considered the viscosity lowering a result of the "breaking up of the fibrils of the pectin," *i. e.*, as due to a change in the properties of the solvent. However, this behavior becomes predictable if we assume a combination between the citrate and the pectin, containing equal parts of each, and less hydrated than the pectin itself.

TABLE III

RELATIVE VISCOSITY OF PECTIN SOLUTIONS WITH SODIUM CITRATE

$c_{H_3Cit.}$	% pectin						
	0.05	0.10	0.15	0.20	0.30	0.40	0.50
0	1.166	1.300	1.409	1.534	1.863	2.178	2.593
0.001	1.169	1.304	1.413	1.536	1.871	2.177	2.595
.002	1.173	1.307	1.421	1.539	1.874	2.179	2.603
.004	1.168	1.313	1.422	1.543	1.872	2.188	2.607
.006	1.164	1.312	1.424	1.548	1.881	2.191	2.622
.008	1.160	1.311	1.424	1.550	1.877	2.186	2.617
.010	1.157	1.308	1.417	1.548	1.876	2.184	2.630
.020	1.138	1.292	1.409	1.542	1.873	2.192	2.628
.050	1.122	1.261	1.367	1.503	1.846	2.168	2.626
.080	1.122	1.250	1.348	1.477	1.803	2.133	2.593
.10	1.122	1.245	1.341	1.469	1.788	2.120	2.577
.25	1.128	1.244	1.333	1.451	1.747	2.053	2.481
.50	1.137	1.255	1.341	1.457	1.752	2.059	2.468
1.00	1.160	1.278	1.368	1.489	1.786	2.084	2.509

The accuracy of the measurements is not sufficient to permit a quantitative discussion of the maximum which occurs at low citrate concentrations. With increasing pectin content, the maximum shifts to higher citrate concentrations, but this relationship does not appear to be linear. It may be assumed tentatively that the citrate concentration for maximum viscosity is proportional to the square root of the pectin concentration.

The behavior described above is not specific for pectin and citric acid. Qualitative measurements have shown that aconitic acid may replace the citrates, agar or gum acacia (not starch or the hexose sugars or sucrose) the pectin. Further investigation along these lines is planned.

Summary

1. The viscosities of pectin solutions containing citric acid or citrates have been measured.
2. The viscosity reaches a maximum at low citrate concentrations, a minimum at higher concentrations.
3. Minimum viscosity occurs when equal concentrations of pectin and citric acid are taken, indicating combination of some kind.
4. The position of the maximum is shifted to higher citrate concentrations by increased pectin content, or by decreased acidity.

HONOLULU, T. H. RECEIVED DECEMBER 1, 1938

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Synthesis of Aliphatic *t*-Butyl Ketones

BY FRANK C. WHITMORE, CLARENCE I. NOLL AND VINCENT C. MEUNIER

The reaction of trimethylacetamide with ethylmagnesium bromide has been reported to give good yields of ethyl *t*-butyl ketone.[1] Since ketones containing the *t*-butyl group are important in the work of this Laboratory, the reaction has been extended to include other aliphatic Grignard reagents. Normal Grignard compounds gave good yields of ketones. With branched Grignard reagents the yield of ketone was low, the predominating product being trimethylacetonitrile. With *t*-butylmagnesium chloride, the yield of trimethylacetonitrile was 73%.

Experimental

Reaction of Trimethylacetamide with Grignard Reagents.—The following describes a typical reaction. Two moles of the Grignard reagent were prepared in 700 cc. of anhydrous ether. The addition of 50.5 g. (0.5 mole) of trimethylacetamide, m. p. 152.5–153.5°, required from one-half to one hour. The reactants were stirred and heated to reflux temperature for sixteen hours. The mixture was decomposed with ice and the ether layer separated. The aqueous layer was acidified with hydrochloric acid and extracted several times with ether. The ether extracts and ether layer were combined and carefully distilled through a fractionating column until the ether was removed. The residual solution was dried with anhydrous sodium sulfate and fractionated through an efficient column.[2] The results are tabulated.

All of the compounds listed have been prepared previously, except those for which analytical data are reported.

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[1] Ramont, Laclotre and Anagnostopoulos, *Compt. rend.*, **185**, 282 (1927).

[2] Whitmore and Lux, THIS JOURNAL, **54**, 3448 (1932); Wilson, Parker and Laughlin, *ibid.*, **55**, 2795 (1933).

REACTION OF GRIGNARD REAGENTS WITH TRIMETHYLACETAMIDE

	RMgX	Ketone	B. p. °C.	B. p. Mm.	n^{20}D	Yield, %	Derivatives of ketones: 2,4-Dinitrophenylhydrazone m. p., °C.	Derivatives of ketones: Semicarbazone m. p., °C.	Derivatives of ketones: Oxime m. p., °C.
1	Methyl	Methyl *t*-butyl (Pinacolone)	105	746	1.3952–1.3960	52	126–127	.....	78.5–79.5
2	Ethyl	Ethyl *t*-butyl	124.5	729	1.4049–1.4052	78	143.5–144.5	.....	84.5–85.5
3	*n*-Propyl	*n*-Propyl *t*-butyl	145	738	1.4103–1.4107	67	116–116.5[d]	.....	78–78.5
4	Isopropyl	Isopropyl *t*-butyl	134–135	744	1.4060–1.4070	20	......	.....	143–144
5	*n*-Butyl	*n*-Butyl *t*-butyl	166	745	1.4162–1.4172	68	......	144.5–145	59.5–60.5[c]
6	Isobutyl	*i*-Butyl *t*-butyl[a]	.....	...	....	..	......	.....	......
7	*s*-Butyl	*s*-Butyl *t*-butyl	156–157	745	1.4158–1.4162	12	......	.....	87–88
8	*t*-Butyl	(Trimethylacetonitrile)[b]	103.5	738	1.3792	..	......	.....	......
9	*n*-Amyl	*n*-Amyl *t*-butyl	184–185	745	1.4208–1.4219	42	99–100[e]	140–140.5	......

[a] Reaction 6 yielded 42% nitrile, unreacted amide, and only 1 g. of ketone from which an oxime, m. p. 72–73°, was made. [b] Trimethylacetonitrile was obtained in 73% yield. It was identified by conversion to ethyl *t*-butyl ketone with ethylmagnesium bromide. [c] *Anal.* Calcd. for $C_9H_{19}NO$: N, 8.91. Found: 8.95. [d] *Anal.* Calcd. for $C_{14}H_{20}N_4O_4$: N, 18.18. Found: 17.99. [e] *Anal.* Calcd. for $C_{16}H_{24}N_4O_4$: N, 16.67. Found: 16.83.

Summary

1. The reaction of trimethylacetamide with normal aliphatic Grignard reagents gives good yields of *t*-butyl ketones.

2. The reaction of trimethylacetamide with *t*-butylmagnesium chloride yields chiefly trimethylacetonitrile.

STATE COLLEGE, PENNA. RECEIVED NOVEMBER 12, 1938

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Identification of Alkyl Phenyl Sulfides, Sulfoxides, and Sulfones[1]

BY V. N. IPATIEFF AND B. S. FRIEDMAN

During the course of the study[2] of the reaction of olefins and alkyl esters of phosphoric and sulfuric acids with thiophenol, it became necessary to develop methods for identifying the resultant alkyl phenyl sulfides.

Unlike the aliphatic sulfides, alkyl phenyl sulfides coördinate very slowly, if at all, with mercuric chloride; so that this excellent method[3a] of identification was of no aid. The other mercuric salts were equally unsatisfactory. With palladous chloride, however, the coördination compounds, $(C_6H_5\text{–}S\text{–}R)_2\cdot PdCl_2$, are formed rapidly and in good yield.[2,3b] These are solid derivatives possessing desirable physical properties in all but a few cases. *t*-Butyl and *t*-amyl phenyl sulfides formed insoluble, brick red powders melting above 250°; analyses of these indicated that the compounds possess the formula, $C_6H_5\text{–}S\text{–}R\cdot 2PdCl_2$. Complexes of the $(C_6H_5\text{–}S\text{–}R)_2\cdot PdCl_2$ type could be obtained from *t*-butyl and *t*-amyl phenyl sulfides only if an excess of the sulfide was used in the preparation of the derivative. These were yellow powders, easily soluble in organic solvents, and melting at 84 and 72–73°, respectively. However, on recrystallization from any of various solvents, or upon standing, there always was obtained the brick red powder accompanied by droplets of the free *t*-alkyl phenyl sulfide. The following reaction apparently takes place

$$2(C_6H_5\text{–}S\text{–}R)_2PdCl_2 \longrightarrow C_6H_5\text{–}S\text{–}R\cdot 2PdCl_2 + 3C_6H_5\text{–}S\text{–}R$$

This characteristic behavior of these derivatives of *t*-butyl and *t*-amyl phenyl sulfides made possible the identification of these sulfides in mixtures with their isomers.

The palladous chloride complex of *active*-amyl phenyl sulfide was an oil, and of *s*-isoamyl phenyl sulfide a solid of indefinite melting point.

To identify the alkyl phenyl sulfides giving unsatisfactory palladous chloride derivatives, as well as to provide additional means for the identification of the other alkyl phenyl sulfides, this investigation was extended to include the preparation of the corresponding sulfones (I). The latter were satisfactory derivatives in only a few instances (see Table I). The sulfones, therefore, were nitrated to give *m*-nitrophenyl alkyl sulfones (II), most of which were then reduced to give the corresponding *m*-aminophenyl alkyl sulfones (III).

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[1] Presented before the Organic Division of the American Chemical Society, Milwaukee, Wisconsin, September 5–9, 1938.

[2] Ipatieff, Pines and Friedman, THIS JOURNAL, **60**, 2731 (1938).

[3] (a) Faragher, Morrell and Comay, *ibid.*, **51**, 2774 (1929); (b) Mann and Purdie, *J. Chem. Soc.*, 1549 (1935).