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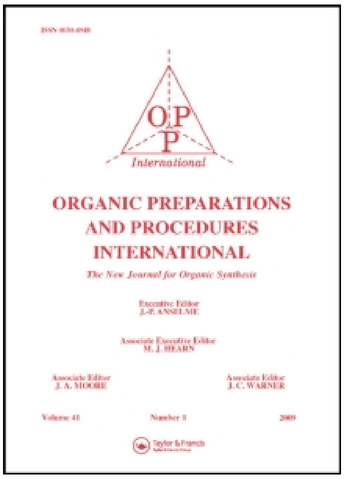

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AROMATIC NITRATION OF 2-PHENYLHYDRAZONES OF 1,2-DICARBONYL COMPOUNDS USING CERIUM(IV) AMMONIUM NITRATE

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Submitted by (11/23/92)

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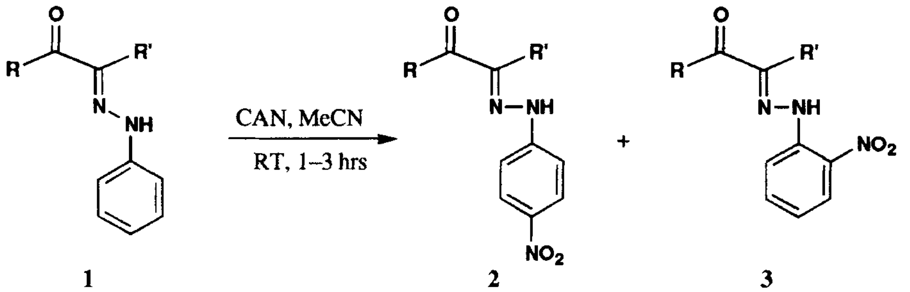
The reactions of organic compounds with salts of cerium(IV) have been studied under various conditions.[1] Reactions of cerium(IV) ammonium nitrate (CAN) with aromatic compounds, however, have not been as extensively investigated.[2] We now report herein our findings on nitration of 2-phenylhydrazones of 1,2-dicarbonyl compounds with CAN.

When 2-phenylhydrazones of 1,2-dicarbonyl compounds (**1**)[3] were treated with CAN in acetonitrile at room temperature for 1-3 hrs, a mixture of the corresponding 4-nitrophenyl and 2-nitrophenyl hydrazones[4-11] **2** and **3** respectively was obtained in good overall yields (Scheme). A slight excess (1.5 equiv.) of CAN was sufficient for complete nitration. All compounds isolated gave satisfactory analytical figures and were characterized by spectroscopic means (IR, mass and NMR); their mps were in agreement with those reported in literature.

A particularly important feature of this reaction is the prevailing mild conditions, as a result of which, neither carbonyl, ester, cyano, nitro groups nor the hydrazone portions undergo reaction with CAN. Thus exclusive formation of ring nitration products with the 4-nitro isomer (**2**) as the major product demonstrates the selectivity of this nitration.



1 2 3

a) R = Me, R' = COMe
b) R = Ph, R' = COMe
c) R = Me, R' = CO_2Et
d) R = Ph, R' = CO_2Et
e) R = OMe, R' = CO_2Me
f) R = OEt, R' = CN
g) R = Ph, R' = NO_2

TABLE 1. Yields and Physical Data of Hydrazones **2** and **3**

Cmpd	Yield (%)	mp. (°C)	lit. mp. (°C)	Cmpd	Yield (%)	mp. (°C)	lit. mp. (°C)
2a	59	228(dec.)	230[a]	**3a**	17	183(dec.)	183–184[g]
2b	55	142–143	143[a]	**3b**	15	144–145	145[h]
2c	64	127–128	127[b]	**3c**	14	93–94	93[b]
2d	60	118–119	118[c]	**3d**	12	150–151	150[c]
2e	57	161(dec.)	160[d]	**3e**	14	138–139	138[d]
2f	66	191–192	193–194[e]	**3f**	16	159–160	161–162[g]
2g	62	147–148	147[f]	**3g**	13	117–118	118[f]

a) Ref. 4 b) Ref. 5 c) Ref. 6 d) Ref. 7 e) Ref. 8 f) Ref. 9 g) Ref. 10 h) Ref. 11.

In conclusion, the method described herein provides a mild and selective mode of ring nitration of 2-phenylhydrazones of 1,2-dicarbonyl compounds with CAN.

EXPERIMENTAL SECTION

Melting points were determined using a Buchi 510 apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer FT-IR 1600 instrument. Proton NMR spectra were obtained on a Varian XL-200, 200 MHz spectrometer using TMS as an internal standard.

General Procedure.- To a solution of 2-phenylhydrazone[3] (**1**, 2.0 mmol) in acetonitrile (20 ml) was added cerium ammonium nitrate (3.00 mmol) and the contents were stirred for 1-3 hrs at room temperature. The reaction mixture was then poured into ice-water and extracted with dichloromethane. The organic layer was washed thoroughly with water and brine and dried over $MgSO_4$. The solvent was removed under reduced pressure to afford a mixture of products **2** and **3** which were separated by column chromatography over silica gel using EtOAc-hexane (2:8) as eluent to give **2** as the first fraction, followed by **3**; they were further purified by crystallization from the appropriate solvent. Spectral data of **2a**: IR ($CDCl_3$): 1676, 1624 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.54 (s, 3

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H, CH_3), 2.64 (s, 3 H, CH_3), 7.51 (d, J = 9 Hz, 2 H, ArH), 8.32 (d, J = 9 Hz, 2 H, ArH), 14.51 (s, 1 H, NH); **3a**: IR: 1675, 1621; ^{1}H NMR: 2.51 (s, 3 H, CH_3), 2.62 (s, 3 H, CH_3), 7.48 (t, J = 8.3 Hz, 1 H, ArH), 7.64 (t, J = 8.3 Hz, 1 H, ArH), 7.73 (d, J = 8.3 Hz, 1 H, ArH), 7.82 (d, J = 8.3 Hz, 1 H, ArH), 14.33 (s, 1 H, NH); **2b**: IR: 1645, 1640; ^{1}H NMR: 2.61 (s, 3 H, CH_3), 7.28–7.61 (m, 7 H, ArH), 8.31 (d, J = 9 Hz, 2 H, ArH), 14.51 (s, 1 H, NH); **3b**: IR: 1648, 1643; ^{1}H NMR: 2.59 (s, 3 H, CH_3), 7.27–7.92 (m, 9 H, ArH), 14.32 (s, 1 H, NH).

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