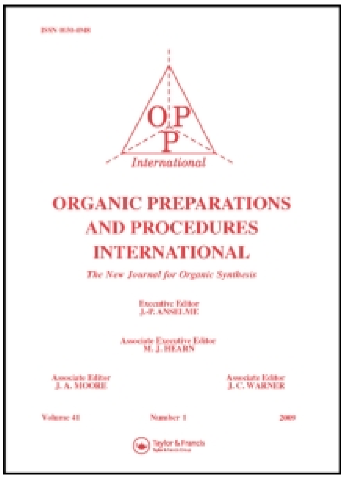


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

A CONVENIENT SYNTHESIS OF 10, 10'-DIMETHYL-9, 9'-BIACRIDYLIDENE

Marion R. Surgi[a]; Julian Tirado-Rives[b]
[a] Material Science Department, Allied-Signal Engineered Materials Research Center, Des Plaines, IL [b] Department of Chemistry, Purdue University West, Lafayette, IN

To cite this Article Surgi, Marion R. and Tirado-Rives, Julian(1988) 'A CONVENIENT SYNTHESIS OF 10, 10'-DIMETHYL-9, 9'-BIACRIDYLIDENE', Organic Preparations and Procedures International, 20: 3, 295 — 298

To link to this Article: DOI: 10.1080/00304948809355826

URL: http://dx.doi.org/10.1080/00304948809355826

Lett., 5 (1968); Paul von R. Schleyer, M. M. Donaldson, R. D. Nicholas and C. Cubas, Org. Syn., Coll. Vol. V, 16 (1973).

3. W. Rowe and T. Dooley, U. S. Patent 4,640,884 (1987); G. Bellman and T. V. Nguyen, PCT Int. Appl. WO 81 03,657 (1981); Chem. Abs., 96 P181794n (1982); R. E. Moore, U. S. Patent 3,383,424 (1968); Sun Oil Co., Neth. Applic. 6,516,807 (1966); Chem. Abs., 65 15249e (1966); R. E. Moore, U. S. Patent 3,819,721 (1974); Chem. Abs., 81 P91141h (1974); R. E. Moore, U. S. Patent 3,594,427 (1971); Chem. Abs., 75 118780f (1971).

* * * * *

A CONVENIENT SYNTHESIS OF 10,10'-DIMETHYL-9,9'-BIACRIDYLIDENE

Submitted by (02/27/87)

Marion R. Surgi*

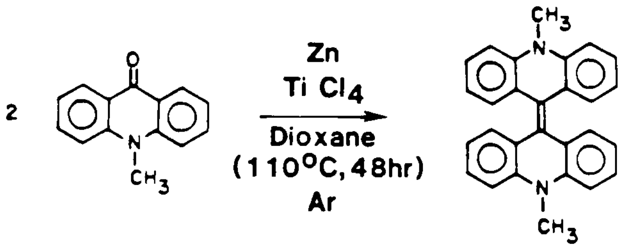
Material Science Department
Allied-Signal Engineered Materials Research Center
50 E. Algonquin Rd., Des Plaines, IL 60016

and

Julian Tirado-Rives

Department of Chemistry
Purdue University
West Lafayette, IN 49707

Recent interest[1,2] in 10,10'-dimethyl-9,9'-biacridylidene (DBA) has prompted our investigation into a more convenient synthesis and extensive characterization of DBA. Lemstead and Hundertmark reported the first synthesis of DBA from N-methylacridone (NMA) using zinc and acetic acid.[3] While Kormendy[4] and Decker[5] were apparently able to repeat this procedure, Nikokavouras and Vassilopoulos[2] following the same procedure, reported poor yields and impure products that were difficult to separate. Nikokavouras et al.[1] used zinc and HCl in ethanol as the coupling agent, but several recrystallizations from pyridine were still necessary to obtain pure material. We now describe a procedure which provides an 80% yield of 94% pure (gc) DBA by a modification of the method of Mukaiyama.[6] NMA, if present in the product, is easily separated from DBA by column chromatography on silica using 9:1 benzene-acetone (v:v) as the solvent. When the isolated product was analyzed by column chromatography and gc, no NMA was found.



NMA DBA

Previous reports suggest that this method[6] is limited to the coupling of carbonyl compounds which contain no atoms with lone pairs more basic than those on an sp^2-hybridized oxygen.[7] When atoms containing lone pairs are present, a significant side-reaction between the coupling reagent and these atoms can occur. While molecules containing both pyridine nitrogens and carbonyl groups have been successfully coupled, we are unaware of reports of the coupling of carbonyl compounds containing substituted aniline nitrogens.

EXPERIMENTAL SECTION

10,10'Dimethyl-9,9'-biacridylidene (DBA).- NMA (5.0 g, 23.9 mmoles) was added to a 3-neck flask (assembled hot) containing 4.7 g (71.7 mmoles) of zinc dust and 200 mL dioxane and the mixture was heated at reflux for 48 hrs. Zinc dust was activated by washing successively with deionized water, ethanol, methanol, and methylene chloride and vacuum dried for 36 hrs. Subsequent handling of the activated zinc was performed in an argon-purged disposable glove box. Under these conditions, zinc dust remained activated for 48 hrs. One neck of the flask was equipped with a septum for sampling the reaction mixture and purging with argon. When refluxing temperature was reached (110°), titanium tetrachloride was added (with stirring) to the reaction flask using a syringe. [CAUTION: Excessive moisture results in violent reactions. For this reason, titanium tetrachloride must be added slowly to react with any water present and to prevent excessive heat liberation.] An aliquot of the reaction mixture can be withdrawn using a syringe and analyzed for the presence of NMA by TLC (9:1 benzene-acetone, silica substrate). After 48 hrs, no NMA was detected and the reaction mixture was quenched with 350 mL of aqueous potassium carbonate (10% by weight) and stirred for 12 hrs. The quenched product which included TiO_2, was filtered using a Celite support to separate TiO_2 from the mixture. The aqueous layer was extracted with methylene chloride and discarded. DBA was then extracted for 8 hrs from the Celite/TiO_2 mixture using methylene chloride in a Soxhelt extractor. This extract was combined with the extract from above and the solvent removed. Some of the product was essentially unextractable as evidenced by the Celite/TiO_2 remaining slightly green after extensive extraction. Any trace amounts of unreacted NMA were probably also adsorbed to the Celite/TiO_2 mixture. The yellow powder obtained was purified by washing with water, followed by ethyl acetate, pyridine, and finally acetone and was shown to be 94% pure by gas chromatography.

An average of 3.7 ±0.3 grams of DBA was obtained from 5.0 grams of NMA in each of three syntheses. The product was characterized as follows: mp. >360°[4]; visible (CH_2Cl_2), λ_{max}: 425 nm; IR (KBr pellet): 1585, 1455, 1340, 1105, 750 cm^{-1}; MS (m/e): 386.3 ($C_{28}H_{22}N_2^{\ddagger}$), 371.2 ($C_{27}H_{19}N_2$+), 353.2 ($C_{28}H_{17}^{+\cdot}$), 281.1 ($C_{21}H_{15}N^{+\cdot}$), 209.0 ($C_{14}H_{13}N_2^{+}$), 208.1 ($C_{14}H_{12}N_2^{+\cdot}$), 193.1 ($C_{28}H_{22}N_2^{+\cdot+\cdot}$), 177.1 ($C_{14}H_9^{+}$), 163.1 ($C_{13}H_7^{+\cdot}$), 73.0 ($C_3H_9N_2^{+}$); ^{1}H-NMR ($CD_2Cl_2$, 200 mHz): δ 7.18 (t, 4H), 7.03 (d, 4H), 6.72 (t, 4H), 6.47 (d, 4H), 3.00 (s, 6H); ^{13}C-NMR (CD_2Cl_2, 200 mHz): δ 143 (calcd. 146), 111 (calcd. 116), 127 (calcd. 127), 120 (calcd. 119), 128 (calcd. 128), 129 (calcd. 132), 125 (calcd. 123), 33 (calcd. 33). Chemical shifts in the ^{13}C-NMR spectra were calculated using algorithms for group additivity given in ref. 8.

Dedication.- This work is dedicated to Renée Elizabeth Surgi on the occasion of her second birthday.

REFERENCES

1. M. Koko, T. Migahara, M. Tamako, S. Yamada and Y. Sano, J. Chem. Soc., Perkin Trans., 2, 441 (1984); R. J. Murphy and G. Svehla, Anal. Chim. Acta, 141, 359 (1982); J. Nikokavouras, A. Vavagannis and G. Vassilopoulos, J. prakt. Chem., 320, 43 (1978); R. Maskiewicz, D. Sogaho and T. C. Bruice, J. Am. Chem. Soc., 101, 5355 (1979).
2. J. Nikokavouras and G. Vassilopoulos, Montash. Chem., 109, 831 (1978); K. Maeda, T. Kashiwabara and M. Tokoyama, Bull. Chem. Soc. Jpn., 50, 473 (1977); M. R. Surgi and J. A. Hodgeson, Anal. Chem., 57, 1737 (1985).
3. K. Lemstead and H. Hundertmark, Ber., 62B, 1065 (1929).
4. K. Kormendy, Acta. Chim. Acad. Sci. Hung., 21, 83 (1959).
5. H. Decker and W. Petsch, J. prakt. Chem., 143, 211 (1935).
6. T. Mukaiyama, T. Sato and J. Hanna, Chemistry Lett., 1041 (1973).
7. J. E. McMurry, M. P. Fleming, K. L. Kees and L. R. Krepski, J. Org. Chem., 43, 3257 (1978).
8. R. M. Silverstein, G. C. Bassler, T. C. Morrill, "Spectroscopic Identification of Organic Compounds", 4th Ed. John Wiley and Sons, New York (1981).