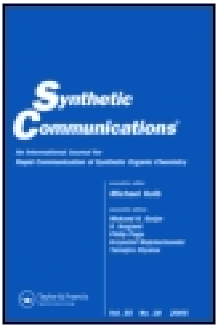


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Photo-Oxidation of Substituted 2-Dicyanomethylene-1,2-dihydropyridines

L. Fuentes [a] , L. A. Bonilla [a] , M. C. Contreras [a] & M. J. Lorenzo [a]

[a] Department of Organic Chemistry , Alcalá de Henares University , Madrid, Spain

To cite this article: L. Fuentes , L. A. Bonilla , M. C. Contreras & M. J. Lorenzo (1992) Photo-Oxidation of Substituted 2-Dicyanomethylene-1,2-dihydropyridines, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 22:14, 2053-2056, DOI: 10.1080/00397919208021339

To link to this article: http://dx.doi.org/10.1080/00397919208021339

SYNTHETIC COMMUNICATIONS, 22(14), 2053-2056 (1992)

PHOTO-OXIDATION OF SUBSTITUTED 2-DICYANOMETHYLENE-1,2-DIHYDROPYRIDINES

L. Fuentes*, L. A. Bonilla, M. C. Contreras and M. J. Lorenzo

Department of Organic Chemistry, Alcalá de Henares University

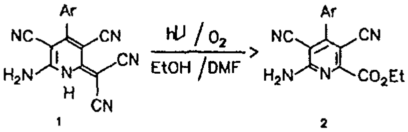
Madrid, Spain

Abstract: About the conversion of dicyanomethylene group to alkylcarboxylate on the photo-oxidation of 2-dicyanomethylene-1,2-dihydropyridines.

In a previous paper[1], we reported the synthesis of 2-dicyanomethylene-1,2-dihydropyridines **1**a-d. We report herein, our preliminary results about the aplication of photo-oxidation of **1** to the synthesis of 2-pyridine carboxylates, compouns for which classical preparation by reaction of the corresponding alcohols with the acids[2] or its acid chlorides[3-6] gives poor or moderate yields. The conversion reported is unusual, which make it a new and efficient method for the synthesis of 2-pyridincarboxylates.

---

* To whom correspondence should be addressed



Compounds 2

Product Nº	Ar	a)Yield (%)	mp· °C
2 a	C_6H_5-	70	244 245
2 b	$p-Cl-C_6H_4-$	69	218 219
2 c	$m-NO_2-C_6H_4-$	81	238 239
2 d	$p-MeO-C_6H_4-$	81	220 221

a) Recrystallized from ethanol

The reaction was accomplished irradiating a 3.3 10^{-2} M oxygenated solution of **1** in DMF-ethanol (4:1) at 350 nm in a quartz vessel or at 545 nm using Rose Bengale as sensitizer. behavior that agrees with a self-sensitized photo-oxidation involving the $^1O_2$ species as an intermediate when irradiation is performed at 350 nm and with a Rose-Bengale sensitized photo-oxidation if **1** is irradiated at 554 nm.

The structure of compounds **2** was established on the basis of analytical and spectroscopic data. The I.r. and ^{1}H-nmr spectra, in all compounds, clearly support the proposed structure **2**. I.r. (KBr) 3460-3215 (NH_2), 2235-2230 (CN) and 1725 (CO) cm^{-1}. ^{1}H-nmr (DMSO-d_6): δ 1.13-1.33 (t, 3H, $OCH_2\underline{CH_3}$); 4.15-4.40 (c, 2H, $O\underline{CH_2}CH_3$); 6.9-8.8 ($H_{arom.}$ + NH_2); for **2d** 3.84 (s, 3H). Mass spectral data are also consistent with the assigned structures. An ulterior confirmation was performed by derivative formation. Thus, by hydrolisis of **2a**, 2-pyridincarboxylic acid was obtained[7], which was decarboxylated to 2-amino-3,5-dicyane-4-phenylpyridine by refluxing in DMSO[8]. On the other hand, when **2a** was treated with hydrochloric acid in ethanol under reflux the 2-amino-3-cyano-4-phenylpyrrol (3,4-b) pyridin-5,7-dione was formed[9].

ACKNOWLEDGEMENTS. We thank the Dirección General de Investigación Científica y Técnica and Comunidad de Madrid for financial support nº PB88-0153 and nº C069/90 respectively.

REFERENCES and NOTES

1. Fuentes L., Vaquero J. J. and Soto J. L., *Synthesis*, 1982, **4**, 320
2. Furst H. and Jelesaroff I., *Arch. Pharm.*, 1950, **283**, 238
3. Vejdelek Z. J. and Protiva M., *Coll. Czech. Chem. Comm.*, 1951, **16**, 344
4. Badgett C. O., Provost Jr R. C., Ogg C. L. and Woodward C. F., *J. Am. Chem. Soc.*, 1945, **67**, 1135
5. Vejdelek Z. J., Trcka V. and Protiva M., *Chem. Listy*, 1952, **46**, 483
6. Pliml J. and Protiva M., *Chem. Listy*, 1953, **47**, 1204

7. To methanol (20 ml) containing 5% aqueous sodium hydroxide (1 ml) was added **2a** (292 mg, 1 mmol). The mixture was stirred at r.t. for 2 h., and then was poured over water (80 ml). The mixture was acidified until pH= 2 by 5% hydrochloric acid. The precipitate formed was collected and recrystallized from 2-propanol. Yield 251 mg (95 %); mp 212-220 °C (dec.); i.r. (KBr): 3412, 3324, 3206, 2236, 1759, 1641, 1568, 1396, 1284 cm^{-1}; ^{1}H-nmr (DMSO-d$_6$) : δ 2.8-4 (br, 1H); 7.58 (s, 5H); 8.30 (s, 2H). Anal. Calcd. for $C_{14}H_8N_4O_2$: C, 63.64; H, 3.05; N, 21.20. Found: C, 63.39; H, 3.16; N, 21.53.

8. A solution of 6-amino-3,4-dicyano-4-phenyl-2-pyridincarboxylic acid (264 mg, 1 mmol) in DMSO (20 ml) was heated under reflux with stirring for 2 h., and then was poured over water (150 ml) acidified by hydrochloric acid. The precipitate formed was separated and the filtrate was extracted with chloroform and concentrated in vacuo. Both solids, the precipitate and the residue obtained by concentration of the chloroformic

extracts, were chromatographed on a silica gel column. The elution with hexane-ethylacetate 6:4 gave 170 mg of the 2-amino-3,5-dicyane-4-phenylpyridine. Yield (77 %); mp. 247-248 °C from ethanol; i.r. (KBr): 3420-3300, 3140, 2220, 1655, 1620, 1580, 1565, 1530, 1485, 1345, 1255, 1230 cm^{-1}; ^{1}H-NMR (DMSO-d$_6$): δ 7.38 (s, 5H); 7.75 (br. s, 2H); 8.42 (s, 1H). Anal. Calcd. for $C_{13}H_8N_4$: C, 70.89; H, 3.66; N, 25.44. Found: C, 71.15; H, 3.50; N, 25.35.

9. To a solution of **2a** (0.58 g, 2 mmol) in ethanol (50 ml) hydrochloric acid (15 ml, 10 N) was added. The mixture was heated under reflux with stirring for 10 h. The precipitate formed was collected and recrystallized from methanol and drops of acetone affording 0.42 g of 2-amino-3-cyano-4-phenylpyrrol (3,4-b)pyridin-5,7-dione. Yield (80 %). mp. 339-341 °C; i.r. (KBr) 3460, 3300-3170, 2215, 1765, 1710, 1600, 1545, 1485, 1370, 1325. ^{1}H-NMR (DMSO-d$_6$) δ: 7.54 (s, 5H), 8.20 (br. s, 2H), 11.40 (s, 1H); Anal. Calcd. for $C_{14}H_8N_4O_2$: C, 63.64; H, 3.05; N, 21.20. Found: C, 63.30; H, 2.97; N, 21.10.

(Accepted in The Netherlands 16 March, 1992)