Mechanism of ipso aromatic substitution by reaction of aryloxy(methoxy)carbenes and diaryloxycarbenes with DMAD

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Abstract: Some aryloxy(methoxy)carbenes and diaryloxycarbenes attack dimethyl acetylenedicarboxylate (DMAD) with aryl group transfer to an alkyne carbon of DMAD. In this study diaryloxycarbenes with different aryl groups that could be transferred competitively, were generated in the presence of DMAD to probe for the mechanism of that ipso aromatic substitution. It was found that a *para* electron-withdrawing substituent, relative to an electron-donating substituent, facilitated migration of an aryl group. Mechanisms in accord with these findings involve initial nucleophilic attack by the carbene at an alkyne carbon of DMAD. That step is followed by either nucleophilic, ipso attack on the aromatic ring or by electron transfer, from the side chain of the aromatic ring into the ring itself.

Key words: aromatic substitution, diaryloxycarbene, DMAD, ipso, nucleophilic.

Résumé : Quelques aryloxy(méthoxy)carbènes et diaryloxycarbènes attaquent l'acétylènedicarboxylate de diméthyle (ACDM) avec un transfert de groupe aryle vers un atome de carbone alcyne du ACDM. Dans le présent travail, dans le but d'étudier le mécanisme de cette réaction de substitution aromatique ipso, on a généré en présence du ACDM des diaryloxycarbènes portant divers groupes aryles qui peuvent être en compétition pour un transfert. On a trouvé que, par opposition à un substituant électrodonneur, un substituant électroaffinitaire facilite la migration d'un groupe aryle. Les mécanismes qui correspondent à ces faits impliquent une attaque nucléophile initiale par le carbène au niveau du carbone de l'alcyne du ACDM. Cette étape est suivie par une attaque nucléophile ipso du noyau aromatique ou par un transfert d'électron à partir de la chaîne latérale du noyau aromatique vers le cycle lui-même.

Mots clés : substitution aromatique, diaryloxycarbène, ACDM, ipso, nucléophile.

[Traduit par la Rédaction]

Introduction

Recently, we (1) reported the results of thermolysis of bis-oxadiazoline **1** in benzene containing dimethyl acetylenedicarboxylate (Scheme 1). The multifunctional product (**2**) must have arisen from a cascade of reactions, including transfer of the aryl ring from oxygen to carbon. Analogous substitution reactions were also observed with a simpler oxadiazoline (**3a**) (1), and with 5,5-dimethyl-2,2-diphenoxy-Δ^3–1,3,4-oxadiazoline (**3b**) (2, 3) (Scheme 2). The only related reaction that we are aware of is that between an aminothiocarbene and diethyl acetylenedicarboxylate, reported by Scherowsky et al. (4) in 1977 (Scheme 3). Although a variety of ipso substitutions on benzene derivatives are known (5), oxy-substituents are not generally among the leaving groups unless there are activating nitro groups in the ring also. It was therefore of interest to try to establish the mechanism of the substitution reactions of Schemes 1 and 2. We now report that competition reactions, with diaryloxycarbenes ((ArO)(Ar′O)C:), gave evidence for preferential transfer of the more electron-deficient aryl group from oxygen to an alkyne carbon atom of DMAD.

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Methods, results, and discussion

The strategy for determining the effect of aryl substituents involved generation of unsymmetric diarylcarbenes (**5**) so as to have internal competition, between the aryl groups in a dipolar (or other) intermediate (**6a**, **7a**), in the step that generates *isomeric* esters (Scheme 4). In all but one case the substituents in the aryl groups were in the *p*-position, and it was assumed that a conformational preference (**6a**, **7a**) would be small at most. It is probably irrelevant because the Curtin–Hammett principle is expected to apply (6). Although intermediates **6a** and **7a** presumably epimerize to **6b** and **7b**, through a small barrier, that too should be irrelevant because intramolecular substitution cannot occur with the ester groups *trans*, as in **6b** and **7b**.

5,5-Dimethyl-2,2-diphenoxy-Δ^3-1,3,4-oxadiazoline (**11**, Ar = Ar′ = Ph), the first 2,2-diaryloxy oxadiazoline (2), was prepared by hydrazinolysis of diphenyl carbonate, subsequent reaction of the hydrazide (**8**) with acetone to afford **9**, oxidative cyclization of **9** to **10** with lead tetraacetate (LTA) in CH_2Cl_2, and acid-catalyzed reaction of **10** with phenol (Scheme 5) (3, 7). Unsymmetric analogues (**11**, one or both aryl groups bearing a substituent) were prepared similarly (3).

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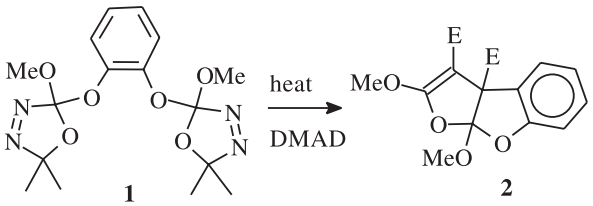
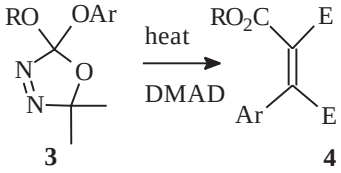
Scheme 1.



(DMAD = dimethyl acetylenedicarboxylate; E = CO_2Me)

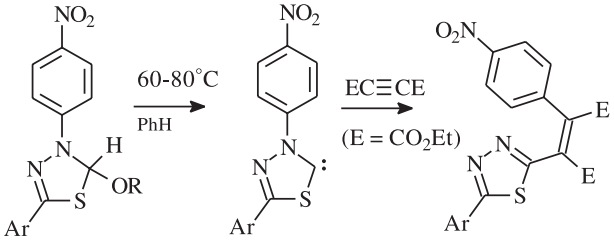
Scheme 2.



(a) R= Me, Ar= *o*-$MeOC_6H_4$; (b) R = Ar = Ph
(DMAD = dimethyl acetylenedicarboxylate;
E = CO_2Me)

Thermolysis of oxadiazolines **11** as benzene solutions containing DMAD, at 110°C in sealed tubes, gave one or both of the isomeric esters (**12**, **13**) in yields (or composite yields) between 28 and 37% (of isolated material) and a diaryl carbonate (**14**) in 25–35% yield (Scheme 6). The esters were separated from other products by means of radial chromatography, which also separated the isomers in the one case that gave both. Assignment of structure followed from the NMR spectra of the products and from the GC–MS patterns. In their EI mass spectra, aryl esters afford base peaks from loss of the fragment ArO in the case of ArOCOC(E)=C(Ar′)E, and from loss of Ar′O in the case of Ar′OCOC(E)=C(Ar)E. It was therefore easy to assign the gross structures of the esters from **11a**–**d** and of the isomeric

Scheme 3.



(R = H, Me)

esters from **11e** (Scheme 6). The geometry (ArOCO and CO_2Me groups *trans*) was established for **12a** by single crystal X-ray diffraction and that geometry was assumed for the other triesters **12**, and for **13e**, on the basis of analogy.

The effects of substituents on the ease of ipso substitution, given by the yield ratios (**13**:**12**) rather than by the absolute yields, are in the order *p*-CN >> *o*-MeO > H > Me > *p*-MeO (Table 1).

It is clear from Table 1 that an electron-withdrawing group in the *p*-position increases the migratory aptitude of an aryl group whereas an electron-donating group decreases it. Unfortunately, most substrates gave only one of the two possible esters and it was not possible to construct a Hammett plot and to estimate the value of ρ. However, the sense of the substituent effect is unmistakable, and the effect cannot be small. We suggest that a likely mechanism to account for the migratory aptitudes is that illustrated with Scheme 7, for the case X=H, Y=CN. The steps to the carbene are well-precedented (8), as are the attack of nucleophilic carbenes on DMAD and other alkynes (9–12) and the reversible ring-opening and ring-closing of cyclopropenes and (or) vinylcarbenes (13–16). Moreover, Boger et al. (17) and Boger and Brotherton-Pleiss (18) have reported reactions of an intermediate (a π-delocalized vinylcarbene) analogous to **15** in Scheme 7. We assume that **15** is equilibrated with cyclopropene **16**, in view of the fact that diphenoxy

Scheme 4.

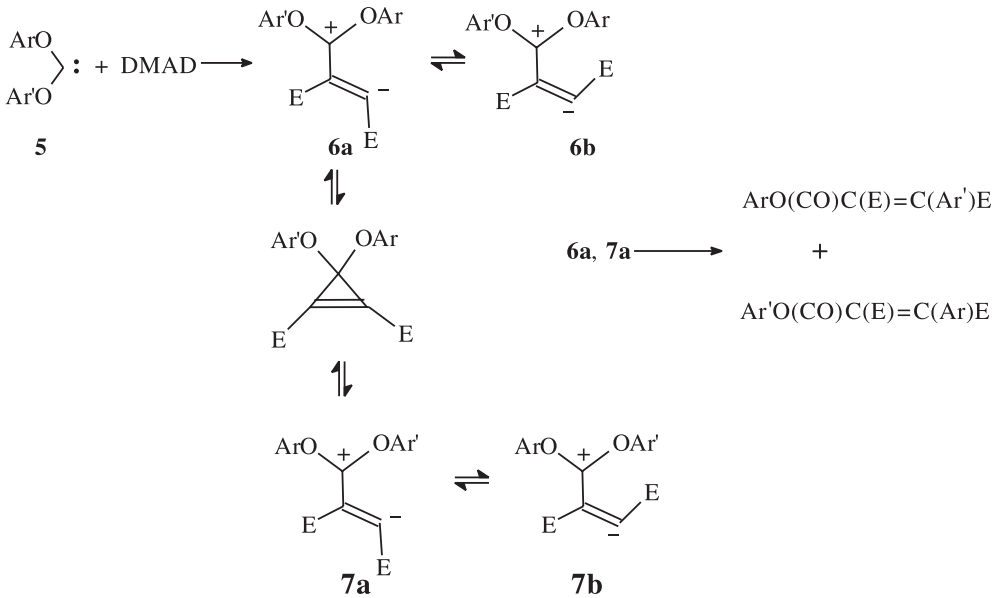
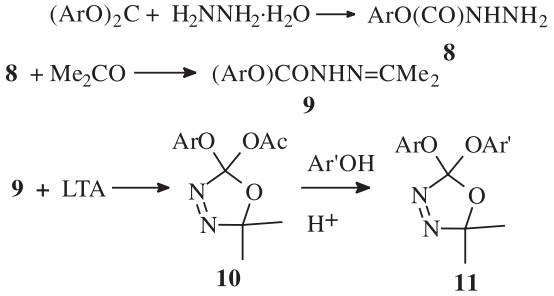


Table 1. Yields (%) of esters (**12**, **13**) and carbonate (**14**) from oxadiazolines (**11**).

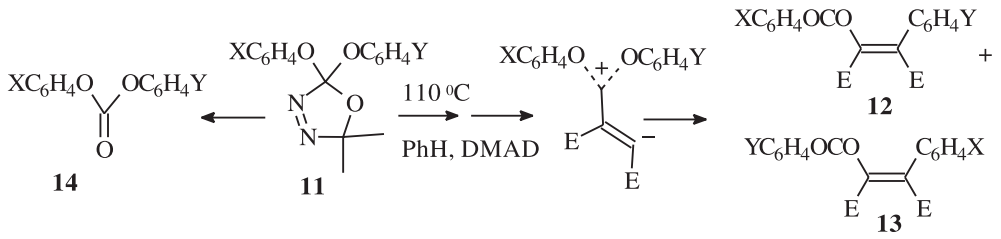
11	12	13	13:12	14
a	37	<2[a]	<0.05	29
b	28	<2[a]	<0.07	26
c	37	<2[a]	<0.05	30
d	38	<2[a]	<0.05	32
e	11	25	2.3	35

[a]Not detected. We did not experience any difficulties with detection of the esters by ^{1}H NMR spectroscopy, and we estimate that the yield of the detected isomer was at least 15-fold greater than that of the isomer that was not detected.

Scheme 5.

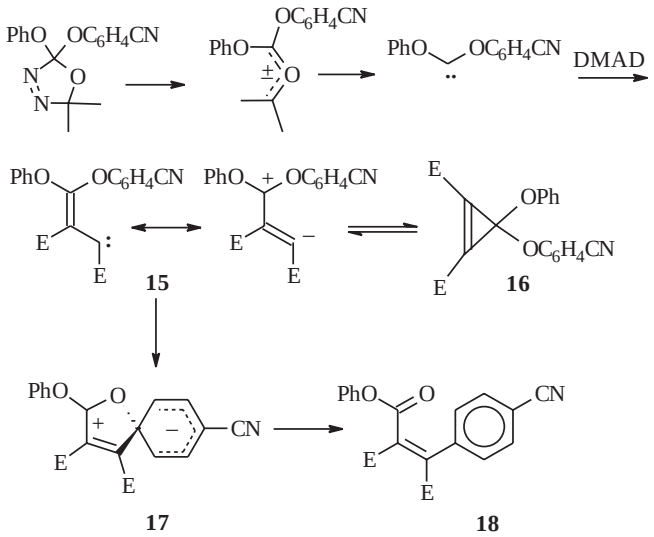


Scheme 6.



(a) X= *p*-OMe, Y= *p*-CN; (b) X= *p*-Me, Y= *p*-CN; (c) X= H, Y= *p*-CN; (d) X= *p* -OMe, Y= H; (e) X= *o*-OMe, Y= H; E = CO_2Me

Scheme 7.

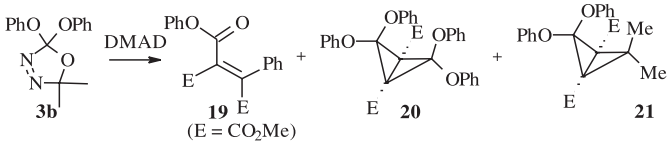


oxadiazoline **3b**, when thermolyzed in the presence of DMAD, affords not only **19** but also **20** and **21** (2) (Scheme 8).

Intermediate **15** also affords **18**, presumably via **17**, which is analogous to the intermediate usually invoked in describing nucleophilic aromatic substitutions (5). Dipolar intermediates in ipso nucleophilic aromatic substitution have been demonstrated many times (19).

A concerted reaction, leading directly from the carbene and DMAD to the product, is unlikely given that aromatic substitutions generally occur through intermediates. However, a more complex stepwise process, involving electron transfer (e.t.) *before* ring closure but leading to the observed

Scheme 8.



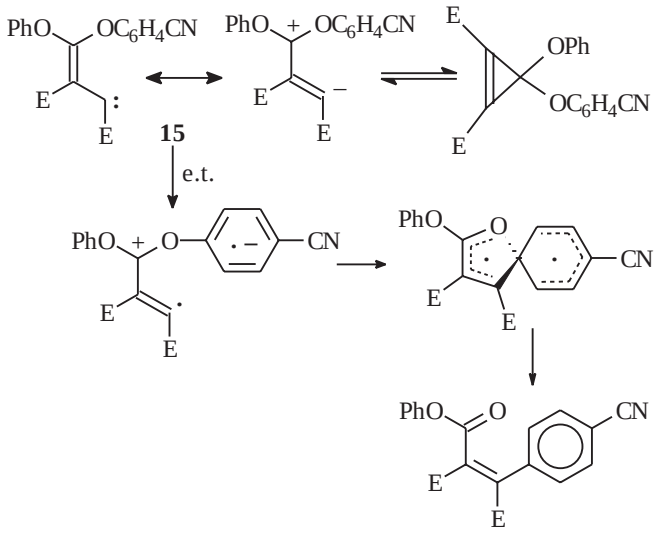
result (Scheme 9) cannot be ruled out with confidence. Some intermolecular chemistry of intermediates similar to **15** is thought to involve electron transfer from a π-delocalized vinylcarbene intermediate, and subsequent coupling of a radical cation and radical anion pair (Scheme 10) (20).

A special interaction must be invoked for the *o*-methoxy substituent, which promoted migration whereas the *p*-methoxy group was not effective. Given that a likely mechanism (Scheme 7) involves a dipolar intermediate, it is logical to propose that the *o*-methoxy group exerts its effect through space, rather than through bonds (Scheme 11). A through-space interaction of the *ortho* methoxy group with the positive center of a dipolar intermediate would help to orient the aryl group for attack, as shown in Scheme 11. Such an involvement would differentiate strongly between the *o*- and *p*-methoxy groups, which presumably have similar conjugative effects.

Summary

Diaryloxycarbenes attack DMAD to afford unsaturated triesters, by attack at the *sp*-carbon and migration of an aryl group from oxygen to the other *sp*-carbon of DMAD. If the aryloxy groups are *para*-substituted, the aryl group that is transferred preferentially is the one that is more

Scheme 9.



electron-deficient. The *ortho*- but not the *para*-methoxy group also promotes migration, presumably by stabilizing an electrophilic site by donation of electron density from the oxygen atom through space. Aryloxymethoxycarbenes (1) probably react with DMAD by an analogous mechanism.

Experimental section

General

NMR spectra were recorded with a Bruker AC-200 or AC-300 NMR spectrometer and IR spectra were obtained with a Biorad FTS-40 spectrophotometer, with the sample in CCl_4. The IR bands are labeled qualitatively with the symbols br, s, and m for broad, strong, and medium intensity bands. Weak bands are not listed. The eluting solvent for radial chromatography was a gradient of ethyl acetate (2.5–10 vol. %) in hexanes. Melting points were obtained with a Thomas Hoover capillary melting point apparatus, and are uncorrected.

Synthesis of diaryl carbonates

Diphenyl carbonate is commercially available. The other diaryl carbonates were prepared as described earlier (3).

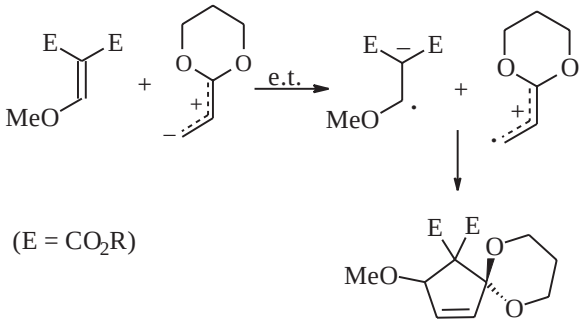
Thermolysis of 11a with DMAD

The procedure described below for thermolysis of **11a** with DMAD is typical.

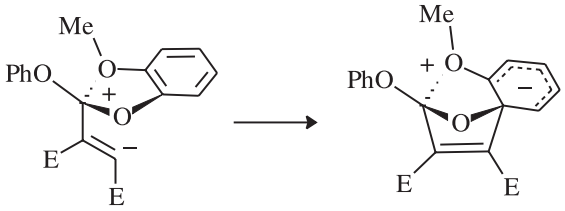
2-(*p*-Cyanophenoxy)-2-(*p*-methoxyphenoxy)-5,5-dimethyl-Δ^3-1,3,4-oxadiazoline (1.03 g, 3.04 mmol) was heated in the presence of DMAD (0.52 g, 3.66 mmol) in 25 mL of benzene (sealed tube) at 110°C for 24 h. Radial chromatography following evaporation of the solvent gave **12a** (37%) and **14a** (29%).

*Triester **12a***: white crystals, mp: 121 to 122°C. EI-MS *m/z* (%): 395 (M, 7), 364 (M – 31, 6), 272 (100), 244 (40), 200 (42), 154 (96), 123 (71), 95 (40), 59 (80). CI-MS (NH_3) *m/z* (%): 413 (M + 18, 19), 396 (M + 1, 17), 272 (100). HRMS *m/z* (%): calcd. for $C_{21}H_{17}NO_7$: 395.1005; found: 395.1026. IR (CCl_4) cm^{-1}: 2955m, 2839m, 2234m, 1746br, 1637m, 1608m, 1505s, 1437m, 1270br, 1232br, 1188br, 1073s, 1038s, 1010s. ^1H NMR (200 MHz, $CDCl_3$) δ: 3.76 (s, 3H, OMe), 3.87 (s, 3H, OMe), 3.92 (s, 3H, OMe), 6.67–6.85 (m, 4H, ArH), 7.58–7.74 (m, 4H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 53.3 (2 × OMe), 55.5, 113.9, 114.5, 117.8, 121.4, 128.5, 128.9, 132.4, 137.2, 143.1, 145.2, 157.7, 162.3, 162.4, 165.8.

Scheme 10.



Scheme 11.



The *E*-configuration of **12a** (ArOCO and CO_2Me groups *trans*) was confirmed by means of single crystal X-ray diffraction.

p-*Cyanophenyl* p-*methoxyphenyl carbonate (**14a**)*: white solid, mp: 103–105°C. EI-MS *m/z* (%): 269 (M, 34), 254 (31), 225 (9), 210 (23), 154 (6), 123 (100), 107 (84), 77 (77), 65 (32). CI-MS (NH_3) *m/z* (%): 287 (M + 18, 48), 269 (M, 89), 123 (100). IR (CCl_4) cm^{-1}: 3004m, 2932m, 2838m, 2232m, 1781s, 1717m, 1605s, 1505s, 1465m, 1296m, 1225s, 1183s, 1041m. ^1H NMR (200 MHz, $CDCl_3$) δ: 3.79 (s, 3H, OMe), 6.88–7.72 (m, 8H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 55.5, 110.1, 114.5, 117.9, 121.5, 121.9, 133.7, 144.2, 151.4, 153.8, 157.7.

Thermolysis of oxadiazoline (11b) with DMAD

Thermolysis of 2(*p*-cyanophenoxy)-5,5-dimethyl-2(*p*-methylphenoxy)-Δ^3-1,3,4-oxadiazoline in the presence of DMAD gave **12b** (26%) and **14b** (28%).

*Triester **12b***: pale yellow oil. EI-MS *m/z* (%): 348 (M – Me), 272 (M – OC_6H_4Me, 100), 244 (23), 200 (23), 176 (14), 154 (46), 107(8), 77 (23), 59 (32), 51 (9). CI-MS (NH_3) *m/z* (%): 397 (M + 18, 33), 380 (M + 1), 272 (M – OC_6H_4Me, 100). HRMS *m/z* calcd. for $C_{21}H_{17}NO_6$: 379.1056; found: 379.1073. IR (CCl_4) cm^{-1}: 2956m, 2234m, 1746s, 1639m, 1610m, 1507s, 1437s, 1269s, 1229s, 1189s, 1075s, 1010s. ^1H NMR (200 MHz, $CDCl_3$) δ: 2.30 (s, 3H, Me), 3.88 (s, 3H, OMe), 3.92 (s, 3H, OMe), 6.66–7.13 (m, ArH of C_6H_4Me), 7.58–7.73 (m, ArH of C_6H_4CN). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 20.7, 53.3 (2 × OMe), 99.8, 113.9,

117.8, 120.3, 120.6, 128.6, 130.0, 132.4, 136.3, 137.2, 145.2, 147.5, 162.1, 162.4, 165.8.

p-*Cyanophenyl* p-*tolyl carbonate* ***14b***: white solid, mp: 91 to 92°C. EI-MS *m/z* (%): 65 (30), 77 (33), 91 (100), 102 (19), 209 (13), 253 (M^+, 23). CI-MS (NH_3) *m/z* (%): 253 (M + 1, 37), 271 (M + 18, 18). HRMS *m/z* calcd. for $C_{15}H_{11}NO_3$: 253.0739; found: 253.0745. IR (CCl_4) cm^{-1}: 2234m, 1783s, 1604m, 1507s, 1287m, 1229s, 1189s, 1167s, 1018m, 1006m. ^1H NMR ($CDCl_3$) δ: 2.36 (s, 3H, Me), 7.12–7.25 (m, 4H, C_6H_4Me), 7.40–7.73 (m, 4H, C_6H_4CN). ^{13}C NMR (50 MHz) δ: 20.8, 110.3, 117.9, 120.4, 122.0, 130.2, 133.8, 136.4, 148.6, 151.3, 154.0.

Thermolysis of oxadiazoline (11c) with DMAD

Thermolysis of 2(*p*-cyanophenoxy)-5,5-dimethyl-2-phenoxy-Δ^3–1,3,4-oxadiazoline in the presence of DMAD gave **12c** (37%) and **14c** (30%).

Triester ***12c***: pale yellow oil. EI-MS *m/z* (%): 365 (M, 2), 334 (M – OMe, 7), 272 (M – OPh, 100), 244 (17), 200 (13), 176 (8), 154 (14), 77 (9), 59 (37). CI-MS (NH_3) *m/z* (%): 383 (M + 18, 84), 272 (M – OPh, 100). IR (CCl_4) cm^{-1}: 2955m, 2233m, 1742b, 1638m, 1593m, 1550m, 1492s, 1436s, 1307m, 1267b, 1233b, 1189s, 1160m, 1074s, 1010s. ^1H NMR (200 MHz, $CDCl_3$) δ: 3.89 (s, 3H, OMe), 3.93 (s, 3H, OMe), 6.77–7.76 (m, 9H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 53.4 (2 × OMe), 114.0, 117.8, 120.7, 126.6, 128.6, 128.7, 129.6, 132.5, 137.1, 145.4, 149.6, 162.0, 165.9.

p-*Cyanophenyl phenyl carbonate* ***(14c)***: white solid, mp: 79 to 80°C. EI-MS *m/z* (%): 239 (M, 33), 195 (22), 167 (28), 140 (5), 121 (13), 102 (21), 77 (100), 65 (35), 49 (30), 43 (76). CI-MS (NH_3) *m/z* (%): 257 (M + 18, 21), 239 (M, 89). IR (CCl_4) cm^{-1}: 2235m, 1782s, 1603m, 1550m, 1507m, 1495m, 1221br, 1186s, 1163s, 1008m. ^1H NMR (200 MHz, $CDCl_3$) δ: 7.26–7.74 (m). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 110.3, 118.0, 120.7, 122.0, 126.7, 130.0, 133.9, 150.7, 151.1, 153.9.

Thermolysis of *p*-methoxyphenoxy phenoxy oxadiazoline (11d) with DMAD

Thermolysis of 2-(*p*-methoxyphenoxy)-2-phenoxy-5,5-dimethyl-Δ^3–1,3,4-oxadiazoline in the presence of DMAD gave **12d** (38%) and **14d** (32%).

Triester ***12d***: light yellow oil. EI-MS *m/z* (%): 370 (M, 2), 339 (M – OMe, 5), 311 (7), 277 (6), 247 (100), 219 (41), 151 (16), 129 (22), 95 (10), 59 (27). CI-MS (NH_3) *m/z* (%): 388 (M + 18, 8), 371 (M + 1, 15), 247 (100). IR (CCl_4) cm^{-1}: 3004m, 2954m, 2839m, 1743br, 1633m, 1505s, 1437m, 1269s, 1232s, 1188s, 1070m, 1039m, 1012m. ^1H NMR (200 MHz, $CDCl_3$) δ: 3.75 (s, 3H, OMe), 3.90 (s, 6H, 2 × OMe), 6.65–7.49 (m, 9H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 53.0, 53.1, 55.5, 114.4, 121.7, 126.3, 127.7, 128.9, 130.4, 132.8, 143.4, 148.0, 157.6, 162.7, 163.4, 167.0.

p-*Methoxyphenyl phenyl carbonate* ***(14d)***: light yellow oil. EI-MS *m/z* (%): 245 (M + 1, 21), 244 (M, 100), 200 (15), 185 (32), 157 (11), 124 (60), 123 (46), 95 (25), 77 (95), 65 (30), 41 (24). CI-MS (NH_3) *m/z* (%): 262 (M + 18, 100), 244 (M, 100). IR (CCl_4) cm^{-1}: 3006m, 2956m, 2838m, 1780s, 1596m, 1507s, 1465m, 1442m, 1298m, 1229s, 1182s, 1103m, 1071m, 1041m, 1010m. ^1H NMR (200 MHz, $CDCl_3$) δ: 3.80 (s, 3H, OMe), 6.88–7.44 (m, 9H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 55.6, 114.5, 120.9, 121.8, 126.2, 129.5, 144.6, 151.1, 152.4, 157.6.

Thermolysis of oxadiazoline 11e with DMAD

Thermolysis of 2(*o*-methoxyphenoxy)-5,5-dimethyl-2-phenoxy-Δ^3–1,3,4-oxadiazoline in the presence of DMAD gave **12e** (11%) and **13e** (25%) as well as **14e** (35%).

Triester ***12e***: pale yellow oil. EI-MS *m/z* (%): 371 (M + 1, 4), 339 (10), 277 (M – 93, 100), 249 (100), 219 (10), 205 (28), 181 (18), 159 (20), 131 (45), 103 (12), 65 (40). CI-MS (NH_3) *m/z* (%): 388 (M + 18, 34), 371 (M + 1, 40), 277 (M – 93, 100). HRMS *m/z* calcd. for $C_{20}H_{19}O_7$ (M + H): 371.1131; found: 371.1108. IR (CCl_4) cm^{-1}: 3005m, 2954s, 2841m, 1745br, 1592s, 1550br, 1493s, 1461m, 1436m, 1226br, 1162m, 1117m. ^1H NMR (200 MHz, $CDCl_3$) δ: 3.80 (s, 3H, OMe), 3.84 (s, 3H, OMe), 3.90 (s, 3H, OMe), 6.77–7.46 (m, 9H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 52.9, 53.0, 55.8, 111.3, 120.8, 121.0, 123.0, 126.1, 129.3, 130.0, 130.1, 131.8, 144.2, 150.1, 156.9, 162.7, 163.9, 166.9.

Triester ***(13e)***: pale yellow oil. EI-MS *m/z* (%): 371 (M + 1, 5), 247 (M – 123, 100), 219 (53), 175 (19), 151 (16), 129 (31), 95 (22), 77 (28), 59 (33). CI-MS (NH_3) *m/z* (%): 388 (M + 18, 38), 371 (M + 1, 12), 247 (M – 123, 100). HRMS *m/z* calcd. for $C_{20}H_{19}O_7$ (M + H): 371.1131; found: 371.1108. IR (CCl_4) cm^{-1}: 2954m, 2841m, 1760m, 1742br, 1633m, 1609m, 1501s, 1436m, 1308m, 1263br, 1232br, 1198br, 1174s, 1110s, 1069m, 1010m. ^1H NMR (200 MHz, $CDCl_3$) δ: 3.74 (s, 3H, OMe), 3.90 (s, 3H, OMe), 3.92 (s, 3H, OMe), 6.63–7.60 (m, 9H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 53.0 (2 × OMe), 55.8, 112.6, 120.7, 122.3, 126.1, 127.3, 128.1, 128.7, 130.3, 132.6, 138.9, 148.2, 151.2, 162.5, 163.0, 167.2.

o-*Methoxyphenyl phenyl carbonate* ***(14e)***: white solid, mp: 58 to 59°C. EI-MS *m/z* (%): 244 (M, 100), 200 (28), 185 (10), 151 (20), 124 (20), 95 (33), 77 (84), 65 (37). CI-MS (NH_3) *m/z* (%): 262 (M + 18, 100), 244 (M, 100). IR (CCl_4) cm^{-1}: 2962m, 2841m, 1784s, 1550br, 1503br, 1465m, 1310m, 1233br, 1191s, 1173s, 1113m. ^1H NMR (200 MHz, $CDCl_3$) δ: 3.89 (s, 3H, OMe), 6.92–7.44 (m, 9H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 56.0, 112.6, 120.7, 120.9, 122.2, 126.1, 127.3, 129.5, 140.0, 151.0, 151.2, 151.6.

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