181. A Novel Synthesis of *tert*-Alkyl Sulfides

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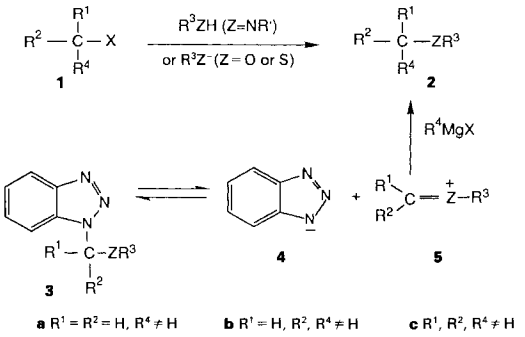
(24.VI.91)

tert-Alkyl sulfides are conveniently prepared from α-(1*H*-benzotriazol-1-yl)alkyl sulfides by displacement of the 1*H*-benzotriazol-1-yl group with *Grignard* reagents. The 1-[α-(alkylthio)alkyl]- and 1-[α-(arylthio)alkyl]-1*H*-benzotriazole intermediates are easily available by several routes: *i*) displacement of the halogen from appropriate halides by sodium salts of thiols, *ii*) condensation of 1*H*-benzotriazole and thiols with carbonyl compounds, or *iii*) lithiation of *N*-substituted 1*H*-benzotriazoles and subsequent treatment with electrophiles.

1. Introduction. – The most important classical methods for the preparation of alkylamines, alkyl ethers, and alkyl sulfides **2** (Z = NR, O, and S, respectively) have involved formation of a C–N, C–O, or C–S bond by nucleophilic substitution at the central saturated C-atom in compounds of type **1** (X = halogen, sulfonate, or similar leaving group; *Scheme 1*). For amines, such methods are rarely high yielding because of the formation of mixtures [1]. For ethers, this reaction (the *Williamson* synthesis) works well for the preparation of primary alkyl ethers **2a** (Z = O), less well for *sec*-alkyl ethers **2b** (Z = O), and not at all for *tert*-alkyl ethers **2c** (Z = O) [2]. For sulfides, satisfactory results are obtained for both **2a** (Z = S) and **2b** (Z = S), but the method fails for *tert*-alkyl sulfides **2c** (Z = S) [3]. In fact, few methods are available for *tert*-alkyl sulfides, although they have been prepared in 20–76% yields from tertiary alcohols and thiols in glacial AcOH in the presence of $HClO_4$ [4]. *tert*-Butyl thiol was converted to *tert*-butyl sulfide by the *Friedel-Crafts* catalysts, $AlCl_3$, HF, BF_3 [5], or H_2SO_4 [6]. It was also found that *tert*-alkyl homoallyl sulfides can be prepared in high yields from dithioacetals and

Scheme 1



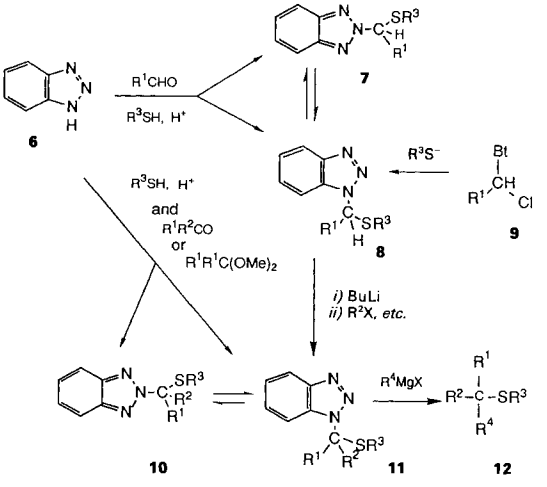
allylstannanes in the presence of $GaCl_3$ [7]. The recent successful use of the novel catalyst system, Me_3SiCl and $InCl_3$, is restricted to the preparation of primary and *sec*-alkyl sulfides in good yields from *O*-(trimethylsilyl)monothioacetals with Et_3SiH and some silylated C nucleophiles [8].

Recent work in our laboratory [9] [10] has shown that *N*-(α-aminoalkyl)-1*H*-benzotriazoles **3** (Z = NR′) reversibly ionize to yield the benzotriazole anion **4** and an iminium cation **5** (Z = NR′). Because of this, compounds **3** (Z = NR′) react with *Grignard* and other organometallic reagents to yield amines **2** (Z = NR′): such reactions occur regardless of the nature of R^1 and R^2, and have been used *inter alia* in the synthesis of alkylated amines [11–13], α-amino-esters [14], β-amino-esters [15] and β-amino-ketones [16], and extended to the preparation of amides [17] and thioamides [18].

These reactions have recently been extended to the oxygen series [19]. Because an oxygen cation of type **5** (Z = O) is less stable than its nitrogen analog, the ionization **3** to **4** + **5** occurs for cases **b** and **c** but not for case **a**. Therefore, the benzotriazole method complements the *Williamson* synthesis, and we have reported [20] the preparation of many ethers of types **2b** (Z = O) and **2c** (Z = O).

Cations of type **5** are still less stable for Z = S. Thus, it appeared that it might be necessary for both R^1 and R^2 in **3** (Z = S) to be other than H for the ionization **3**→**4** + **5** to be sufficiently favored to allow the preparation of sulfides **2** (Z = S) by this route. However, it is precisely such sulfides **2c** (Z = S) which are not easily available by the classical route. We now report that the successful outcome of these speculations has resulted in a novel synthesis of *tert*-alkyl sulfides **12**. *N*-[α-(alkylthio)alkyl]- or *N*-[α-(arylthio)alkyl]-1*H*-benzotriazoles **8**, available by the two alternative routes indicated in *Scheme 2*, are converted in two steps into products **12** *via* intermediates **11**. Compounds **11** can also be prepared in some cases directly by reaction of **6** with ketones and thiols.

Scheme 2[a])



Bt = 1*H*-Benzotriazol-1-yl

[a]) For definition of R^1, R^2, R^3, and R^4 see *Tables 1* and *3*.

Results and Discussion. – *Preparation of* N-*[α-(Alkylthio)alkyl]- and* N-*[α-(Arylthio)-alkyl]-1* H-*benzotriazoles.* Compounds of types **8** and **11** can be prepared by four different routes.

Route 1. From N-*(α-Haloalkyl)benzotriazoles* (**9**→**8**). The displacement of halogen from such 1*H*-benzotriazolyl derivatives by S nucleophiles is facile. Thus, 1-(1*H*-benzotriazol-1-yl)-1-chlorobutane (**9a**) reacted with sodium thiophenoxide in MeOH at 20° to afford 1-(1*H*-benzotriazol-1-yl)-1-(phenylthio)butane (**8a**) in 80% yield. However, an attempted reaction of 1-(1*H*-benzotriazol-1-yl)-1-chloro-2-methylpropane with sodium thiophenoxide failed to give the corresponding sulfide **8b** (R^1 = i-Pr); presumably the increased steric hinderance prevented the nucleophilic displacement.

Route 2. Condensation of Benzotriazole **6** *with Thiols and Aldehydes* (**6**→**7** and **8**). Good yields of sulfides were realised from the condensations of aliphatic aldehydes, 1*H*-benzotriazole, and thiophenol in the presence of catalytic amounts of TsOH in refluxing benzene with azeotropic removal of H_2O. These reactions gave isomer mixtures **7** and **8** which could be separated by column chromatography. The 1*H* to 2*H* isomer ratios (*Table 1*) estimated from the integrals of the ^{1}H-NMR signals for the crude products reveal the predominance of the 1*H* isomers **8** in all these cases. The thermodynamic equilibria for these mixtures are reported and discussed in [21].

Route 3. Condensation of 1 H-*Benzotriazole* (**6**) *with Thiols and Ketones or Ketals* (**6**→**10** and **11**). In contrast to the displacement reaction mentioned above, the acid-catalyzed condensations of 1*H*-benzotriazole and thiols also succeeded with ketones and led to the formation of *tert*-alkyl sulfides with an α-1*H*-benzotriazol-1-yl group. Thus the

Table 1. *Preparation of α-(1* H-*Benzotriazol-1-yl)alkyl Sulfides from Aldehydes and Ketones*

No.	R^1	R^2	R^3	M.p.[a] [°C]	Yield [%]	Ratio[b] 1*H*/2*H*	Eluent for column chromatography
7a	Pr	–	Ph	oil	80	70:30	Hexane/CH_2Cl_2 3:1
8a	Pr	–	Ph	oil			
7b	i-Pr	–	Ph	69–70	75	67:33	Hexane/CH_2Cl_2 3:1
8b	i-Pr	–	Ph	57–57.5			
7c	Et	–	Ph	oil	78	70:30	Hexane/CH_2Cl_2 4:1
8c	Et	–	Ph	oil			
7d	i-Pr	–	*m*-CH_3–C_6H_4	oil	73	71:29	Hexane/CH_2Cl_2 2:1
8d	i-Pr	–	*m*-CH_3–C_6H_4	oil			
10a	Me	Me	Ph	75–76	11	66:34	Hexane/CH_2Cl_2 3:1
11a	Me	Me	Ph	oil			
10b	–$(CH_2)_4$–		Ph	80–81	34	78:22	Hexane/$CHCl_3$ 2:1
11b	–$(CH_2)_4$–		Ph	97–98			
10c	–$(CH_2)_5$–		Ph	76–78	47	50:50	Hexane/CH_2Cl_2 2:1
11c	–$(CH_2)_5$–		Ph	96–98			
10d	–$(CH_2)_6$–		Ph	70–71	41	75:25	Hexane/CH_2Cl_2 4:1
11d	–$(CH_2)_6$–		Ph	oil			
10e	–$(CH_2)_5$–		$PhCH_2$	123–125	62	43:57	Hexane/$CHCl_3$ 2:1
11e	–$(CH_2)_5$–		$PhCH_2$	75–77			
10f	–$(CH_2)_4$–		C_8H_{17}	oil	56	70:30	Hexane/$CHCl_3$ 4:1
11f	–$(CH_2)_4$–		C_8H_{17}	oil			
10g	–$(CH_2)_5$–		C_8H_{17}	oil	53	60:40	Hexane/CH_2Cl_2 4:1
11g	–$(CH_2)_5$–		C_8H_{17}	oil			

[a]) All compounds gave satisfactory elemental analyses. [b]) Taken from ^{1}H-NMR of crude products.

sulfides **10a–d** and **11a–d** were obtained as mixtures by the reaction of 1*H*-benzotriazole and benzenethiol with acetone and several cyclic ketones. In the cases of acetone, cyclopentanone, and cycloheptanone, the 1*H*-isomers predominated (66–81%). From cyclohexanone, the 1*H* and 2*H* isomers were formed in comparable amounts, probably because of the 1,3-diaxal interactions in this more rigid system. 2-Methylcyclohexanone, under similar conditions, failed to afford the required 1*H*-benzotriazol-1-yl derivative but gave instead 1-methyl-2-(phenylthio)cyclohexene. Presumably, the steric interactions in the benzotriazole derivative were too great and spontaneous elimination occurred. Acetophenone failed to afford significant amounts of condensation products which is ascribable to the low electrophilicity of the C=O group and to steric crowding in the required products.

Reaction of 1*H*-benzotriazole with 2,2-dimethoxypropane and benzenethiol afforded the 1*H*-benzotriazol-1-yl derivative **11a** (55%) and its 2*H*-isomer **10a** (17%) in much better yields than were obtained from acetone (**11a**: 7%, **10a**: 4%).

Route 4. From N-*[α-(Alkylthio)alkyl]-1*H*-benzotriazole Anions and Electrophiles* (**8**→**11**). Treatment of the *sec*-alkyl sulfides **8a** and **8b** with BuLi readily affords the α-lithio derivatives. These reacted with electrophiles (alkyl halides or carbonyl compounds) to provide excellent yields of *tert*-alkyl sulfides. The α-H-atoms of the *sec*-alkyl sulfides are activated by the electron-withdrawing 1*H*-benzotriazol-1-yl group and by the ability of sulfur to stabilize the anion. Although some of these *tert*-alkyl sulfides can also be prepared by the condensation of benzotriazole and thiols with ketones, the *tert*-alkyl sulfides obtained *via* lithiation of *sec*-alkyl sulfides would be difficult to get from bulky carbonyl compounds in reaction with 1*H*-benzotriazole and arenethiols. However, lithiation of *sec*-alkyl sulfides followed by treatment with electrophiles constitutes a versatile and high-yielding method for the preparation of tertiary sulfides of type **11**.

The lithio derivative of **8a** reacts with MeI, $PhCH_2Br$, and benzaldehyde to give the alkylated products **11h**, **11i**, and **11j**, respectively, in good yields (*Tables 1* and *2*). Compound **11j** was isolated as a 1:1 mixture of diastereoisomers. Similarly reactions of the lithio derivative of **8b** with $PhCH_2Br$, 1-bromobutane, and MeI gave the expected products **11k**, **11l**, and **11m**, in high yields (*Tables 1* and *2*).

Synthesis of tert-*Alkyl Sulfides by Displacement of the 1*H*-Benzotriazol-1-yl Group.* The *tert*-alkyl sulfides with an α-(1*H*-benzotriazol-1-yl) group fail to react with *Grignard* reagents in Et_2O or THF, but in toluene at 85–95° the 1*H*-benzotriazol-1-yl group is

Table 2. *Preparation of* tert-*Alkyl Sulfides with an α-(1*H*-Benzotriazol-1-yl) Group* via *Lithiations*

No.	R^1	R^2	R^3	M.p. [°C]	Yield [%]	Eluent for column chromatography
11h[a])	Pr	Me	Ph	oil	99	–
11i	Pr	$PhCH_2$	Ph	99–101	83	CH_2Cl_2
11j	Pr	PhCH(OH)	Ph	135–137	78	–
11k[b])	i-Pr	$PhCH_2$	Ph	118–120	92	–
11l	i-Pr	Bu	Ph	76– 78	95	–
11m	i-Pr	Me	Ph	oil	98	–

[a]) Compounds **11h–j** were prepared by reaction of **8a** with the following electrophiles (R^2X in *Scheme 2*): **11h**: MeI; **11i**: $PhCH_2Br$; **11j**: PhCHO.

[b]) Compounds **11k–m** were prepared by reaction of **8b** with the following electrophiles (R^2X): **11k**: $PhCH_2Br$; **11l**: BuBr; **11m**: MeI.

displaced smoothly to afford *tert*-alkyl sulfides **12**. Bimolecular displacement of the 1*H*-benzotriazol-1-yl group in **11** by the *Grignard* reagent is unlikely as it is impeded by steric hindrance. As in previous analogous transformations [22], the reaction is believed to proceed *via* ionisation of the N–C(SPh) bond followed by reaction of the resulting cation **5** (Z=S) with the *Grignard* reagent. The *tert*-alkyl sulfides **11** fail to isomerize in toluene unless catalyzed by acids such as TsOH [21]. This again indicates that the MgX^+ component of the *Grignard* reagent or RMgX itself binds to the 1*H*-benzotriazol-1-yl group of **11** assisting in the heterolytic cleavage of the N–C bond and the subsequent reaction of the cation with the *Grignard* reagent.

Attempts to prepare *sec*-alkyl sulfides by the reaction of α-(1*H*-benzotriazol-1-yl)-alkyl sulfides of type **8b** with *Grignard* reagents failed. The formation of anions by the abstraction of the α-H-atom by the *Grignard* reagents was suggested by the intense color of the intermediate solutions. The α-(1*H*-benzotriazol-1-yl)alkyl sulfides of type **11** react with *Grignard* reagents to give *tert*-alkyl sulfides **12** in satisfactory to good yields (51–77%, *Table 3*). Sulfides **12** are produced from both the 1*H* and the 2*H* isomers of α-(1*H*-benzotriazol-1-yl)alkyl sulfides, thus these isomers need not be separated. When the displacement of benzotriazole was carried out with $PhCH_2MgBr$, small amounts (3–5%) of vinyl-sulfide elimination products were isolated in a few cases; *i.e.* reactions with **11c**, **11e**, and **11k**. However, reaction with PhMgCl or (hex-1-ynyl)magnesium iodide gave mixtures containing vinyl sulfides [23] as major components (70–90%). Sulfides **12** were purified by column chromatography with hexane as eluent (*Table 3*).

^1H- and ^{13}C-NMR Spectra. The symmetrical 2*H* isomers of α-(1*H*-benzotriazol-1-yl)alkyl sulfides show *AA'BB'* splitting patterns in their ^{1}H-NMR spectra. The H–C(4) and H–C(7) signals are shifted to *ca.* 7.87 ppm, and the H–C(5) and H–C(6) signals appear at *ca.* 7.34 ppm. In the case of *sec*-alkyl sulfides **7** and **8**, the NC*H* signal appears in the region 5.8–6.2 ppm. The methine protons of compounds **7e** and **8e** are unobservable due to signal overlap with complex aromatic patterns. In the case of sulfides **10** and **11**, the *ortho*-H-atoms of the phenylthio substituent resonate in the region 6.6–6.9 ppm. In the *sec*-alkyl sulfides **7** and **8**, these protons are shifted to 7.0–7.5 ppm. The ^{13}C-NMR spectra of compounds **7**, **8**, **10**, and **11** display the characteristic pattern for benzotriazole,

Table 3. *Preparation of* tert-*Alkyl Sulfides* **12a–j**

No.	From	R^1	R^2	R^3	R^4	M.p.[a]) [°C]	Total yield [%]
12a	**11a**	Me	Me	Ph	$PhCH_2$	56–58[b])	58
12b	**11b**	$-(CH_2)_4-$		Ph	$PhCH_2$	oil	54
12c	**11c**	$-(CH_2)_5-$		Ph	$PhCH_2$	oil	69
12d	**11h**	Pr	Me	Ph	$PhCH_2$	oil	64
12e	**11k**	i-Pr	$PhCH_2$	Ph	$PhCH_2$	56–58	64
12f	**11l**	i-Pr	Bu	Ph	$PhCH_2$	oil	75
12g	**11m**	i-Pr	Me	Ph	$PhCH_2$	oil	64
12h	**11e**	$-(CH_2)_5-$		CH_2Ph	$PhCH_2$	oil	51
12i	**11f**	$-(CH_2)_4-$		C_8H_{17}	$PhCH_2$	oil	61
12j	**11g**	$-(CH_2)_5-$		C_8H_{17}	$PhCH_2$	oil	77
12k	**11g**	$-(CH_2)_5-$		C_8H_{17}	Allyl	oil	65
12l	**11f**	$-(CH_2)_4-$		C_8H_{17}	p-CH_3–$C_6H_4CH_2$	oil	53

[a]) All compounds gave satisfactory elemental analyses or HRMS.
[b]) [24]: M.p. 59.5–60°.

and in the aliphatic region the NCH of α-(1*H*-benzotriazol-1-yl)alkyl sulfides resonate at 67–83 ppm.

All the *tert*-alkyl sulfides **12** were characterized by ^{1}H- and ^{13}C-NMR spectroscopy. The methylene protons of the benzylic substituent of **12e** are diastereotopic and are observed as an *AB* system.

Conclusions. – The reaction of *tert*-alkyl sulfides with α-(1*H*-triazol-1-yl) groups with *Grignard* reagents provides a convenient method for the preparation of a variety of symmetrical and unsymmetrical *tert*-alkyl sulfides.

Experimental Part

General. THF and Et_2O were dried over 4-Å molecular sieves and distilled from sodium/benzophenone before use. 1-(1*H*-Benzotriazol-1-yl)-1-chlorobutane [24] and 1-(1*H*-benzotriazol-1-yl)-1-chloro-2-methylpropane [20] were prepared by the literature methods. M.p.: determined with a hot-stage microscope, uncorrected. Column chromatography: with MCB silica gel (230–400 mesh). The ^{1}H- and ^{13}C-NMR spectra: *Varian-VXR-300-NMR* spectrometer. The ^{1}H chemical shifts referenced to TMS are expressed in ppm and the coupling constants (*J*) given in Hz. The ^{13}C chemical shifts are referenced to $CDCl_3$ or (D_6)DMSO and are reported in ppm. Elemental analyses: *Carlo-Erba 1106* instrument under the supervision of Dr. *D. Powell.*

*1-(1*H*-Benzotriazol-1-yl)-1-(phenylthio)butane* (**8a**). *1-(1*H*-Benzotriazol-1-yl)-1-chlorobutane* (**9a**; 2.09 g, 10 mmol) was added to a soln. of the Na salt of benzenethiol prepared from benzenethiol (9 mmol) and Na (9 mmol) in MeOH, and the mixture stirred at r.t. for 10 h under N_2. The reaction product was poured into ice-water, extracted with $CHCl_3$ (4 × 15 ml) and dried ($MgSO_4$). The solvent was evaporated and the residue purified by column chromatography using benzene/$CHCl_3$ as eluent.

*General Procedure for the Condensation of 1*H*-Benzotriazole, Thiols, and Carbonyl Compounds.* A mixture of 1*H*-benzotriazole (10 mmol), a thiol (10 mmol), and the pure carbonyl compound (10 mmol) was refluxed in benzene (100 ml) in the presence of TsOH (0.2 g) under a *Dean-Stark* head. After the collection of H_2O in the trap ceased (12–24 h) the mixture was poured into aq. NaOH soln. (300 ml, 5%) and shaken well to remove unreacted 1*H*-benzotriazole and thiol. Et_2O (200 ml) was added to the mixture and the org. layer separated, washed with H_2O, dried ($MgSO_4$), and the solvent removed. The 1*H* and 2*H* isomers were obtained by flash chromatography of the crude product. Compounds **7a**/**8a** to **10g**/**11g** were prepared by this procedure (*Tables 1* and *2*). A better method for **10a**/**11a** is given below.

Preparation of **10a** *and* **11a** *from 2,2-Dimethoxypropane.* A mixture of 1*H*-benzotriazole, 2,2-dimethoxypropane, and benzenethiol (10 mmol of each) was refluxed in benzene (100 ml) for 24 h in the presence of a catalytic amount of TsOH. Most of the benzene and the MeOH formed during the reaction were slowly distilled off and the residue was poured into aq. NaOH (200 ml, 5%) and shaken. The product was extracted with Et_2O, the Et_2O layer washed with H_2O, dried ($MgSO_4$), and the solvent removed. The isomers were separated by flash chromatography using hexane/CH_2Cl_2 4:1.

Preparation of tert-*Alkyl Sulfides with* α-*(1*H*-Benzotriazol-1-yl) Groups* via *Lithiation of* **8**. *General Procedure for* **11h–m**. To a soln. of the 1-(arylthio)-1-(1*H*-benzotriazol-1-yl)alkane **8** (3.5 mmol) in dry Et_2O (25 ml), BuLi (3.5 mmol in hexane) was added slowly *via* a syringe at −78° under N_2. The mixture was stirred for 10 min at −78°, and the electrophile (3.5 mmol) in dry Et_2O (5 ml) was added in one portion. The mixture was stirred for 2–3 h, allowed to warm to r.t. and stirred overnight. The product was quenched with aq. NH_4Cl, extracted with Et_2O, the Et_2O layer washed with H_2O, dried ($MgSO_4$), and the solvent removed. The crude product was purified by column chromatography or recrystallization (*Table 3*).

*2-(1*H*-Benzotriazol-1-yl)-1-phenyl-2-(phenylthio)pentan-1-ol* (**11j**). Two diastereoisomers of **11j** in a 1:1 ratio were obtained from **8a** and benzaldehyde. The product was obtained as a diastereoisomeric mixture by recrystallization. The tentative ^{1}H-NMR ($CDCl_3$) assignments: diastereoisomer 1: 8.40–6.76 (*m*, 14H); 5.89 (*d*, *J* = 4.0, 1H); 3.89 (*d*, *J* = 4.0, 1H); 2.79–2.01 (*m*, 2H); 1.21 (*m*, 2H); 0.79 (*m*, 3H); diastereoisomer 2: 8.40–6.76 (*m*, 14H); 5.55 (*d*, *J* = 3.6, 1H); 3.72 (*d*, *J* = 3.6, 1H); 2.79–2.01 (*m*, 2H); 1.63 (*m*, 2H); 0.85 (*m*, 3H).

Preparation of tert-*Alkyl Sulfides from (1*H*-Benzotriazol-1-yl)alkyl Sulfides and of* Grignard *Reagents. General Procedure for* **12a–j**. To a soln. of the *tert*-alkyl sulfide **10** or **11** (2.5 mmol) in Et_2O (15 ml) was added dropwise a soln. of the *Grignard* reagent (15 mmol) in Et_2O and the mixture stirred. Toluene (15 ml) was added to the soln. and solvent evaporated off, until the temp. of the mixture reached 85–95°. Heating and stirring of the

resulting mixture was continued and the reaction monitored by TLC. After complete disappearance of the starting material (4–6 h), the mixture was poured slowly into cold H_2O and extracted with Et_2O (100 ml). The org. layer was separated, washed with H_2O, dried ($MgSO_4$), and the solvent removed. The crude product was purified by flash chromatography with hexane.

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