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Characterization of the Products of the Reactions of Magnesium Hydride with Isopropylborate and Aluminum Isopropoxide in Tetrahydrofuran

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Exchange of hydrogen with isopropoxy groups in the reactions of magnesium hydride with isopropylborate and aluminum isopropoxide in THF has been demonstrated and the formation of mixed 'isopropoxy-hydride' complexes of boron and aluminum magnesium have been characterized by infrared, nmr, X-ray powder diffraction and elemental analysis. The selectivity of mixed 'alkoxyhydride' complexes as reducing agents toward cyclic and bicyclic ketones has been investigated.

Introduction

We have been engaged for some time in the reactions of magnesium hydride with alkyls, amides, alkoxides, halides and hydrides of magnesium, aluminum and boron, and have prepared successfully THF-soluble alkylmagnesium hydrides [1], dialkylaminomagnesium hydrides [2], alkoxymagnesium hydrides [3], hydridomagnesium halides [4] and mixed metal hydrides [5, 6]. Complexes such as alkoxymagnesium hydrides and dialkylaminomagnesium hydrides have been shown to behave as stereoselective reducing agents toward cyclic and bicyclic ketones [7]. We have also prepared some complex metal hydrides of magnesium of empirical formula $LiMg(NR_2)H_2$ and $LiMg(OR)H_2$ by the reaction of MgH_2 with LiOR and $LiNR_2$ compounds [8].

$$LiNR_2 \text{ (or LiOR)} + MgH_2 \xrightarrow{THF} LiMg(NR_2)_2 \text{ or } LiMg(OR)H_2 \quad (1)$$

Since reactions of MgH_2 with $B(OR)_3$ and $Al(OR)_3$ have not been studied, it was thought worthwhile to study these reactions in order to prepare mixed 'alkoxyhydride' complexes of magnesium with boron and aluminum and determine their reducing effectiveness toward cyclic and bicyclic ketones.

Experimental

Reactions were performed under dry nitrogen at the bench or in a glove box equipped with a recirculating system using manganese oxide to remove oxygen [9]. Infrared spectra were obtained on a Perkin-Elmer 621 spectrophotometer using KBr and CsI cells. NMR spectra were recorded on a Varian-A-60 spectrometer. X-Ray powder diffraction pattern data were obtained on a Philips-Norelco X-ray unit using a 114.5 mm camera with nickel filtered CuKα radiation. Samples were sealed in a 0.5 mm capillary and exposed to X-rays for 6 hours. 'd' spacings were read on a precalibrated scale equipped with a viewing apparatus. Line intensities were estimated visually.

Analyses

Gas analyses were accomplished by hydrolysis of samples with HCl on a standard vacuum line equipped with a Teopler pump. Aluminum was determined by adding excess EDTA and back-titrating with standard zinc acetate at pH 4 in 50% ethanol with dithizone as an indicator. Magnesium was determined by EDTA titration at pH 10 using Erichrome Black T as an indicator. When aluminum was present, it was masked by complexation with triethanolamine. Boron was estimated as boric acid in the presence of mannitol. Isopropoxy groups present in the complexes were determined as isopropanol by hydrolysis of the samples with water and analyzing the filtrate by glc.

Materials

Solvents were distilled immediately prior to use over lithium aluminum hydride (ether) or sodium aluminum hydride (THF). The ketones 2-methylcyclohexanone, 3,3,5-trimethylcyclohexanone and

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camphor were purified by distillation or sublimation under reduced pressure.

Diphenylmagnesium (Ph_2Mg) was prepared by heating a mixture of triply sublimed magnesium (Dow Chemical Co.) and diphenylmercury at 155° for 40 hours. The crude reaction mixture was extracted with freshly distilled ether and the resulting solution standardized by magnesium analysis. Diethylmagnesium was prepared by stirring a mixture of diethylmercury with magnesium metal at 60–80 °C for 8 hr, followed by extraction of the crude reaction mixture with ether. Lithium aluminum hydride ($LiAlH_4$) was obtained from Ventron, Metal Hydrides Division. A solution was prepared by refluxing $LiAlH_4$ in ether overnight followed by filtration through a glass-fritted funnel (medium) using pre-dried Celite Analytical Filter-Aid (Johns-Manville). The clear solution was standardized by aluminum analysis.

Aluminum isopropoxide was prepared by the reaction of aluminum metal with isopropanol in presence of mercuric chloride as a catalyst and the product distilled under reduced pressure (80 °C/0.3 mm). Isopropylborate (140 °C) was prepared by azeotropic removal of water from a mixture of boric acid, benzene and isopropanol [10].

Preparation of MgH_2 Slurry in THF

40 ml of a 0.5 *M* solution of $LiAlH_4$ (20.0 mmol) in diethyl ether was added dropwise to a magnetically stirred solution 50 ml of 0.4 *M* of diphenylmagnesium (20.0 mmol) in ether. This reaction mixture was stirred at room temperature for 1 hour and the insoluble white solid formed was filtered. The solid was then washed 3–4 times with freshly distilled ether and finally a slurry in THF was prepared. *Anal.* calcd. for MgH_2 = 1.00:2.00. Found: 1.00:2.02.

Redistribution Reaction Between AlH_3 and $Al(O\text{-}Pr^i)_3$ in THF

Preparation of $AlH(OPr^i)_2$

To 8.0 mmol of $Al(OPr^i)_3$ in THF (25 ml) was added 10 ml of 0.4 *M* THF solution of AlH_3 (4.0 mmol) dropwise with continuous stirring at 0 °C. The reaction mixture was warmed to room temperature and stirred for additional 30 min. The resulting clear solution was analyzed and its infrared spectrum recorded. *Anal.* calcd. for $AlH(POr^i)_2$, $Al:H:Pr^iOH$ = 1.00:1.00:2.00. Found: 1.00:0.98:2.03. The infrared spectrum showed a strong band at 1850 cm^{-1} characteristic of $\nu Al\text{–}H$ stretching vibrations.

Preparation of $AlH_2(OPr^i)$

20 ml of a 0.4 *M* solution of AlH_3 (8.0 mmol) in THF was added dropwise to a well stirred solution of $Al(OPr^i)_3$ (4.0 mmol) in THF (15 ml) at 0 °C. The reaction mixture was stirred for 1 h at room temperature and the clear solution analyzed. *Anal.* calcd. for $AlH_2(POr^i)$; $Al:H:Pr^iOH$ = 1.00:2.00:1.00. Found: 1.00:1.96:1.01. The infrared spectrum of the solution exhibited a strong band at 1822 cm^{-1} due to $\nu Al\text{–}H$ stretching vibration.

Preparation of Isopropoxymagnesium Hydride, $HMgOPr^i$

To a magnetically stirred slurry of MgH_2 (6.0 mmol) in THF (30 ml) was added dropwise a THF solution of isopropanol (5.95 mmol in 10 ml of THF). The reaction mixture was stirred at room temperature for 24 hours, after which time the solvent was removed under vacuum. Elemental analysis of the resulting solid showed that it contained magnesium and hydrogen in the molar ratio 1.00:0.97. The solid was insoluble in THF and formed a suspension.

Preparation of $Mg[Al(OPr^i)_4]_2$

Magnesium metal (0.28 g) was dissolved in a solution of aluminum isopropoxide (4.76 g) in isopropanol (50 ml) in the presence of $HgCl_2$ (0.01 g) catalyst, by refluxing for 40 hours. A colorless clear solution was obtained. An excess of isopropanol was removed and the product was dried under vacuum. The resulting viscous liquid was distilled at 110°/0.1 mm (90% yield). *Anal.* Found: Mg, 4.17; Al, 9.84; Pr^iO, 85.86. Calcd. for $Mg[Al(OPr^i)_4]_2$: Mg, 4.18; Al, 9.82; Pr^iO, 86.00%.

Reaction of MgH_2 with $Mg[Al(OPr^iO_4]_2$ in THF

When 5.7 mmol of $Mg[Al(OPr^i)_4]_2$ solution in THF (35 ml) was allowed to react with a slurry of MgH_2 (5.65 mmol) in THF (30 ml) for 3 hours at room temperature, the magnesium hydride dissolved and a clear solution resulted. Analysis of the resulting solution revealed that it contained Mg, Al, H and Pr^iOH in ratios 1.00:1.03:0.96:4.05.

Reactions of MgH_2 with Isopropylborate and Aluminum Isopropoxide in THF in the Ratios 1:1 and 1:2

Isopropylborate, aluminum isopropoxide or isoproxyaluminum hydride in THF was added dropwise to a THF slurry of MgH_2 or $HMgOPr^i$ in the appropriate ratios and the reaction mixture stirred magnetically at room temperature for 2–3 hours. The resulting clear solution was analyzed (Table I) and the infrared and NMR spectra recorded. When the solvent was removed under vacuum, a white solid formed in the case of the aluminum isopropoxide reactions whereas a highly viscous mass resulted in the isopropylborate reactions. The X-ray poweder diffraction patterns of the aluminum compounds were recorded.

TABLE I. Reactions of Magnesium Hydride with Isopropylborate and Aluminum Isopropoxides.

S. No.	Reactants (mmol)		THF (ml)	Reaction Time (h)	Analysis (Ratio) H:Mg:Al:OPr^i	NMR Data in THF Gem-Dimethyl doublet (δ ppm)
	MgH_2	$M(OR)_3$				
		$Al(OPr^i)_3$				
1	4.00	4.02	45	3	1.94:1.00:1.05:3.03	1.17, 1.19, 1.27
2	3.45	6.85	60	2	1.95:1.00:1.97:5.98	1.17, 1.20, 1.27, 1.36, 1.54, 1.58
		$HAl(OPr^i)_2$				
3	4.25	4.20	50	3	2.89:1.02:1.00:2.07	1.17, 1.22
		$H_2Al(OPr^i)$				
4	4.05	4.08	50	5	3.87:1.00:1.02:1.05	1.17 (broad)
		$B(OPr^i)_3$				
5	3.80	3.85	50	4	1.97:1.00:1.04:3.07	1.16, 1.12
6	3.00	5.95	70	2	1.92:1.00:1.97:5.11	1.13

X-ray pattern:

$[MgH_2 + Al(OPr^i)_3]$ = 10.0 vs, 8.75 s, 8.00 s, 4.15 m, 3.50 w, 3.25 vs.
$[MgH_2 + 2Al(OPr^i)_3]$: Same as above but a weaker pattern.

Reaction of $HMgOPr^i$ with $Al(OPr^i)_3$ in THF

To a suspension of $HMgOPr^i$ (3.85 mmol) in THF (20 ml) was added dropwise a solution of 3.90 mmol of $Al(OPr^i)_3$ in THF (25 ml). The reaction mixture was stirred at room temperature for 3 hours, during which time a clear solution resulted. Analysis of this solution showed Mg, Al, H and OPr^i in ratios 1.00: 1.04:0.98:3.97, which corresponded to $MgAl(OPr^i)_4H$.

Reduction procedure

To a 25 ml flask containing a magnetic stirring bar and fitted with a septum cap and two syringe needles as nitrogen inlet and outlet, 1 ml of a 0.2 *M* solution of ketone in THF was added. The flask was cooled to 0° and a sufficient amount of the hydride solution was then added by syringe to provide the desired excess and the reaction mixture was vigorously stirred. After 26 hours the reaction mixture was hydrolyzed using saturated aqueous ammonium chloride solution. The products were analyzed by glc. A diglycerol column (90°) was used to separate the products in the cases of 3,3,5-trimethylcyclohexanone, 4-tert-butylcyclohexanone and camphor.

Results and Discussion

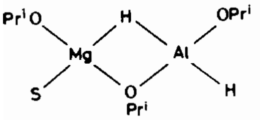
The preparation of $HMgAlH_4$ and $HMgBH_4$, the half complex metal hydrides of $Mg(AlH_4)_2$ and $Mg(BH_4)_2$, have been reported recently [5, 11]. Although MgH_2 is insoluble in THF, both $HMgAlH_4$ and $HMgBH_4$ exhibited significant solubility. The major interest in the preparation of $HMgBH_4$ and $HMgAlH_4$ was to impart solubility to a Mg–H compound so that a soluble Mg–H compound could be evaluated as a reducing agent toward organic substrates. Unfortunately, these compounds did not exhibit any unusual selectivity toward the organic substrates that were screened. Since it is now well understood that the selectivity of complex metal hydrides as reducing agents [12] depend to a considerable extent on their steric bulk (*e.g.*, lithium trimethoxyaluminum hydride is more selective than lithium aluminum hydride), we thought it important to prepare mixed 'alkoxy-hydride' complexes of magnesium with aluminum and boron that should indeed possess a high steric requirement.

In order to prepare mixed 'isopropoxy-hydride' complexes of magnesium and aluminum, aluminum isopropoxide was allowed to react with an active MgH_2 slurry in THF, in 1:1 and 2:1 molar ratios (eqns. 2–3). A clear solution resulted in both cases within 2–3 hours at room temperature. The infrared spectrum of the clear solution of the reaction of MgH_2 with $Al(OPr^i)_3$ in 1:1 ratio in THF (eqn. 2) showed the presence of the Al–H stretching absorption at 1762 cm^{-1} and a strong band at 1130 cm^{-1} which could be due to $\nu[(C–O) + Pr^iO]$ [13]. The strong band at 972 cm^{-1} is assigned to ν(C–O) (bridging). The spectrum also showed the presence of ν(Al–O) [14] and ν(Mg–O) [15] bands at 675 and 430 cm^{-1}, respectively. Thus, the presence of Al–H (terminal) and Mg–O stretch-

$$MgH_2 + Al(OPr^i)_3 \xrightarrow{THF} Pr^iOMgAl(OPr^i)_2H_2 \quad (2)$$

$$MgH_2 + 2Al(OPr^i)_3 \xrightarrow{THF} Mg[Al(OPr^i)_3H]_2 \quad (2)$$

ing absorptions suggests that during complex formation an exchange of hydrogen with isopropoxy group takes place. Proton NMR spectrum of the reaction product in THF solution showed the presence of three sets of doublets due to gem-dimethyl groups at δ 1.17, 1.19 and 1.27 ppm. The product has been found to cleave THF rapidly at higher temperatures (under refluxing conditions) and since it was not soluble in common hydrocarbon solvents, molecular association studies were not possible. Although without molecular association information it is not possible to assign a correct structure, on the basis of available spectroscopic data structure I seems reasonable. The positions of these signals are different from those due to $Al(OPr^i)_3$ (δ 1.17, 1.37 and 1.57 ppm). The up-field doublet (1.17 ppm) is probably due to the terminal isopropoxy group attached to aluminum and the two lower field doublets are proposed to be due to the terminal isopropoxy group attached to magnesium (1.19 δ) and to the bridging alkoxy group (1.27 δ) respectively [16]. When the solvent (THF) was removed from the reaction mixture, a white crystalline solid material was obtained. The X-ray powder diffraction pattern of the solid was found to be different from that of a mixture of MgH_2 and $Al(OPr^i)_3$ or $Mg(OPr^i)_2$ and $H_2Al(OPr^i)$, thus suggesting the formation of a new compound.



(I) (I)

The infrared spectrum of the clear solution produced in the reaction of MgH_2 with two mole equivalents of aluminum isopropoxide (eqn. 3) showed strong and medium intense bands at 1800 and 1760 cm^{-1}, assignable to νAl–H. Medium intense bands at 1130 cm^{-1} and 972 cm^{-1} are assigned to ν[(C–O) + Pr^i] and ν(C–O) respectively. The presence of the Al–O and Mg–O is indicated by the bands at 675 and 430 cm^{-1} respectively. Since two bands have been observed in the Al–H stretching region and the lower band (1760 cm^{-1}) is at the position where the Al–H stretching absorption of $Pr^iOMgAl(OPr^i)_2H_2$ occurs, it is suggested that a mixture of complexes (1) and $Mg[Al(OR)_3H]_2$ are present (eqn. 4). The nmr spectrum of the solution is quite complicated and shows at least six sets of doublets due to gem-dimethyl protons. Furthermore, when the THF solvent was removed from the solution of reaction (3) and the solid material was analyzed by X-ray powder diffraction, a pattern similar to that of complex I was observed thus indicating the disproportionation of $Mg[Al(OPr^i)_3H]_2$ as shown in eqn. 4.

$$Mg[Al(OPr^i)_3H]_2 \longrightarrow Pr^iOMgAl(OPr^i)_2H_2 + Al(OPr^i)_3 \qquad (4)$$

When an equimolar amount of $HAl(OPr^i)_2$ or $H_2Al(OPr^i)$ was added to a slurry of MgH_2 in THF, a clear solution resulted after 3–5 hours reaction time. The solutions were analyzed by elemental and spectroscopic analysis, indicating the compounds $Pr^iOMgAl(OPr^i)H_3$ (V) and $Pr^iOMgAlH_4$ (VI). The infrared spectrum of the product (V) showed the presence of an Al–H stretching band at 1760–36 cm^{-1} and also showed a band at 430 cm^{-1} due to Mg–O. The proton nmr spectrum exhibited two sets of doublets in 1:1 ratio due to two types of isopropoxy groups (bridging and terminal). In complex (VI) Al–H stretching absorption could be seen in the region 1756–30 cm^{-1} as a strong band and a band at 430 cm^{-1}, suggesting the presence of Mg–O. The nmr spectrum of this product in THF showed only one set of doublets due to gem-dimethyl protons.

$$MgH_2 + HAl(OPr^i)_2 \rightarrow Pr^iOMgAl(OPr^i)H_3 \ (V) \qquad (5)$$

$$MgH_2 + H_2Al(OPr^i) \rightarrow Pr^iOMgAlH_4 \ (VI) \qquad (6)$$

The hydrogen migration from magnesium to aluminum seems to be well documented in the reaction of $HMgOPr^i$ with $Al(OPr^i)_3$. When the reactants in THF were mixed in equimolar proportions, the infrared spectrum of the resulting solution showed an Al–H stretching band at 1802 cm^{-1} suggesting that the hydrogen migrated from magnesium to aluminum and was replaced by an isopropoxy group from aluminum.

$$HMgOPr^i + Al(OPr^i)_3 \rightarrow Pr^iOMgAl(OPr^i)_3H \ (VII) \qquad (7)$$

The same product (VII) with a similar infrared spectrum was obtained in the reaction of magnesium hydride with $Mg[Al(OPr^i)_4]_2$ [17] in equimolar ratio. The $Mg[Al(OPr^i)_4]_2$ was prepared by the reaction of magnesium metal with aluminum isopropoxide in isopropanol in the presence of a catalytic amount of mercuric chloride (eqn. 8)

$$Mg + 2Al(OPr^i)_3 + 2Pr^iOH \xrightarrow{HgCl_2} Mg[Al(Opr^i)_4]_2 \qquad (8)$$

$$MgH_2 + Mg[Al(OPr^i)_4]_2 \xrightarrow{THF} 2Pr^iOMgAl(OPr^i)_3H \qquad (9)$$

The infrared spectrum of the solution (eqn. 10) showed a terminal B–H stretching band at 2290 cm^{-1}, suggesting hydrogen migration from magnesium to boron. The proton nmr spectrum of the re-

TABLE II. Infrared Spectral Data of 'Isopropoxy-Hydride' Complexes.

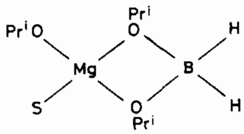
$HMgOPr^i$	$Al(OPr^i)_3$	$AlH(OPr^i)_2$	$AlH_2(OPr^i)$	MgH_2 + $Al(OPr^i)_3$	MgH_2 + $2Al(OPr^i)_3$	MgH_2 + $AlH_2(OPr^i)$	MgH_2 + $AlH(OPr^i)_2$	$HMgOPr^i$ + $Al(OPr^i)_3$	$B(OPr^i)_3$	MgH_2 + $B(OPr^i)_3$	MgH_2 + $2B(OPr^i)_3$
1460s	1430w	1850s	1822s	1762vs	1800s	1756–30vs	1760–36vs	1802m	1468s	2290s	2285s
1378s	1385vs	1430b	1440wb	1725sh	1760m	1430wb	1435wb	1762sh	1420vsb	2230sh	2140sh
1365s	1372vs	1382sh	1385m	1460–40wb	1430wb	1378s	1376s	1430wb	1390vs	2155w	1460sh
1350m	1360sh	1373vs	1375s	1375s	1370s	1363sh	1360sh	1372s	1325vs	1465mb	1400–1380vs
1260w	1338sh	1125vs	1120vs	1350w	1130vs	1130s	1130s	1130vs	1170s	1420mb	1340vs
1150vsb	1200sh	1065b	1062b	1130vs	1025wb	965s	1026w	1030wb	1120vs	1325vs	1120vs
985s	1155sb	950s	950s	1070b	972s	825sh	968s	974s	950vs	1122vs	1070sb
830m	1120vs	825wb	820sh	1030wb	821s	785s	822s	822s	835s	1070sb	984s
720m	1020sb	790b	790s	972s	792s	755s	787s	793s	600s	980s	950sb
575sb	938vs	715s	730vs	821s	733s	730s	750s	735s	660vs	950sb	890sh
510m	900vs	665sb	670m	792s	675s	620m	674sh	675s	590m	890mb	832m
430s	850m	630sb	640m	733s	600m	590w	630m	600m	455m	835m	660s
330m	825m	560w	560wb	675s	562m	560w	568w	563m	395w	660s	576s
	695s	500w	500w	600m	460w	485w	540w	460w		572s	562s
	670s	450w	450w	562m	430m	430w	480w	430m		560s	510w
	600m		400wb	460w			430m			510w	430m
	555m			430m						435m	
	525m										
	470m										
	420m										

TABLE III. Reduction Reactions of Cyclic and Bicyclic Ketones with the 'Isopropoxy-Hydrides'.

Ketone	Hydride/Ketone	Reaction Conditions	Recovered Ketone (%)	Products (% relative yield) Axial-OH	Eq-OH
$MgH_2 + 2Al(OPr^i)_3 \rightarrow Mg[Al(OPr^i)_3H]_2$					
2-methylcyclohexanone	2:1	0 °C, 24 hr	0	65.1	34.9
3,3,5-trimethylcyclohexanone	2:1	0 °C, 24 hr	0	72.1	27.9
4-tert-butylcyclohexanone	2:1	0 °C, 24 hr	0	12.8	87.2
Camphor	2:1	0 °C, 24 hr	0	87.7	12.3
$MgH_2 + Al(OPr^i)_3 \rightarrow Pr^iOMg(OPr^i)_2H_2$					
2-methylcyclohexanone	2:1	0 °C, 24 hr	0	70.9	29.1
3,3,5-trimethylcyclohexanone	2:1	0 °C, 24 hr	0	69.9	30.1
4-tert-butylcyclohexanone	2:1	0 °C, 24 hr	0	9.9	90.1
Camphor	2:1	0 °C, 24 hr	0	88.3	11.7

sulting solution showed two types of isopropoxy groups (Table I). The same complex was also obtained in the reaction of $HMgOPr^i$ with $HB(OPr^i)_2$.

$$MgH_2 + B(OPr^i)_3 \xrightarrow{THF} Pr^iOMgB(OPr^i)_2H_2 \text{ (VIII)} \quad (10)$$



In the reaction of MgH_2 with $B(OPr^i)_3$ in 1:2 ratio (eqn. 11), the infrared spectrum of the resulting clear solution showed a strong band at 2285 cm^{-1}, due to B–H stretching, and surprisingly only one isopropoxy group signal. This observation could be due to rapid exchange of terminal and bridging groups, or to the existence of the compound as an ion pair $Mg^{+2}[B(OR)_3H]_2^-$. When the solvent was removed from the above reaction, a sticky solid resulted which corresponds to $Mg[B(OPr^i)_3H]_2$ on elemental analysis. Since $B(OPr^i)_3$ is a liquid (b.p. 140 °C) which can easily be removed under high vacuum, the possibility of $Mg[B(OPr^i)_3H]$ having disproportionated to a mixture of $Pr^i(OMgB(OPr^i)_2H_2$ and $B(OPr^i)_3$ can be ruled out.

$$MgH_2 + 2B(OPr^i)_3 \rightarrow Mg[B(OPr^i)_3H]_2 \text{ (IX)} \quad (11)$$

Four representative ketones, 2-methylcyclohexanone, 4-tert-butylcyclohexanone, 3,3,5-trimethylcyclohexanone and camphor, were selected for evaluating the stereoselectivity of the new hydrides prepared in this study. Reductions were carried out at 0° in THF solution and the samples were hydrolyzed after 2 hr reaction time, followed by the glc analysis of the resulting alcohol products. The results of these studies are given in Table III. It can be seen that the reagents behave similarly to $LiAlH(OMe)_3$ [12, 18, 19].

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