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A SIMPLE SYNTHESIS OF 1,6-DIENES

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Summary

Imidoyl chlorides react with 3.3—6.0 molar equivalents of allylmagnesium bromide to give substituted 1,6-dienes in 32—67% yields.

Imidoyl chlorides are an interesting class of organic compounds [1,2]. Some recent applications of imidoyl chlorides in organic synthesis include the preparation of mesoionic compounds [3], 1,4-diaza-1,3-butadienes [4], imines and amines [5]. Several types of novel organometallic complexes of imidoyl halides have also been reported [4,6]. We now wish to report that imidoyl chlorides can experience double allylation by allylmagnesium bromide to give substituted 1,6-dienes in reasonable yields.

In 1906, Marquis [7] reported that phenylmagnesium bromide reacts with PhC(Cl)=NPh to give benzophenone in modest yield. The latter is presumably generated by hydrolysis of the corresponding Schiff base, since such compounds were isolated by Busch and Fleischmann [8,9], using RMgX, where R = Ph, α-$C_{10}H_7$, CH_3, C_2H_5 and later by Gilman and Morton [10] using *o*-anisylmagnesium bromide. A mixture of *N*,*N*-diphenylbenzamidine and *N*-(1,2-diphenylethylidene)aniline was obtained by treatment of PhC(Cl)=NPh with benzylmagnesium chloride.

The reaction of imidoyl chlorides with allylmagnesium bromide is an interesting and useful one. Reaction of equimolar amounts of I (R = *p*-BrC_6H_4, R' = Ph) and allyl-Grignard for 2 h afforded 4% of the 1,6-diene II (R = *p*-BrC_6H_4, R' = Ph) and less than 4% of the anticipated Schiff base. The latter was obtained, in similar yield, using a 2/1 ratio of allylmagnesium bromide to I, with II being formed in 6% yield along with small amounts of at least five other products. While these results were disappointing, we were gratified to observe that the use of excess Grignard (i.e. 3.3—6.0/1.0 mol ratio of C_3H_5MgBr/I) results in a clean

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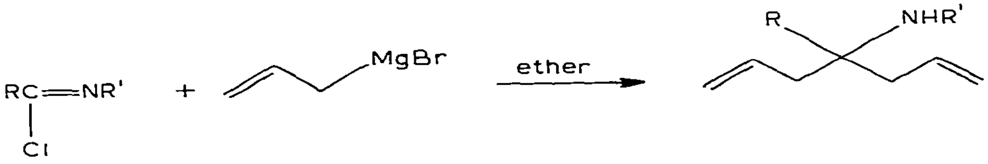
TABLE 1

IMIDOYL CHLORIDE—ALLYLMAGNESIUM BROMIDE REACTIONS

I (R =, R′ =)	C_3H_5MgBr/I	Reaction time, (h)	Yield of II (%)	B.p. (°C/mmHg)	Analysis found (calcd.) (%))		
					C	H	N
Ph, p-$CH_3C_6H_4$	6/1	0.5	65	180/4	86.14 (85.59)	8.62 (8.36)	
Ph, p-ClC_6H_4	4.7/1	0.5	63	190/3.5	76.21 (76.62)	7.08 (6.77)	4.94 (4.70)
p-BrC_6H_4, Ph	4.2/1	1.0	67	165/3	67.14 (66.67)	5.92 (5.89)	4.15 (4.09)
p-$CH_3OC_6H_4$, Ph	3.3/1	2.0	32	200/3 [b]	82.14 (81.87)	7.73 (7.90)	5.00 (4.77)
2-Furyl, p-$CH_3OC_6H_4$	4/1	21 [a]	40	150/4	76.65 (76.29)	7.87 (7.47)	

[a] Refluxed for the last 3.5 hours. [b] M.p. 74–76°C.



(I) (II)

and general reaction to give the 1,6-dienes in 32—67% yields (Table 1-yields were not optimized). With the exception of the 2-furyl substrate, I (R = 2-furyl, R' = 4-$CH_3OC_6H_4$) the reactions were quite facile. The structures of the products were identified on the basis of analytical and spectral (IR, NMR, mass spectral) data (Table 2). The infrared spectra of II gave absorptions at 3380—3600 cm^{-1} due to NH, and at 1620—1644 cm^{-1} for the double bond stretching vibration. Molecular ion peaks were observed in the mass spectra of II, with loss of an allyl unit, and then propene, being the principal fragmentations. The nuclear magnetic resonance spectra are also in accord with the assigned structure, with the four allylic protons occurring at δ 2.66—2.76 and the unsaturated protons appearing as a multiplet at δ 4.76—6.06.

TABLE 2

PERTINENT SPECTRAL DATA FOR II

II (R =, R' =)	IR [a] (cm^{-1})		^1H NMR, δ (ppm) [b]	MS (*m/e*)
	ν(NH)	ν(C=C)		
Ph, *p*-$CH_3C_6H_4$	3465	1620	2.17 (s, 3 H, CH_3), 2.74 (m, 4 H, allyl protons), 3.95 (s(br), 1 H, NH), 4.80—6.06 (m, 5 H, olefinic protons), 6.40 (d, 2 H, *J* 8 Hz, protons *meta* to the CH_3 group), 6.95 (d, 2 H, protons *ortho* to CH_3), 7.40 (m, 5 H, Ph protons)	277, 236, 194
Ph, *p*-ClC_6H_4	3430	1644	2.72 (m, 4 H, allyl protons), 4.00 (s(br), 1 H, NH), 4.80—6.00 (m, 6 H, olefinic protons), 6.34 (d, 2 H, *J* 8 Hz, protons *meta* to Cl), 6.96 (d, 2 H, protons *ortho* to Cl), 7.40 (m, 5 H, Ph protons)	297, 256, 214
p-BrC_6H_4Ph, Ph	3380	1636	2.70 (m, 4 H, allyl protons), 3.95 (s(br), 1 H, NH), 4.76—6.00 (m, 6 H, olefinic protons), 6.40—7.70 (m, 9 H, aromatic protons)	343, 341, 302, 300, 260, 258
p-$CH_3OC_6H_4$, Ph	3467	1624	2.76 (m, 4 H, allyl protons), 3.82 (s, 3 H, OCH_3), 4.02 (s(br), 1 H, NH), 4.80—6.08 (m, 6 H, olefinic protons), 6.30—7.56 (m, 9 H, aromatic protons)	293, 252, 210
2-Furyl, *p*-$CH_3OC_6H_4$	3600	1640	2.66 (m, 4 H, allyl protons), 3.70 (s, 3 H, OCH_3), 4.05 (s(br), 1 H, NH), 4.85—6.00 (m, 6 H, olefinic protons), 6.20—7.00 and 7.43 (m, 7 H, protons of benzene and furan rings)	283, 242, 200

[a] $CHCl_3$ solution. [b] $CDCl_3$ with tetramethylsilane as internal standard.

It is noteworthy that the presence of catalytic amounts of cuprous halide in the reaction of I with allylmagnesium bromide results in reduced product yields. For example, treatment of I (R = Ph, R′ = p-$CH_3C_6H_4$) with the Grignard reagent and 10 mol% of cuprous bromide gave II (R = Ph, R′ = p-$CH_3C_6H_4$) in 58% yield.

The reaction of imidoyl chlorides with excess allylmagnesium bromide constitutes a simple synthesis of 4-substituted- 1,6-dienes. Furthermore, the presence of an amino substituent at the 4-position is of considerable potential in its own right since, for example, methylation (at nitrogen) and subsequent elimination would give the 1,3,6-triene.

Experimental

Elemental analyses were determined by Canadian Microanalytical Service, Limited, Vancouver, and by Guelph Chemical Laboratories, Guelph, Ontario. A Unicam SP1100 spectrometer, equipped with a calibration standard, was used for infrared spectral determinations, and Varian T60 and MS9 instruments were used for recording ^1H NMR and mass spectra, respectively. The imidoyl chlorides were synthesized as previously described [3].

Typical procedure for the reaction of imidoyl chlorides with allylmagnesium bromide

Allylmagnesium bromide (7.0 mmol) in anhydrous ether (30 ml) was freshly prepared from allyl bromide and magnesium. A few drops of I (R = Ph, R′ = p-ClC_6H_4, 0.374 g, 1.5 mmol) in ether (10 ml) was added to the rapidly stirred Grignard reagent.

After one minute, the remaining imidoyl chloride solution was added in one portion. The reaction mixture was stirred at room temperature for 30 minutes and then poured into a saturated aqueous ammonium chloride solution. The product was extracted with ether, and the ether extract was dried and concentrated. Purification by chromatography (5/1 hexane/ether) gave II, R = Ph, R′ = p-ClC_6H_4 as a pale yellow oil which was distilled. Yield 0.280 g (63%).

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