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REACTIONS OF ACETONE AND ISOPROPYL ALCOHOL WITH THE PRODUCTS OF REDUCTION OF TITANIUM CHLORIDES WITH METALLIC MAGNESIUM

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Summary

Reactions of low-valent titanium complexes (formed by reduction of $TiCl_3 \cdot 3$ THF and $TiCl_3 \cdot 4$ i-PrOH with Mg in nitrogen) with acetone and isopropanol were investigated. It was observed that acetone is hydrogenated by the products of the system $TiCl_3 \cdot 3$ THF + Mg + N_2. These products also dehydrogenate isopropanol to acetone and pinacoline. Isopropanol present in the coordination sphere of $TiCl_3 \cdot 4$ i-PrOH reacts with Mg giving exclusively alkoxide derivatives.

Introduction

The possible synthesis of amines (and other organic nitrogen compounds) by means of complexes containing the nitride bond as the nitrogen source it important but as yet unresolved. The following reactions leading to the formation of amines are known:

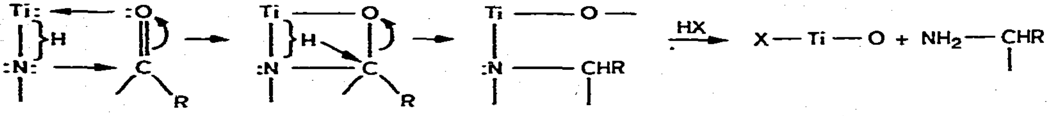
$$TiCl_4 + N_2 + C_{10}H_8 \xrightarrow{H^+} \text{naphthylamines (ref. 1)} \qquad (1)$$

$$Cp_2TiCl_2 + Mg + N_2 + R_2CO \xrightarrow{H^+} R_2CHNH_2, (R_2CH)_2NH \text{ (ref. 2)} \qquad (2)$$

$$(CH_3)_3SiCl + Li + N_2 \xrightarrow{\text{transition metal}} N[Si(CH_3)]_3 + LiCl \text{ (ref. 3)} \qquad (3)$$

$$Cp_2TiPh_2 \xrightarrow[\Delta]{N_2,\ 90\text{-}100\ \text{atm}} PhNH_2, PhNHNH_2 \text{ (ref. 4)} \qquad (4)$$

Van Tamelen [2] obtained 3-pentylamine and bis(3-pentylamine) in 6 to 13% yield (with respect to bound N_2) from diethyl ketone in the system [Cp_2TiCl_2 + Mg + N_2]. He isolated the amines after hydrolysis with water, but he did not give any data showing whether the carbonyl compound was reduced to the alcohol or not. The following mechanism has been proposed for this reaction:



(5)

[$TiCl_3 \cdot 3\ THF + Mg + N_2$] is a simpler system than that used by Van Tamelen. In this system the compound $NTiMg_2Cl_2 \cdot THF$ (I) is formed [5] as a result of reduction of titanium chloride with magnesium and the reaction of low valence titanium complexes with molecular nitrogen. In compound I nitrogen is in the nitride form, i.e. in the state which on alkaline hydrolysis liberates ammonia. The only reaction of compound I with carbonyl compounds described in the literature is the reaction with benzoyl chloride, which leads to the formation of $NTiCl(COPh)_{1.5}$. In this case the formation of organic nitrogen compounds was not observed.

On the other hand, the reaction of $TiCl_3 \cdot 3\ THF$ with Mg under argon gives a mixture [M]:

$$TiCl_3 \cdot 3\ THF + Mg \xrightarrow{THF, Ar} [M] \qquad (6)$$

The first paper describing the use of [M] in organic syntheses was a report concerning the reductive coupling of carbonyl compounds leading to the formation of alkenes [6]:

$$[M] + R_2C{=}O \rightarrow R_2C{=}CR_2 \qquad (7)$$

Mixture [M] reacts also as an oxygen-removing agent [7]:

$$[M] + (RO)_3PO \rightarrow (RO)_3P \qquad (8)$$

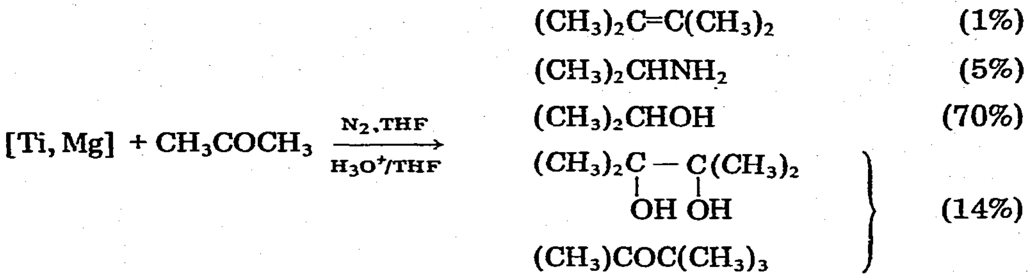
$$[M] + R_2SO \rightarrow R_2S \qquad (9)$$

Therefore investigation of reactions of the products obtained from the system $TiCl_3 \cdot 3\ THF + Mg + N_2$ in THF (in which $NTiMg_2Cl_2$ is the main component) with carbonyl compounds was thought to be of interest and we chose acetone as the model carbonyl compound. In the later parts of the present work the symbol used to denote the solution of products obtained from the system $TiCl_3 \cdot 3\ THF + Mg + N_2$ in THF will be [Ti, Mg]:

$$TiCl_3 \cdot 3\ THF + Mg + N_2 \xrightarrow[N_2]{THF} [Ti, Mg] \qquad (10)$$

Results

The reaction of [Ti, Mg] with acetone takes place according to the following scheme:



$$[\mathrm{Ti,Mg}] + \mathrm{CH_3COCH_3} \xrightarrow[\mathrm{H_3O^+/THF}]{\mathrm{N_2,THF}} \begin{array}{ll} \mathrm{(CH_3)_2C{=}C(CH_3)_2} & (1\%) \\ \mathrm{(CH_3)_2CHNH_2} & (5\%) \\ \mathrm{(CH_3)_2CHOH} & (70\%) \\ \left.\begin{array}{l} \mathrm{(CH_3)_2\underset{OH}{C}-\underset{OH}{C}(CH_3)_2} \\ \mathrm{(CH_3)COC(CH_3)_3} \end{array}\right\} & (14\%) \end{array} \qquad (11)$$

The yields are calculated with respect to acetone. 2,3-Dimethylbut-2-ene is formed before hydrolysis of the mixture, and the other products after hydrolysis. Isopropanol is the main product. The mixture [Ti, Mg] used in the reaction with acetone was modified in various ways and the results of these studies are shown in Table 1. The fact that hydrolysis was necessary for the isolation of products of reaction 11 indicates that alkoxide bonds are formed and that the formation of these bonds is accompanied by hydrogenation of the carbonyl carbon atom.

Another reaction possible in this system is the formation of a compound containing the structural unit $(CH_3)_2C(\text{metal})$—O—metal. In order to find out which of these reactions takes place we hydrolysed the product of reaction 11 using deuterium oxide. The resulting labelled isopropanol, $(CH_3)_2CHOD$, indicates that [Ti, Mg] either contained a compound having the Ti—H bond or Mg—H bond or that it is able to transfer hydrogen atoms from the solvent to an acceptor such as the carbonyl carbon atom. The products of the coupling reaction were observed also in conditions where the reaction mixture [Ti, Mg] was made free from all unreacted magnesium. This excludes the possibility that magnesium was responsible for the coupling process.

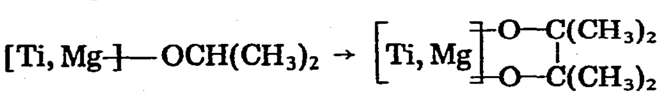
The reduction of acetone to magnesium or titanium isopropoxide by the [Ti, Mg] system made it necessary to investigate the reactions of isopropanol with this system:

$$[\mathrm{Ti,Mg}] + \mathrm{(CH_3)_2CHOH} \rightarrow \text{products} \qquad (12)$$

The results are shown in Table 2.

In the distillate obtained after evaporation of the mixture of products resulting from reaction 12 we observed neither unreacted isopropanol (for the molar ratio Ti/isopropanol 1/1) nor volatile products resulting from this substance. Since the products could be isolated only after hydrolysis, the following reactions must have taken place:

$$[\mathrm{Ti,Mg}] + \mathrm{(CH_3)_2CHOH} \rightarrow [\mathrm{Ti,Mg}]\!-\!\mathrm{OCH(CH_3)_2}$$



$$[\mathrm{Ti,Mg}]\!-\!\mathrm{OCH(CH_3)_2} \rightarrow \left[\mathrm{Ti,Mg}\right]\!\begin{array}{l} -\mathrm{O{-}C(CH_3)_2} \\ \qquad\;\; | \\ -\mathrm{O{-}C(CH_3)_2} \end{array} \qquad (13)$$

Further evidence for the eqns. 13 was afforded by hydrogen evolution studies.

The presence of isopropanol in the post-reaction mixture from the very start of the reaction in the molar ratio Ti/>CHOH 1/1 does not decrease the

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TABLE 1

REACTIONS OF THE PRODUCTS OF THE SYSTEM $TiCl_3 \cdot 3\ THF + Mg + N_2$ WITH ACETONE

Reactants and molar ratio		Yield based on CH_3COCH_3 (%)					Yield of NH_3 (%)	Yield of $(CH_3)_2CHNH_2$ calculated for combined N_2 (%)
		$(CH_3)_2CHNH_2$	$(CH_3)_2CHOH$	$(CH_3)C{=}C(CH_3)_2$	pinacone and pinacoline	CH_3COCH_3		
[Ti,Mg] + CH_3COCH_3	1/1	5.0	70	1.0	14	10	82	6.5
[Ti,Mg] + CH_3COCH	1/25	0	0.9	0	2	97	76	0
[Ti,Mg] + Na + CH_3COCH_3	1/3/1	1.1	16.0	0	64	19	50	2.0
[Ti,Mg] + NaH + CH_3COCH_3	1/3/1	4.1	67	4.0	13	12	79	5.0
[Ti,Mg] + CCl_4 + CH_3COCH_3	1/1/1	0	65	0	27	8	63	0
[Ti,Mg] + I_2 + CH_3COCH_3	1/2/1	0	68	1.0	20	11	75	0
$TiCl_4$ + Na + CH_3COCH_3	1/3/1	0.6	29	2.0	15.4	53	20	3.0
Cp_2TiCl_2 + Na + CH_3COCH_3	1/3/1	1.0	49	0	22	28	41	2.4

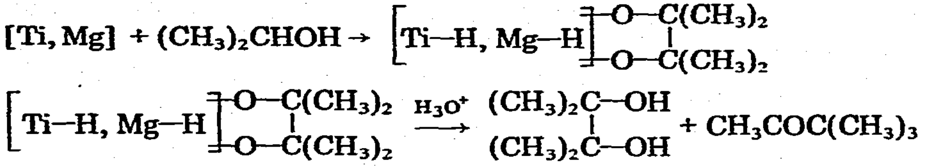
TABLE 2

REACTION OF THE SYSTEM $TiCl_3 \cdot 3$ THF + Mg + N_2 + $(CH_3)_2CHOH$ AND [Ti,Mg] + $(CH_3)_2CHOH$

Molar ratio of reagents	Time of addition of isopropanol	Distillate (%)				Hydrolysate (%)				NH_3 (%)
$Ti/Mg/(CH_3)_2CHOH$		$(CH_3)_2CHNH_2$	CH_3COCH_3	pinacone	$(CH_3)_2CHOH$	$(CH_3)_2CHNH_2$	CH_3COCH_3	pinacone	$(CH_3)_2CHOH$	
1/4/1	At the beginning of the reaction	0	0	0	0	0	0	0	100	76.0
1/4/1	24 h after the beginning of reaction 10	0	0	0	0	0	0	26.0	73	71.0
1/4/4	At the beginning of the reaction	0	0	0	0	0	0	0	100	3.7
1/4/4	24 h after the beginning of reaction 10	0	1.5	0	6.0	0.5	1.0	1.2	79	60.0

nitrogen-binding activity, but higher concentrations of isopropanol have an inhibiting effect on the reaction with molecular nitrogen.

We observed that a considerable quantity of pinacone was formed from isopropanol when it was added to the solution 24 hours after the start of reaction 10:



$$[\mathrm{Ti,Mg}] + (CH_3)_2CHOH \rightarrow \left[\mathrm{Ti{-}H, Mg{-}H}\right]\begin{matrix} -O-C(CH_3)_2 \\ | \\ -O-C(CH_3)_2 \end{matrix}$$

$$\left[\mathrm{Ti{-}H, Mg{-}H}\right]\begin{matrix} -O-C(CH_3)_2 \\ | \\ -O-C(CH_3)_2 \end{matrix} \xrightarrow{H_3O^+} \begin{matrix} (CH_3)_2C-OH \\ | \\ (CH_3)_2C-OH \end{matrix} + CH_3COC(CH_3)_3 \qquad (14)$$

Thus the system [Ti,Mg] on standing must acquire dehydrogenating and coupling properties. Isopropylamine was formed in very small amounts.

The results of these studies prompted us to investigate the reaction of $TiCl_3 \cdot 4$ i-PrOH with magnesium and with magnesium and acetone. In the system $TiCl_3 \cdot 4$ i-PrOH, isopropanol is in the coordination sphere of the metal, i.e. in the direct neighbourhood of the titanium atom which undergoes reduction:

$$TiCl_3 \cdot 4\ \text{i-PrOH} + Mg \rightarrow TiCl_2 \cdot 4\ \text{i-PrOH} + MgCl_2 \qquad (15)$$

$$TiCl_2 \cdot 4\ \text{i-PrOH} + Mg \rightarrow (\text{titanium in valence state} < 2) \cdot (\text{i-PrOH})_x \rightarrow$$

$$\text{alkoxides of Ti and Mg and other products} \qquad (16)$$

In this situation isopropanol can undergo dehydrogenation to a larger extent than when it is dissolved in the reaction mixture. Deoxygenation of isopropanol is also possible. The results of our investigation of this reaction are shown in Table 3.

It was also of interest to know if the product of reactions 15 and 16 would react with acetone giving bound isopropanol (reduction) and pinacone (coupling). Therefore we performed reactions 17-19. The results are shown in Table 4.

$$TiCl_3 \cdot 4\ \text{i-PrOH} + Mg \xrightarrow{N_2} \text{products (a)} \qquad (17)$$

$$\text{products (a)} + (CH_3)_2C{=}O \xrightarrow{N_2} \text{products (b)} \qquad (18)$$

$$\text{products (b)} + H_3O^+ \xrightarrow[THF]{N_2} (CH_3)_2C{=}O + (CH_3)_2CHOH \qquad (19)$$

TABLE 3

REACTION OF THE SYSTEM $TiCl_3 \cdot 4$ i-PrOH + Mg + ADDITIONAL REAGENT + N_2

Molar ratio of reagents	Distillate (%)		Hydrolysate (%)	
$TiCl_3 \cdot 4$ i-PrOH/Mg/additional reagent	$(CH_3)_2CHOH$	CH_3COCH_3	$(CH_3)_2CHOH$	CH_3COCH_3
1/4/4Na	0	0	96	0
1/4/4NaH	30	0	68	0
1/4/2AlEt$_3$	0	0	96	0
1/4/—	0.5	0.5	96	

TABLE 4

REACTIONS OF THE SYSTEM $TiCl_3 \cdot 4$ i-PrOH + Mg ACCORDING TO EQNS. 17-19

Molar ratio of reagents		Yields of products with respect to the amount of CH_3COCH_3 and $(CH_3)_2CHOH$					
$TiCl_3 \cdot 4$ i-PrOH/Mg/acetone		Amount of products in THF distillate before hydrolysis after 24 h of the reaction (%)		Amount of products after hydrolysis with water of the residue of the distillation (%)		Amount of products after hydrolysis with H_2SO_4 of the residue (%)	
		$(CH_3)_2CHOH$	CH_3COCH_3	$(CH_3)_2CHOH$	CH_3COCH_3	$(CH_3)_2CHOH$	CH_3COCH_3
	1/4/2	0	0	93	5	2	0,1
4 moles of Na added	1/4/2	33	1.5	60,3	3.1	1,5	0,5
2 moles of AlEt added	1/4/2	0	0.12	65	10	20,7	4,0
4 moles of NaH added	1/4/2	27	0,2	71	1.1	0,7	0,1

Discussion

In contrast to complex Ti and Mg compounds prepared under argon, complex compounds of these metals which contain nitride bonds remove oxygen from acetone only to a small degree but even so the C=O bond is ruptured. The main product (after hydrolysis) is isopropanol and therefore the main reaction is the attack on the C=O double bond.

Hydrolysis with D_2O gives $(CH_3)_2CHOD$ so the first product of the reaction involves the alkoxide bond which is formed as a result of the migration of hydrogen: $(CH_3)_2CH{-}O{-}$metal. The relatively high yield of the coupling products, i.e. pinacone and pinacoline (14%), indicates a considerable contribution from the reaction in which the transition state can be represented as $(CH_3)_2C{-}O{-}$metal. The low yield of isopropylamine is probably due to the low power of the [Ti, Mg] mixture as the oxygen-removing agent. For this reason the concentration of reactive $(CH_3)_2C^+$, $(CH_3)_2C\colon$ or $(CH_3)_2CH^{\bullet}$ is low.

Modifications of $NTiMg_2Cl_2 \cdot THF$ by means of reducing and oxidising agents such as NaH, CCl_4 and I_2 did not cause enhancement of the amine yield, although the oxidising agents CCl_4 and I_2 should have a considerable effect on the Ti—N bond by increasing the valence state of titanium (eqn. 20).

$$[N{-}Ti^x] + CCl_4, I_2 \rightarrow [N{-}Ti^{x+1}{-}Cl, I] \qquad (20)$$

However, this had no effect on the reactivity of $[N{-}Ti^x]$ with respect to $(CH_3)_2CO$. It is also possible that isopropylamine is formed from a nitrogen compound other than $NTiMg_2Cl_2 \cdot THF$ existing in reaction mixture 10 or from its isomer.

The nitrides which are formed in the system $[Cp_2TiCl_2 + Mg + N_2]$ as reported by Van Tamelen also react with carbonyl compounds giving low yields of organic nitrogen compounds. The two systems are compared in Table 5. Organic nitrogen compounds obtained from the $[Cp_2TiCl_2 + Mg + N_2]$ system are formed in 6 to 13% yield.

The reactions of [Ti,Mg] with acetone, viz., (a) hydrogenation of C=O bond to give a $>$CHO—metal system; (b) decomposition of C=O bond followed by coupling to give a $(CH_3)_2C{-}O{-}$metal$-O{-}C(CH_3)_2$ system; (c) the formation of isopropylamine precursor, probably having the formula $(CH_3)_2CH{-}NH{-}$metal; (d) the synthesis of 2,3-dimethyl-but-2-ene, prompted us to investigate

TABLE 5

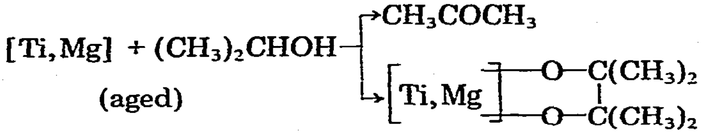
COMPARISON OF REACTIVITIES OF CARBONYL COMPOUNDS WITH NITRIDE NITROGEN IN $[Cp_2TiCl_2 + Mg + N_2]$ and $[TiCl_3 \cdot 3\ THF + Mg + N_2]$

Molar ratio Ti/Mg	$[Cp_2TiN_2 + Mg + N_2]$ + carbonyl compound	$[TiCl_3 \cdot 3\ THF + Mg + N_2]$ + CH_3COCH_3
	1/4	1/2.5
Solvent	THF	THF
Time of reaction of carbonyl compound with the titanium-containing system (h)	120	24
Yield of primary amine (%)	4-8	5
Yield of secondary amine (%)	7.5	0
Yield of alcohol (%)	No information	70

the reaction of [Ti, Mg] with $(CH_3)_2CHOH$. Isopropanol added to the mixture $TiCl_3 \cdot 3\,THF + Mg + N_2$ at the beginning of the reaction in the molar ratio Ti/$(CH_3)_2CHOH$ 1/1 does not inhibit the formation of nitride complexes from N_2, but at higher molar ratios it does. In distillates obtained after the evaporation of the post-reaction mixture [Ti, Mg] + $(CH_3)_2CHOH$ we could not detect isopropanol even when working at the molar ratio Ti/$(CH_3)_2CHOH$ 1/4, but isopropanol appeared after hydrolysis of the residue. There is therefore no doubt that reaction 21 takes place.

$$[\mathrm{Ti,Mg}] + (CH_3)_2CHOH \rightarrow [\mathrm{Ti,Mg}]\!\!-\!OCH(CH_3)_2 \qquad (21)$$

In the case when isopropanol was added to "aged" [Ti, Mg] (24 h after the start of reaction 10) we observed the formation of isopropanol dehydrogenation products, i.e. acetone and pinacone (eqn. 22). This observation is of



$$\underset{\text{(aged)}}{[\mathrm{Ti,Mg}]} + (CH_3)_2CHOH \begin{cases} \rightarrow CH_3COCH_3 \\ \rightarrow [\mathrm{Ti,Mg}]\begin{matrix} -O-C(CH_3)_2 \\ | \\ -O-C(CH_3)_2 \end{matrix} \end{cases} \qquad (22)$$

importance since the mixture [Ti,Mg] always retains its hydrogenating property and converts acetone to $(CH_3)_2CH{-}O{-}$metal and $(CH_3)_2C{-}O{-}$met.$-O-C(CH_3)_2$. In a further investigation of this system we examined the reactivity of $TiCl_3 \cdot 4$ i-PrOH.

When $TiCl_3 \cdot 4$ i-PrOH dissolves in THF, isopropanol appears in the solution; the ligand exchange reaction 23 therefore must take place.

$$TiCl_3 \cdot 4\,\text{i-PrOH} + THF \rightleftharpoons TiCl_3 \cdot 3\,\text{i-PrOH}(THF)_x + (CH_3)_2CHOH \qquad (23)$$

The reaction with nitrogen does not take place at Ti/Mg molar ratios at which it is observed in the case of the $TiCl_3 \cdot 3$ THF complex. The reduction of tinanium to low valence states in which it exists in the complexes reacting with N_2 takes place when larger amounts of magnesium are used. During the reaction of $TiCl_3 \cdot 4$ i-PrOH with Mg we observed evolution of hydrogen.

By hydrolysis of the product of reaction 16 we obtained only isopropanol. The above three observations indicate that the reaction of $TiCl_3 \cdot 4$ i-PrOH with Mg in THF leads to a mixture of magnesium isopropoxide Mg[OCH—$(CH_3)_2$] and products of the type $[\mathrm{Ti,Mg}]\!\!-\!O{-}CH(CH_3)_2$. It is probable that these products react with N_2 and that the post-reaction mixture consists of magnesium isopropoxide and compounds containing nitride and alkoxide bonds.

Experimental

Titanium trichloride tetrahydrofuranate was prepared according to Theile [8]. 30 g of aluminium foil strips were allowed to react with 38 g of $TiCl_4$ (0.2 mol) in 300 ml of tetrahydrofuran for 2 days at room temperature. A blue crystalline precipitate appeared on the bottom of the flask and on the surface of the foil. The foil was removed from the reactor and the precipitate was filtered. After washing with two 50 ml portions of THF and drying, 54.5 g of the complex was obtained. The yield is 73%. (Analysis found: C, 38.6; H, 6.38; Cl, 28.07; Ti, 13.0. $C_{12}H_{24}O_3Cl_3Ti$ calcd.: C, 38.89; H, 6.48; Cl, 28.73; Ti, 12.9%.)

Synthesis of $TiCl_3 \cdot 4$ i-PrOH was performed according to H.L. Schlafer and R. Gotz [9].

Nitrogen and argon were dried and freed from oxygen by passing through columns containing BTS catalyst (Fluka), P_2O_5, KOH and molecular sieves.

Tetrahydrofuran was first dried by keeping for 1 day over KOH and 1 day over $LiAlH_4$. Then it was refluxed over fresh $LiAlH_4$ for several hours and distilled through a column. Immediately after the distillation it was freed from oxygen by bringing up to the boiling point repeatedly under a pressure in the range 0.2 to 0.4 Torr.

Synthesis of Yamamoto complex and analogous reactions: 20 ml of THF was added to 2.0 g (5.4 mmol) of $TiCl_3 \cdot 3$ THF and 0.33 g (13.5 mmol) of Mg under nitrogen. During 15 to 20 min stirring at room temperature the colour of the reaction mixture changed from blue to green and then black. After 90 min the acetone (or other appropriate reagent) was added by means of a hypodermic syringe. Several reactions were performed by adding different reactants [$(CH_3)_2CHOH$; NaH etc.] at the beginning of the reaction in the molar ratios indicated in the tables.

The organic products were analysed after evaporating (or hydrolysis and evaporating) by GLC using Giede 18.4-3 apparatus. Two columns: 3 m Carbowax 1500 on Chromosorb W AW and 3 m of SE30 on Chromosorb W AW 60 to 80 mesh were employed; flame ionization detector; N_2 flow 40 to 60 ml/min.

Evolution of H_2 was measured with a gas burette and the gas analysed by this same apparatus using katharometer detector and argon gas flow.

Acknowledgements

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