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REACTION OF 2,4,6-CYCLOOCTATRIEN-1-ONE WITH ORGANOMETALLIC REAGENTS

THE EFFECT OF HEXAMETHYLPHOSPHORAMIDE

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Abstract—Addition of triethylaluminium, ethyllithium, and ethylmagnesium bromide to 2,4,6-cyclooctatrien-1-one proceeded principally in a 1,2-manner. The subsequent work-up caused ring cleavage to yield 4,6,8-decatrien-3-one. Lithium diethylcopper gave a 1,4-adduct, 7-ethylcycloocta-3,5-dien-1-one (66%). The presence of hexamethylphosphoramide (HMPA) brought about a marked increase of the proportion of 1,4-adduct in the reactions of ethyllithium and ethylmagnesium bromide. The results were discussed together with the reactions of other α,β-unsaturated ketones under similar reaction conditions.

INTRODUCTION

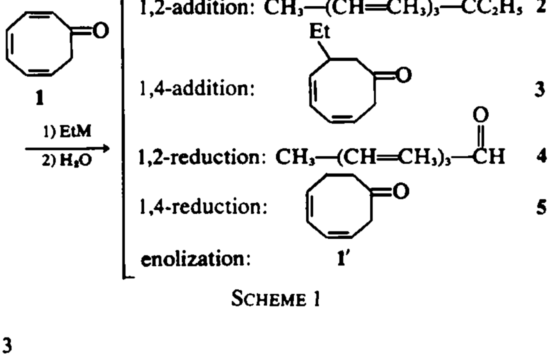
Besides the well-established valence isomerism between 1,3,5-cyclooctatriene and bicyclo [4.2.0]octa-2,4-diene structures,[1] there are several papers describing the facility of ring transformation of 1,3,5-cyclooctatriene compounds bearing heteroatoms at the methylene carbon, such as 7-azide-1,3,5-cyclooctatriene,[2] 7-oximino-1,3,5-cyclooctatriene,[2] 2,4,6-cyclooctatrien-1-one[3] or cyclooctatetraene oxide[4] under non-photochemical conditions. Kröner[5] reported a facile ring cleavage of the cyclic trienols obtained by lithium aluminium hydride reduction or Grignard addition of 2,4,6-cyclooctatrien-1-one **1** to aliphatic trienals or trienones, respectively, on heating.

Recently we reported a ring contraction of **1** to esters of 2,5-cyclohexadienylacetic acid in the reaction with the alkoxide of primary and secondary alcohols.[6] The formation of alkyl(2,4,6-cycloheptatrienyl)methanols in the Grignard addition of cyclooctatetraene oxide[7] would also belong to the same category. This paper is one of our continuing studies on the cyclooctatriene compounds and describes the reaction of organometallic reagents with **1** with particular reference to the effect of the solvent and HMPA as an additive on the orientation of the addition. HMPA is known for its strong donating power to the cationic center of organometallic reagents, enhancing the anionic character of the carbon-metal bond.[8]

RESULTS AND DISCUSSION

*Reaction of **1** with Organometallics*: The reaction of **1** with organometallic reagents can be supposed to proceed, like ordinary α,β-unsaturated ketones, in several ways: 1,2-addition, 1,4-addition, 1,2-reduction, 1,4-reduction. However, the special structure of **1** imposed by three conjugated double bonds in an eight membered ring was found to alter the relative preference among these routes and in the structure of the products after work-up. Scheme 1 is a brief illustration of the reaction of **1** with various organometallics which include ethyllithium ethylmagnesium bromide, triethylaluminium, and lithium diethyl copper.

The reaction of **1** with triethylaluminium in petroleum ether proceeded with ring cleavage to give 4,6,8-decatrien-3-one **2** as a principal product in a 46% yield. Traces of 7-ethylcycloocta-3,5-dien-1-one **3**, 2,4,6-octatrien-1-al **4**, 3,5-cyclooctadien-1-one **5** were obtained, and recovered **1** (7·8%). Kröner[5] reported that 2,4,6-cyclooctatrien-1-ol isomerized thermally with ring cleavage to **4**. Thus, **4** derives from 1,2-reduction of **1** by triethylaluminium. **2** Over Pd-BaCO$_3$ absorbed three molar equivalents of hydrogen to yield decan-3-one **6**. A similar result was obtained in the reaction of ethylmagnesium bromide with **1** in ether, though the yield of **3** (2%) was a little higher. The ring cleaved product **2** in this case showed a different more complex NMR pattern in olefinic proton region compared with that obtained from



SCHEME 1

triethylaluminium. However, both ring-cleaved products could be hydrogenated over Pd-$BaCO_3$ to **6**, indicating that these are isomers with respect to the three conjugated double bonds.

Kröner[5] showed that the reaction product of methylmagnesium iodide with **1** was thermally unstable and gave 3,5,7-nonatrien-2-one and 4,6,8-nonatrien-2-one. IR and NMR spectra of the reaction product of ethylmagnesium bromide with **1** suggested the presence of a similar mixture, but further analyses were not attempted. Triethylaluminium gave only **2**, but the cis-trans configuration of the isomers still remains to be clarified.

The results described above suggest that triethylaluminium added to **1** preferentially in a 1,2-manner, like the Grignard reagent. The structure of the precursor which led to **2**, however, may not be the same as that in the Grignard reaction. In order to collect information on the structure of the precursor, the reaction mixture obtained with triethylaluminium was directly hydrogenated over Pd-$BaCO_3$ and then hydrolyzed. Gas chromatography, NMR and IR spectra showed that the saturated product mainly consisted of 7-ethylbicyclo[4.2.0]octan-7-ol (49%) and 1-ethylcyclooctanol (14%). Prior hydrolysis to the hydrogenation of the reaction mixture gave only **6**, and neither decan-3-ol nor 1-ethylcyclooctan-1-ol was detected. The NMR spectrum of the reaction mixture in n-hexane prior to work-up also suggested the presence of a compound of bicyclo[4.2.0]octa-2,4-diene structure, since its four olefinic protons (δ 5·95) appeared at position similar to those of 1,3-cyclohexadiene (δ 5·78). These evidences support the idea that the 1,2-adduct obtained from **1** and triethylaluminium assumes a bicyclo[4.2.0]octa-2,4-diene structure rather than a cyclooctatriene structure and on hydrolysis the resultant alcohol rapidly transforms into the open-chain unsaturated ketone **2**. The origin of the difference in the structure of the open-chain products between the reaction of triethylaluminium and that of ethylmagnesium bromide is difficult to understand. In THF solvent, the reactions of triethylaluminium and triethylborane with **1** did not take place even at reflux, and **1** was recovered.

On the other hand, lithium diethylcopper,[9] which is known to add to α,β-unsaturated ketones preferentially in a 1,4-manner, gave almost exclusively **3** in a 66% yield, which absorbed two equivalents of hydrogen over Pd-$BaCO_3$ to yield 3-ethylcyclooctanone **7**. In contrast to the 1,2-adduct, the dienone is stable on distillation and gas chromatographic analysis. The 1,4-adduct formation by lithium diethylcopper has been discussed by House[9] in terms of the facile attack to the double bond of conjugated ketones and relative inertness of the reagent toward carbon-oxygen bond.

1,2- and 1,4-Additions: Since the thermally unstable 1,2-adduct transforms into the aliphatic unsaturated ketone during gas chromatographic analysis, the ratio of 1,2- and 1,4-addition was determined by the relative peak areas of the aliphatic and cyclic ketones. The results obtained with ethyllithium and ethylmagnesium bromide under various reaction conditions are summarized in Table 1, where the products obtained from reduction or enolization are not included, since they account for only a minor portion of the products under the conditions. The yield of the addition products generally amounted to 66–33%. Experiment 6 in Table 1 was performed at −70°C to examine the effect of the conformational mobility of **1** on the course of the addition, because it is known that the inversion rate of the tub-form of **1** slows down below −43°C.[10] No appreciable change in product ratio was observed. Comparison of experiments 7 and 8 indicates that 1,4-addition tends to increase on going from petroleum ether to diethyl ether as solvent. More pronounced increases of 1,4-addition were observed in the presence of HMPA with both ethylmagnesium bromide and ethyllithium. Obviously, the ether solvent and HMPA molecules coordinated to the organometallic reagents play an important role in determining the mode of the addition. Reaction of **1** with ethylmagnesium bromide gave a higher proportion of 1,2-adduct (92%) exceeding that of ethyllithium (78–82%), in contrast to the generally accepted difference in the product distribution between Grignard reagent and alkyllithium in the addition to α,β-unsaturated ketones.[11] In our control experiments under the same conditions in ether, 2-cyclohexen-1-one produced 59% of the 1,2-adduct with ethylmagnesium bromide as compared to 91% with ethyllithium. Methylvinyl ketone similarly afforded 46% and 83% of the 1,2-adduct, respectively.

Addition of HMPA can be considered to affect the course of the reaction of organometallic reagents with carbonyl compounds in the following ways: (1) increase of ionic character of carbon-metal bond of the reagents, (2) increased bulkiness of the reagents coordinated by solvent or added ligand, (3) change of interaction between carbonyl oxygen and metal ($>C{=}O\cdots M$).

It is generally believed[12] that alkylmetal compounds are associated in hydrocarbon or ether solvents, but react with ketones in their monomeric forms. The observed dependence of 1,4-addition on a variety of solvents and the presence of HMPA in the present reactions of **1** could be reasonably interpreted by a steric factor where the increased bulkiness of the reagents bearing donor solvents or HMPA would retard 1,2-attack to the carbonyl carbon of the relatively rigid tub-form of **1**, but would disturb 1,4-addition less. This interpretation is further supported by the reactions of **1** with other alkyl magnesium and lithium reagents of different "intrinsic bulkiness".

Table 1. Relative ratio of adduct of 1 with ethyl metallic reagents

Run No.	1 mMol	EtM	mMol (mol/l)	Additive (mMol)	Solvent	Temp °C	Time min	Product Ratio[d] 1,2-Add.%	1,4-Add.%
1	40·0	Et_3Al	50·0 (2·5)[a]		Petrol[c] ether	−25 ~ 23	180	98·0	2·0[f]
2	16·7	Et_3Al	20·0 (4·0)[a]	—	THF	reflux	20	0	0[h]
3	20·0	EtMgBr	50·0 (0·5)[b]	—	Et_2O	reflux	30	92·0	8·0[f]
4	4·0	EtMgBr	5·0 (0·33)[b]	HMPA (5·0)	Et_2O	reflux	30	77·9	22·1[g]
5	4·0	EtMgBr	5·0 (0·33)[b]	HMPA (10·0)	Et_2O	reflux	30	56·3	43·7[g]
6	4·0	EtLi	10·0 (0·3)[a]	—	Et_2O	−70	210	78·2	21·8[g]
7	1·0	EtLi	2·0 (0·3)[a]	—	Et_2O	reflux	30	81·9	18·1[g]
8	4·0	EtLi	5·0 (0·4)[a]	—	Petrol[c] ether	reflux	30	100[e]	0[g]
9	4·0	EtLi	5·0 (0·4)[a]	HMPA (5·0)	Petrol[c] ether	reflux	30	23·6	76·4[g]
10	4·0	EtLi	5·0 (0·4)[a]	HMPA (10·0)	Petrol[c] ether	reflux	30	0	100[g]
11	16·7	EtLi	20·0 (0·4)[a]	CuI (10·0)	Et_2O	−60	40	0·5	99·5[f]

[a] The concentration was determined by acid-titration.

[b] Calculated amount based on the amount of magnesium.

[c] Fraction of 30–40°C.

[d] Relative areas of the corresponding peaks in gas chromatograms. Normalized as 1,2% + 1,4% = 100.

[e] A considerable amount of unknown high boiling material was also founded.

[f] Vales for distillated.

[g] Vales for the concentrate after work-up.

[h] No reaction.

Table 2. Relative ratio of adducts of 1 with Grignard and alkyllithium reagents

Run No.	Organometallic reagents	1,2-Add.%	1,4-Add.%
12	CH_3MgI[b]	95·9	4·1
4	C_2H_5MgBr[a]	92·0	8·0
13	$i\text{-}C_3H_7MgBr$[b]	40·6	59·4
14	CH_3Li[c]	100	trace
7	C_2H_5Li[a]	81·9	18·1
15	$i\text{-}C_3H_7Li$[c]	35·7	64·3

[a] Cited from Table 1.

[b] Values for hydrogenated product of distillate.

[c] Values for hydrogenated product of the concentrate after work-up.

As shown in Table 2, the proportion of 1,4-addition was found to increase in proportion to the size of alkyl group both in Grignard reagents and alkyllithiums.

In summary, the mode of the addition of organometallics to 1 is dependent on the coordinative ability of the reaction medium as well as the nature of organometallic reagent, and the increasing order of 1,4-addition for the ethyl reagents can be arranged as follows: Et_3Al (petrol. ether) ≤ EtLi (petrol. ether) < EtMgBr (Et_2O) < EtLi (Et_2O) < EtMgBr (1 equiv. HMPA) < EtMgBr (2 equiv. HMPA) < EtLi (1 equiv. HMPA) < Et_2CuLi < EtLi (2 equiv. HMPA).

Enolization of α,β-Unsaturated Ketones: The reaction of saturated ketones with n-butylmagnesium bromide in HMPA at 80°C proceeds exclusively to form the corresponding magnesium enolates, which reacted with alkyl halides or tosylates to yield alkylated ketones in good yields.[13] Reactions of 2-cyclohexen-1-one or methylvinyl ketone with ethylmagnesium bromide in ether in the presence of two equivalents of HMPA resulted in marked increase of the recovered ketones and the formation of high boiling material. The similar function of added ligands is noted in the literature.[14] Evolution of nearly an equivalent amount of ethane to the recovered 2-cyclohexen-1-one was also observed on addition of the ketone to the mixture of the reagents and HMPA in ether. Thus, the reaction of α,β-unsaturated ketones would be considered to suffer from the enolization promoted by HMPA even under ordinary reaction condition at reflux in ether. Table 3 includes the reaction of 2-cycloocten-1-one with ethyllithium under various conditions. Al-

Table 3. Reaction of 2-cycloocten-1-one with ethyllithium.

Run No.	Ketone	EtLi mMol (mol/l)	solvent	Additive HMPA mMol	Product ratio[a] I	II	III	IV	V	VI
16	4	5 (0.63)	Et_2O	—	67.8	6.0	28.7	0.8	1.1	0.8
17	4	5 (0.25)	Petrol ether	—	72.7	2.2	5.0	0.0	12.3	7.8
18	4	5 (0.25)	Petrol ether	5	10.6	0.0	68.8	1.3	0.0	19.3
19	4	5 (0.25)	Petrol ether	10	50.0	4.7	1.5	41.1	0.0	2.7

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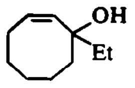

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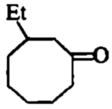

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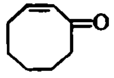

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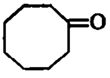

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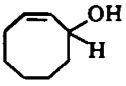

VI. Unknown

[a]Relative peak areas of GLC for distillate.

though the concurrent formation of a considerable amount of polymeric material prevents accurate estimation, the product distribution indicates the similar effect of the medium containing HMPA.

In sharp contrast with the results for these unsaturated ketones, enolization seems not to interfere with the present organometallic addition of **1**, and the comparable yields of addition products were obtained irrespective of the kind of solvent or the amount of HMPA (up to three equivalents). This inertness of the hydrogens at C(8) to enolization is in accordance with the observation described by Roberts et al[10] that the C(8) hydrogens were very resistant to the base-catalyzed deuterium exchange in D_2O-dioxane. An interpretation based on an unfavourable arrangement of the hydrogen and carbonyl group for the resistance of **1** to enolization could not be applied in this case, since the dihedral angle of nearly 90° is estimated by Dreiding model of the tub-form of **1**. A plausible explanation would derive from one or both of the following electronic factors: (1) a repulsive interaction caused by a close proximity of the developing π-electrons to π-electrons of the C-4 double bond; (2) instability by forming an antihomoaromatic ring system composed of six π-electrons of the three double bonds and lone-pair electrons in view of the existence of the corresponding homoaromatic cation.[15]

EXPERIMENTAL

Materials. 2,4,6-Cyclooctatrien-1-one **1** was prepared by the base catalyzed isomerization of cyclooctatetraene oxide,[4] in 60–80% yields, b.p. 68–69°C/3 mm Hg, n_D^{25} 1·5776. 2-Cycloocten-1-one was obtained by Jones oxidation of 2-cycloocten-1-ol. Triethylaluminium was a commercial product (Ethyl Corporation, N.Y.). Commercial hexamethylphoshoramide was distilled prior to use. Manipulation of the solutions of air- and water-sensitive reagents, triethylaluminium and ethyllithium, was done in a dry nitrogen box. All reactions were carried out under a nitrogen atmosphere.

Reaction of **1** *with triethylaluminium*. In a 300 ml flask equipped with reflux condenser, thermometer, magnetic stirrer, and an inlet tube for nitrogen, a solution of 4·80 g (40 mmol) of **1** in petroleum ether (30 ml) was placed and the flask was thoroughly flushed with nitrogen. The mixture was cooled to −25°C and a solution of 6·8 ml (50 mMol) of triethylaluminium in petroleum ether (15 ml) was added in a period of 7 min. No gas was evolved during the addition. Temperature of the mixture was gradually raised to room temp during 3 h under stirring. The mixture was hydrolyzed by addition of wet ether (100 ml) and then 10 ml of water, and filtered. The precipitate was washed with three portions of 40 ml of ether. The combined solutions were washed twice with water and dried over anhydrous magnesium sulfate. Distillation gave 3·55 g (54%) of yellow liquid, b.p. 73–76°C/2 mm Hg, n_D^{25} 1·5745. IR (neat): $\nu_{C=O}$ 1680 cm^{-1}; $\nu_{C=C}$ 1660, 1630, 1610 cm^{-1}; $\delta_{C=CH}$ (cis) 725 cm^{-1}; $\delta_{C=CH}$ (trans) 925 cm^{-1}. NMR (CCl_4): δ, 1·09 (t, 3H; J = 7 Hz), 1·89 (d, 3H; J = 8 Hz), 2·50 (q, 2H; J = 7 Hz), 6·40 (m, 5H), 7·62 (two d, 1H; J = 11, 15 Hz). UV (MeOH): λ max 216 nm (ϵ = 5400), 313 nm (ϵ = 23600).

Hydrogenation of the product (1·76 g) in 20 ml methanol over Pd–$BaCO_3$ absorbed 740 ml of hydrogen (97% of the theoretical amount, 766 ml), and the following distillation gave decan-3-one **6** and a small amount (2·0%) of 3-ethylcyclooctanone **7**, b.p. 91°C/50 mmHg. The former was confirmed by comparison with an authentic sample (IR, GLC and its semicarbazone).

Reaction of **1** *with lithium diethylcopper*. An ethereal lithium diethylcopper solution was prepared at −60°C in a 300 ml three necked flask (as in the previous experiment) by addition of a calculated amount of filtered ethyllithium (40 mMol) in ether to a mixture of 3·8 g (20·0 mMol) of cuprous iodide in ether (30 ml) at −60°C. After a solution of 2·0 g (16·7 mMol) of **1** in ether (30 ml) was added the mixture was stirred for 40 min at −60°C. Temperature of the mixture was raised gradually to −20°C during 1 h and the mixture was hydrolyzed by addition of saturated aqueous ammonium chloride (100 ml). The water layer was extracted three times with ether and the combined ethereal solution was washed once with water.

After drying over anhydrous magnesium sulfate and concentration, the residue was distilled to yield light yellow liquid, 1·6 g (66%), b.p. 84–95°C/2 mm Hg. The product containing a small amount (0·5%) of **2** was purified by preparative gas chromatography. IR (neat): $\nu_{C=O}$ 1700 cm^{-1}; $\nu_{C=C}$ 1660, 1630 cm^{-1}. NMR (CCl_4): δ, 0·92 (t, 3H), 1·38 (m, 2H), 2·37 (m, 3H), 3·10 (d, 2H), 5·78 (m, 4H). UV (MeOH): λ_{max} 230 nm ($\epsilon = 7700$), cf. 1,3-cyclooctadiene: λ_{max} 230 nm ($\epsilon = 6000$). Calc for $C_{10}H_{14}O$: C; 79·94, H; 9·35. Found: C; 79·56, H; 9·60%.

Hydrogenation of the purified product (239 mg) absorbed two molar equivalents of hydrogen (72 ml) to yield 3-ethyl-cyclooctanone **7** on distillation, which coincided with the product obtained in the reaction of 2-cycloocten-1-one with ethyllithium (gas chromatography and IR).

Reaction of **1** *with ethylmagnesium bromide.* Ethylmagnesium bromide in ether was prepared from 5·5 g (50 mMol) of ethylbromide and 1·2 g (50 mg-atom) of magnesium in the usual procedure. A solution of 2·4 g (20 mMol) of **1** in ether (10 ml) was added to the Grignard solution at room temperature in a period of 5 min, and the mixture was stirred under reflux for 30 min. The mixture was cooled with ice-water and hydrolyzed. Distillation after work-up gave light yellow liquid, 1·9 g (57%), b.p. 75·0–77·7°C/2·5 mm Hg. Hydrogenation of the product yielded a mixture of decan-3-one **6** (92%) and 3-ethylcyclooctanone **7** (8%).

Effect of the presence of HMPA. The following general procedure was used to see the effect of HMPA on the ratio of 1,2- and 1,4-addition. An ethylmagnesium bromide solution obtained from 0·70 g (6 mMol) of ethylbromide and 0·12 g (5 mg-atom) of magnesium in ether (15 ml) and a calculated amount (5·0 mMol) of ethyllithium solution (in petroleum ether or diethyl ether) were used for the reaction. To an ethyllithium solution (5·0 mMol, 0·4 mol/l) one or two equivalents of HMPA (0·90 g and 1·80 g, respectively) in 5 ml solvent was added, and the mixture was refluxed under stirring for 30 min. A solution of 0·48 g (4·0 mMol) of **1** in 5 ml solvent was added to the cooled mixture at 5°C. After stirred at the temperature for 30 min, the mixture was refluxed under stirring for 30 min and then hydrolyzed by addition of saturated aqueous ammonium chloride solution (100 ml). The water layer was extracted with three 20 ml portions of ether. The combined solution was dried and concentrated. The ratio of 1,2- and 1,4-adduct in the product was determined by the gas chromatogram of the concentrate on 3 mm × 2 m column of 10% Reoplex 400 on 60–80 mesh Celite 545.

Reaction of 2-cycloocten-1-one with ethyllithium. A filtered ethereal ethyllithium solution of known concentration (8 mMol, 0·63 mol/l) was added to a mixture of 0·50 g (4·0 mMol) of 2-cycloocten-1-one in ether (10 ml) at 5°C and the mixture was stirred at the temperature for 30 min. The mixture was then refluxed under stirring for 1·5 h, cooled and hydrolyzed. The water layer was extracted with three 20 ml portions of ether. After drying and concentration of the combined solution, distillation gave 0·10g of liquid and a considerable amount of polymeric residue. When HMPA was used as an additive, a mixture of ethyllithium and one or two equivalents amount of HMPA was refluxed for 30 min prior to the addition of the ketone solution. The composition of the distillate obtained under several reaction conditions are listed in Table 3.

Reaction of other Grignard reagents and alkyllithiums. To methylmagnesium iodide [1·42 g (10 mMol) of methyl iodide and 0·24 g (10 mg-atom) of magnesium in 15 ml ether] prepared in the usual manner was added a solution of **1** [0·48 g (4 mMol)] in ether (10 ml). The mixture was stirred for 30 min at 5°C and refluxed for 30 min under stirring. The cooled solution was hydrolyzed and worked up. Distillation yielded 0·38 g (67%) of light yellow liquid, b.p. 74°C/3 mm Hg, n_D^{25} 1·5670. After the product was hydrogenated over Pd-$BaCO_3$, ratios of 1,2- and 1,4-adduct was determined by gas chromatography on a column (3 mm × 2 m) of 10% SE-30 on 60–80 mesh Celite 545. By the same procedure, 0·48 g (4·0 mMol) of **1** was allowed to react with methyllithium (8 mMol) or isopropyllithium (7 mMol) in ether. After evaporation of the ethereal reaction mixture, the residue was dissolved in 5 ml methanol and hydrogenated over 5% Pd-$BaCO_3$. The products were analyzed by gas chromatography.

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