

Synthesis of Symmetrically Disubstituted 1,1'-Diphenyl-1,1'-azoalkanes

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As part of our work on diarylazoalkanes^{1,2,3}, a series of symmetrically disubstituted 1,1'-diaryl-1,1'-azoalkanes (**4**) were prepared from alkyl aryl ketones (**1**) via the azines (**2**) and the corresponding hydrazines (**3**) employing a modification of the method previously used by Cohen et al.⁴ For comparison, previously known derivatives⁴ (X = H, 4-CH₃, 4-Cl, 4-OCH₃) are also dealt with in this communication. A study of the effects of the substituted groups on the rate of decomposition and product distribution will be presented elsewhere.

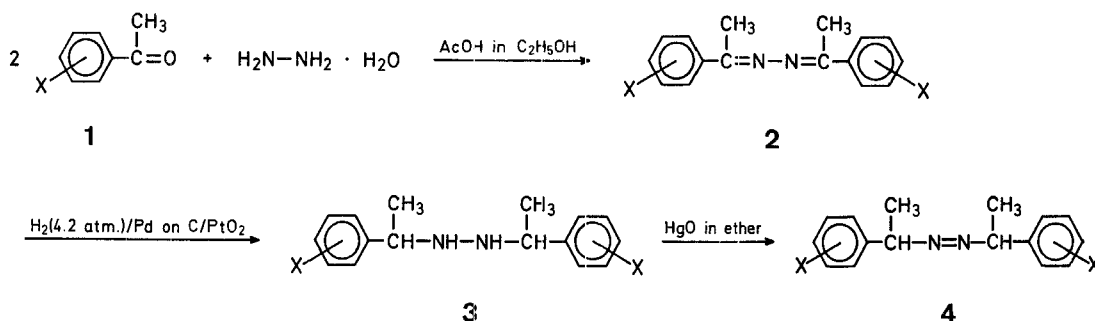
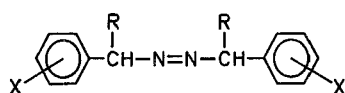


Table 1. Symmetrically Disubstituted Diarylazoalkanes from the Corresponding Hydrazines



X	R	Yield %	m. p. ^a	Analysis	U. V. log (359 mμ)
H ^b	CH ₃	47	71–72.5°	calc. C 80.67 H 7.57 N 11.76 found 80.77 7.86 11.94	1.69
4-CH ₃ ^b	CH ₃	65	77.5–78.5°	calc. C 81.20 H 8.27 N 10.52 found 81.38 8.40 10.64	1.73
4-C ₂ H ₅	CH ₃	61	46–47°	calc. C 81.71 H 8.80 N 9.60 found 81.63 8.84 9.52	1.74
4-OCH ₃ ^b	CH ₃	37	89–90°	calc. C 72.48 H 7.38 N 9.40 found 72.31 7.56 9.39	1.91
4-F	CH ₃	22	56–57°	calc. C 70.07 H 5.84 N 10.22 found 70.31 6.01 10.00	1.67
4-Cl ^b	CH ₃	35	106–107.5°	calc. C 62.51 H 5.23 N 9.11 found 62.53 5.49 9.40	1.79
3-CH ₃	CH ₃	50	38–39.5°	calc. C 81.20 H 8.27 N 10.52 found 81.23 8.17 10.43	1.72
3-OCH ₃	CH ₃	25	69.5–71°	calc. C 72.48 H 7.38 N 9.40 found 72.57 7.53 9.40	1.73
3-F	CH ₃	34	40–41°	calc. C 70.07 H 5.84 N 10.22 found 69.88 5.87 10.34	1.66
3-Cl	CH ₃	52	39–40.5°	calc. C 62.51 H 5.23 N 9.11 found 62.36 5.40 9.08	1.70
3-CF ₃	CH ₃	10	9–10°	calc. C 57.76 H 4.28 N 7.48 found 57.76 4.29 7.21	1.28
2-OCH ₃	CH ₃	43	56.5–58°	calc. C 72.48 H 7.38 N 9.40 found 72.19 7.42 9.24	1.67
2-OCH ₃	H	60	70–71°	calc. C 71.11 H 6.67 N 10.37 found 71.19 6.72 10.44	1.83 ^c

^a Capillary tube, 3°/min.

^b see Ref.⁴

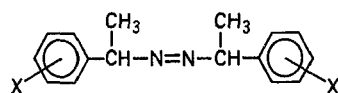
^c at 355 mμ

Employing the original method of Cohen et al.⁴, some of the azo compounds **4** (X = 4-CH₃, 4-C₂H₅, 4-OCH₃, 4-F) were synthesized with only moderate success; the method failed in making the *meta* derivatives and the parent compound from oxidation of the corresponding hydrazine with hydrogen peroxide⁴ even after several trials with different experimental conditions. Consequently, we employed a different oxidation procedure found in this laboratory which uses mercuric oxide as the oxidizing agent in ether as solvent. The improvement observed with this procedure can be attributed to the following factors:

(1) The hydrazines (**3**) are more soluble in ether than in aqueous solution and this provides more favorable conditions for the reaction with the mercuric oxide which is dispersed in the solution.

(2) The more volatile ether provides better temperature control of the exothermic reaction and thus prevents thermal decomposition of the azo compounds.

Table 2. N.M.R. Parameters of Some Diarylazoalkanes



X	Chemical Shifts, δ , ppm					
	CH _{3(d)}	CH _(q)	C ₆ H _{4(m)}	OCH _{3(s)}	CH ₃	CH _{2(q)}
H	1.47	4.58	7.29	—	—	—
4-CH ₃	1.44	4.25	7.18	—	2.31 _(s)	—
3-CH ₃	1.46	4.53	7.11	—	2.33 _(s)	—
4-C ₂ H ₅	1.45	4.53	7.17	—	1.23 _(t)	2.62
4-F	1.46	4.60	7.24	—	—	—
3-F	1.48	4.58	7.10	—	—	—
4-Cl	1.47	4.53	7.27	—	—	—
3-Cl	1.50	4.57	7.27	—	—	—
3-CF ₃	1.50; 1.56 ^a	4.70	7.55	—	—	—
4-OCH ₃	1.43	4.51	7.03	3.73	—	—
3-OCH ₃	1.57	4.57	6.96	3.72	—	—
2-OCH ₃	1.38; 1.42 ^a	5.07	7.15	3.71; 3.76 ^a	—	—
	CH ₂ , 4.98 _(s)		7.10	3.78	—	—

^a Double sets of peaks are probably due to rotational isomers.

(3) Mercuric oxide appears to be a more effective oxidizing agent than hydrogen peroxide for this system.

(4) Observation of the color change (HgO, yellow → Hg, black) makes it easy to detect the end of the reaction, avoiding possible further oxidation of 4 to ketazines (2).

Based on the results observed it appears that the procedure described here is not only easier to use, but is also applicable to a greater variety of compounds, and is a good general method for the preparation of secondary (or primary) azo compounds.

1,1'-Diphenyl-1,1'-azoalkanes; General Procedure:

The symmetrically disubstituted N,N'-bis-[1-phenylethyl]-hydrazine (~0.05 mol) dissolved in absolute ether (100 ml) was treated with freshly made mercuric oxide (0.05 mol) from reaction of mercury(II)-chloride with sodium hydroxide. (No reaction occurred when commercially made mercuric oxide, red or yellow form, was used). After stirring at room temperature for several hours the yellow color of the mercuric oxide disappeared. The ether solution was filtered and dried over magnesium sulfate and evaporated under reduced pressure to obtain the azo compounds as colorless crystalline materials (except that the p-Cl derivative was light yellow⁴ and the m-CF₃ isomer was a light brown liquid). The melting point, extinction coefficient at 359 m μ , elemental analyses, overall yield and N. M. R. parameters for these new azo compounds

are listed in Table 1 and 2. The same method of synthesis was also successfully used for one compound of another series^{5,6}, 2,2'-dimethoxy ω , ω' -azotoluene, with good results.

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