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Study on Synthesis of Azo-Coupling Products of 3-Aminotropolone

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Abstract: 3-Acetamidotropolone **1** reacted with *p*-substitutedbenzenediazonium chloride in pyridine to afford 3-acetamido-5-(4-substitutedphenylazo)tropolones **2a~f**. Hydrolysis of compounds **2a~f** gave 3-amino-5-(4-substitutedphenylazo)tropolones **3a~f** which could not be obtained directly from reactions of 3-aminotropolone with *p*-substitutedbenzenediazonium chloride. The structures of these new compounds **2a**, **2c~f**, **3a**, **3c~f** were confirmed from the elemental analysis and spectral data.

Keywords: 3-Acetamidotropolone, 3-aminotropolone, synthesis, azo-coupling, electrophilic substitution.

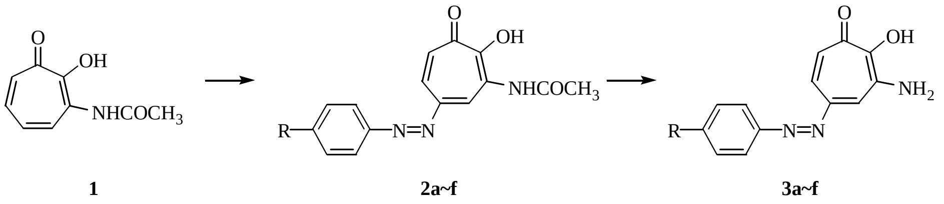
It is generally known that due to their special structures, tropolpone compounds demonstrate virtually the same aromaticity as benzene compounds, thus undergoing electrophilic substitution reactions with electrophilic reagents. The researches about this have been reported in many papers, especially about the reactions of 3-acetyltropolone[1], 3-acetamidotropolone[2], 3-cinnamoyltropolone[3], 3-iso-propenyl-tropo-lone[4], 3-(2-quinilinyl) tropolone[5] with various electrophilic reagents. But, the substituted 3-amino products can not be obtained directly from the reactions of 3-aminotropolone with the electrophilic reagents because of bearing hydroxyl and amino groups, which have paradoxical orientation effect in the seven-member aromatic ring. For this reason, this thesis presumed a route that 3-acetamido-5-paraphenylazotropolone **2a~f** were synthesized from 3-acetamidotropolone, then the objective compounds 3-amino-5-parapheny-l azotropolone **3a~f** could be derived from the hydrolysis of **2a~f** in acidic solution. The results proved that the process was feasible and were summarized as follows (**scheme 1**).

Results and Discussion

Azo-coupling reaction of 3-acetamidotropolone

Like other tropolone compounds, the azo-coupling reaction of 3-acetamidotropolone proceeds with aniline or para-aniline diazonium salt in pyridine solution cooled by ice water, the products **2a~f** were obtained in yield of 35.12%~92.49%.

Scheme 1



2a, 3a	R=H
2b, 3b	R=CH_3
2c, 3c	R=OCH_3
2d, 3d	R=Br
2e, 3e	R=Cl
2f, 3f	R=NO_2

The structures of compounds **2a~f** were confirmed by elemental analysis and spectral data. Take ^{1}H-NMR of compound **2c** for an example, δ 2.31 ppm (s, 3H), methyl hydrogen of the acetyl group; δ 3.94 ppm (s, 3H), the methoxyl hydrogen in the benzene ring; δ 7.26 ppm (d, 2H, J=8.2 Hz), the hydrogen adjacent to the methoxyl group in benzene ring; δ 7.52 ppm (d, 1H, J=10.2 Hz), the hydrogen at position 7 in tropolone ring; δ 7.68 ppm (d, 2H, J=8.2 Hz), the hydrogen adjacent to the azo group in benzene ring; δ 7.95 ppm (dd, 1H, J=10.2, 2.4 Hz), the hydrogen at position 6 in tropolone ring; δ 7.18 ppm (br, 1H), the hydrogen of amino group; δ 7.95 ppm (d, 1H, J=2.4 Hz), the hydrogen at position 4 in tropolone ring. IR (KBr cm^{-1}) 3352, 3295 absorptions of NH group and OH group; 1683, 1598 corresponding to the carboxyl group in acetamido group and ketone group in tropolone ring. All the above data showed that the electrophilic substitution occurred in position 5. The structures of other compounds could also be confirmed by their spectral data and elemental analysis (**Table 1**, **Table 2**).

Hydrolysis of azo-coupling products of 3-acetamidotropolone

Compounds **2a~f** were refluxed in 50% sulfuric acid for 1.5 h ~ 3 h, the hydrolyzed products **3a~f** could be given in yield of 59.1%~89.66%. The signals of δ 2.31ppm and δ 9.18ppm in ^{1}H-NMR disappeared, and peak of the carboxyl of acetamido group (1683 cm^{-1}) also disappeared in IR, but the signal of NH_2 was shown in IR and ^{1}H-NMR spectra, which illustrated that the acetamido group was hydrolyzed, and the 5-azo-coupling products of 3-aminotropolone were obtained.

Table 1 Physical constant and elemental analysis of compounds **2a~f, 3a~f**

Compound	Yield(%)	mp.(℃)	Elemental analysis					
			C(%)		H(%)		N(%)	
			Cald.	Found	Cald.	Found	Cald.	Found
2a	35.12	183~184	63.63	63.54	4.63	4.38	14.84	14.96
2b	92.49[a]	196~197[b]	64.64	64.70	5.09	5.18	14.13	14.34
2c	75.79	185~186	61.34	61.57	4.83	4.66	13.41	13.61
2d	58.67	234~235	49.76	49.85	3.32	3.14	11.60	11.78
2e	61.05	202~203	56.73	56.48	3.81	3.64	13.23	13.44
2f	54.55	237~239	54.91	54.66	3.66	3.54	17.07	17.35
3a	85.92	201~202	64.72	64.53	4.60	4.38	17.42	17.59
3b	85.41[c]	178~179[d]	65.87	65.67	5.13	5.24	16.46	16.69
3c	77.80	164~165	61.99	62.07	4.83	4.58	15.49	15.76
3d	86.61	279~280	48.79	48.59	3.12	3.06	13.13	13.36
3e	59.10	282~282	56.66	56.39	3.63	3.44	15.24	15.25
3f	89.66	297~298	54.57	54.55	3.50	3.37	19.57	19.68

a: lit.[2]80%; b: lit.[2]184~185℃; c: lit.80%;d: lit.224℃.

Table 2 IR, ^{1}H-NMR data of compounds **2a~f, 3a~f**

Compounds	υ (cm^{-1})(KBr)	^{1}H-NMR(δ , ppm)(CDCl$_3$)
2a	3352 (NH), 3294 (OH), 1688 (C=O), 1598 (C=O)	2.32 (s, 3H, COCH$_3$), 7.27~9.98 (m, 8H, ArH), 9.19 (br, 1H, NH)
2b	3350 (NH), 3290 (OH), 1680 (C=O), 1600 (C=O)	2.30 (s, 3H, COCH$_3$), 2.41 (s, 3H, CH3), 7.26~9.95 (m, 7H, ArH), 9.17 (br, 1H, NH)
2c	3353 (NH), 3292 (OH), 1684 (C=O), 1596 (C=O)	2.31 (s, 3H, COCH$_3$), 3.94 (s, 3H, OCH$_3$), 7.26~9.95 (m, 7H, ArH), 9.18 (br, 1H, NH)
2d	3352 (NH), 3293 (OH), 1683 (C=O), 1592 (C=O)	2.32 (s, 3H, COCH$_3$), 7.29~9.99 (m, 7H, ArH), 9.19(br, 1H, NH)
2e	3353 (NH), 3294 (OH), 1680 (C=O), 1599 (C=O)	2.31 (s, 3H, COCH$_3$), 7.28~9.97 (m, 7H, ArH), 9.20 (br, 1H, NH)
2f	3352 (NH), 3292 (OH), 1682 (C=O), 1598 (C=O)	2.33 (s, 3H, COCH$_3$),7 .29~9.99 (m, 7H, ArH), 9.24 (br, 1H, NH)
2e	3350 (NH), 3291 (OH), 1686 (C=O), 1602 (C=O)	2.30 (s, 3H, COCH$_3$), 7.27~9.96 (m, 8H, ArH), 9.19 (br, 1H, NH)
3a	3446 (NH), 3372 (NH), 3202 (OH), 1634 (C=O)	7.24~9.86 (m, 8H, ArH), 7.14 (br, 2H, NH$_2$)
3b	3440 (NH), 3370 (NH), 3200 (OH), 1630 (C=O)	2.44 (s, 3H, CH3), 7.23~9.82 (m, 7H, ArH), 7.18 (br, 2H, NH$_2$)
3c	3444 (NH), 3374 (NH), 3205 (OH), 1636 (C=O)	3.95 (s, 3H, OCH$_3$), 7.22~9.86 (m, 7H, ArH), 7.19 (br, 2H, NH$_2$)
3d	3442 (NH), 3372 (NH), 3202 (OH), 1624 (C=O)	7.22~9.88 (m, 7H, ArH), 7.14 (br, 2H, NH$_2$)
3e	3444 (NH), 3370 (NH), 3200 (OH), 1628(C=O)	7.25~9.80 (m, 7H, ArH), 7.10 (br, 2H, NH$_2$)
3f	3445 (NH), 3376 (NH), 3208 (OH), 1614(C=O)	7.27~9.83 (m, 7H, ArH), 7.19 (br, 2H, NH$_2$)

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