ice bath. The mixture was stirred at room temperature for 4 hr. and then was added, during 45 min., to a stirred solution of 6.23 g. (0.0246 mole) of dichlorodiphenylsilane in 50 ml. of ether. The mixture was hydrolyzed and the organic layer was worked up in the usual manner. The residual material was washed with petroleum ether (b.p. 60–70°) and an insoluble substance was filtered off. This was dissolved in benzene and chromatographed on a column of alumina to give 1.36 g. (15%) of product, m.p. 170–172°. Recrystallization from petroleum ether (b.p. 77–115°) raised the melting point to 172.5–174°.

Anal. Calcd. for $C_{26}H_{22}Si$: C, 86.15; H, 6.12; Si, 7.74. Found: C, 86.49, 86.30; H, 6.32, 6.34; Si, 7.70.

The petroleum ether (b.p. 60–70°) was removed from the first filtrate, and the residue was distilled under reduced pressure to give two unidentified fractions and 4.1 g. of residue which could not be further purified.

Acknowledgment.—This research was supported in part by the United States Air Force under contract AF 33(616)-6463 monitored by the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio.

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The Reduction of 3-Ethyl-3-methylvaleronitrile by Grignard Reagents in the Presence of Ferric Chloride[1]

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Received April 30, 1963

In an attempt to catalyze the reaction of *t*-butylmagnesium chloride with 3-ethyl-3-methylvaleronitrile, it was observed that the nitrile was reduced in reasonable yields to the corresponding aldehyde.

Hauser and Humphlett[2] predicted that the Grignard reagent should be capable of reducing nitriles, but were not able to isolate hexanal from the reaction of *t*-butylmagnesium chloride with hexanenitrile. Mosher and co-workers[3] reinvestigated the reaction and studied the action of ethyl, isopropyl, and *t*-butyl Grignard reagents on trimethylacetonitrile. They found that the amount of reduction product increased while normal addition decreased as branching of the Grignard reagent increased. However, the yields of trimethylacetaldehyde obtained amounted to only 5–17% as the reaction temperature was varied from 35–150°.

When 3-ethyl-3-methylvaleronitrile was treated with *t*-butylmagnesium chloride in the present investigation, no reaction occurred in refluxing ether for up to 139 hours. The introduction of a small amount of ferric chloride, however, caused a fairly rapid change in the infrared absorption spectrum of a hydrolyzed sample of the reaction mixture. After continued heating, there was obtained 31% of 3-ethyl-3-methylvaleraldehyde.

Further study of the reaction of 3-ethyl-3-methylvaleronitrile with *t*-butylmagnesium chloride in the presence of ferric chloride did not lead to improved yields of the aldehyde. When isobutylmagnesium iodide was substituted for *t*-butylmagnesium chloride, 3-ethyl-3-methylvaleraldehyde resulted in 51% yield.

The reaction of trimethylacetonitrile with *t*-butylmagnesium chloride and ferric chloride was examined briefly. Trimethylacetaldehyde was isolated in 20% yield along with traces of carbonyl and hydroxyl containing compounds.

An attempt to reduce hexanenitrile by means of *t*-butylmagnesium chloride and ferric chloride afforded *t*-butyl pentyl ketone plus tarry condensation products.

Experimental[4]

Reaction of 3-Ethyl-3-methylvaleronitrile with *t*-Butylmagnesium Chloride and Ferric Chloride.—A Grignard reagent, prepared from 24.3 g. (1 g.-atom) of magnesium and 102 g. (1.1 moles) of *t*-butyl chloride in 350 ml. of anhydrous ether, was added during 1 hr. to a mixture of 25 g. (0.2 mole) of 3-ethyl-3-methylvaleronitrile, 3 g. of ferric chloride, and 100 ml. of anhydrous ether. The reaction mixture was stirred and refluxed for 200 hr., and hydrolyzed with 1:1 cold hydrochloric acid. The ether layer was separated, washed, dried, and concentrated in the usual manner. The residue was distilled through a 25-cm. helices-packed column to give 8 g. (31%) of 3-ethyl-3-methylvaleraldehyde, b.p. 165–170°, n^{25}_{D} 1.4258, plus an uncharacterized high-boiling residue.

Anal. Calcd. for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 74.54; H, 12.20.

Its 2,4-dinitrophenylhydrazone melted at 88–89° after recrystallization from ethanol.

Anal. Calcd. for $C_{14}H_{20}N_4O_4$: C, 54.53; H, 6.54. Found: C, 54.30; H, 6.34.

Reaction of 3-Ethyl-3-methylvaleronitrile with Isobutylmagnesium Iodide and Ferric Chloride.—A titrated[5] ether solution of 0.45 mole of isobutylmagnesium iodide was added dropwise to a mixture of 25 g. (0.2 mole) of 3-ethyl-3-methylvaleronitrile, 3 g. of ferric chloride, and 100 ml. of anhydrous ether. The resulting mixture was stirred and refluxed for 186 hr., and then hydrolyzed and worked up as in the previous experiment. There was obtained 13.1 g. (51%) of 3-ethyl-3-methylvaleraldehyde, b.p. 165–170°, n^{25}_{D} 1.4257. The high-boiling residue (10.5 g.) was not investigated.

Reaction of Trimethylacetonitrile with *t*-Butylmagnesium Chloride and Ferric Chloride.—A mixture of 1.26 moles of *t*-butylmagnesium chloride and 0.75 g. of ferric chloride in 500 ml. of anhydrous ether was stirred for 0.5 hr., and then a solution of 41.5 g. (0.5 mole) of trimethylacetonitrile in 100 ml. of dry ether was added during 2 hr. The reaction mixture was stirred and refluxed for 28 hr., hydrolyzed with hydrochloric acid, and worked up in the usual fashion. There was obtained 3.6 g. of trimethylacetaldehyde, b.p. 60–70°, n^{20}_{D} 1.3809–1.3827; the corresponding 2,4-dinitrophenylhydrazone melted at 203–207° (lit.[3] m.p. 205–207°). An additional 5 g. of trimethylacetaldehyde, codistilled with the ether, was recovered as the 2,4-dinitrophenylhydrazone. The total yield of trimethylacetaldehyde was 8.6 g. (20%). The aqueous phase from the hydrolysis of the original reaction mixture was extracted continuously for 2 days with 250 ml. of ether. After drying and evaporating the ether, a trace of residue was left. It showed characteristic infrared absorptions for hydroxyl and carbonyl groups.

Reaction of Hexanenitrile with *t*-Butylmagnesium Chloride and Ferric Chloride.—A solution of approximately 2 moles of *t*-butylmagnesium chloride in 700 ml. of anhydrous ether was added dropwise to a mixture of 48.5 g. (0.5 mole) of hexanenitrile, 3 g. of ferric chloride, and 150 ml. of dry ether. The reaction mixture

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[1] This work was supported by grant no. 918-A from the Petroleum Research Fund.

[2] C. R. Hauser and W. J. Humphlett, *J. Org. Chem.*, **15**, 359 (1950).

[3] H. S. Mosher and W. T. Mooney, *J. Am. Chem. Soc.*, **73**, 3948 (1951); E. J. Blanz, Jr., and H. S. Mosher, *J. Org. Chem.*, **23**, 492 (1958).

[4] All melting and boiling points are uncorrected. The carbon-hydrogen analyses were performed by the Weiler and Strauss Laboratories, Oxford, England.

[5] H. Gilman, P. D. Wilkinson, W. P. Fishel, and C. H. Meyers, *J. Am. Chem. Soc.*, **45**, 150 (1923).

was stirred and refluxed for 39 hr. and hydrolyzed with 500 ml. of 1:1 hydrochloric acid. The ether was removed by distillation and the residue was heated on a steam bath for 1 hr., with occasional shaking. The aqueous phase was separated and extracted with three 100-ml. portions of ether. The extracts and organic phase were combined, dried over anhydrous magnesium sulfate, and concentrated. The residue was distilled to give 3.8 g. (2.4%) of *t*-butyl pentyl ketone, b.p. 45–55° (1 mm.), n^{25}_{D} 1.4190–1.4240; semicarbazone, m.p. 139–140° (lit.[6] m.p. 140–140.5°); 2,4-dinitrophenylhydrazone, m.p. 76–77° (lit.[6] m.p. 99–100°); and 46 g. of an intractable tar.

Anal. Calcd. for $C_{16}H_{24}O_4N_4$: C, 57.13; H, 7.19; N, 16.66. Found: C, 57.09; H, 7.14; N, 16.18.

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Preparation of *t*-Alkylphosphonic Dichlorides[1]

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Received May 3, 1963

The aluminum chloride-catalyzed reaction of alkyl halides with phosphorus trichloride[2a,b] has broad utility for the synthesis of *sec*-alkylphosphonic dichlorides. However, the usefulness of this reaction for the straightforward synthesis of *t*-alkylphosphonic dichlorides appeared to be limited to the preparation of *t*-butylphosphonic dichloride. Kosolapoff and Crofts[3] found that starting with *t*-amyl chloride, a mixture of *t*-butyl- and amylphosphonic dichlorides was obtained and the separation of these two products by fractional distillation was difficult. Experiments in this laboratory confirmed these results; we were never able to prepare *t*-amylphosphonic dichloride that, by proton magnetic resonance spectrograms, was free of *t*-butylphosphonic dichloride. However, the finding of Kinnear and Perren[2b] that isobutyl chloride gave *t*-butylphosphonic dichloride suggested that 1-halo-2-alkylalkanes could be used to prepare *t*-alkylphosphonic dichlorides.

Our investigations show that the use of 1-halo-2-alkylalkanes apparently provides a general preparation of *t*-alkylphosphonic dichlorides by the reaction of Kinnear and Perren. The yields of pure products are only 20–40%, while the yields of gross high-boiling material are still only 40–50%. In all cases the foreshots obtained in distillation under high vacuum were small, and as much as half of the high-boiling material reremained as a heel even when bath temperatures were raised to over 100° at about 0.2-mm. pressure. We have not studied any range of experimental conditions in an attempt to improve yields, since our object was to obtain about 50 g. of pure product without regard to optimizing conditions for yield.

Experimental

One mole of alkyl bromide was added slowly to 1 mole of phosphorus trichloride plus 1 mole of anhydrous aluminum chloride in 400 ml. of methylene chloride at about 0°. After the reaction mixture had been stirred overnight at room temperature, the mixture was poured slowly, with good manual agitation, over a mixture of ice and solid carbon dioxide. The mixture with ice was allowed to warm up slowly to between −20 and −10°, and the phases were separated in a separatory funnel. After the mixture was dried with anhydrous calcium chloride, the methylene chloride was pumped off from the organic phase and distillation carried out at about 0.2 mm.

The three *t*-alkylphosphonic dichlorides that were prepared in this manner are listed in Table I. All three compounds are clear, colorless liquids at room temperature. Proton magnetic resonance spectrograms for these compounds and for *t*-butylphosphonic dichloride (all 10% by volume in carbon tetrachloride) were obtained with the Varian Associates Model 4300 B spectrometer at 40 Mc. The doublet for the β-methyl protons occupies the same position for all three of the higher *t*-alkylphosphonic dichlorides (41.1 and 67.4 c.p.s. downfield from tetramethylsilane as an internal standard) but is displaced to 44.3 and 69.1 c.p.s. for the *t*-butylphosphonic dichloride. From the spectrograms it is estimated that the three higher phosphonic dichlorides contain not more than a few per cent of the *t*-butyl compound. Even the small peaks to the lowfield side of the main doublet for these compounds may not be due to the *t*-butyl doublet, but may be due to other protons in these molecules.

TABLE I

t-ALKYLPHOSPHONIC DICHLORIDES

Compound	C, % Found	C, % Calcd.	H, % Found	H, % Calcd.	P, % Found	P, % Calcd.	Cl, % Found	Cl, % Calcd.	Yield of high boilers, %	Yield of product, %	Approximate[a] b.p at 0.2–0.3 mm., °C.
2-Methylbutyl-2-phosphonic dichloride	31.6	31.7	5.9	5.9	16.0	16.4	36.3	37.5	50	32	55
3-Methylamyl-3-phosphonic dichloride	34.6	35.5	6.7	6.5	14.5	15.3	34.3	34.9	50	40	70
3-Methylheptyl-3-phosphonic dichloride	40.8	41.6	7.3	7.4	12.9	13.4	29.9	30.7	40	22	90

[a] Crude measurements made during purification of compounds.

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[1] The information contained in this article was developed during the course of work under contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

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The Photoinitiated Oxidation of Tertiary Phosphites

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Received April 25, 1963

During a study of the photochemical phenylation of tri-*n*-butyl phosphite with iodobenzene,[1] we observed the formation of a significant amount of a third ma-

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(1) For a preliminary report of this study, see J. B. Plumb and C. E. Griffin, *J. Org. Chem.*, **27**, 4711 (1962).