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

Fission of *t*-Butyl Alkyl Ketones in the Schmidt Reaction

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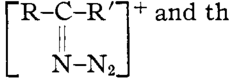
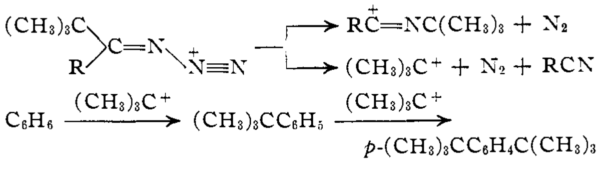
Several *t*-butyl alkyl ketones were treated with hydrazoic acid in benzene and in toluene under the usual conditions of the Schmidt reaction. Rearrangement of the *t*-butyl group occurred to the extent of only 1–11%. The principal reaction was a cleavage of the intermediate iminodiazonium ion to give the *t*-butyl derivative of the aromatic hydrocarbon solvent. The reaction is explained as a β-fission similar to that observed for certain carbonium ions. By-products of the reaction include isomeric ketones formed by rearrangement of the original ketones by the sulfuric acid.

The ready availability of highly branched aliphatic ketones containing *t*-alkyl groups[2] suggested a study of the rearrangement of tertiary groups in the Schmidt reaction. The action of hydrazoic acid on unsymmetrical dialkyl ketones usually produces N-alkyl amides resulting from the migration of the bulkier group. This fact has been explained by the preferential formation of one geometric isomer of an iminodiazonium ion  $\left[\begin{array}{c}\mathrm{R{-}C{-}R'}\\ \| \\ \mathrm{N{-}N_2}\end{array}\right]^+$ and the subsequent *trans*-migration of an alkyl group.[3] Preliminary attempts to effect migration of *t*-butyl and pentamethylethyl groups resulted in very low yields of N-alkyl amides or their hydrolysis products.

Three *t*-butyl alkyl ketones (R = methyl, ethyl and *t*-butyl) were then studied by a uniform procedure in which constant molar ratios of carbonyl compound, sulfuric acid, sodium azide and benzene were maintained under the usual conditions of the Schmidt reaction. The main products in each case were *t*-butylbenzene and di-*t*-butylbenzene formed by alkylation of the solvent by the *t*-butyl group from the ketone. A similar cleavage has been described by Schuerch and Huntress for trialkylacetic acids[4] and by Smith for pivalophenone.[5] However, an aromatic hydrocarbon was not employed as solvent for the reactions and the fate of the cleaved tertiary group was either different or undetermined. The alkylbenzenes were separated effectively in high purity by fractional distillation and identified through their corresponding nitro derivatives and by a comparison of infrared spectra. The yields accounted for 24–56% of the ketone used, whereas the amount of *t*-butylamine from the normal Schmidt rearrangement was less than 11%. No evidence of rearrangement of the smaller alkyl group was detected. The rather low material balance suggested that *t*-butylbenzene was sulfonated during the reaction. This fact was confirmed by a recovery of only 28% of *t*-butylbenzene from a mixture in benzene and sulfuric acid treated under conditions identical to the Schmidt reaction. When toluene was substituted for benzene in an attempt to suppress sulfonation of the hydrocarbon product, the yield of *t*-butyltoluene from ethyl *t*-butyl ketone was 72%. Infrared analysis indicated that the product was mainly *p*-*t*-butyltoluene containing about 10% of the *meta* isomer. This composition is the same as that obtained by several Friedel–Crafts alkylations of toluene under mild conditions.[6]

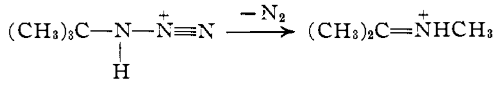
The cleavage likely occurs concurrently with rearrangement of the iminodiazonium ion. The fragment resulting from loss of a molecule of nitrogen from this ion is stabilized by a β-fission in which the *t*-butyl group is cleaved as a carbonium ion. This type of fission is well known. β-Eliminations accompany Wagner–Meerwein and pinacol rearrangements in which the cleavage is beta to an electronically deficient carbon atom[7] and the Beckmann rearrangement in which the transition state is similar to that in the Schmidt reaction.[8] The absence of isobutylene in the evolved nitrogen and of the dimers and trimers of isobutylene in the liquid organic products suggests that the *t*-butylcarbonium ion is never free but is cleaved in a transition state involving a molecule of benzene.



$$\begin{array}{c}(\mathrm{CH_3})_3\mathrm{C} \\ \mathrm{R}\end{array}\!\!>\!\mathrm{C{=}N{-}\overset{+}{N}{\equiv}N} \longrightarrow \begin{cases}\mathrm{R\overset{+}{C}{=}NC(CH_3)_3} + \mathrm{N_2}\\ (\mathrm{CH_3})_3\mathrm{C}^+ + \mathrm{N_2} + \mathrm{RCN}\end{cases}$$

$$\mathrm{C_6H_6} \xrightarrow{(\mathrm{CH_3})_3\mathrm{C}^+} (\mathrm{CH_3})_3\mathrm{CC_6H_5} \xrightarrow{(\mathrm{CH_3})_3\mathrm{C}^+} p\text{-}(\mathrm{CH_3})_3\mathrm{CC_6H_4C(CH_3)_3}$$

The nitriles produced by the cleavage were hydrolyzed to the corresponding acids. In one case it was shown that considerable hydrolysis to the acid occurred at 15–25° during the Schmidt reaction. A 10% yield of trimethylacetic acid was obtained from hexamethylacetone by an ether extraction of the cold aqueous layer from the Schmidt reaction. Alkaline hydrolysis then produced an additional 37% of this acid along with ammonia, methylamine and *t*-butylamine. The methylamine is probably produced by a degradation of the *t*-butyl radical in a manner previously suggested.[4] Here a molecule of hydrazoic acid acts in place of the benzene to capture the tertiary group. Loss of nitrogen and rearrangement of a methyl group then produces a protonated N-methyl ketimine from which the methylamine is formed upon hydrolysis.



$$(\mathrm{CH_3})_3\mathrm{C}{-}\underset{\displaystyle\mathrm{H}}{\underset{|}{\mathrm{N}}}{-}\overset{+}{\mathrm{N}}{\equiv}\mathrm{N} \xrightarrow{-\mathrm{N_2}} (\mathrm{CH_3})_2\mathrm{C}{=}\overset{+}{\mathrm{N}}\mathrm{HCH_3}$$

An interesting side light on the behavior of saturated ketones in concentrated sulfuric acid was observed in conjunction with this study. Small quan-

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[1] This paper is based on the M.S. thesis of S. C. Paviak, The Pennsylvania State University, 1954.

[2] W. C. Percival, R. B. Wagner and N. C. Cook, THIS JOURNAL, **75**, 3731 (1953).

[3] M. S. Newman and H. L. Gildenhorn, *ibid.*, **70**, 317 (1948); P. A. S. Smith, *ibid.*, **70**, 320 (1948).

[4] C. Schuerch, Jr., and E. H. Huntress, *ibid.*, **71**, 2233 (1949).

[5] P. A. S. Smith and J. P. Horwitz, *ibid.*, **72**, 3718 (1950).

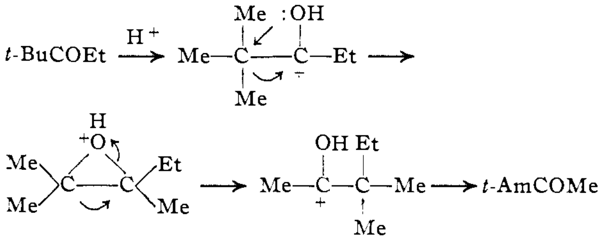
[6] M. J. Schlatter and R. D. Clark, *ibid.*, **75**, 361 (1953).

[7] F. C. Whitmore and E. E. Stahly, *ibid.*, **55**, 4153 (1933); F. C. Whitmore, *Chem. Eng. News*, **26**, 671 (1948).

[8] A. H. Blatt and R. P. Barnes, THIS JOURNAL, **56**, 1148 (1934); **57**, 1330 (1935).

tities of ketones recovered from the Schmidt reactions were identified as isomers of the reactants. Thus, methyl *t*-amyl ketone was formed from ethyl *t*-butyl ketone and methyl pentamethylethyl ketone from hexamethylacetone. In one experiment, the rearrangement of ketone accounted for 21% of the reaction product. The isomerization of hexamethylacetone by sulfuric acid in benzene solution has been observed recently in connection with alkylation studies.[9] We have shown that the rearrangement of ethyl *t*-butyl ketone to methyl *t*-amyl ketone in sulfuric acid occurs in the absence of hydrazoic acid or aromatic hydrocarbon. By stirring the ketone with concentrated sulfuric acid for three days at 30–50°, a mixture of ethyl *t*-butyl ketone (91%) and methyl *t*-amyl ketone (9%) was obtained. The product was analyzed by fractional distillation and infrared spectroscopy.

The simplest mechanism by which the two methyl groups may be exchanged for the carbonyl group is by two concerted substitutions involving the two protonated ketones and a protonated oxide intermediate. Other paths are possible but involve many more ionic intermediates.



Experimental

Preparation of Ketones.—Pinacolone, b.p. 105° at 738 mm., n^{20}D 1.3970, was prepared from acetone[10] and distilled twice through a six-plate column. Ethyl *t*-butyl ketone[11] was made in 52% yield by the action of ethylmagnesium bromide on trimethylacetamide.[12] Fractional distillation gave a product boiling at 123–124° at 735 mm., n^{20}D 1.4048–1.4052. The hexamethylacetone was made from *t*-butylmagnesium chloride and trimethylacetyl chloride.[13]

Reactions of Ketones with Hydrazoic Acid.—The reactants and products for six experiments are summarized in Table I. The ketone, concentrated sulfuric acid and distilled aromatic hydrocarbon were mixed and cooled with stirring to 15–25° by means of an ice-bath. Sodium azide was introduced in small portions over a period of two hours from a solids injector. The evolved nitrogen was collected over water at atmospheric pressure. In the first experiment the mixture was heated to complete the reaction. Vigorous evolution of nitrogen occurred at 40–50°. Better control was obtained in subsequent reactions by stirring at 25–35° for several hours before the heating period. Experiments 4 and 6 were carried out simply by stirring for five hours at this lower temperature. The theoretical amount of nitrogen based on the ketone was obtained in the last three experiments. In the others, a quantity of nitrogen equivalent to the sodium azide was evolved. Stirring was sufficient to produce an emulsion of the two layers.

TABLE I

SCHMIDT REACTIONS OF *t*-BUTYL ALKYL KETONES

Expt.	R	RCOC$(CH_3)_3$ Moles	Solvent,[a] ml.	H_2SO_4	NaN_3	Products (yields, %)
1	CH_3	0.40	300 B	204	0.48	*t*-Butylbenzene (30) *p*-Di-*t*-butylbenzene (9) *t*-Butylamine (3) Ammonia (26)
2	CH_3	.30	300 B	154	.36	*t*-Butylbenzene (43) *p*-Di-*t*-butylbenzene (13) *t*-Butylamine (0.6) Ammonia (11)
3	C_2H_5	.30	300 B	154	.36	*t*-Butylbenzene (32) *p*-Di-*t*-butylbenzene (7) *t*-Butylamine (0.3) Ammonia (19) Propionic acid (17) Methyl *t*-amyl ketone (5)
4	C_2H_5	.30	400 T	154	.36	*t*-Butyltoluene[c] (72) *t*-Butylamine (11) Ammonia (71)
5	*t*-C_4H_9	.30	300 B	154	.36	*t*-Butylbenzene (23) *p*-Di-*t*-butylbenzene (0.7) *t*-Butylamine (9) Methylamine (26) Ammonia (27) Pennone[d] (21)
6	*t*-C_4H_9	.60[b]	800 T	308	.72	*t*-Butyltoluene[c] (14) *t*-Butylamine (5) Methylamine (30) Ammonia (49) Trimethylacetic acid (47) Pennone[d] (6)

[a] B = benzene, T = toluene. [b] Recovered ketone in this experiment was 28%. The yields of products in this case are based on ketone reacted. [c] Approximately 90% *para*–10% *meta* by infrared analysis. [d] 3,3,4,4-Tetramethyl-2-pentanone.[19]

The sulfuric acid layer was washed with two 100-ml. portions of hydrocarbon and poured onto 200–400 g. of ice. The combined hydrocarbon layers were washed free of sulfuric acid and fractionated through a 12-plate column. *t*-Butylbenzene was collected at 69° at 26 mm., 81.5° at 46 mm.; $n^{20.5}$D 1.4928, n^{25}D 1.4900; 2,4-dinitro-*t*-butylbenzene, m.p. 63.5–64.5° (reported 61–62°).[14] *p*-Di-*t*-butylbenzene was obtained from the distillation residues and crystallized from isopropyl alcohol, m.p. 78.0–78.5°; 2-nitro-1,4-di-*t*-butylbenzene, m.p. 86–87° (reported 88–89°).[15] *t*-Butyltoluene boiled at 62° at 8 mm., n^{25}D 1.4896.[16] Further identification was made by alkaline permanganate oxidation to *p*-*t*-butylbenzoic acid, m.p. 162–164° (reported 164°).[17] The infrared spectrum exhibited absorption peaks characteristic of both the *meta* and *para* isomers. A rough estimate of the composition was made at 12.8 and 14.2 μ assuming the extinction coefficients reported for the pure isomers.[6] At these wave lengths calculations indicated 8 and 12%, respectively, of the *meta* isomer.

In the last four experiments, the aqueous sulfuric acid layers were well extracted with ether; the ether in turn was extracted with dilute sodium hydroxide solution. In addition to recovered hydrocarbon solvent, rearranged ketones were obtained from the ethereal solutions by fractional distillation. From experiment 3, 2.9 g. of ketonic material was obtained, b.p. 122–123.5° at 737 mm. Fractional crystallization of the 2,4-dinitrophenylhydrazones gave two derivatives, m.p. 108–110° and m.p. 91–93°, neither of which corresponds to that of the original ketone, m.p. 146°. The former was identified as the 2,4-dinitrophenylhydrazone of methyl *t*-amyl ketone, m.p. 109–111°.[18] The latter derivative may have been the 2,4-dinitrophenylhydrazone of methyl neopentyl ketone, m.p. 98°. Sufficient material was not available for further purification or for a mixed m.p. From experiments 5 and 6, solid ketone, b.p. 168–171° at 735 mm., m.p. 56–60° was isolated in 9.0-g. and 3.8-g. quantities, respectively. Refractionation through

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[9] S. Barton, F. Morton and C. R. Porter, *Nature*, **169**, 373 (1952).

[10] G. A. Hill and E. W. Flosdorf, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 462.

[11] F. C. Whitmore, C. I. Noll and V. C. Meunier, THIS JOURNAL, **61**, 683 (1939).

[12] Prepared in 62% yield by a method described for isobutyramide, R. E. Kent and S. M. McElvain, *Org. Syntheses*, **25**, 59 (1945).

[13] Reference 2. We are grateful to these authors for a generous sample of this ketone.

[14] J. F. McKenna and F. J. Sowa, THIS JOURNAL, **59**, 471 (1937); J. B. Shoesmith and A. Mackie, *J. Chem. Soc.*, 2336 (1928).

[15] D. I. Legge, THIS JOURNAL, **69**, 2086 (1947).

[16] C. G. LeFevre, R. J. LeFevre and K. W. Robertson, *J. Chem. Soc.*, 487 (1935).

[17] C. S. Marvel, *et al.*, THIS JOURNAL, **66**, 915 (1944).

[18] F. C. Whitmore, *et al.*, *ibid.*, **63**, 651 (1941).

a 1.1 $\times$ 9 cm. column packed with ${}^5/_{32}$ in. single turn glass helices gave seven fractions boiling at 168–169° at 735 mm., m.p. 57–59°. The infrared spectrum established the presence of a carbonyl group (5.87 μ) as the only functional group. The 2,4-dinitrophenylhydrazone melted at 181–182° and the semicarbazone at 198–199°.

Anal. Calcd. for $C_{10}H_{21}N_3O$: C, 60.30; H, 10.55. Found: C, 60.40; H, 10.37.

This ketone was identified by the above constants as 3,3,4,4-tetramethyl-2-pentanone (pennone). The identification was confirmed by oxidation of 2 g. of the ketone with 52% nitric acid (following the procedure of Locquin and Sung[19]) to give $\alpha,\alpha,\beta,\beta$-tetramethylbutyric acid which melted sharply at 194–195° (uncor.).

Trimethylacetic acid was obtained from the alkaline wash solution from experiment 6 by acidification with sulfuric acid and extraction with ether. Fractional distillation gave 4.5 g., b.p. 161° at 735 mm., m.p. 33°; *p*-bromophenacyl ester, m.p. 75–76°.

Isolation and purification of the N-*t*-butyl amide was less successful than direct hydrolysis to *t*-butylamine. The aqueous layers in experiments 2 and 3 were neutralized with barium hydroxide and sodium hydroxide, respectively. After filtration of insoluble barium sulfate and sulfonate, the aqueous solutions were evaporated almost to dryness under vacuum and extracted with hot ethyl acetate. Water was removed by azeotropic distillation, after which the residue was filtered and concentrated. The crystallized amides were mixtures of $RCONH_2$ and $RCONHC(CH_3)_3$ as shown by hydrolysis with 20% potassium hydroxide solution. Acetic and propionic acids were identified as their *p*-bromophenacyl esters melting at 84–85° and 63–64°, respectively. *t*-Butylamine and ammonia were identified as described below.

The amides were hydrolyzed directly in experiments 1, 4, 5 and 6. The sulfuric acid layers were neutralized with 50% sodium hydroxide and excess base added to make the final solution 20% by weight in sodium hydroxide. Hydrolysis was effected over a period of 3–5 days by stirring and heating just below the reflux temperature to prevent excessive frothing. Ether, ammonia and amines were swept by a very slow stream of air into traps containing concentrated hydrochloric acid. The hygroscopic hydrochlorides obtained by evaporation of the excess hydrochloric acid were dried over calcium chloride in a desiccator. *t*-Butylamine hydrochloride was separated by extraction with anhydrous butanol and crystallized from that solvent. The picrate prepared from the free amine melted at 199–201° (reported 198°).[20] Methylamine hydrochloride was extracted into and crystallized from hot absolute ethanol. The amine was identified as N-methylphthalimide, m.p. 131–132° (reported 134°).[21] The residues of ammonium chloride gave a positive test with Nessler reagent and sublimed from 332 to 348°.

The alkaline solution from the hydrolysis was acidified with sulfuric acid in experiment 6. Steam distillation gave 16.1 g. of trimethylacetic acid, m.p. 31–33°; *p*-bromophenacyl ester, m.p. 75–76°.

Rearrangement of Ethyl *t*-Butyl Ketone by Sulfuric Acid.—Concentrated sulfuric acid, 33 g., was added dropwise with stirring to 25 g. of the ketone cooled in an ice-bath. The yellow solution was stirred for two days at room temperature and then warmed to 55° for three hours. After cooling overnight to room temperature, the mixture was poured onto 100 g. of ice and washed well with four 20-ml. portions of water. Fractionation through a 1.1 $\times$ 34 cm. column packed with ${}^1/_8$ in. single turn glass helices gave eight fractions, 18.2 g. (73%) of material boiling at 123–123.5°, $n^{25}\mathrm{D}$ 1.4022–1.4027. The remainder of the liquid in the column was then distilled to dryness at a pressure of 50 mm. Two fractions, 6 g., of distillate were obtained, $n^{25}\mathrm{D}$ 1.4030 and $n^{25}\mathrm{D}$ 1.4035. Infrared absorption spectra were determined from 2 to 13 μ for authentic samples of ethyl *t*-butyl ketone, b.p. 123–124° at 735 mm., $n^{25}\mathrm{D}$ 1.4022; methyl *t*-amyl ketone, b.p. 128° at 740 mm., $n^{25}\mathrm{D}$ 1.4080; methyl neopentyl ketone, b.p. 124° at 740 mm., $n^{25}\mathrm{D}$ 1.4012; and the various fractions from the above reaction. Methyl *t*-amyl ketone was easily identified by absorption peaks at 7.37, 8.79 and 12.87 μ. By the conventional methods of quantitative analysis, fractions 1–8 were found to contain 5% of methyl *t*-amyl ketone; fraction 9, 15% and fraction 10, 26%. From these data calculations indicate a total of 9% rearrangement of ethyl *t*-butyl ketone to methyl *t*-amyl ketone. No evidence of methyl neopentyl ketone could be detected.

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[19] R. Locquin and W. Sung, *Bull. soc. chim. France*, [4] **35**, 753 (1924); *Compt. rend.*, **178**, 1179 (1924).

[20] R. Brown and W. E. Jones, *J. Chem. Soc.*, 782 (1946).

[21] E. J. Sakellarios, *Helv. Chim. Acta*, **29**, 1675 (1946).

[Contribution from the Noyes Chemical Laboratory, University of Illinois]

The Condensation of *t*-Butylmagnesium Chloride with Duryl *o*-Isopropenylphenyl Ketone[1]

By Reynold C. Fuson, William D. Emmons[2] and Shaler G. Smith, Jr.

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It has been shown that duryl *o*-isopropenylphenyl ketone (I in text) reacts with *t*-butylmagnesium chloride in the 1,6-manner. The point of attachment of the *t*-butyl group is, significantly, the *para* position of the benzene ring rather than in the vinyl side chain. Catalytic hydrogenation converted the product, 4-*t*-butyl-2-isopropenylphenyl duryl ketone, to 4-*t*-butyl-2-isopropylphenyl duryl ketone, which has been synthesized by an independent method.

Alkylation of duryl phenyl ketone at the *para* position of the phenyl ring by the action of certain Grignard reagents corresponds to a 1,6-addition followed by oxidation of the adduct.[3] Attempts to achieve 1,6-addition in analogously constituted linear ketones failed, however.[4] We therefore turned to hindered diaryl ketones having a vinyl group in a conjugate position. The present paper reports a study of the behavior of one of these, duryl *o*-isopropenylphenyl ketone (I), toward the *t*-butyl Grignard reagent.

This ketone might conceivably undergo attack not only at the *para* position but also at the terminal position of the vinyl side chain. Experiment showed that *para* alkylation occurs, the product being 4-*t*-butyl-2-isopropenylphenyl duryl ketone (II). The yield was low, however, and, since no other products have been identified, 1,6-addition involving the side chain cannot be excluded as a possibility.

The structure of the butylated ketone was established by reference to 4-*t*-butyl-2-isopropylphenyl duryl ketone (III) to which it could be converted by hydrogenation. The saturated ketone was made, in turn, by treating *p*-*t*-butylphenyl duryl ketone (IV) with the isopropyl Grignard reagent and by the action of *t*-butylmagnesium chlo-

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[2] Rohm and Haas Fellow, 1949–1950; Socony-Vacuum Oil Co. Fellow, 1950–1951.

[3] R. C. Fuson and R. Tull, This Journal, **71**, 2543 (1949).

[4] R. C. Fuson and W. Y. Libby, *J. Org. Chem.*, **16**, 626 (1951).