Pergamon

Tetrahedron Letters 40 (1999) 7413–7416

TETRAHEDRON
LETTERS

Organolithium reagents bearing nonlinear optical chromophores. Synthesis of triarylmethane dyes

Cécile Arbez-Gindre,[a] Constantinos G. Screttas,[a,*] Céline Fiorini,[b] Claudia Schmidt[b] and Jean-Michel Nunzi[b,*]

[a]*National Hellenic Research Foundation, Institute of Organic and Pharmaceutical Chemistry, Vas. Constantinou 48, 11635 Athens, Greece*

[b]*Commissariat à l'Energie Atomique, Leti-Technologies Avancées, Département d'Electronique et d'Instrumentation Nucléaire, Groupe Composants Organiques, Service de Physique Electronique, Saclay, 91191 Gif sur Yvette, France*

Received 29 April 1999; accepted 27 July 1999

Abstract

Stilbenyllithiums bearing donor groups were generated by the halogen–metal exchange reaction and are shown to be useful in C–C and C–heteroelement forming reactions. A series of triarylmethane dyes has thus been prepared.
© 1999 Elsevier Science Ltd. All rights reserved.

Keywords: lithium; lithium compounds; carbenium ions; phosphorous compounds; electronic spectra.

The synthesis of organolithium reagents capable of introducing, in a regiospecific manner, a stilbenyl moiety into various organic or organometallic structures and the evaluation of a benzylic-type carbon bearing a positive charge as an electron acceptor in donor–acceptor substituted stilbenes, constitute the subject of the present communication.

This work was carried out in view of the continuing interest in compounds with nonlinear chromophores, among which stilbenes are important.[1] Although the nonlinear properties are intrinsic[2] to the stilbene unit per se, second order nonlinear optical (NLO) properties can only be manifest when the centrosymmetry is lifted by an appropriate substitution. In particular, *p,p′*-substitution by an electron acceptor and an electron donor group enhances the phenomenon.[1] Therefore, in designing stilbenyllithium derivatives, one has to consider the compatibility of the above mentioned groups with the C–Li functionality. We thus decided to develop a method of generating stilbenyllithium reagents of the general structure *p,p′*-D-C_6H_4-CH=CH-C_6H_4-Li, where D is a donor group such as RO- or R_2N-. We also describe here the utility of these reagents in C–C or C–heteroelement forming reactions. More specifically, we report the synthesis of a series of stilbene substituted methanols as well as the linear optical properties of the corresponding triarylmethane dyes. In the case of one compound, the second order NLO properties

---

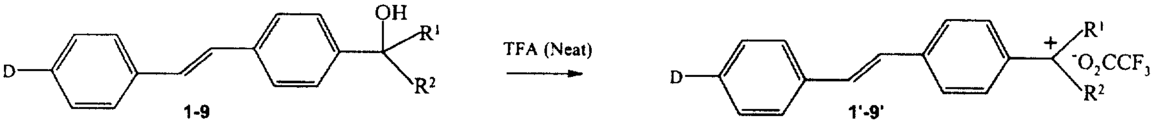
* Corresponding authors.

0040-4039/99/$ - see front matter © 1999 Elsevier Science Ltd. All rights reserved.
PII: S0040-4039(99)01446-X

have been determined using a time resolved non-degenerate six-wave mixing method (SWM).[3] The experiment consists of a transient polar orientation of the molecules in solution using purely optical means. This results in the recording of a transient second order susceptibility χ^2 which can be read out via second harmonic generation. Analysis of the second harmonic generated signal is directly related to the molecular characteristics such as hyperpolarisability β or the difference between the molecular moment in the excited and in the ground states $\Delta\mu$. Unlike the more conventional method of EFISH (Electric-Field-Induced-Second-Harmonic-Generation), SWM can, as in the case of the present work, be applied to ionic salts which, because of their conductivity in solution, cannot be oriented using static field poling.[4]

The reagents can be conveniently prepared by the bromine–lithium exchange reaction using stibenyl bromides readily accessible by the Horner–Emmons synthesis. Compared to other methods investigated, the bromine–lithium exchange reaction was found to give the best results.[5] Depending on whether the donor is an alkoxy- or a dialkylamino group, different solvents, as well as other reaction conditions, have to be employed for optimal results. 4-Bromo-4′-dimethylamino-stilbene undergoes bromine–lithium exchange with *n*-butyllithium in tetrahydrofuran (THF) at temperatures up to –40°C, whereas the corresponding methoxy-derivative requires diethyl ether as a solvent at 0–5°C. Under these conditions, the competing Wurtz coupling reaction between the stilbenyllithium generated and the butyl bromide is suppressed almost completely, and in the case of the methoxystilbenyllithium, complications from *ortho*-metallation are absent. Thus, yields of methoxy- or dimethylamino stilbenyllithiums of 92–95% have been realised, along with a 5–8% yield of the debrominated starting stilbene derivative.

The stilbenyllithiums were added to a series of aromatic ketones, ethyl benzoate and diethyl carbonate,[6] to produce carbinols **1**–**9** (Scheme 1). The same organolithiums were used in C–Si, C–S, C–Sn and C–P bond forming reactions, giving compounds **10**–**15**. The triarylmethanols **1**–**9** were converted to the corresponding triarylmethyl cations **1′**–**9′** by dissolving them in neat trifluoroacetic acid (TFA) (Eq. 1). Table 1 summarises absorption maxima, molar extinction coefficient and transition dipole moment data deduced from linear absorption spectroscopy.



(1)

1 D = Me_2N; $R^1 = R^2 =$ phenyl (89%; mp 206-207°C)
2 D = Me_2N; $R^1 =$ D-stilbenyl ;$R^2 =$ phenyl (96%; mp 254-255°C)
3 D = Me_2N; $R^1 = R^2 =$ D-stilbenyl (92%; mp>341°C)
4 D = Me_2N; $R^1 =$ phenyl; $R^2 =$ 1-naphthyl (93%; mp 163-164°C)
5 D = Me_2N; $R^1 =$ phenyl; $R^2 =$ *o*-tolyl (84%; mp 148-150°C)
6 D = Me_2N; R^1, $R^2 =$ 1,2-(*o,o*′-diphenylenyl)ethane (96%; mp 94-96°C)
7 D = Me_2N; R^1, $R^2 =$ *o,o*′-diphenylenylthioether (96%; mp 179-180°C)
8 D = MeO; $R^1 = R^2 =$ phenyl (69%; mp 156-157°C)
9 D = MeO; $R^1 = R^2 =$ D-stilbenyl (89%; mp 214-215°C)

10 D = Me_2N; A = $P(O)(OPh)_2$ (38%; mp 259-260°C)
11 D = Me_2N; A = $P(O)(OEt)_2$ (84%; mp 141-142°C)
12 D = Me_2N; A = $SiMe_3$ (95%; mp 142-144°C)
13 D = Me_2N; A = $SnBu_3$ (74%; mp 66-67°C)
14 D = Me_2N; A = SMe (87%; mp 205-207°C)
15 D = MeO; A = $SiMe_3$ (95%; mp 167-168°C)

Scheme 1.

The results in Table 2 were deduced from six-wave mixing experiments where the second order NLO properties of **1** are compared to those of the well defined reference[3] compound Disperse Red 1 (DR1).

Table 1

compound	λ_{max} (nm)	ε_{532nm} (mol^{-1}lcm^{-1})	ε_{max}	μ(D)
1′	540	70731	75850	11.4
2′	591	45422	143800	14.4
3′	608	33870	112450	15.8
4′	508 (614)	33898	58206	13.4
5′	(436) 550	69400	90520	11.9
6′	(380, 442) 564	24096	44635	13.6
7′	(313, 384) 520	12143	11200	5.6
8′	638	9862	62130	13.15
9′	684	6820	99100	17.3

Table 2

molecule	I^{SHG} (a. u.)	τ SWM (ps)	$\Delta\mu$ (D)	μ (D)	$\beta(0)$ (Cm^{3}V^{-2})
1′	35880	42	7	11.4	$3.7{*}10^{-49}$
DR1	20370	162	7[7]	7.7	$0.95{*}10^{-49}$

The data show that the static hyperpolarisability (ω=0) β (0) of the dye corresponding to **1**, is of the same order of magnitude as that found for DR1, although the excited state lifetime for compound **1′**, which limits the SWM signal lifetime τ SWM, is very short.

Acknowledgements

This work was supported by the European Training and Mobility of Researchers Network Contract No. ERBFMRXCT 96-0047.

References

1. (a) Bosshard, C.; Sutter, K.; Prêtre, P.; Hullinger, J.; Flörsheimer, M.; Kaatz, P.; Günter, P. In *Advance in Nonlinear Optics 1*; Garito, A. F.; Kajzar, F., Eds. Organic Nonlinear Optical Materials. Gordon and Breach: Amsterdam, 1995. (b) *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S.; Zyss, J., Eds.: Mass Academic: Boston, 1987; Vol. 1(2), p. 23. (c) *Nonlinear Optical Properties of Organic Molecules and Polymers*; Nalwa, H. S.; Miyata, S., Eds.; CRC Press: Boca Raton, 1997; p. 89.
2. (a) Oudar, J. L. *J. Chem. Phys.* **1977**, *67*, 446. (b) Marder, S. R.; Gorman, C. B.; Meyers, F.; Perry, J. W.; Bourhill, G.; Bredas, J. L.; Pierce, B. M. *Science* **1994**, *265*, 632.
3. Fiorini, C.; Charra, F.; Nunzi, J.-M. *J. Opt. Soc. Am. B* **1994**, *11*, 2347.
4. Paci, B.; Schmidt, C.; Fiorini, C.; Nunzi, J.-M, Arbez-Gindre, C.; Screttas, C. G. Accepted for publication in *J. Chem. Phys.*
5. Preparation of **1**: A solution of 4-bromo-4′-dimethylamino-stilbene (5 mmol) in THF (35 mL) was cooled to –80°C. After 10 min, *n*-BuLi (3.5 mL, 1.87 M in methylcyclohexane (MCH)) was added rapidly. The mixture was stirred for 2 h while the temperature was allowed to reach –40°C. Benzophenone (5 mmol) was then added. The solution was stirred without cooling for 2 h and hydrolysed at room temperature. The product was extracted with CH_2Cl_2. Evaporation to dryness afforded **1** as a yellow solid recrystallised from isopropanol and purified by column chromatography on silica gel (1.8 g, 4.45 mmol, 89%). Mp: 206–207°C. ^{1}H NMR (300.13 MHz, $CDCl_3$): 2.78 (s, 1H, O*H*); 2.98 (s, 6H, $(CH_3)_2N$); 6.72 (d, ^3J=7.9 Hz, 2H); 6.89 (d, ^3J=16.3 Hz, 1H, -*H*C=CH-); 7.03 (d, ^3J=16.3 Hz, 1H, -HC=C*H*-); 7.32 (m, 16H). ^{13}C NMR (75.47 MHz, $CDCl_3$): 40.4; 81.9; 112.3; 123.6; 125.5; 127.1; 127.5; 127.8; 128.1; 129.0; 137.1; 145.1; 146.80; 150.10. Anal. calcd for $C_{29}H_{27}NO$ (MW=405.20); C, 85.89; H, 6.71; N, 3.45. Found: C, 85.16; H, 6.78; N, 3.36. ES: *m/z*: 405.20: *m/z*+18: 387.20: *m/z*+23: 427.1. Preparation of **8**: A solution of 4-bromo-4′-methoxy-stilbene (6.6 mmol) in Et_2O (60 mL) was cooled to 3°C. After 10 min, *n*-BuLi (3.5 mL, 1.87 M in MCH) was added rapidly. The mixture was stirred for 2 h at

3°C and cooled to –40°C. Benzophenone (6.6 mmol) was then added and the solution stirred without cooling for 2 h and hydrolysed at room temperature. The product was extracted with Et_2O. Evaporation to dryness afforded **8** as a white solid recrystallised from MCH (1.8 g, 4.58 mmol, 69%) and purified by column chromatography on silica gel. Mp: 156–157°C. ^1H NMR (300.13 MHz, $CDCl_3$): 2.79 (s, 1H, O*H*); 3.82 (s, 3H, CH_3O); 6.89 (d, $^3J=8.7$ Hz, 2H); 6.95 (d, $^3J=16.3$ Hz, 1H, -*H*C=CH-); 7.05 (d, $^3J=16.3$ Hz, 1H, -HC=C*H*-); 7.34 (m, 16H). ^{13}C (75.47 MHz, $CDCl_3$): 55.20; 81.80; 114.0; 125.7; 125.9; 127.2; 127.6; 127.7; 127.8; 128.10; 128.40; 130.0; 136.5; 145.7; 146.7; 159.2. Anal. calcd for $C_{28}H_{24}O_2$ (MW=392.50): C, 85.68; H, 6.17. Found: C, 85.32; H, 6.17. ES: *m/z*: 392.30; *m/z*+23: 414.1.

6. Greve, D. R.; Schougaard, S. B.; Geisler, T.; Petersen, J. C.; Bjørnholm, T. *Adv. Mat.* **1997**, *9*, 1113.
7. Liptay, W. *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 177.