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LETTERS

The Gomberg-type dimerization of bifluorenylidene radicals: an X-ray crystallographic investigation[☆]

Laura E. Harrington,^a James F. Britten^a and Michael J. McGlinchey^{a,b,*}

^aDepartment of Chemistry, McMaster University, 1280 Main St. W., Hamilton, ON L8S 1L5, Canada

^bDepartment of Chemistry, University College Dublin, Belfield, Dublin 4, Ireland

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Abstract—The reaction of phenylethynyllithium with 9-bromofluorene yields 9,9'-bifluorenylidene, **8**, 9,9'-bifluorenyl, **9**, and a molecule **10**, of formula C₅₂H₃₂, in which coupling has occurred between a 9,9'-bifluorenyl fragment and a 9,9'-bifluorenylidene moiety such that a C(9) position of the former is attached to a C(3) site of the latter. This parallels the unsymmetrical radical coupling of triphenylmethyl radicals, which leads to the Gomberg dimer, rather than hexaphenylethane. The structure of **10** has been elucidated by X-ray crystallography, and a mechanistic rationale is offered.

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1. Introduction

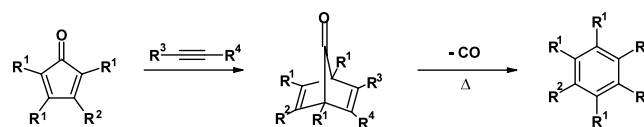
We have recently reported studies on the dynamic behavior of sterically hindered systems containing five-, six- or seven-membered rings containing such bulky substituents as phenyl, β -naphthyl, chloro or ferrocenyl moieties (**1–4**).¹ In continuation of these investigations, we have targeted 9-fluorenylpentaphenylbenzene, **5**, as a ligand with the potential to exhibit restricted or correlated rotation. Although fluorenyl-substituted benzenes have been reported,² there has not been a systematic study of the influence of these bulky groups on their neighboring substituents in a fully substituted system. The synthesis of **5** required the unsymmetrical alkyne 9-phenylethynylfluorene, **6**, which would then be used in a Diels–Alder addition to the appropriate cyclopentadienone, prior to thermolysis and cheletropic elimination of carbon monoxide, as exemplified in Scheme 1.

The original preparation of 9-phenylethynylfluorene, **6**, involved nucleophilic displacement of bromide from 9-bromofluorene using a phenylethynyl Grignard reagent; however, the reported yield was only 10%.³ Nevertheless, the possibility of a single-step synthesis by

nucleophilic attack on 9-bromofluorene using phenylethynyl-lithium was considered, and the reaction was carried out at -78°C in an attempt to minimize carbene formation. However, the reaction yielded numerous products, and we now report the structures and possible mechanisms of formation of the major fractions.

2. Results and discussion

When 9-bromofluorene was treated with phenylethynyl-lithium at -78°C , allowed to warm slowly to room temperature and hydrolyzed, several products were obtained after chromatographic separation. Two of these were readily identified both spectroscopically and by X-ray crystallography as the known molecules 9,9'-bifluorenylidene, **8**,⁴ and 9,9'-bifluorenyl, **9**⁵ (combined yield 16%). The mass spectrum of the third product, **10**



1. R¹ = R² = R³ = R⁴ = phenyl
2. R¹ = R² = R³ = R⁴ = β -naphthyl
3. R¹ = R³ = R⁴ = phenyl; R² = ferrocenyl
4. R¹ = R³ = R⁴ = β -naphthyl; R² = ferrocenyl
5. R¹ = R² = R³ = phenyl; R⁴ = 9-fluorenyl

Scheme 1. Diels–Alder synthesis of sterically crowded benzene derivatives.

Keywords: X-ray crystallography; fluorenyl radicals; Gomberg dimerization.

[☆] Supplementary data associated with this article can be found at doi:10.1016/j.tetlet.2003.09.050

* Corresponding author. Tel.: 353-1-716-2880; fax: 353-1-716-2127; e-mail: michael.mcglinchey@ucd.ie

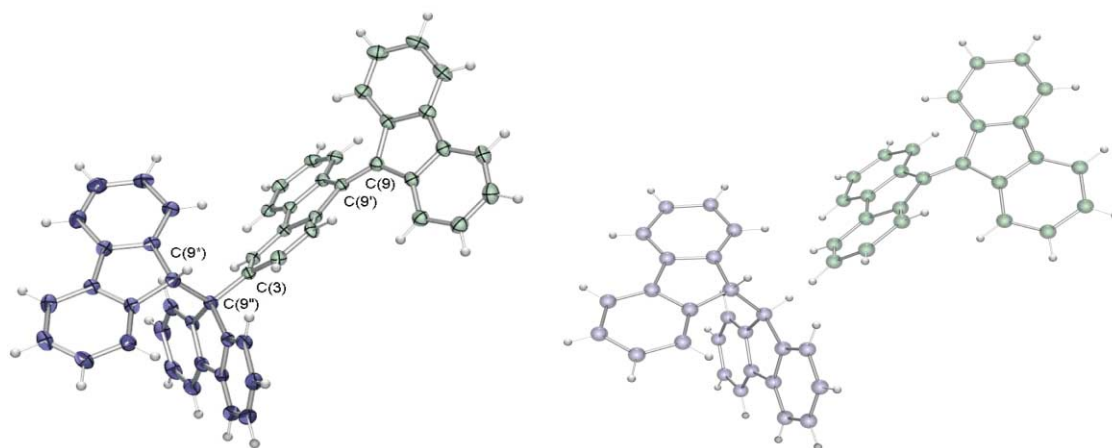


Figure 1. X-Ray crystal structure of (a) the tetramer **10** (50% thermal ellipsoids), and (b) comparison with the combination of fragments **8** and **9**.

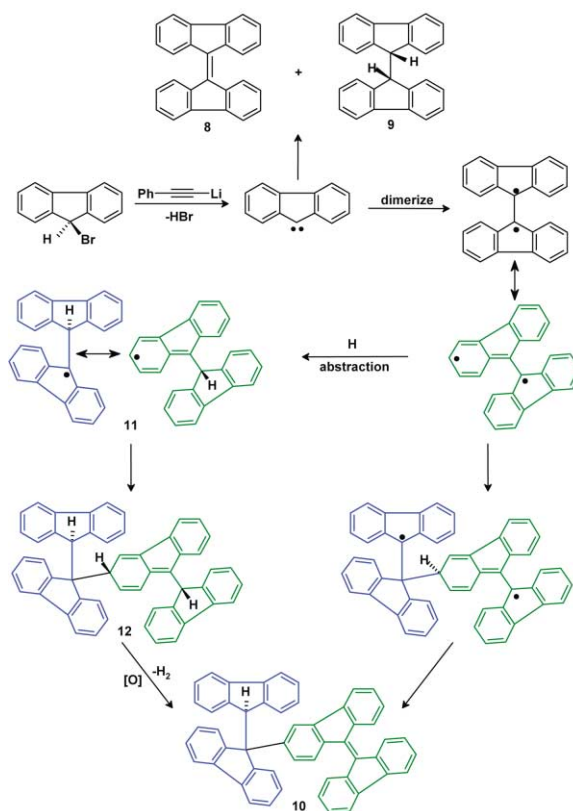
(12% yield), revealed a molecular weight of 656, corresponding to the formula $C_{52}H_{32}$, and indicating the formation of a dimer of **8**, that is, a tetramer of fluorenylidene. Since a variety of such tetramers could be readily envisaged, the product was characterized by X-ray crystallography and the resulting structure appears as Figure 1(a).

The tetramer **10** is comprised of a 9,9'-bifluorenyl fragment linked to a 9,9'-bifluorenylidene moiety such that a C(9) position of the former is attached to a C(3) site of the latter (C–C 1.545(4) Å). The steric crowding between the two fluorenylidene fragments causes a twisting such that the interplanar angle is 35°; this compares favorably with the dihedral angles reported in other 9,9'-bifluorenylidenes which lie in the range 31–34°.⁶ Moreover, the structure of the 9,9'-bifluorenyl unit in **10** closely resembles that found in the parent system such that the two fluorenyls adopt a gauche conformation.⁷ Figure 1(b) illustrates the remarkable similarity between **10** and its analogous molecular components **8** and **9**.

It seems evident that the products **8**, **9** and **10** arise from a fluorenylidene moiety generated by dehydrobromination of 9-bromofluorene. It has been claimed that treatment of 9-bromofluorene with KOH in DMSO at room temperature yields 9,9'-bifluorenylidene, **8**, 'almost quantitatively',⁸ but Bethel reported the formation of small quantities of 'an amorphous brown solid' of unknown identity.⁹ Fluorenylidene carbene is well known to adopt a triplet ground state,¹⁰ (although the singlet state is also accessible)¹¹ and so dimerization and radical abstraction to yield **8** and **9** are not unexpected processes; however, the fluorenylidene tetramer, **10**, has not been previously reported. Furthermore, other investigations involving such fluorenyl-derived radicals or carbenes have not reported the formation of tetrameric products.¹²

One can envisage two possible routes to **10**: the first would involve generation of the triplet diradical form of **8**, abstraction of one hydrogen to form the known

radical **11**,¹³ dimerization to **12**, and finally aerial oxidation to give the final product. The second, and perhaps more attractive option, would proceed via initial coupling of the diradical forms of **8**; subsequent migration of a single hydrogen then yields **10** directly, as illustrated in Scheme 2. However, a feature common to both mechanisms is the coupling between a radical located at a 9-fluorenyl position with a radical site on the phenyl periphery of the molecule. This parallels the classic 'Gomberg-type' dimerization of triphenylmethyl radicals, which, for steric reasons, do not yield the



Scheme 2. Proposed mechanism for the formation of tetramer, **10**.

expected hexaphenylethane.¹⁴ One might speculate that the triplet diradical state of bifluorenylidene is relatively long-lived because of the sterically mandated non-planar orientation of the two C₁₃H₈ moieties, thereby hindering radical coupling, as in Tomioka's now classic triplet carbenes.¹⁵

Other minor products were obtained after chromatographic separation. Their mass spectra were inconclusive, they provided very complicated NMR spectra, even over a range of high and low temperatures and, unfortunately, they did not yield crystals. Consequently, their structures remain to be unraveled.

In light of this unexpected result, an alternative route to 9-phenylethynylfluorene, **6**, was undertaken. We chose to repeat a more recent synthesis¹⁶ that begins with addition of phenylethynyllithium to fluorenone; subsequent treatment of the 9-phenylethynylfluorene-9-ol with BF₃ and triethylsilane¹⁷ furnishes the desired hydrocarbon in respectable yield (Scheme 3). Since **6** is known to undergo ready rearrangement to the corresponding allene, **7**,³ its structure has now been unambiguously confirmed by X-ray crystallography, as shown in Figure 2.

The C≡C bond length is 1.195(2) Å and the fluorenyl substituent is almost exactly perpendicular to the

PhC≡C plane (91.2°), though it is bent away by 129.7° from the linear alkyne. All other bond lengths and angles are within acceptable ranges.

3. Conclusion

Treatment of 9-bromofluorene with an alkynyl-lithium reagent unexpectedly yields the tetramer, **10**, in which a 9,9'-bifluorenyl fragment and a 9,9'-bifluorenylidene are linked by a Gomberg-type radical coupling, as determined by X-ray crystallography.

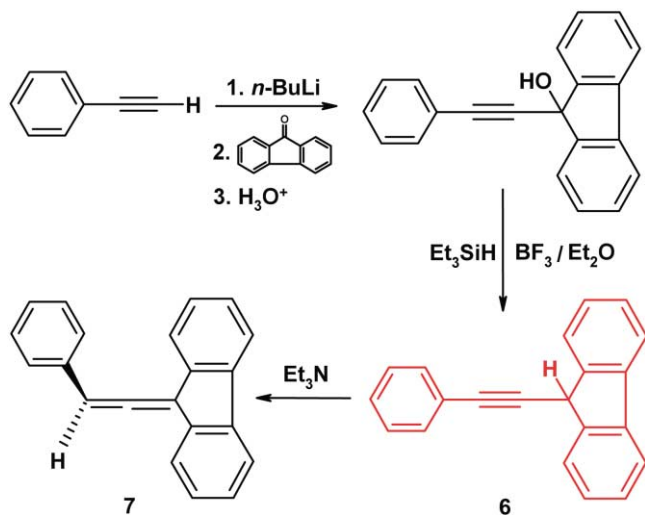
Supporting information available: Experimental procedures and characterization for compounds **6** and **10**, as well as X-ray crystallographic collection and refinement details and structural data. Crystal data for **6** and **10** has been deposited with the Cambridge Crystallographic Data Center (CCDC # 217750, 217751).

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Scheme 3. Synthetic route to phenylethynylfluorene, **6**.

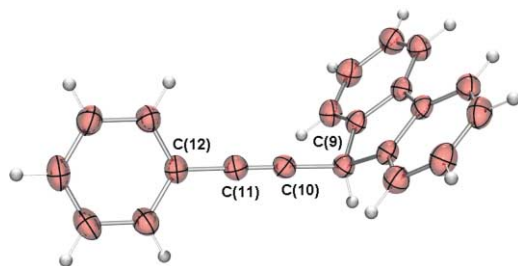


Figure 2. X-Ray crystal structure of the unsymmetrical alkyne, **6** (50% thermal ellipsoids).

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