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SYNTHESIS OF PYRIDAZINE DERIVATIVES—XVI

METHYL SUBSTITUTED IMIDAZO(1.2-b)PYRIDAZINES BY SYNTHESIS AND HOMOLYTIC METHYLATION[1]

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Abstract—Several Me substituted imidazo[1.2-b]pyridazines have been synthesized and NMR data for some of them are included and discussed. Homolytic methylation of imidazo[1.2-b]pyridazine revealed a marked selectivity and afforded a mixture of 7-methyl-, 8-methyl- and 7,8-dimethylimidazo[1.2-b]-pyridazine which could be separated by gas chromatography.

IN AN earlier communication[2] we described the synthesis of 2-methylimidazo[1,2-b]-pyridazine, the only so far known representative of Me substituted imidazo[1.2-b]-pyridazines. Our present investigation of homolytic methylation on the parent azabicycle required authentic specimens of different Me substituted derivatives. Several of these have now been synthesized by an adaptation of a recently described method for the preparation of substituted imidazo[1.2-b]pyridazines,[2,4] i.e. we employed a properly substituted 3-amino-6-chloropyridazine (I) and condensed it with α-bromoacetaldehyde or an α-bromoketone. The resulting Me substituted 6-chloroimidazo[1.2-b]pyridazine (III) was subsequently dehalogenated over Pd–C as catalyst to IV. Another possibility is to start with a substituted 3-aminopyridazine (II) to form directly the required imidazo[1.2-b]pyridazine (IV). According to these methods we have prepared 2-, 6-, 7- and 8-methyl-, 2,3-, 2,6-, 2,7-, 2,8- and 7,8-dimethyl-, 2,3,6-, 2,3,7-, 2,3,8- and 2,7,8-trimethyl- and 2,3,7,8-tetramethyl-imidazo-[1.2-b]pyridazine.

In addition to NMR spectra of some imidazo[1.2-b]pyridazines recorded previously,[2] in Table 1 are presented proton chemical shifts and coupling constants for some Me substituted imidazo[1.2-b]pyridazines described in this paper. From these data the following observations and correlations can be made. It appears that the most deshielded proton is H_6 as already observed with other imidazo[1.2-b]-pyridazines.[2] Usually a replacement of a proton in an aromatic ring by a Me group results in an increase in the shielding of the proton, bound on a C adjacent to that bearing a Me group[5,6] and this observation holds also for Me substituted imidazo[1.2-b]-pyridazines under investigation. It is of interest to note that the Me groups attached to C_2 and C_3 appear to have the same chemical shift and that the Me group on C_7 always appears at a higher field than does that on C_8.

Since it is known that in a fused aromatic system ring current in one ring may influence the proton chemical shift in the other ring,[5] it was of interest to examine if this holds in the case of imidazo[1.2-b]pyridazines. As in the case of the related imidazo[1.2-b]pyridine[7] it might be expected that if the imidazo[1.2-b]pyridazine ring system is expected to have truly aromatic character, the ring current of the

TABLE 1. NMR SPECTRA TABULATION OF

Compound	Chemical shift −τ									
	H_2	H_3	H_6	H_7	H_8	2-Me	3-Me	6-Me	7-Me	8-Me
6-Chloro-8-methyl-imidazo(1.2-b)pyridazine	2·23 (d)	2·08 (d)	(d)	3·08						7·32 (d)
6-Chloro-7-methyl-imidazo(1.2-b)pyridazine	2·23 (d)	2·08 (d)			2·03 (d)				7·52 (d)	
2,3,7,8-Tetramethyl-imidazo(1.2-b)pyridazine			1·96 (s)			7·53 (s)	7·53 (s)		7·72 (d)	7·44 (d)
6-Chloro-2,3,7,8-tetra-methylimidazo(1.2-b)-pyridazine						7·53 (s)	7·53 (s)		7·64 (d)	7·40 (d)
2,3-Dimethylimidazo-(1.2-b)pyridazine			1·74 (q)	3·12 (q)	2·20 (q)	7·51 (s)	7·51 (s)			
2,6-Dimethylimidazo-(1.2-b)pyridazine		2·35 (s)		3·17 (d)	2·26 (d)	7·51 (s)		7·46 (s)		

s = singlet; d = doublet; q = quartet.

π-excessive imidazole ring would cause to shift the pyridazine protons upfield, whereas the π-deficient pyridazine ring would have an opposite effect and shift the imidazole protons downfield. This could be confirmed from a correlation of NMR spectra of imidazole and pyridazine in deuterochloroform[8–10] with that of imidazo[1.2-b]-pyridazine. There is a remarkable shift of the imidazole protons downfield from 2·75 in imidazole to 2·21 for H_2 and 2·01 for H_3 in imidazo[1.2-b]pyridazine that enables to discern both protons in the parent and substituted bicyclic azaheterocycle. On the other hand, the proton on the C adjacent to the ring N in the 6-membered ring is shifted upfield from 0·76 in pyridazine to 1·70 in imidazo[1.2-b]pyridazine. Thus, this ability to sustain an induced ring current[11] may classify imidazo[1.2-b]pyrida-zines among truly aromatic compounds.

With regard to coupling constants which are presented in Table 1, it should be noted that in the NMR spectrum of 2,6-dimethylimidazo[1.2-b]pyridazine the long-range spin–spin coupling constant, J_{H_3,H_8}, is not discernible since the signal for H_3 is partly overlapped with the signal for H_8.

The 8-Me protons in 6-chloro-8-methylimidazo[1,2-b]pyridazine are appreciably coupled to the proton H_7 and the same is true for the 7-Me isomer where coupling of the same magnitude with H_8 is observed. However, there are no observed couplings of the 6-, 7- or 8-Me group to other ring protons, except as mentioned above. Similar observations have been made with heteroaromatic molecules when Me groups were attached to a C atom with a higher electron density.[12–14] Also in the related imidazo[1.2-a]pyridine ring system such couplings were not observed,[7,15] except for the 6-Me derivative.

From a recent review of homolytic substitutions of heterocyclic compounds[16] it follows that in methylation studies thermal homolysis of diacetyl peroxide in solution at moderate temperatures was most frequently employed. However, to our knowledge

SOME IMIDAZO(1.2-b)PYRIDAZINES (IN $CDCl_3$)

Coupling constants, c/s								
$J_{H_7, 8\text{-}Me}$	J_{H_2, H_3}	$J_{H_6, 7\text{-}Me}$	J_{H_6, H_8}	$J_{7\text{-}Me, 8\text{-}Me}$	J_{H_7, H_8}	J_{H_8, H_7}	J_{H_6, H_8}	$J_{2\text{-}Me, H_3}$
1·5	1·0							
	1·0	1·5	0·8					
				~0·5				
				~0·5				
					9·5	4·5	2·0	
					9·5			~0·5

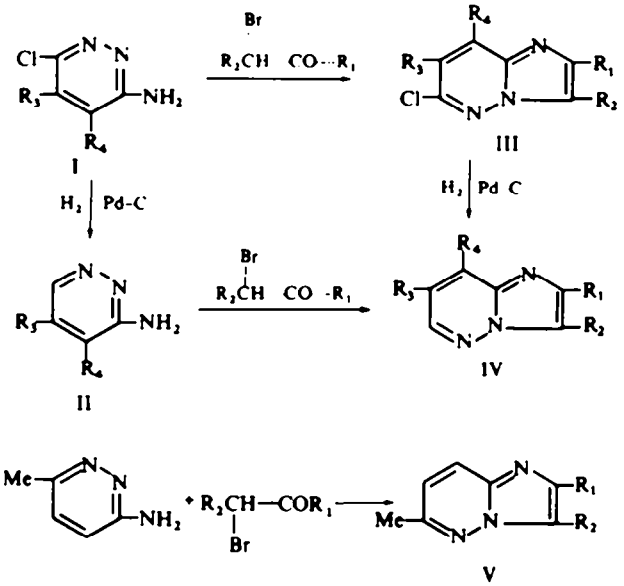
there are no reported homolytic methylations of imidazoles or pyridazines. Known are homolytic phenylations on pyridazine and these afforded 4-phenylpyridazine,[17] whereas from 1-methyl imidazole a mixture of the 2- and 5-isomer in the ratio of 2:1 has been obtained.[18] We have now treated imidazo[1.2-b]pyridazine with a solution of peroxyacetic acid, prepared from acetic anhydride and hydrogen peroxide, and a product was obtained in which the presence of methyl substituted imidazo[1.2-b]-pyridazines was detected by means of NMR spectroscopy. The formation of such products was undoubtedly due to the formation of some diacetyl peroxide as a result of the conversion of peroxyacetic acid in the presence of an excess of acetic anhydride.[19]

The crude product was successfully fractionated by gas chromatography on a column packed with Celite and containing as liquid phase polypropylene glycol adipate (Reoplex 400), which has been used formerly for the separation of different heterocyclic bases.[20] The elution pattern revealed that the product consisted of the unreacted starting compound and a mixture of 7-methyl-, 7,8-dimethyl- and 8-methylimidazo[1.2-b]pyridazines in the ratio of about 1:2:4.

Methylation was repeated and a solution of excess pure diacetyl peroxide in ether was employed in thermal homolysis. Using the same technique for the chromatographic separation of the resulting mixture and after examining the relative retention times it could be shown that exactly the same three methylated imidazo[1.2-b]-pyridazines were formed. There was no parent compound present and the mixture consisted of 8-methyl-, 7-methyl- and 7,8-dimethylimidazo[1.2-b]pyridazines formed in the ratio of about 1:2:5.

These results suggest that homolytic methylation of imidazo[1.2-b]pyridazine leads preferentially to an attack of the Me radical on position 8 with a subsequent formation of the 7,8-dimethyl derivative. Evidently, under the conditions employed, there was no attack on the imidazole ring since the corresponding derivatives could

not be identified in the reaction mixture at all. The marked positional selectivity para to the ring N of the pyridazine ring in homolytic reactions was demonstrated already in phenylations[17] whereas, contrarily, homolytic decomposition of diacyl peroxides in the presence of pyridine disclosed a preferential formation of 2-alkylpyridines.[21]



EXPERIMENTAL

M.ps: Kofler m.p. apparatus are corrected; UV spectra: Beckman Model DU spectrophotometer; NMR spectra: Varian model A-60 spectrometer, 10% (w/w) $CDCl_3$ solns, TMS as an internal standard.

3,6-Dichloro-4-methylpyridazine[22,23] was prepared from the corresponding pyridazone and upon amonolysis a mixture of 3-amino-6-chloro-4-methylpyridazine and 3-amino-6-chloro-5-methylpyridazine was obtained.[22] Both isomers were separated after acetylation as described by Linholter *et al.*[22] 3-Amino- and 3-amino-6-methylpyridazine were prepared according to the procedure employed by Grundmann,[24] whereas for the synthesis of 3-amino-6-chloro-4,5-dimethylpyridazine the procedure of Satoda *et al.* was followed.[25] Methyl 1-bromoethylketone was best prepared according to the procedure described by Catch *et al.*[26]

6-Chloro-7,8-dimethylimidazo[1.2-b]*pyridazine* (III, $R_1 = R_2 = H$, $R_3 = R_4 = Me$)

A mixture of bromoacetaldehyde diethylacetal (6·0 g), HBr (1·5 ml, $d = 1·38$) and water (1·5 ml) was heated under reflux for 2 hr and thereafter poured into EtOH (50 ml). The stirred soln was neutralized with solid $NaHCO_3$ and filtered. To the soln 3-amino-6-chloro-4,5-dimethylpyridazine (2·1 g, 0·013 mole) was added and the mixture was stirred for 5 hr at room temp. The reaction mixture was evaporated to dryness *in vacuo* and the residue was dissolved in water (30 ml), neutralized with solid $NaHCO_3$ and the mixture left aside on ice overnight. The separated product was filtered off, washed with few ml water and dried on air. For analysis the compound was purified by sublimation at 50°/0·1 mm Hg, m.p. 85–86°. Yield of the crude product was 0·7 g (29%). Crystallization from EtOH can be also used for purification. (Found: C, 52·54; H, 4·40; N, 22·70. $C_8H_8ClN_3$ requires: C, 52·91; H, 4·44; N, 23·14%); λ_{max}^{EtOH} 2260 and 3270 Å (ε 29,750 and 4400).

In essentially the same way the following compounds were prepared:

(i) Compound III ($R_1 = R_2 = R_4 = H$, $R_3 = Me$) was obtained in 41% yield, m.p. 108–109° (from H_2O). (Found: C, 49·93; H, 4·01; N, 25·03 $C_7H_6ClN_3$ requires: C, 50·17; H, 3·61; N, 25·07%).

(ii) Compound III (R_2 = R_4 = H, R_1 = R_3 = Me) was obtained in 47% yield, m.p. 190° from EtOH : H_2O, 1 : 2. (Found: C, 52·54; H, 4·40; N, 23·08. $C_8H_9ClN_2$ requires: C, 52·91; H, 4·44; N, 23·14%.)

(iii) Compound III (R_4 = H, R_1 = R_2 = R_3 = Me) was obtained in 38% yield, m.p. 142° from H_2O. (Found: C, 55·12; H, 5·08; N, 21·70. $C_9H_{10}ClN_2$ requires: C, 55·26; H, 5·15; N, 21·48%).

(iv) Compound III (R_1 = R_2 = R_3 = H, R_4 = Me) was obtained in 21% yield, m.p. 38–39° from n-hexane. (Found: C, 50·02; H, 3·44; N, 24·92. $C_7H_6ClN_2$ requires: C, 50·17; H, 3·61; N, 25·07%).

(v) Compound III (R_2 = R_3 = H, R_1 = R_4 = Me) was obtained in 24% yield, m.p. 105–106° from H_2O. (Found: C, 53·06; H, 4·71; N, 22·93. $C_8H_9ClN_2$ requires: C, 52·91; H, 4·44; N, 23·14%).

(vi) Compound III (R_3 = H, R_1 = R_2 = R_4 = Me) was obtained in 31% yield, m.p. 125–127° from n-hexane. (Found: C, 55·11; H, 5·10; N, 21·29. $C_9H_{10}ClN_2$ requires: C, 55·26; H, 5·15; N, 21·48%).

(vii) Compound III (R_2 = H, R_1 = R_3 = R_4 = Me) was obtained in 52% yield, m.p. 112° from EtOH : H_2O, 3 : 1. (Found: C, 55·32; H, 5·30; N, 21·20. $C_9H_{10}ClN_2$ requires: C, 55·26; H, 5·15; N, 21·48%).

(viii) Compound III (R_1 = R_2 = R_3 = R_4 = Me) was obtained in 49% yield, m.p. 80° from EtOH : H_2O, 2 : 1. (Found: C, 57·02; H, 5·92; N, 20·22. $C_{10}H_{12}ClN_2$ requires: C, 57·25; H, 5·77; N, 20·03%).

(ix) Compound III (R_3 = R_4 = H, R_1 = R_2 = Me) was obtained in 43% yield, m.p. 140–141° from EtOH. (Found: C, 52·68; H, 4·61; N, 22·97. $C_8H_9ClN_2$ requires: C, 52·91; H, 4·44; N, 23·14%).

In all these cases for 0·01 mole of the corresponding pyridazine 0·02 moles of bromoacetone or 0·013 moles of methyl 1-bromoethylketone or bromoacetaldehyde prepared from 5 g of its diethylacetal were used.

7,8-*Dimethylimidazo*[1.2-b]*pyridazine* (IV, R_1 = R_2 = H, R_3 = R_4 = Me)

Compound III (R_1 = R_2 = H, R_3 = R_4 = Me, 0·01 mole) was dissolved in MeOH (50 ml) and a soln of KOH (0·56 g) in MeOH (10 ml) and Pd–C (1 g of 5%) were added. The reaction mixture was stirred in an atmosphere of H_2 at room temp until the required amount of H_2 was absorbed. The catalyst was then removed by filtration and the solvent evaporated to dryness *in vacuo* so that temp did not exceed 35°. The residue was dissolved in H_2O (15 ml) and repeatedly extracted 5 times with $CHCl_3$. The combined extracts were dried with $MgSO_4$, filtered and the solvent evaporated *in vacuo* to dryness. After crystallization from n-hexane the pure compound was obtained, m.p. 124°, yield 93%. (Found: C, 65·12; H, 6·35; N, 28·72. $C_8H_9N_3$ requires: C, 65·28; H, 6·16; N, 28·55%); λ_{max}^{EtOH} 3220 Å (ε 3870).

Following the above procedure other imidazo[1.2-b]pyridazines were prepared. All compounds with m.p. under 80° crystallize after standing on ice for some time.

(i) Compound IV (R_1 = R_2 = R_4 = H, R_3 = Me) was obtained in 95% yield, m.p. 132° from n-hexane. (Found: C, 63·00; H, 5·46; N, 31·44. $C_7H_7N_3$ requires: C, 63·14; H, 5·30; N, 31·56%).

(ii) Compound IV (R_2 = R_4 = H, R_1 = R_3 = Me) was obtained in 90% yield, m.p. 78° from n-hexane. (Found: C, 65·09; H, 6·30; N, 28·41. $C_8H_9N_3$ requires: C, 65·28; H, 6·16; N, 28·55%).

(iii) Compound IV (R_1 = R_2 = R_3 = H, R_4 = Me) was obtained in 72% yield, m.p. 43–44° from n-hexane. (Found: C, 63·10; H, 5·42; N, 31·90. $C_7H_7N_3$ requires: C, 63·14; H, 5·30; N, 31·56%).

(iv) Compound IV (R_3 = R_4 = H, R_1 = R_2 = Me) was obtained in 88% yield, m.p. 58–59° from n-hexane. (Found: C, 65·12; H, 6·28; N, 28·81. $C_8H_9N_3$ requires: C, 65·28; H, 6·16; N, 28·55%).

(v) Compound IV (R_4 = H, R_1 = R_2 = R_3 = Me) was obtained in 92% yield, m.p. 129° from n-hexane. (Found: C, 66·92; H, 6·98; N, 26·06. $C_9H_{11}N_3$ requires: C, 67·05; H, 6·88; N, 26·07).

(vi) Compound IV (R_2 = R_3 = H, R_1 = R_4 = Me) was obtained in 85% yield, b.p. 132°. (Found: C, 65·02; H, 6·08; N, 28·36. $C_8H_9N_3$ requires: C, 65·28; H, 6·16; N, 28·55%).

(vii) Compound IV (R_3 = H, R_1 = R_2 = R_4 = Me) was obtained in 78% yield, b.p. 145°. (Found: C, 66·88; H, 6·81; N, 26·22. $C_9H_{11}N_3$ requires: C, 67·05; H, 6·88; N, 26·07%).

(viii) Compound IV (R_2 = H, R_1 = R_3 = R_4 = Me) was obtained in 97% yield, m.p. 123° from n-hexane. (Found: C, 67·22; H, 7·02; N, 25·67. $C_9H_{11}N_3$ requires: C, 67·05; H, 6·88; N, 26·07%).

(ix) Compound IV (R_1 = R_2 = R_3 = R_4 = Me) was obtained in 95% yield, m.p. 127–128° from n-hexane (Found: C, 68·36; H, 7·66; N, 24·04. $C_{10}H_{13}N_3$ requires: C, 68·54; H, 7·48; N, 23·98%).

2-*Methylimidazo*[1.2-b]*pyridazine* (IV, R_2 = R_3 = R_4 = H, R_1 = Me)

Compound II (R_3 = R_4 = H, 0·95 g) was heated under reflux with a soln of bromoacetone (2 g) in EtOH (25 ml) for 3 hr. The solvent was removed *in vacuo*, the residue dissolved in water (20 ml), the soln neutralized with a sat. $NaHCO_3$aq and extracted 3 times with 25 ml $CHCl_3$. The $CHCl_3$ layer was separated and dried with $MgSO_4$, filtered and evaporated *in vacuo* to dryness. The oily residue was treated

with n-hexane (5 ml) and left on ice overnight. The separated product was identical with the previously prepared compound.[2]

Using 3-amino-6-methylpyridazine and the appropriate bromocarbonyl compound, the following methyl substituted imidazo[1.2-b]pyridazines were prepared:

(i) Compound V ($R_1 = R_2 = H$) was obtained in 45% yield, m.p. 125° from n-hexane. (Found: C, 63·02; H, 5·48; N, 31·34. $C_7H_7N_3$ requires: C, 63·14; H, 5·30; N, 31·56%).

(ii) Compound V ($R_2 = H$, $R_1 = Me$) was obtained in 36% yield, m.p. 96° from n-hexane. (Found: C, 65·36; H, 6·34; N, 28·86. $C_8H_9N_3$ requires: C, 65·28; H, 6·16; N, 28·55%).

(iii) Compound V ($R_1 = R_2 = Me$) was obtained in 32% yield, m.p. 56° from n-hexane. (Found: C, 66·96; H, 7·02; N, 25·92 $C_9H_{11}N_3$ requires: C, 67·05; H, 6·88; N, 26·07%).

Homolytic methylation of imidazo[1.2-b]pyridazine

(a) A soln of peroxyacetic acid was prepared as follows: Ac_2O (100 ml) was cooled to 10°, conc H_2SO_4 (0·1 g) was added and thereafter to the stirred and externally cooled soln H_2O_2 (20 ml of 30%) was added portionwise so that the temp did not exceed 50°. The soln was left aside for 1 hr, anhyd NaOAc (0·2 g) was added and the mixture filtered. To this soln imidazo[1.2-b]pyridazine (5·0 g) was added and the mixture heated at 70° for 8 hr. The reaction mixture was evaporated *in vacuo* at 40° and the remaining yellow oil was dissolved in water (50 ml), neutralized with solid Na_2CO_3 and extracted 5 times with $CHCl_3$ (40 ml portions). The combined extracts were dried over $MgSO_4$ and the solvent evaporated *in vacuo*. The remaining yellow oil (2·5 g) was used without further purification for chromatographic separation.

(b) A soln of diacetyl peroxide in ether was prepared from Na_2O_2 (15 g)[27] and was used straight away. A soln of imidazo[1.2-b]pyridazine (2·0 g) in glacial AcOH (60 ml) was treated with the above soln of diacetyl peroxide and the reaction mixture heated at 70°. The ethereal soln of diacetyl peroxide was added during 2 hr and ether was at the same time distilled off from the reaction mixture. After the addition was complete, heating was continued for 3 hr, the solvent was evaporated *in vacuo*, the residue was made alkaline with 20% NaOH aq and extracted with $CHCl_3$ (5 portions of 30 ml). The combined extracts were dried over $MgSO_4$ and after the solvent was removed *in vacuo* there remained 1·7 of yellow oil which was used for further investigations.

Chromatographic separation

Gas chromatography was carried out on a Podbielniak Chromacron No. 9580 gas chromatograph equipped with stainless steel column, 100 cm long and 4 mm internal diameter. Column packing consisted of 15% (w/w) polypropylene glycol adipate (Reoplex 400) on 60 to 80-mesh Celite 545. Column was preconditioned for 1 hr at a temp of 175°. Samples (1 μl) were injected as a soln of 10 mg of the reaction mixture in 0·2 ml of $CHCl_3$. As carrier gas argon was introduced at a flow rate of 60 ml per min.

In order to ascertain just which compounds could be present in the reaction mixture, relative retention times were determined. These have been determined from sharp, well-defined peaks as follows: 8-methylimidazo[1.2-b]pyridazine 312 sec, imidazo[1.2-b]pyridazine 456 sec, 2,6-dimethylimidazo[1.2-b]pyridazine 529 sec, 7,8-dimethylimidazo[1.2-b]pyridazine 556 sec, 7-methylimidazo[1.2-b]pyridazine 692 sec, and 2,3,7,8-tetramethylimidazo[1.2-b]pyridazine 894 sec. Since the principal impurity normally found in imidazo[1.2-b]pyridazine is its 6-chloro derivative, this compound was also examined and a retention time of 874 sec established. No effort was made to maintain the quantitative relationship of the methylimidazo[1.2-b]pyridazines examined as standards to those in the reaction mixture, as we were primarily interested in qualitative rather than quantitative date.

Chromatographic separation of both reaction products was effected as indicated above and from the area of peaks the quantitative relationship of particular compound was evaluated. In the reaction product of imidazo[1.2-b]pyridazine and a soln of peroxyacetic acid there were identified 7-methyl-, 7,8-dimethyl- and 8-methylimidazo[1.2-b]pyridazine in the ratio of 1:2:4·3 and a small quantity of the parent imidazo-[1.2-b]pyridazine. On the other hand, imidazo[1.2-b]pyridazine after treatment with diacetyl peroxide afforded a product, which could be separated into 8-methyl-, 7-methyl- and 7,8-dimethylimidazo[1.2-b]-pyridazine in the ratio of 1·1·8·5·2. This mixture contained no unreacted parent compound.

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