Direct Geminal Dimethylation of Ketones and Exhaustive Methylation of Carboxylic Acid Chlorides Using Dichlorodimethyltitanium

Manfred T. Reetz*, Jürgen Westermann, and *Suk-Hun Kyung*

Fachbereich Chemie der Universität Marburg,
Hans-Meerwein-Straße, D-3550 Marburg

The reaction of ketones with an excess of $(CH_3)_2TiCl_2$ (**6**) leads to the replacement of the carbonyl oxygen atom by two methyl groups. This mild method of direct geminal dimethylation involves Grignard-type addition followed by formation of tertiary carbocations which are captured by methyltitanium species. Additional functional groups such as primary alkyl chlorides, thioethers, aromatics, ethers, and esters are tolerated, but not thioketals. The procedure has been applied to the synthesis of (±)-cuparene (**44**). Similarly, carboxylic acid chlorides are converted to *tert*-butyl derivatives.

Direkte geminale Dimethylierung von Ketonen und erschöpfende Methylierung von Carbonsäurechloriden mit Dimethyltitandichlorid

Die Reaktion von Ketonen mit einem Überschuß von $(CH_3)_2TiCl_2$ (**6**) führt zum Ersatz des Carbonyl-Sauerstoffatoms durch zwei Methylgruppen. Diese milde Methode der direkten geminalen Dimethylierung beinhaltet Grignard-artige Addition gefolgt von der Bildung tertiärer Carbokationen, die von Methyltitan-Spezies abgefangen werden. Zusätzliche funktionelle Gruppen wie primäre Alkylchloride, Thioether, Aromaten, Ether oder Ester werden toleriert, nicht aber Thioketale. Die Methode wurde bei der Synthese von (±)-Cuparen (**44**) herangezogen. In ähnlicher Weise werden Carbonsäurechloride in *tert*-Butylderivate übergeführt.

The geminal dimethyl structural unit occurs frequently in terpenes, steroids and compounds of theoretical interest. Compounds containing these and other types of quarternary carbon atoms are generally prepared via multistep syntheses using a variety of techniques [1]. An attractive strategy calls for geminal dimethylation of ketones, i. e., the position specific replacement of the carbonyl oxygen by two methyl groups. This can be accomplished by a three step sequence $1 \rightarrow 2 \rightarrow 3 \rightarrow 4$ involving Wittig olefination, Simmons-Smith cyclopropanation and hydrogenolysis [2].
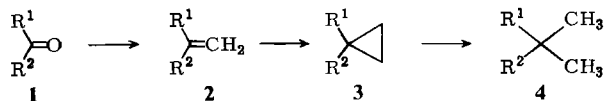

Although this sequence has been applied successfully in several instances [2], we sought a direct method. Previously, it had been shown that certain ketones are geminal dimethylated by a 3−4 fold excess of $Al(CH_3)_3$ in a closed vessel at 120−180°C [3].

However, the yields are meager due to competing enolization and rearrangements under such drastic conditions. Since we had already demonstrated that tertiary alkyl chlorides (prepared classically from ketones) react chemoselectively with Lewis acidic titanium reagents of the type CH_3TiCl_3 (5) or $(CH_3)_2TiCl_2$ (6) to form methylated alkanes at low temperatures[4], it seemed promising to devise a direct route employing titanium reagents. Here we describe the direct conversion $1 \rightarrow 4$ using $(CH_3)_2TiCl_2$ (6) under mild conditions[5].

$$1 \xrightarrow{(CH_3)_2TiCl_2 \ (6)} 4$$
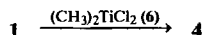
Optimization

Since the Ti−O bond is thermodynamically very strong (≈ 115 kcal/mol)[6], any reaction which leads to such a bond is expected to have a pronounced driving force[7]. Furthermore, we anticipated a mechanism in which methyltitanium reagents add to the carbonyl function, followed by an S_N1 process and capture of the carbonium ion by excess reagent. Thus, initial experiments employed CH_3TiCl_3 (5) and $(CH_3)_2TiCl_2$ (6) in combination with cyclohexanone in a polar ionizing solvent (e.g., CH_2Cl_2). The bis-etherate of CH_3TiCl_3 can be prepared simply by reacting ether solutions of CH_3MgX or CH_3Li with $TiCl_4$[8]. Unfortunately, ether-free solutions of CH_3TiCl_3 are not accessible by this route, so that $Zn(CH_3)_2$[*] must be used[4,9]. The same applies to $(CH_3)_2TiCl_2$[5,9]. Stock solutions of 5 and 6 in CH_2Cl_2 are accessible in $\geq 90\%$ yield simply by choosing the correct ratio of components.

$$Zn(CH_3)_2 \begin{cases} \xrightarrow{2 \ TiCl_4} CH_3TiCl_3 \quad 5 \\ \xrightarrow{TiCl_4} (CH_3)_2TiCl_2 \quad 6 \end{cases}$$
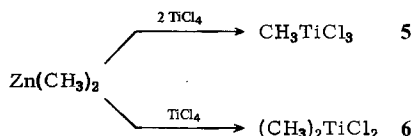
Various quantities of $Zn(CH_3)_2$ were allowed to react with $TiCl_4$ in CH_2Cl_2 followed by the addition of 10 mmol of cyclohexanone (7). The product mixtures consisted of the tertiary carbinol 8, the chloride 9 and the desired 1,1-dimethylcyclohexane (10), the product distribution depending upon the relative amounts of $Zn(CH_3)_2$ and $TiCl_4$ (Table 1).

7   8   9   10
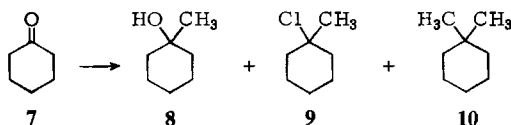
Table 1 allows for several important conclusions. One equivalent of CH_3TiCl_3 alone does not result in clean carbinol formation at room temperature (entry 1). This is very likely due to an elimination reaction of the initial Grignard-type adduct to form 1-methyl-cyclohexene, which undergoes further unknow reactions with titanium species[9]. At $-30\,°C$ a double or triple excess of CH_3TiCl_3 affords the tertiary chloride 9, but not 10

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[*] Pure $Zn(CH_3)_2$ is extremely *pyrophoric*. However, CH_2Cl_2 solutions are much less so and can be conveniently handled (much like *n*-butyllithium)[9].

Table 1. Geminal Dimethylation of Cyclohexanone[a]

Entry	TiCl$_4$ (mmol)	Zn(CH$_3$)$_2$ (mmol)	temp. (°C)	time (h)	conversion (%)		
					8	9	10
1	10	5	+22	1	– [b]	–	–
2	20[c]	10	–30	2	<10	85	–
3	30[c]	10	–30	4	–	>90	–
4	20	15	–30	2	–	40	50
5	10	10	–30	0.25	>90[d]	–	–
6	10	10	–30	4	>90[d]	–	–
7	20	20	–30	4	–	–	>85
8	22	22	–30 → +22	2	–	–	>90
9	22	22	–30	0.5	55	35	10
10	22[c]	22[c]	–30 → +22	2	–	–	>90[e]
11	10	20	–30 → +22	4	>90	–	–

[a] In all cases 10 mmol of **7** was used in CH$_2$Cl$_2$. – [b] Non-identified oligomeric residue. – [c] Half of the amount of reagent was initially used and the rest added after addition of **7**. – [d] If the reaction is allowed to run for 24 h, 1-methylcyclohexene and oligomeric material is formed. – [e] The yield of distilled **10** was 72%; no attempt at optimizing the isolation procedure was made.

(entries 2,3). In contrast, a 1:1 ratio of ketone and (CH$_3$)$_2$TiCl$_2$ results in clean formation of the carbinol **8** (entries 5,6). Thus, the reaction stops at the mono-addition stage, although the system contains an additional active methyltitanium species. In contrast, a double excess of (CH$_3$)$_2$TiCl$_2$, i.e., four methyl groups per carbonyl function, induces smooth geminal dimethylation (entries 7, 8, 10). If this reaction is quenched with H$_2$O prior to completion, all three products **8, 9** and **10** are observed. The results are in line with the following carbonium ion mechanism: a 1:1 mixture of **6** and **7** results in the Grignard-type adduct **11**. In the absence of additional **6**, the product of aqueous workup is the tertiary carbinol **8**, unless long reaction times (24 h) are chosen which lead to unidentified decomposition products. If an additional equivalent of **6** is present, it induces ionization and methylation via **11** → **12** → **10** and/or **11** → **9** → **10**. Mechanistically related is the direct methylation of tertiary carbinols and diols using **6**, a process in which intermediates of the type **11** are very likely involved[5]. For example, methylcyclohexanol (**8**) reacts with an excess of **6** to form **10**. In fact, tertiary lithium *alcoholates* are also converted to methylated alkanes using dichlorodimethyltitanium[10].
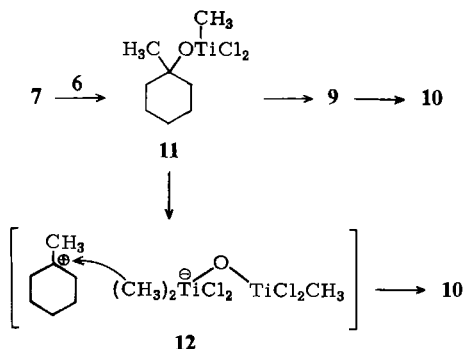
Attempts to circumvent the use of $Zn(CH_3)_2$ failed. For example, if an ether solution of $TiCl_4$ is treated with two parts of methyllithium at $-78\,°C$ and the resultant etherate of **6** reacted with 0.5 parts of **7**, only carbinol formation sets in. Thus, a polar and ionizing solvent is necessary for geminal dimethylation.

It should be noted that $Zn(CH_3)_2$ in the presence of catalytic amounts of $TiCl_4$ fails to induce dimethylation. The same applies to various mixtures of $Al(CH_3)_3$ and $AlCl_3$. However, the combination of two parts $Al(CH_3)_3$ and two parts $TiCl_4$ reacts with one part of **7** in CH_2Cl_2 at $-25\,°C$ (5 h) to form $85-90\%$ of **9**[5,9].

Synthetic Applications

The utility of the above procedure using a two-fold excess of $(CH_3)_2TiCl_2$ in CH_2Cl_2 is illustrated by the following examples. The numbers in brackets refer to isolated yields. Ketones activated by cyclopropyl or aryl groups should be reacted at lower temperatures ($-40\,°C$ to $0\,°C$).
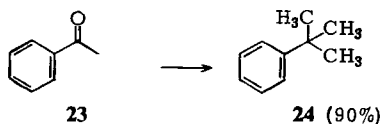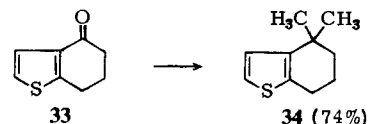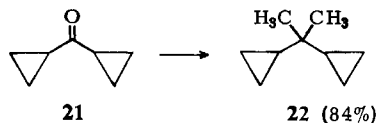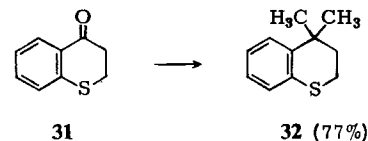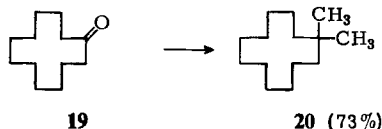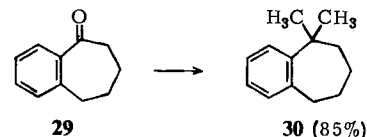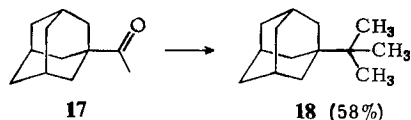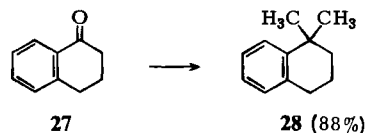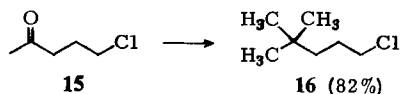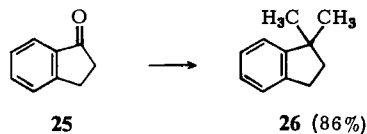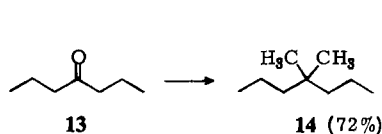
The results show that a variety of acyclic and cyclic ketones can be smoothly geminal dimethylated, including those which lead to compounds having two neighboring quaternary C-atoms (17 → 18). Such functional groups as primary alkyl chlorides (15 → 16), cyclopropyl groups (21 → 22), thioethers (31 → 32) and thiophene (33 → 34) are tolerated. Chemoselectivity is also observed in certain methoxy substituted aryl ketones, which are precursors of synthetic tetrahydro-cannabinoids[10]. The latter contain *meta*-substitution patterns, i.e., they are compounds which cannot be synthesized by Friedel-Crafts *tert*-alkylation. Finally, ester groups do not prevent dimethylation, e.g., a 1:1 mixture of cyclohexanone and ethyl acetate reacts with 6 to form > 80% of 10[5,9].

The reactive and Lewis acidic property of $(CH_3)_2TiCl_2$ imposes limitations concerning chemoselectivity. For example, thioketal functions seem to deactivate the reagent, possibly via complexation. Thus, a 1:1 mixture of cyclopentanone and its diethyl thioketal fails to react with 6 to afford 1,1-dimethylcyclopentane[9].

Another restriction has to do with α,β-unsaturated ketones. In an attempt to apply the procedure to 35, *two* dimethylated products 37 and 38 were formed in a ratio of about 1:1 (75% yield). Again, the intermediacy of a carbonium ion, in this case the ambident allyl cation 36, seems plausible. Pulegone (39) affords one major product 40 (≈ 70%) in addition to several non-identified components. 41 could not be isolated.
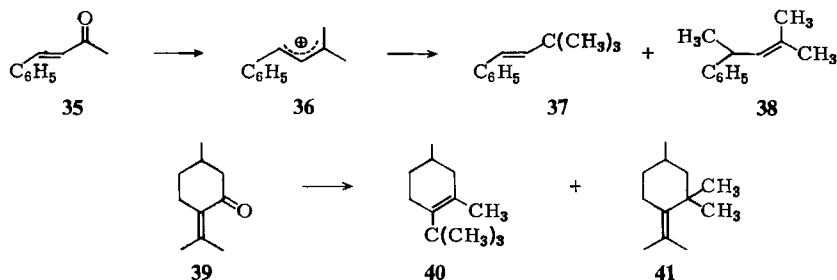
The first application of the present procedure to a natural product pertains to the simple synthesis of (±)-cuparene (44) from (±)-cuparenone (42), which in turn is readily accessible from cyclopentanone in three steps[11]. Direct geminal dimethylation afforded a 1:1 mixture of 44 and 45, conversion being > 95%. The isolated yield (34%) of 44 is low due to steric conjestion[5], but the simplicity of the procedure relative to previous multistep strategies[12] underlines its value. Parenthetically, dry HCl converts 45 into the corresponding tertiary chloride, which can be methylated to 44 using $Zn(CH_3)_2$ and catalytic amounts of $TiCl_4$ (overall conversion ≈ 60%).
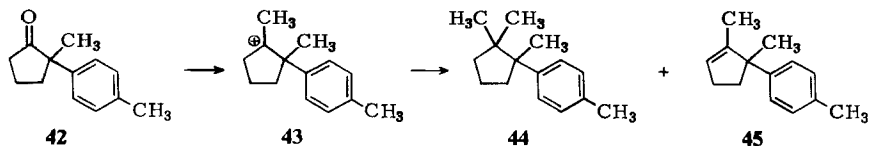

Recently, *Posner* repeated our synthesis using optically active 42[13]. As expected, cuparene (44) turned out to be *racemic*. This speaks for the carbonium ion 43, which

undergoes rapid racemizing aryl or methyl group migration prior to capture by methyl-titanium species.

In conclusion, direct geminal dimethylation of a number of structurally different ketones is possible using $(CH_3)_2TiCl_2$. However, if the ketone contains a great deal of additional functionality, or if rapid rearrangements are anticipated, alternative multistep procedures are likely to be the method of choice[2]. Recently, a one-pot reaction based on the Tebbe reagent has been described by *Grubbs*[14]. Although its scope is presently unexplored, it may emerge as a useful complementary method.

Geminal Trimethylation of Carboxylic Acid Chlorides

Since carboxylic acid chlorides are known to react with such classical reagents as CH_3Li, CH_3MgX or $Zn(CH_3)_2$ to form carbinols or ketones, it seemed worthwhile to attempt geminal trimethylation with an excess of $(CH_3)_2TiCl_2$. Indeed, adding one part of benzoyl chloride (**46**) to a CH_2Cl_2 solution containing 2.5 parts of $Zn(CH_3)_2$ and two parts of $TiCl_4$ resulted in $\approx 90\%$ conversion to *tert*-butylbenzene (**24**)[14]. Aliphatic acid chlorides are also per-methylated, e. g., **47** → **48** (35%).
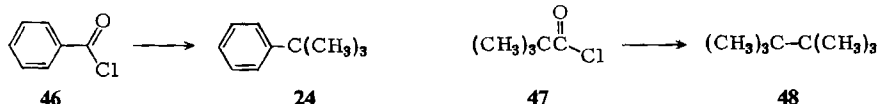
This work was supported by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie.*

Experimental Part

Dichloromethane was dried by distilling over P_2O_5. Titanium tetrachloride was distilled under an atmosphere of dry nitrogen. – ^{1}H NMR spectra: Varian T-60, Bruker WH-400, δ values, TMS as external standard. – ^{13}C NMR spectra: Varian CFT-20. – MS: Varian CH 7a, ionization energy 70 eV.

Synthesis of Dimethylzinc: The following procedure has been adapted from *Nützel*[15].

A mixture of 140 g of Zn dust and 15 g of CuO in a dry 500 ml three-necked round-bottomed flask is heated gently with a Bunsen burner in a current of H_2*[)]. During the heating process the flask is rotated fairly continuously by hand. At the beginning the color of the mixture is fairly black, at the end it should be gray. If it is yellow, local overheating has occurred and the substance is unsuitable for reaction with CH_3I. At the beginning the mixture is rather thick, and some degree of lump formation may occur. At the end of the activation process the hot gray mixture is somewhat fluid. The flask is then purged with N_2 and cooled to room temperature. A reflux condenser (preferably metal due to safety reasons) and a dropping funnel are then attached, N_2 being kept over the Zn/Cu mixture. Then 141 g (1 mol) of freshly distilled CH_3I are slowly added via the dropping funnel. The exothermic reaction should begin before all of the CH_3I has been added. After addition, the mixture is heated at $65 - 70\,°C$ for about 18 h. We have observed that sometimes the reaction is finished after about 10 h. The flask is then allowed to come to room temperature and is then cooled to $-78\,°C$. The reflux condenser is exchanged by a dry Liebig cooler, during which a slow stream of N_2 is maintained. If the flask is not cooled to $-78\,°C$, some

*[)] Excess H_2 should be led into a ventilated hood via a rubber tube!

of the Zn(CH$_3$)$_2$ is blown into the air, where it *immediately ignites*. The end of the Liebig cooler has a receiving system of 3 or 4 flasks, each containing about 50 ml of dry CH$_2$Cl$_2$. The receiving flasks are cooled with a dry ice/aceton bath and distillation is begun at atmospheric pressure. An oil bath is used to heat the flask, the bath temperature reaching 200 °C toward the end of the distillation. The product has a tendency to condense in the Liebig cooler, so that heating with a powerful heating gun or Bunsen burner is necessary. Due to safety reasons the whole operation should be performed in a hood. The yield of Zn(CH$_3$)$_2$ is 70 – 75%, i. e., the CH$_2$Cl$_2$ solutions are about 3 – 4 molar. The content can be determined by weighing or by NMR integration of the methyl peak of Zn(CH$_3$)$_2$ (singlet at δ = – 0.43) relative to the CH$_2$Cl$_2$ signal. These stock solutions can be kept in the refrigerator for weeks without decomposition. Neat Zn(CH$_3$)$_2$ is highly *pyrophoric*, but the CH$_2$Cl$_2$ solutions are much less so and can be handled like *n*-butyllithium (serum caps, springes, etc.).

Synthesis of Dichlorodimethyltitanium (**6**)[16]: In a dry 100 ml flask equipped with an N$_2$-inlet 8.35 g (4.8 ml, 44 mmol) of clean TiCl$_4$ is mixed with 80 ml of dry CH$_2$Cl$_2$. Upon cooling to – 30°C, 44 mmol of Zn(CH$_3$)$_2$ (e. g., 11 ml of a 4 M CH$_2$Cl$_2$ solution) is slowly added via a syringe, the mixture being agitated with a magnetic stirrer. Stirring is continued for 10 minutes. Conversion to (CH$_3$)$_2$TiCl$_2$ is $\geq$ 90%[9].

General Procedure for Geminal Dimethylation of Ketones

To the above stirred solution containing $\approx$ 40 mmol of (CH$_3$)$_2$TiCl$_2$ is added a ketone (20 mmol) at – 30°C. The mixture is slowly allowed to come to room temperature during a period of about 2 h and is then poured onto ice water. The aqueous phase is extracted with ether and the combined organic phases washed with H$_2$O and NaHCO$_3$. After drying over MgSO$_4$, the solvent is removed and the product distilled (e. g., using a Kugelrohr) or crystallized. In case of aryl or α,β-unsaturated ketones, addition is best performed at – 40°C and the mixture allowed to come to 0°C prior to the usual workup.

Most of the compounds prepared here have been described in the literature. The ^{1}H NMR spectra and comparison with authentic samples or literature data confirmed the structures: **10**[17], **14**[18], **16**[19], **18**[20], **20**[21], **22**[3], **24**[3], **26**[3], **28**[22], **30**[23], **32**[24], **34**[25], **37**[26], **38**[3], **48**[27].

1-Chloro-4,4-dimethylpentane (**16**)[19]: Isolated by Kugelrohr distillation (35°C/22 torr). – ^{1}H NMR (CCl$_4$): δ = 0.9 (s, 9H), 1.2 – 1.8 (m, 4H), 3.4 (t, 2H).

C$_7$H$_{15}$Cl (131.6)   Calc. C 62.44 H 11.23   Found C 62.09 H 11.12

1-tert-Butyl-2,4-dimethyl-1-cyclohexene (**40**): The ^{1}H NMR spectrum of the crude product mixture shows about 70% of **40** as well as several other non-identified compounds. A sample of pure **40** was obtained by gas chromatography (SE 30 column, 120°C). – ^{1}H NMR (CCl$_4$): δ = 0.9 (d, 3H), 1.1 (s, 9H), 1.2 – 2.0 (m, 10H). – MS: m/e = 166 (37%), 152 (11), 151 (100), 123 (19), 110 (20), 109 (73), 96 (13), 95 (86), 83 (12), 82 (12), 81 (39), 69 (28), 67 (25), 57 (49).

C$_{12}$H$_{22}$ (166.3)   Calc. C 86.67 H 13.33   Found C 86.41 H 13.38

Synthesis of (±)-Cuparene (**44**)[12]: To a solution of 13 mmol of (CH$_3$)$_2$TiCl$_2$ in about 20 ml dry CH$_2$Cl$_2$ was added at – 25°C 2-methyl-2-*p*-tolylcyclopentanone (**42**)[11] (1.0 g, 5.3 mmol) dissolved in 3 ml of CH$_2$Cl$_2$. The solution was stirred at – 25°C for 3 h and was then allowed to come to room temperature (1 h). The mixture was worked up according to the general procedure. The crude product contained a 1 : 1 mixture of **44** and **45**, as measured by ^{1}H NMR spectroscopy. Pure **44** was separated by preparative gaschromatography (SE 30 column, 190°C): 0.37 g (34%). – ^{1}H NMR (CCl$_4$): δ = 0.53 (t, 3H), 1.03 (s, 3H), 1.23 (s, 3H), 1.60 (m, 6H), 2.25 (s, 3H), 7.20 (q, 4H). – IR (Film): 2950 (ss), 2860 (s), 1520 (m), 725 (m) cm^{-1}. – MS (70 eV): m/e = 202 (30%, M$^{\oplus}$), 145 (28), 132 (100). – ^{13}C NMR (CDCl$_3$): δ = 19.7, 20.8, 24.3, 24.4, 26.4, 36.9, 39.8, 50.3, 126.9, 128.2, 134.7, 144.5.

General Procedure for Exhaustive Methylation of Carboxylic Acid Chlorides

The mixture of 25 mmol of $(CH_3)_2TiCl_2$ in about 40 ml of CH_2Cl_2 is treated with 10 mmol of a carboxylic acid chloride at $-40\,°C$. In case of aromatic carboxylic acid chlorides the mixture is allowed to come to $0\,°C$ within 2 h (in case of aliphatic derivatives: room temperature). Workup is the same as in geminal dimethylation of ketones.

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