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IONIC HYDROGENATION OF THE ETHYLENE BOND AND THE DOUBLE BOND OF THE CARBONYL GROUP

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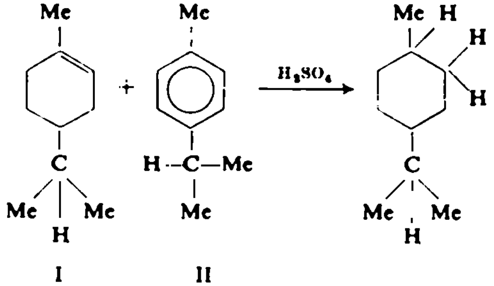
Abstract—The action of triethylsilane and excess trifluoracetic acid upon cyclic and acyclic olefines at room temperature results in a selective hydrogenation when the olefin has two substituents at the ethylene carbon. Excess of trifluoroacetic acid is essential for the reaction. Under more drastic conditions (heating in ampoules at 140° or using a large excess of trifluoroacetic acid) cyclic and acyclic olefines with unbranched structure and inner double bond are capable of undergoing hydrogenation although this is sometimes accompanied by isomerization. In addition to triethylsilane, cycloheptatriene and saturated branched hydrocarbons have been used as hydride-ion donors. It has been found that the action of trifluoroacetic acid and triethylsilane on ketones yields trifluoroacetates of corresponding alcohols. If at least one of the ketone radicals is phenyl, hydrogenation is more likely to result in the formation of a hydrocarbon. Benzophenone and acetophenone give after 15–20 hr at 50–60° diphenylmethane (90%) and ethylbenzene (70%) respectively.

ONE of the possible ways to hydrogenate a multiple bond, in particular ethylene, is by addition of proton and hydride ion.

In the ionic hydrogenation of dihydrolimonene (I) by sulphuric or hydrofluoric acid and *p*-cymene (II) it was concluded that *p*-cymol donates the hydride-ion.[1-3]



I II

Similarly, it was shown[4] that methyl styrene and allyl alcohol are hydrogenated by

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* Translated by A. L. Pumpiansky, Moscow.

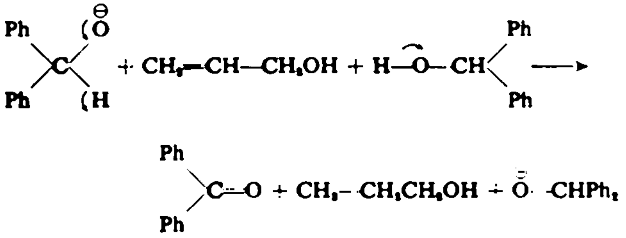
[1] V. N. Ipatieff, H. Pines, R. C. Olberg, *J. Amer. Chem. Soc.* **70**, 2132 (1948).

[2] H. Pines, A. Weizmann and V. N. Ipatieff, *J. Am. Chem. Soc.* **70**, 3859 (1948).

[3] H. Pines, D. Strehlau and V. N. Ipatieff, *Jl Am. Chem. Soc.* **71**, 3534 (1949), **72**, 1563, 5521 (1950).

[4] S. V. Vitt, and N. S. Martinkova, *Izvest. Akad. Nauk. SSSR, Otdel. khim. Nauk* 525 (1964).

benzhydrol and its alcoholate:



In the ionic hydrogenation of olefines using trifluoroacetic acid as a proton donor and trisubstituted silane as donating hydride ion,[5] it found that, at room temperature, methylcyclohexene, methylcyclopentene, 2-methyl-2-butene and 2-methyl-1-pentene are hydrogenated to the respective saturated hydrocarbons. Using a molecular ratio 1:1:2 of olefine: triethylsilane: trifluoroacetic acid, the yield of saturated hydrocarbons is as high as 80%. Unbranched olefines, cyclic and acyclic (cyclohexene, 1-hexene, 2-hexene, 1-heptene, 2-heptene) fail to hydrogenate under these conditions. This is also the case with 4-methyl-2-pentene at 20–50° with a 1:1:2 ratio of olefine: silane:trifluoroacetic acid, but if a catalytic amount of sulphuric acid is added, hydrogenation does take place to form 2-methylpentane.

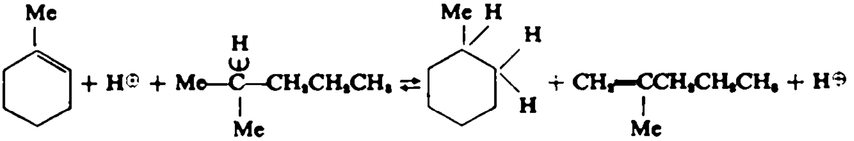
Methyldiethylsilane, triethylsilane, mono-, di-, and triphenylsilanes have been investigated as hydride ion donors. Their donating capacity was found to increase on passing from monophenylsilane to diphenylsilane and decrease from diphenylsilane to triphenylsilane.

A similar regularity has been observed[6] in the behaviour of phenyl substituted silanes on hydrogen exchange with LAD and hydrocarbons such as cycloheptatriene have been studied as hydride donors.

It is well known that cycloheptatriene in losing a hydride ion gives rise to a stable tropylium ion.

Consequently, we have shown that cycloheptatriene in the presence of trifluoroacetic acid reacts with methylcyclohexene forming methylcyclohexane. The yield of hydrogenation product, however, is low probably due to partial polymerization of cycloheptatriene and of the products of its partial hydrogenation.

We have also tried saturated hydrocarbons with a tertiary carbon atom, as hydride-ion donors,[1-3,7,8] and found that methylcyclohexene in trifluoroacetic acid yields methylcyclohexane and 2-methyl-1-pentene, in accordance with the following equation:



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[5] Z. N. Parnes, V. I. Zdanovich, E. E. Kugucheva, G. I. Bassova and D. N. Kursanov, *Dokl. Akad. Nauk SSSR* **166**, 122 (1966).

[6] D. N. Kursanov, V. N. Setkina and Yu. N. Novikov, *Izvest. Akad. Nauk. SSSR, Otdel. khim. Nauk.* 1911 (1964).

[7] W. Haaf and H. Koch, *Liebigs Ann.* **638**, 122 (1960).

[8] G. M. Kramer, *J. Org. Chem.* **30**, 2671 (1965).

Similarly, the reactions of methylcyclopentene and methylcyclohexane in trifluoroacetic acid gave a mixture of methylcyclohexene and methylcyclopentane together with starting hydrocarbons. The ionic mechanism of the reaction is substantiated by the following facts and considerations.

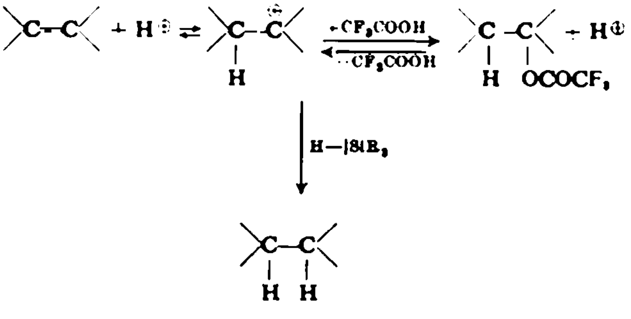
1. When an olefine is mixed with trifluoroacetic acid in the absence of silane the solution turns dark and on standing gives a precipitate. This appears to be due to ionic polymerization. In the presence of silane there is practically no polymerization and the solution remains colourless even when heated. Apparently the carbonium-ion being formed reacts faster with silane, abstracting a hydride-ion.

2. The ionic reaction mechanism is in accordance with the selectivity of hydrogenation of branched olefines as only in these cases are tertiary carbonium ions formed directly. These are known to be much more stable than secondary ions, the energy of which is reported[9] to be 11 kcal/mole higher than that of tertiary carbonium ions.

3. Of the unbranched olefines investigated only styrene, which on proton addition forms a carbonium-ion stabilized by the adjacent phenyl, undergoes hydrogenation under mild conditions.

4. The ionic mechanism explains the hydrogenation of 4-methyl-2-pentene on addition of trifluoroacetic acid in the presence of catalytic amounts of sulphuric acid. Under these conditions, isomerization of 4-methyl-2-pentene to 2-methyl-2-pentene takes place and the latter then yields a tertiary carbonium atom on protonation.

In olefines having two substituents at the ethylene carbon, hydrogenation is possible only in an excess of trifluoroacetic acid, the equilibrium in reaction I is almost completely shifted towards trifluoroacetate formation when equimolar amounts of olefin and acid are used.[10] Further addition of acid causes the trifluoroacetate to be protonated and the equilibrium is shifted towards the formation of carbonium ion:



I

With an unbranched olefine, when the trifluoroacetic acid–olefine ratio is 2:1, the reaction does not yield a saturated hydrocarbon, but if the ratio is increased to 3·5:1, hydrogenation takes place. Thus 2-hexene gives a poor yield of hexane and cyclohexene is partly converted to cyclohexane, methylcyclopentene, and methylcyclopentane. Similar results are obtained when the reaction is carried out at 140° in

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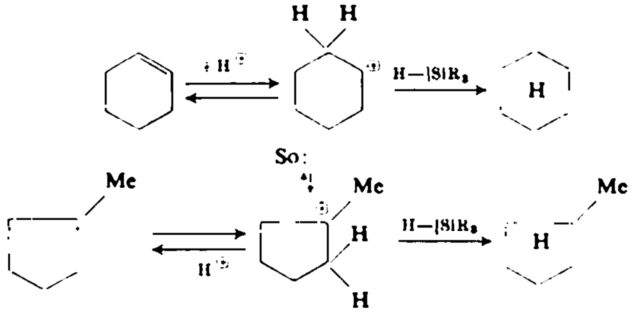
[9] A. G. Evans, *The Reaction of Organic Halides in Solution*, p. 25. The Manchester University Press, England (1946).

[10] C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, pp. 752, 767. Cornell University Press, Ithaca, New York (1953).

sealed ampoules at olefine:silane:acid ratio of 1:1:2. The formation of methylcyclopentene, methylcyclopentane and cyclohexane from cyclohexene may be accounted for by the following scheme:

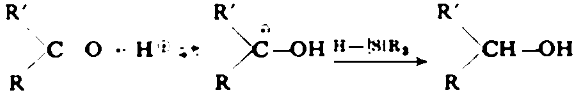


It is to be noted that methylcyclohexanol trifluoroacetate fails to react with triethylsilane but addition of an equimolecular amount of trifluoroacetic acid to the reaction mixture gives rise to methylcyclohexane in the same yield as on hydrogenation of methylcyclohexene using a olefine:silane:acid ratio of 1:1:2. Secondary trifluoroacetate, in particular that of cyclohexanol, does not react with triethylsilane even in the presence of an equimolecular amount of trifluoroacetic acid.

Olefins with a terminal double bond, such as 1-hexene, when heated in ampoules at 140° using a olefine:silane:acid ratio of 1:1:2 give no hydrogenation products. When trifluoroacetic acid was used in large excess (3·5 fold) the reaction products contained 2-hexene and hexane. It is possible that isomerization of 1-hexene into 2-hexene was followed, under the experimental conditions, by hydrogenation leading to hexane.

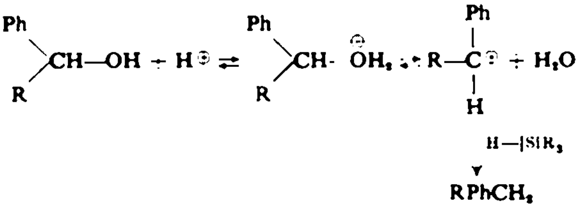
It was anticipated that a double carbon-oxygen bond would also undergo hydrogenation under the experimental conditions and ketones such as methyl ethyl ketone and cyclohexanone when used in a ketone:silane:trifluoroacetic acid ratio of 1:1—2:2 yield after 10–15 hr at 55° trifluoroacetates of the respective alcohols. However, in ketones containing at least one benzene ring adjacent to the CO group hydrogenation is more complete and the latter is converted to a methylene group. Thus the hydrogenation of aryl ketones results in good yield of hydrocarbons, acetophenone and benzophenone yielding ethylbenzene (70%) and diphenylmethane (94%) respectively.

The mechanism of the reaction may be described by the following scheme:



$$R'RC{=}O + H^{\oplus} \rightleftarrows R'R\overset{\oplus}{C}{-}OH \xrightarrow{H-SiR_3} R'RCH{-}OH$$

With R′ = Ph the following reaction may take place:



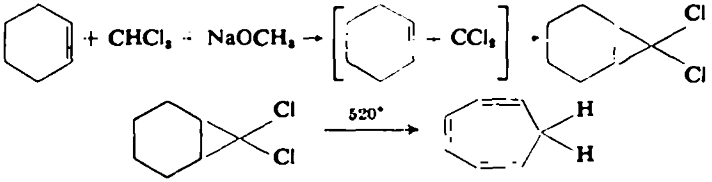
$$PhRCH{-}OH + H^{\oplus} \rightleftarrows PhRCH{-}\overset{\oplus}{O}H_2 \rightleftarrows R{-}\overset{Ph}{\underset{H}{C^{\oplus}}} + H_2O;\quad R{-}\overset{Ph}{\underset{H}{C^{\oplus}}} \xrightarrow{H-SiR_3} RPhCH_2$$

The introduction into the benzene ring of an electron-withdrawing substituent *para* to the CO, e.g. a protonated dimethylamino group slows down the reaction considerably. Thus, the Michler ketone is converted to bis-dimethylaminodiphenyl methane after the reaction mixture has been heated for 40 hr at 90–95°.

EXPERIMENTAL

Trifluoroacetic acid used had $H_0 = -3{\cdot}15$ as determined by Hammett method, with 2,4-dichloro-6-nitroaniline as indicator.[11] Silanes were prepared from $SiHCl_3$ by Grignard reaction.[12] Hydrocarbons were synthesized by conventional procedures or kindly supplied by the laboratory of B. A. Kazansky.

Cylcoheptatriene was obtained by Winberg's method[13] by the following scheme:



To purify the resulting cycloheptatriene from toluene it was converted to tropylium bromide.[14] The tropylium salt was reduced with LAH to cycloheptatriene.

Starting and end products were analysed by GLC. Qualitative determinations were effected on chromatograph Chrom-1 with flame ionization detection and a column filled with 13% β,β'-dioxypropionitrile on a diatomite brick for hydrocarbons, and 10% Tween-20 on a INZ-600 brick for ketons. N was used as carrier gas. The column was 2 meters in length and 4 mm diam. It was operated for hydrocarbons at 24–26° and 160–180 mm N press in the evaporator. Peaks were identified by introducing into the specimen authentic samples. In order to substantiate the identity of compounds with coinciding peaks the analysis was repeated on the column filled with reoplex 400.

Quantitive determinations of hydrocarbons were carried out on the chromatograph "Willy Guide", "GCHF-18/2T". The column was 2 m. in length and 6 mm i.d. and filled with 10% reoplex 400 on a diatomite brick using He as carrier-gas, at 36°.

We made use of the method of inner standardization (or labelling).[15] Before carrying out the analysis a weighed quantity of a known substance whose heat conductivity was equivalent to that of the substance to be determined was introduced into the weighed specimen. The calculation was made in terms of the formula:

$$Pi = P\frac{t_{x1}h_{x1}}{t_x h_x}$$

where Pi is the amount of the substance being determined in the specimen (mg),
P is the amount of the reference substance introduced.
t_x is the retention time of the reference substance,
t_{x1} is the retention time of the substance being determined,
h_x is the peak height of the reference substance,
h_{x1} is the peak height of the substance being determined.

I. *The determination of the ability of different olefines to undergo ionic hydrogenation*

Hydrogenation was effected by using trifluoroacetic acid as proton donor and triethylsilane as ion donor. The reaction was carried out (a) at 50° during 10 hr, and (b) at 20° during 120 hr. The olefine:triethylsilane:trifluoroacetic acid ratio was 1:1:2.

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[11] L. P. Hammett and M. A. Paul, *J. Am. Chem. Soc.* **56**, 830 (1934).

[12] J. W. Jenkins, N. L. Lavery, P. R. Guenther and H. W. Post, *J. Org. Chem.* **13**, 862 (1948).

[13] H. E. Winberg, *J. Org. Chem.* **24**, 264 (1959); USP, 283106 (1958).

[14] D. N. Kursanov and M. E. Vol'pin, *Dokl. Akad. Nauk. SSSR* **113**, 339 (1957).

[15] V. I. Kurko, *Gazokhromatograficheskу analysis pistchevykh produktov. Zh. Pistchevaya promyshlennost*. Moskva (1965).

To mixture of triethylsilane (0·01 mole) and trifluoroacetic acid (0·02 mole) the olefin (0·01 mole) was added slowly. The resulting mixture was poured into water, the hydrocarbon layer separated and the aqueous layer extracted with ether or benzene. The combined organic layers were then neutralized, washed with water, dried, distilled and analysed by GLC. The experimental results are summarized in Table 1.

TABLE 1. HYDROGENATION OF OLEFINES UNDER MILD CONDITIONS

Starting olefine	Hydrogenation	Hydrogenation product
1-Hexene	No	—
2-Hexene	No	—
4-Methyl-2-pentene	No	—
2-Methyl-2-butene	Yes	2-Methylbutane
2-Methyl-1-pentene	Yes	2-Methylpentane
Cyclohexene	No	—
1-Methylcyclohexene	Yes	Methylcyclohexane
1-Methylcyclopentene	Yes	Methylcyclopentane
Styrene	Yes	Ethylbenzene

The reaction of methylcyclohexene, triethylsilane and trifluoroacetic acid (1:1:1·5 ratio) was carried out at 60° during 5 hr plus 100 hr at 20° gave triethylsilane trifluoroacetate in a 40% yield of theory, b.p. 150–151°, n_D^{20} 1·3748. Lit., b.p. 153°; n_D^{20} 1·3720.[16] (Found: C, 42·34, 42·50; H, 6·36, 6·63; F, 24·68, 24·95, $(C_2H_5)_3SiOCOCF_3$ requires: C, 42·11; H, 6·58; F, 25%.)

When during the reaction with a tenfold excess of trifluoroacetic acid the evolving gas was entrapped at room temp the yield of hydrogen was 4% of theory. The same experiment gave methylcyclohexane in a 88% yield.

TABLE 2. DEPENDENCE OF METHYLCYCLOHEXANE YIELD ON THE AMOUNT OF CF_3COOH PER 1 MOLE OF METHYLCYCLOHEXENE AND 1 MOLE OF TRIETHYLSILANE

CF_3COOH (mole)	Yield of methylcyclohexane (%)	
	at 50° for 10 hr	at 20° for 120 hr
1	6	4
1·5	40	—
2	67	73
2·5	72	68
3	71	70
4	72	73
5	67	67
10	—	78*

* The reaction took 1 hr.

II. *Interaction of trifluoroacetate and silane*

Methylcyclohexyltrifluoroacetate was synthesized from methylcyclohexene and trifluoroacetic acid in the presence of conc H_2SO_4, b.p. 67·0–69·5° at 38 mm, n_D^{20} 1·3900. Lit.[18], b.p. 47·5° at 10 mm, n_D^{20} 1·3891.

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[16] H. Anderson and G. N. Stanislow, *J. Org. Chem.* **18**, 1716 (1953).

[17] P. DiGiorgio, W. Strong, L. Sommer and F. Whitmore, *J. Am. Chem. Soc.* **68**, 1380 (1946).

[18] V. N. Setkina, D. N. Kursanov and E. V. Bykova, *Izvest. Akad. Nauk SSSR. Otdel. khim. Nauk* 1367 (1962).

(a) A soln of methylcyclohexyltrifluoroacetate (0·013 mole) in triethylsilane (0·013 mole) was left for 190 hr at 20°. GLC showed that the reaction gave only traces of methylcyclohexane (0·8% of theory). In 1400 hr the analysis was repeated but the percentage of methylcyclohexane practically unchanged.

(b) To a soln of methylcyclohexyltrifluoroacetate (0·006 mole) and triethylsilane (0·006 mole), trifluoroacetic acid (0·06 mole) was added and the mixture left for 150 hr at 20°. GLC showed the products to contain methylcyclohexane in a 76% yield of theory.

(c) Cyclohexyltrifluoroacetate was synthesized from cyclohexene and trifluoroacetic acid in the presence of conc. H_2SO_4, b.p. 63·5° at 39 mm, n_D^{20} 1·3840. Lit.[10], b.p. 150° at 759 mm, n_D^{20} 1·3827. Equimolecular amounts of cyclohexyltrifluoroacetate, triethylsilane and trifluoroacetic acid were heated at 20° for 170 hr. After conventional treatement the mixture was investigated by GLC and showed a complete absence of cyclohexane.

III. *Search for hydrogenation conditions of unbranched olefines*

Raising the temperature. Experiments were conducted for 10 hr at 140° in sealed ampoules at olefine–triethylsilane–trifluoroacetate acid ratio of 1:1:2. No 1-hexene was hydrogenated under these conditions. With 2-hexene and cyclohexene the chromatogram revealed small peaks of hexane and cyclohexane, respectively. In the case of cyclohexene, peaks characteristic of methylcyclopentene and methylcyclopentane were also found.

Increasing the amount of fluoroacetic acid to 3·5 moles per 1 mole of olefine and 1 mole of silane gave with 2-hexene and cyclohexene the same results as obtained at 140°. On the other hand, 1-hexene was partly hydrogenated to form hexane. It might be suggested that the first step of the reaction involves isomerization of 1-hexene to 2-hexene followed by its hydrogenation.

Addition of H_2SO_4 in catalytic amounts failed to bring about hydrogenation of cyclohexene at 50° during 20 hr. However, under these conditions 4-methyl-2-pentene was hydrogenated giving methylpentane in a 70% yield. This seems to be due to acid isomerization of 4-methyl-2-pentene to 2-methyl-3-pentene which then undergoes hydrogenation.

IV. *Miscelleneous donors of hydride-ion*

(a) *Phenyl-substituted silanes.* To phenyl-substituted silane (0·01 mole) methylcyclohexene (0·03 mole) was added and then trifluoroacetic acid (0·05 mole). In 100 hr the mixture was treated as usual. The yield of methylcyclohexane amounted to 8% for monophenylsilane, 30–45% for diphenylsilane, and 13% for triphenylsilane per hydrogen abstracted as hydride of the silane involved in the reaction.

(b) *Hydrocarbons.* To a mixture of 2-methylpentane (0·01 mole) and methyl-1-cyclohexene (0·01 mole), trifluoroacetic acid (0·02 mole) was added. The mixture was heated for 30 hr at 50° and then treated as usual. Chromatographic analysis revealed the presence of methylcyclohexene, methylcyclohexane, 2-methylpentane, and 2-methyl-1-pentene.

When the reaction of methyl-1-cyclopentene, methylcyclohexane, and trifluoroacetic acid was carried out using the same ratio of components and under the same conditions the reaction products were found contain methylcyclopentane together with starting products. When using cycloheptatriene as hydride-ion donor the conditions of the reaction were as follows: to 0·01 mole of methylcyclohexene and 0·03 mole of trifluoroacetic acid, 0·03 mole of cycloheptatriene in decane solution was added and the mixture kept at 90° for 1–5 hr. GLC revealed 5–6% of methylcyclohexane of theory in the reaction products. It also pointed to the presence of a tropylium ion, identified as chloroplatinate.

V. *Ionic hydrogenation of the carbonyl group*

(a) *Methylethylketone.* To the ketone (0·01 mole) and trifluoroacetic acid (0·02 mole) was added dropwise with stirring 0·01 mole of silane taking care that the temp did not exceed 50° and the mixture was kept at 55°. The whole system was carefully protected from moisture. After 10 hr heating the mixture was neutralized with K_2CO_3, the organic layer separated, the aqueous layer extracted by ether and the ethereal extracts combined with the organic layer. On removing ether the dried products were distilled. GLC showed the fraction boiling below 120° to contain the starting ketone, silane, trifluoroacetate of 2-butanol and 2-butanol. The fraction boiling above 170° was repeatedly distilled *in vacuo* and yielded hexaethyldisiloxane, b.p. 99–101° at 10–12 mm, n_D^{20} 1·4341. Lit., 233°, at 734 mm.

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[10] E. J. Bourne, M. Stacey, J. C. Tatlow and R. Warrall, *J. Chem. Soc.* 3268 (1958).

n_D^{20} 1·4340.[17] A special experiment showed that treatment of triethylsilanol trifluoroacetate with K_2CO_3 gave hexaethyldisiloxane in a quantitative yield. The percentage of resulting hydrogenation product corresponded to that of hexaethyldisiloxane being 40% of theory.

(b) *Cyclohexanone*. Experiments were carried out as above. The reaction products were distilled without preliminary treatment and the fraction boiling at 150–200° was collected. This was washed with bisulphite and boiled with KOHaq for 3 hr. The hydrolysate was poured into a sat. NaClaq, the organic layer was separated and combined with ethereal extracts. The ethereal soln was washed with sat NaClaq until neutral. The dried soln was distilled over CaO and analysed for lapile H. The fraction free of solvent weighed 5·02 g, the specimen 0·831 mg, the percentage of active H was 0·67, the analysed mixture contained 66·60% of cyclohexanol, alcohol was obtained in a 55% yield of theory.

Hydrogenation of cyclohexanone at the ketone:acid:silane ratio of 1:2:2 for 20 hr at 55° gave rise to cyclohexanol in a 74% yield.

(c) *Acetophenone*. 0·01 mole of ketone was heated at 55° with 0·03 mole of trifluoroacetic acid and 0·03 mole of silane. The reaction was run as described for methylethylketone. After standing 15 hr, the reaction mixture was distilled on a column with 13 ideal plates and fractions containing ethylbenzene were collected (the content of ethylbenzene being checked by GLC). Quantitative determinations were carried out on the device KhT-63 (gas balance, reoplex 20% inner reference compound-toluene), yield of ethylbenzene was 70% of theory.

(d) *Benzophenone*. The component's ratio was 1:3:3. The reaction mixture was heated for 20 hr at 55–60°. The reaction course was followed by chromatography on alumina in the system CCl_4–Chf (1:3). Without preliminary decomposition a fraction boiling above 200° was separated which gave after freezing b.p. 200° and after freezing out diphenylmethane m.p. 23–24° in a 94% yield of theory. The m.p. of the tetranitroderivative was found to be 171°, lit. 171°.[20]

(e) *Michler' ketone*. Experiments were carried out in argon sweep with the components ratio 1:10:4 for 40 hr at 90–95°. The reaction mass disintegrated after dissolution into layers with the upper one gradually becoming pale and white crystals appearing on the flask walls. The reaction mixture was poured into a soda soln, the products extracted with benzene and the extract washed with water. The dried soln was freed of the solvent and cold alcohol added to the ppt. The latter after recrystallization from alcohol, yielded 75% of bis-dimethylaminodiphenylmethane, m.p. 89–90°; lit., m.p. 91°.[21]

[20] G. Parkes and R. Morley, *J. Chem. Soc.* 1478 (1936).

[21] M. Nathansohn and P. Müller, *Ber. Dtsch. Chem. bes.* **22**, 1882 (1889).