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CLAISEN AMINO REARRANGEMENT AS A METHOD FOR SYNTHESIS OF C-CYCLOALKENYLANILINES

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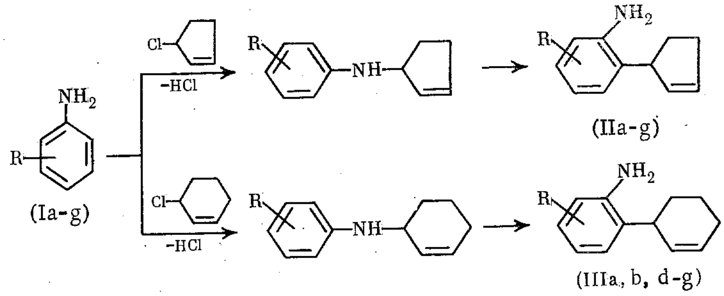
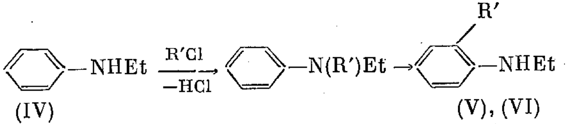
The Claisen amino rearrangement, which proceeds with unusual ease when aniline is reacted with 4-chloro-2-pentene, is autocatalytic and leads to C-alkylated compounds via the intermediate formation of the N-alkylated product [1].

We found that allylic cycloalkenyl chlorides, like 3-chlorocyclopentene and 3-chlorocyclohexene, react in a similar manner with aromatic amines:



R = H (a), 2-Me (b), 3-Me (c), 4-Me (d), 4-MeO (e), 2-Cl (f), 2,4-Me$_2$ (g).

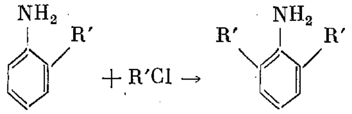


R' = 2-cyclopenten-1-yl (V); 2-cyclohexen-1-yl (VI).

The reaction was run in excess aniline, which serves as the solvent and ties up the liberated HCl as the hydrochloride.

Based on the GLC analysis data, employing the N-alkylated products, the reaction begins with replacement of the H atom of the amine by the cycloalkenyl group. The formed N-alkylanilines are then selectively rearranged by the aniline hydrochloride to 2-(2-cycloalkenyl)-anilines. The process can be stopped at the step of forming the N-substituted product by adding triethylamine to the reaction mixture. In contrast to aromatic amines, the hydrochlorides of aliphatic amines do not catalyze the rearrangement.

The reaction proceeds at ~20°C and is accompanied by the evolution of heat. 3-Chlorocyclopentene reacts so vigorously that quite strong cooling is necessary. The obtained 2-(2-cycloalkenyl)anilines can react anew with 3-chlorocyclopentene and 3-chlorocyclohexene to give the 2,6-disubstituted products:



R' = 2-cyclopenten-1-yl (VII), 2-cyclohexen-1-yl (VIII).

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TABLE 1. Synthesis of o-(2-Cycloalkenyl)anilines

Compound	Starting aniline	T., °C	Time, h	Yield, %	bp, °C (p, mm Hg)	n^{20}_D	Found/Calculated, %			Infrared spectrum ν_{NH_2}, cm^{-1}
							C	H	N	
Alkylating agent 3-chlorocyclopentene										
(IIa)	(Ia)	120	2	78	112–113(3)	1,5850	83,08/83,02	8,06/8,18	8,68/8,80	3450, 3370
(IIb)	(Ib)	140	3	79	110–111(2)	1,5794	83.10/83,24	8,68/8,67	8.01/8,09	3480, 3390
(IIc)	(Ic)	140	3	85	112–115(2)	1,5775	83.14/83,24	8.63/8,67	8.01/8.09	3450, 3370
(IId)	(Id)	140	3	71	109–112(2)	1,5768	83.31/83,24	8.85/8,67	8.12/8,09	3440, 3360
(IIe)	(Ie)	140	3	58	130–132(2)	1,5815	76.10/76,19	7,93/7,94	7,63/7,40	3440, 3360
(IIf)	(If)	140	3	52	122–125(2)	1,5898	68.48/68,22	6,26/6,22	7,26/7,24	3470, 3380
(IIg)	(Ig)	130	2	73	128–129(2)	1.5708	83,39/83,42	9.08/9,09	7,53/7.49	3470, 3380
(V)	(IV)	140	3	80	115–117(1)	1,5636	83,34/83.42	9.16/9,09	7,50/7,49	3420 (νNH)
Alkylating agent 3-chlorocyclohexene										
(IIIa)	(Ia)	150	10	81	118–120(2)	1,5852	83,53/83,24	8.52/8,67	7,76/8,09	3450, 3370
(IIIb)	(Ib)	140	10	74	132–136(2)	1,5770	83.40/83,42	9.14/9,09	7,56/7.49	3470, 3380
(IIId)	(Id)	160	12	80	120–121(1)	1.5781	83.51/83,42	9.01/9,09	7,35/7,49	3460, 3380
(IIIe)	(Ie)	160	12	60	150–151(1)	1,5796	77,27/76,85	8.50/8.37	6,96/6,90	3450, 3370
(IIIf)	(If)	150	12	68	128–130(1)	1,5928	69.40/69,40	6,72/6,75	6,73/6,75	3480, 3400
(IIIg)	(Ig)	140	10	86	121–123(1)	1,5723	83,27/83,58	9,37/9,45	6,79/6,97	3480, 3400
(VI)	(IV)	140	10	82	110–111(1)	1.5654	83.19/83,58	9.26/9,45	6,74/6,97	3410 (νNH)

Together with the main product, namely the 2,6-di-(2-cycloalkenyl)aniline, a substantial amount of decomposition products is formed.

The structure of the obtained compounds was proved by the spectra. The IR spectra of (II) and (III) have the absorption bands of a primary amino group (two broad bands in the 3300-3500 cm^{-1} region). The PMR spectrum of (IIa) has five groups of signals: for the methylene (1.60-2.20 ppm) and methine (3.58 ppm) protons, and the protons of the CH=CH bond (5.70 ppm), amino group (3.40 ppm), and aromatic ring. The latter give a complex multiplet in the 6.40-6.80 ppm region, which is characteristic for a strongly bonded ABCD system that describes the o-position of substituents. In addition, the position of the substituents in the ring is confirmed by the ^{13}C NMR spectrum of (IIa). This spectrum, with a broad-band suppression based on the protons, consists of 11 signals, which are characteristic for compounds with an unsymmetrical arrangement of the substituents in the aromatic ring. The values of the chemical shifts, calculated by the additive scheme, coincide satisfactorily with the experimental values in the case of the o-substituent.

EXPERIMENTAL

The IR spectra were obtained on a UR-20 spectrophotometer, the PMR spectra were obtained on a Tesla BS-487B instrument, and the ^{13}C NMR spectra were obtained on a Bruker HX-90 instrument, using HMDS as the internal standard. The GLC analysis was run on an LCM-7A chromatograph, using a 3 m × 4 mm column packed with SE-30 deposited on Chromaton N-AW-DMCS, in a helium stream (30 ml/min). The 3-chlorocyclopentene and 3-chlorocyclohexene were obtained by known procedures immediately before use.

2-(2-Cyclopentenyl)aniline (IIa). With stirring and cooling with tap water, to 46.5 g (0.5 mole) of aniline was added in drops 10.2 g (0.1 mole) of freshly prepared 3-chlorocyclopentene. Then the reaction mixture was kept for 2 h at 120°, cooled, and the congealed mass was treated with alkali solution. The organic layer was separated and dried over KOH. The residue from distilling off the excess aniline was practically pure (IIa), which was additionally purified by vacuum-distillation. Infrared spectrum (ν, cm^{-1}): 3450, 3370, 3060, 2850, 1625, 1500, 1460, 1290, 760. PMR spectrum (in CCl_4, δ, ppm): 1.60-2.20 m (4H, 2-CH_2), 3.40 s (2H, NH_2), 3.58 m (1H, CH), 5.70 m (2H, CH=CH), 6.40-6.80 m (4H, Ar). ^{13}C NMR spectrum (neat, δ, ppm): 31.2 ($C^{5'}$), 47.2 ($C^{1'}$), 116.0 (C^6), 118.5 (C^4), 127.1 ($C^{2'}$), 127.6 ($C^{5'}$), 129.9 ($C^{2'}$), 132.4 (C^3), 133.6 ($C^{3'}$), 144.6 (C^1).

Products (IIb-g) were obtained in a similar manner (Table 1).

2,6-Di(2-cyclopentenyl)aniline (VII). With stirring, to 47.7 g (0.3 mole) of (IIa) at 20° was added dropwise 10.2 g (0.1 mole) of 3-chlorocyclopentene. The mixture was kept for 3-4 h at 140°. The reaction product was isolated the same as (IIa) to give 13.5 g (60%) of (VII), bp 155-158° (1 mm), n^{20}_D 1.5672. Infrared spectrum (ν, cm^{-1}): 3480, 3390, 3060, 2860, 1630, 1460, 760. PMR spectrum (δ, ppm): 1.63-2.22 m (8H, 4-CH_2), 3.22 m (2H, 2-CH), 3.50 s (2H, NH_2), 5.68 m (4H, 2-CH=CH), 6.65 s (3H, Ar). Found: C 85.55; H 8.44; N 6.13%. $C_{16}H_{19}N$. Calculated: C 85.33; H 8.44; N 6.22%.

2-(2-Cyclohexenyl)aniline (IIIa). With stirring, to 46.5 g (0.5 mole) of aniline at 20° was added dropwise 11.6 g (0.1 mole) of 3-chlorocyclohexene. Slight heating up was observed, and the mass congealed on cooling. The reaction mixture was heated for 10 h at 150°. The reaction product was isolated the same as (IIa). Infrared spectrum (ν, cm^{-1}): 3450, 3370, 3025, 2870, 1620, 1500, 1460, 1290, 760. PMR spectrum (δ, ppm): 1.55-1.87 m (6H, 3-CH_2), 3.14 m (1H, CH), 3.34 s (2H, NH_2), 5.62 m (2H, CH=CH), 6.36-6.85 m (4H, Ar).

Compounds (IIIb, d-g) were obtained in a similar manner (see Table 1).

2,6-Di(2-cyclohexenyl)aniline (VIII). Obtained the same as (VII) from 52 g (0.3 mole) of (IIIa) and 11.6 g (0.1 mole) of 3-chlorocyclohexene. Yield of (VIII) 16.2 g (64%), bp 168-170° (1 mm), n^{20}_D 1.5779. Infrared spectrum (ν, cm^{-1}): 3460, 3370, 3025, 2860, 1620, 1450, 750. PMR spectrum (δ, ppm): 1.63-1.92 m (12H, 6-CH_2), 3.22 s (2H, 2-CH), 3.54 s (2H, NH_2), 5.65 m (4H, 2-CH=CH), 6.75 m (3H, Ar). Found: C 85.74; H 8.94; N 5.45%. $C_{18}H_{23}N$. Calculated: C 85.49; H 9.09; N 5.53%.

CONCLUSIONS

The reaction of 3-chlorocycloalkenes with excess aromatic amine leads to o-(2-cycloalkenyl)-substituted aromatic amines.

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