Homolytic Aromatic Substitution of Heterocyclic Compounds. Part XIII. Arylation and Heteroarylation of Coumarin and Benzo[*b*]furan Using Triazenes as the Source of Radicals. An Experimental and Theoretical Study (1)

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The homolytic arylation (substituents in the phenyl radical: none, *p*-methyl, *p*-fluoro, *p*-chloro, *p*-bromo, *o*-chloro, 2,4-dichloro, 3,5-dichloro, 2,3,4-trichloro, 2,3,5-trichloro, *o*-carbomethoxy, *p*-carboethoxy, and *o*-phenyl) and heteroarylation (2-thiazolyl, 2-benzothiazolyl, 3-pyridyl) of coumarin and benzo[*b*]furan has been studied. The radicals were generated by thermal decomposition of the corresponding 1,3-diaryltriazenes in the presence of isoamyl nitrite. Homolytic substitution of coumarin takes place exclusively in the position 3, in agreement with the prediction based on SCF-MO free valences. In the case of benzo[*b*]furan, all the reactivity indices (F, S_r, and A_r) predict the position 2 to be most reactive, in agreement with the experimental results. Comparison of the mass spectra of the products indicates similarities between the spectra of arylcoumarins and arylbenzo[*b*]furans and the existence of a common intermediate in their fragmentation pattern, *viz.*, the benzo[*b*]furan cation radical.

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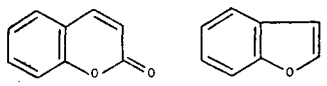
Introduction.

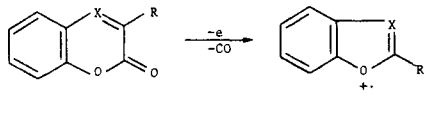
There are only a few papers available in the literature dealing with homolytic substitution reactions of coumarin (I) and benzo[*b*]furan (II). Rondestvedt and Vogl have



I II

shown (2) that the decomposition of *p*-nitrobenzenediazonium chloride in aqueous acetone in the presence of cuprous chloride as the catalyst (the Meerwein reaction (3)) leads to substitution of coumarin in the position 3 giving 3-*p*-nitrophenylcoumarin in a 40% yield. The authors did not mention any other possible isomers. The free-radical phenylation of benzo[*b*]furan was studied by Spagnolo and co-workers (4). They generated phenyl radicals by thermal decomposition of N-nitrosoacetanilide at 40° and obtained 2-phenylbenzo[*b*]furan (76% yield) as the main reaction product accompanied by 4-phenylbenzo[*b*]furan (17.5%) and traces of four other isomers. Whereas these experimental results seem to be in agreement with the expected preferred reactivity of the positions adjacent to the heteroatom in free-radical substitutions in the heterocyclic series (5), they do not agree with theoretical predictions based on the calculated free valences for coumarin (6) and benzo[*b*]furan (7). According to some calculations (6,7e), the positions 4 in coumarin and 3 in benzo[*b*]furan should be more reactive than the positions 3 and 2, respectively. Because of this discrepance we have decided to carry out an experimental and theoretical study of homolytic substitution in coumarin and benzo[*b*]furan. In a recent publication we have described a simple and rapid synthesis of 1,3-diaryltriazenes (8) which can be used as the source of aryl radicals in homolytic arylations. The use of this method enabled us to synthesize new arylsubstituted coumarins and benzo[*b*]furans and to study the course of a free-radical substitution reaction at the same time (Schemes 1 and 2).

It is known that in mass spectrometry of coumarin and its derivatives (9) the principal mode of fragmentation involves the elimination of carbon monoxide and the formation of the benzo[*b*]furan radical cation. Thus, the mass spectra of arylbenzo[*b*]furans, used as the principal means of their identification, should be very similar to those of the corresponding arylcoumarins starting from the M^+ - CO fragment. A similar situation has been observed with many aromatic and heteroaromatic compounds containing the carbonyl group (*e.g.*, 1,4-benzoxazin-2-ones, *A*, X = N, and 1,3-benzoxazoles, *B*, X = N (10)).



A B

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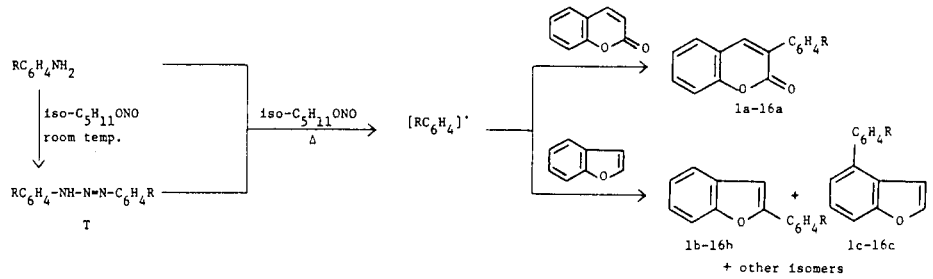
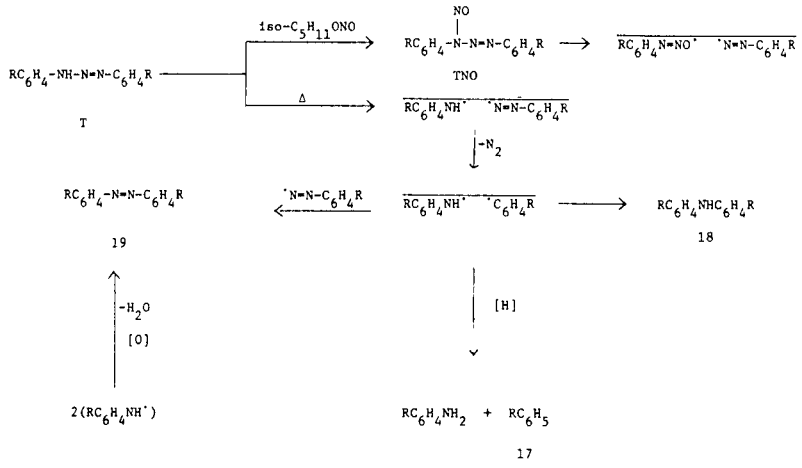


In **1** through **13**, R = H (**1**), 4-Me (**2**), 4-F (**3**), 4-Cl (**4**), 4-Br (**5**), 2-Cl (**6**), 2,4-Cl_2 (**7**), 3,5-Cl_2 (**8**), 2,3,4-Cl_3 (**9**), 2,3,5-Cl_3 (**10**), 2-COOMe (**11**), 4-COOEt (**12**), 2-Ph (**13**). In addition to RC_6H_4, the other groups are 3-pyridyl (**14**), 2-thiazolyl (**15**), and 2-benzothiazolyl (**16**).

Scheme 1. Thermal decomposition of arylamines or 1,3-diaryltriazenes in the presence of isoamyl nitrite and coumarin or benzo[*b*]furan.



Scheme 2. Principal secondary products obtained in the thermal decomposition of triazenes.

Table I

Relative Amounts of Products Obtained in Homolytic Arylation of Benzo[*b*]furan

Radical	Yield, % (a)	Relative Amounts of Isomers, % (b) Position			VPC (d) T_R, sec (t, °)
		2	4	Other (c)	
C_6H_5·	55	59.5	21.5	19.0	248, 184, 212, 226 (220)
		75.9 (e)	17.5 (e)	6.6 (e)	
p-MeC_6H_4·	45	63.0	18.6	18.4	330, 242, 300 (220)
p-ClC_6H_4·	50	65.0	18.5	18.5	240, 186, 210, 224 (240)
p-FC_6H_4·	48	63.0	19.4	17.6	145, 116, 127, 133 (240)
p-$EtOOCC_6H_4$·	40	70.0	16.5	13.5	337, 267, 305, 319 (240)
o-$C_6H_5C_6H_4$·	59	56.0	25.0	19.0	2330, 2200, 2260 (f)

(a) Determined using the internal reference method.
(b) Average values obtained by gas chromatography (VPC) on OV-1 and SE-30 columns.
(c) 7 + 6 + 5.
(d) OV-1 column.
(e) Reference 4.
(f) Kováts indices were determined using normal C_{22} to C_{24} alkanes (13).

Table II

Principal Fragments and Their Relative Intensities Observed in the Mass Spectra of 3-Aryl- and 3-Heteroarylcoumarins (a)

RC_6H_4 in **1a-16a**	Compound No.	Fragments (relative intensity, %) M^+	$M^+ - CO$	$M^+ - CO - HCO$	Other fragments and m/2e
C_6H_5 (b)	**1a**	22 (100)	194 (50)	165 (40)	139, 111, 105 ($C_6H_5CO^+$), 97, 82.5, 77, 69, 63
p-MeC_6H_4	**2a**	236 (100)	208 (44.5), 207 (30)	179 (9), 178 (15)	165, 146, 117, 91, 89, 76
p-FC_6H_4	**3a**	240 (100)	212 (60)	183 (52)	146, 123 ($FC_6H_4CO^+$), 120, 106, 91.5
p-ClC_6H_4	**4a**	258 (30), 256 (100)	230 (17), 228 (50)	201 (2.5), 199 (7)	221 ($M^+ - Cl^\cdot$), 165 ($M^+ - Cl^\cdot - 2CO$), 146, 139 ($ClC_6H_4CO^+$), 110, 96, 89, 82.5, 82, 81.5
p-BrC_6H_4	**5a**	302 (100), 300 (100)	274 (50), 272 (50)	245 (3), 243 (2)	221 ($M^+ - Br^\cdot$), 165 ($M^+ - Br^\cdot - 2CO$), 164, 163, 146, 111, 110.5, 83, 82.5, 82, 81.5, 81, 69.5, 69, 63
o-ClC_6H_4	**6a**	258 (out), 256 (out)			221 ($M^+ - Cl^\cdot$, 100), 165 ($M^+ - Cl^\cdot - 2CO$), 146, 139, 110, 96, 82.5, 82, 81.5, 81
2,4-$Cl_2C_6H_3$	**7a**	294 (1), 292 (6), 290 (3)			257 ($M^+ - Cl^\cdot$, 40), 255 ($M^+ - Cl^\cdot$, 100), 201, 199 ($M^+ - Cl^\cdot - 2CO$), 164, 163 ($M^+ - 2Cl^\cdot - 2CO$), 146, 82, 81.5, 81
3,5-$Cl_2C_6H_3$	**8a**	294 (10), 292 (60), 290 (100)	266 (6), 264 (36), 262 (65)		235, 233, 201, 199 ($M^+ - Cl^\cdot - 2CO$), 164, 163 ($M^+ - 2Cl^\cdot - 2CO$), 146, 128.5, 128, 127.5, 127, 113, 99.5, 82, 81.5, 81
2,3,4-$Cl_3C_6H_2$	**9a**	328 (2), 326 (5), 324 (7)			239 ($M^+ - Cl^\cdot$, 13), 291 (68), 289 (100), 237 ($M^+ - 2Cl^\cdot$, 7), 235 (10), 233 (11), 198, 197, 163, 146, etc.
2,3,5-$Cl_3C_6H_2$	**10a**	328 (out), 326, 324			293 ($M^+ - Cl^\cdot$, 12), 291 (68), 289 (100), 237 ($M^+ - 2Cl^\cdot$, 1.5), 235 (8), 233 (12), 199, 198, 197, 163, 146
o-$MeOOCC_6H_4$	**11a**	280 (90)	252 (20)		249 ($M^+ - OMe^\cdot$, 90), 221 ($M^+ - COOMe^\cdot$, 100), 193, 165, 163, 146, 135, 110.5, 105, 82.5, 82
p-$EtOOCC_6H_4$	**12a**	294 (66)	266 (26)		249 ($M^+ - OEt^\cdot$, 100), 238, 221 ($M^+ - COOEt^\cdot$, 40), 193, 165, 146, 110.5
3-Pyridyl	**14a**	223 (40)	195 (25)		166 (12), 146 (60), 118 (60), 79 (40), 70 (70), 43 (100)
2-Thiazolyl	**15a**	229 (100)	201 (42)		58 (90), 146
2-Benzothiazolyl (c)	**16a**	279 (20)	251 (10)		169, 146 (75), 135 (94), 118 (100), 94, 63, 43 (90)

(a) The spectra were registered on a Varian MAT 111 instrument at 80 eV.
(b) This peak was preceded by a lower intensity peak of the same mass and giving the same fragments. These are obviously the peaks due to fragments formed from the 4-isomer.
(c) This spectrum was recorded on an MS 50 mass spectrometer.

EXPERIMENTAL

Coumarin - Arylation Products (11).

Triazenes, T (*cf.* Scheme 1), decomposed at 100-120° in the presence of coumarin and an excess of isoamyl nitrite give a single arylation product (12) detected by gas chromatography and identified by coupled gas chromatography-mass spectrometry (13). In the case of the phenyl derivative **1a**, the same product was obtained by thermal decomposition of dibenzoyl peroxide in the presence of coumarin. This observation confirms the free-radical nature of the Meerwein reaction. The site of the free-radical attack is the position 3 of coumarin and, in the case of the *p*-nitrophenyl derivative, the product obtained in this reaction is the same as the compound described by Rondestvedt and Vogl (2) (m.p. 260-262°). 3-Phenylsubstituted coumarins, **2-12a**, including the above *p*-nitrophenyl derivative, can be easily identified by gas chromatography (12) using the Kováts index for 3-phenylcoumarin and the increments of the index (ΔI) for the substituent groups measured on the same column with respect to the corresponding aromatic hydrocarbons (14).

In the case of the heteroaryl derivatives **13a-15a**, thermal decomposition of the corresponding heterocyclic amines was used. The yields were determined by gas chromatography (internal reference) and were found to be comparable to those obtained in the Meerwein reaction. Similarly as in other reactions of this type, a number of secondary products were observed, among them the respective aromatic hydrocarbons, RC_6H_5 (**17**), formed from the aryl radicals by abstraction of hydrogen from the substrate. The lowest yield was observed with methyl anthranilate. In this case, the two major reaction products were methyl benzoate and the nitrogen-containing derivative **19** (R = COOme). Compound **19** is most likely formed by cage recombination of the aryl and arylazo radicals or by oxidation of secondary diamines formed by dimerization of arylamino radicals. The derivative **19** was identified by its mass spectrum which gives a molecular ion M^+ with m/e = 198, and the following characteristic fragments: $M^+ - (OCH_3)$ at 267, $M^+ - 2(OCH_3)$ at 236, $M^+ - C_6H_5$ at 163, and $M^+ - (C_6H_5 + N_2)$ at 135 (100%). Other fragments were observed at 120, 105 (C_6H_5 - CO), 92, and 77 ($C_6H_5^+$).

Another commonly observed secondary product in this type of reaction is diarylamine **18** formed by cage recombination of aryl and arylamino radicals (R = H; 2,4-dichloro in **18**). Formation of these compounds seems to indicate that at higher temperatures and in the presence of an excess of isoamyl nitrite the N-nitroso intermediate (TNO) postulated by Fišera and co-workers (15) is not formed or its formation represents a reaction competitive with the thermal decomposition of the respective triazene.

Benzo[*b*]furan.

In contrast to coumarin, the arylation of benzo[*b*]furan carried out at 120° leads to the formation of several isomers one of which is the prevailing reaction product. The results summarized in Table I indicate that the relative amounts of isomers formed are practically independent of the nature of the aryl radical. The lower percentage for the most abundant isomer found in our reactions (~60%) is due to the difference in the reaction temperature. Whereas our experiments had been carried out at 120°, the reactions performed by Tiecco's group were run at 40° (4). The same distribution of the different isomeric phenyl derivatives is obtained in the free-radical phenylation of the benzo[*b*]furan ring using phenyl radicals generated by thermal decomposition of of dibenzoyl peroxide at 120° (4).

The mass spectra of the four isomers obtained in the reaction closely resemble each other (see below) and, because of this, it was not possible to determine the position of substitution by this technique. The isomers were identified by proton nmr spectroscopy. The reaction mixture was chromatographed on a column and the fraction containing the most abundant isomer was isolated. Its nmr spectrum (deuteriochloroform/TMS, δ H-3 6.98 ppm, singlet) enabled us to assign this compound the structure

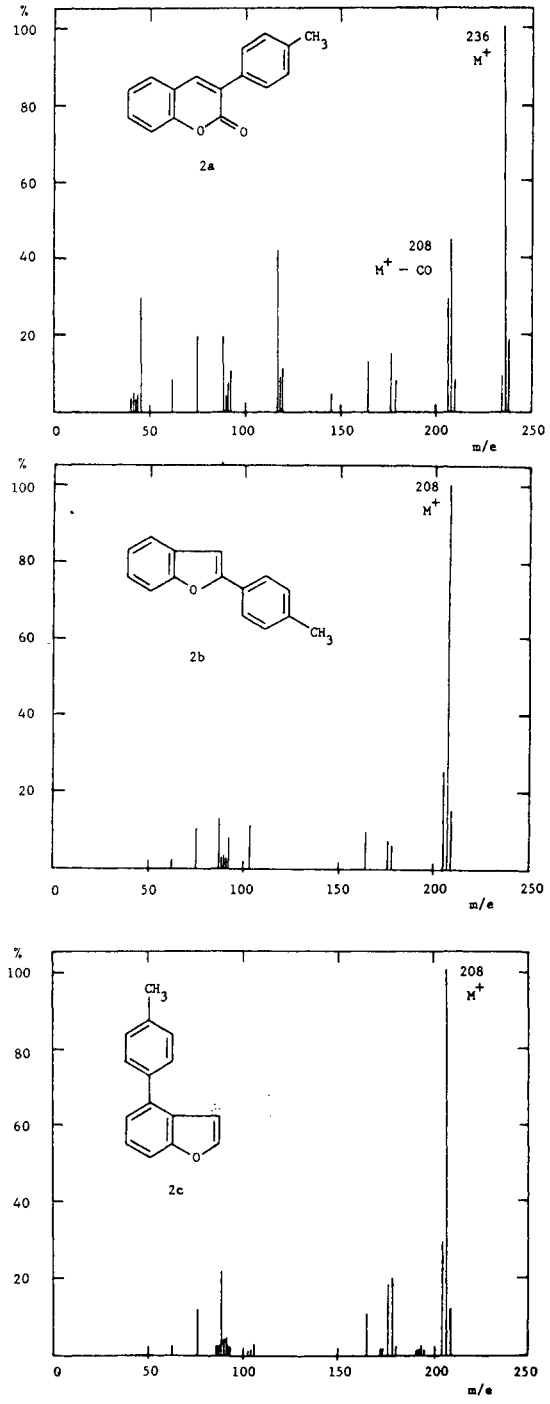


Figure 1. Mass spectra of 3-*p*-tolylcoumarin (**2a**), 2-*p*-tolylbenzo[*b*]furan (**2b**), and 4-*p*-tolylbenzo[*b*]furan (**2c**).

of 2-phenylbenzo[*b*]furan, **1b**. In the case of benzo[*b*]furan itself, this proton gives a doublet at 6.7 ppm. The same procedure carried out with 3-aminopyridine as the source of radicals confirmed the most reactive position in substitution (δ H-3 6.97 ppm) as well as the formation of another isomer (21.5%) whose retention time was analogous to that of 4-phenylbenzo[*b*]furan, **1c**, prepared by a described method (4). As far as the identification of products in other reaction mixtures is concerned, the 2- and 4-substituted products posed no problems. Their gas chromatograms were analogous to those of 2- and 4-phenylbenzo[*b*]furan using the addivity principle for Kováts indices for the R groups attached to the benzene ring.

The preferential reactivity of benzo[*b*]furan in the position 2 is thus analogous to the reactivity of the same position in furan (16). The other two most reactive positions in benzo[*b*]furan are the positions 4 and 7, *i.e.*, both are the *ortho* positions in the benzene ring, whereas the positions 5 and 6 are *meta* and the position 3 is *meta* with respect to the heteroatom.

Characteristic Features in the Mass Spectra of 3-Arylcoumarins and 2-Arylbenzo[*b*]furans.

The principal fragments and their relative intensities (with respect to the base peak) observed in the mass spectra of 3-aryl- and 3-heteroarylcoumarins are summarized in Table II.

The essential features of the spectra are as follows: (a) The molecular ion, M^+, gives a very intense peak. The M^+ peak is usually the base peak except in the following cases: (i) In *o*-chlorophenyl derivatives **6a**, **7a**, **9a**, and **10a**, the base peak corresponds to $M^+ - Cl$, (ii) In the esters **11a** and **12a** (base peak at m/e = $M^+ - OMe$ and $M^+ - OEt$); (iii) In the heteroarylcoumarins **14a** and **16a**. It seems worth mentioning that in 3-(2-thiazolyl)coumarin there is a very intense peak at m/e = 58 (90%) which is characteristic of thiazoles containing no substituents in positions 4 and 5 (17). (b) The second important fragment which is the base peak in coumarin itself (9) corresponds to a loss of carbon monoxide from the molecular ion ($M^+ - CO$). As a rule, its intensity is about 50% of that of the molecular ion and it is quite sensitive to the effect of substituents in the aromatic ring of 3-arylcoumarins. In some cases (**1a**, **2a**, **3a**, **4a**), this fragment is accompanied by a fragment $M^+ - CO - HCO$. (c) In 3-dichlorophenylcoumarins one observes fragments of low intensity at m/e 201, 199 ($M^+ - Cl - 2CO$) and at 164 and 163 ($M^+ - 2Cl - 2CO$). In 3-*p*-chlorophenylcoumarin and 3-*p*-bromophenylcoumarin, a fragment corresponding to $M^+ - Cl^- - CO$ (m/e = 165) is observed. (d) All the spectra contain a fragment at m/e = 146 corresponding to coumarin. This seems to indicate a certain weakness of the bond between the coumarin system and the aryl or heteroaryl substituent. (e) Finally, all the spectra of coumarin derivatives are characterized by the presence of doubly charged ions, especially in the case of halophenylcoumarins (X = Cl, Br), $(M^+ - X)/2$, $(M^+ - X - 2CO)/2$.

The mass spectra of 2-aryl- and 4-arylbenzo[*b*]furans are quite similar and, in some cases, the only difference is the relative intensity of the individual fragments. Thus, it is not possible to distinguish 2-arylbenzo[*b*]furans from their 4-aryl isomers by mass spectrometry (Table III).

The principal fragments and their relative intensities are the result of isomerization of 2-aryl- and 4-arylbenzo[*b*]furans. They are quite analogous to the fragments obtained from the corresponding 3-arylcoumarins (except for the $M^+ - CO$ fragment).

A comparison of these three mass spectra of 3-*p*-tolylcoumarin, 2-*p*-tolylbenzo[*b*]furan and 4-*p*-tolylbenzo[*b*]furan (Figure 1) indicates that the benzo[*b*]furan cation radical is a common intermediate in the fragmentation process (10). In all cases, except for the ester **12b** (or **12c**), the molecular ion is the base peak and the principal fragments are those obtained by fragmentation of benzo[*b*]furan (*e.g.*, peaks formed by loss of CO and HCO). Also, doubly charged fragments corresponding to $M^+/2$ (82.5) are observed in the spectra of **1b**, **3b**, **4b**, **12b**, and $M^+ - HCO/2$.

Theoretical Treatment.

The HMO calculations were carried out in the usual way on an IBM 1130 computer. The following empirical parameters were adopted for the Coulomb integrals, α_X, and the resonance integrals, β_{CX} (18).

Table III

Principal Fragments and Their Relative Intensities

Observed in the Mass Spectra of 2-Aryl- and 4-Arylbenzo[*b*]furans (a)

RC_6H_4	Compound No.	Fragments (relative intensity, %)
C_6H_5	**1b**	*194* (100), 165 (38.5), 97 (16), 82.5 (14), 82 (23), 81.5 (6), 77 (3), 69.5 (6)
	1c	*194* (100), 165 (43.6), 97 (10), 82.5 (7), 82 (22), 81.5 (5.5), 77 (2), 69.5 (9)
p-MeC_6H_4	**2b**	*208* (100), 202 (31), 179 (6), 178 (8), 104 (12.8), 165 (8.4), 91 (8), 89 (15), 76 (11), 63 (4)
	2c	*208* (100), 202 (30), 179 (21), 178 (16), 104 (8), 165 (11), 91 (3), 89 (23.5), 76 (14), 63 (4)
p-FC_6H_4	**3b**	*212* (100), 184 (6), 183 (38.2), 106 (20.6), 91 (12), 91.5 (12), 92 (3), 81.5 (3), 82 (7), 81 (6)
	3c	*212* (100), 184 (6), 183 (35.4), 106 (8), 91 (6), 91.5 (8), 92 (5), 81.5 (6), 82 (8), 81 (6)
p-ClC_6H_4	**4b**	*230* (32), *228* (100), 199 (3), 165 (30), 116 (18), 82.5 (12), 82 (23), 81.5 (12), 81 (17.5) 69.5, 69
	4c	*230* (35), *228* (100), 199 (4), 165 (30), 116 (8), 82.5 (13), 82 (20), 81.5 (15), 81 (6), 69.5, 69
p-$EtOOCC_6H_4$	**12b**	*266* (80), 238 (28), 221 (100), 193 (12.6), 165 (34.8), 110.5 (19.6), 96.5 (5), 82.5 (30.4), 69.5 (10)
	12c	*266*, 238, 221, 193, 165, 110.5, 96.5, 82.5, 69.5
o-$C_6H_5C_6H_4$	**13b**	271 (20), *270* (100), 269 (55), 268 (15), 253 (10), 241 (15), 239 (15), 226 (4)
	13c	271, 270, 269, 268, 253, 241, 239, 226
3-Pyridyl	**14b**	196 (14.3), *195* (100), 194 (4), 167 (11.5), 166 (15.7), 140 (9), 139 (13.4), 97.5 (8.6), 84 (5.6), 70 (6), 69.5 (5.4), 69 (5.4), 63 (4)
	14c	196, *195*, 194, 167, 166, 160, 139, 97.5, 84, 70, 69.5, 69, 63

(a) Molecular ions are in italics. The principal fragments in benzo[*b*]furan are 119 (9), *118* (100), 90 ($M^+ - CO$, 30), 89 (29), 63 (13.4), 62 (5.5), and 59 (5.1).

$\alpha_{O(endo)} = \alpha_C + 2\beta_{CC}$ $\beta_{CO} = 0.8\beta_{CC}$

$\alpha_{O(keto)} = \alpha_C + \beta_{CC}$ $\beta_{CO} = \beta_{CC}$

In the calculations the endocyclic oxygen was assumed to contribute two π electrons, the keto oxygen one π electron into the π system.

The SCF-MO calculations were carried out on the same computer using the PPP (Pariser-Parr-Pople) method (19). The systems were assumed to be planar and to have idealized geometry. All the ring bond lenghts were taken as 1.40 Å, the C-O bond length in the keto group of coumarin was taken as 1.20 Å. The rings were assumed to be regular hexagons and pentagons. The following parameters were used in the calculations (20,21).

	C	O (endo)	O (keto)
W_p	-11.16	-33.90	-17.70
p^2,q^2	11.13	18.60	15.23

The resonance integrals β_{pq} were determined using Kon's formula (22), $\beta_{pq} = k/r_{pq}^6$, where k is a parameter depending on the nature of the atoms p and q and r_{pq} is the distance between the atoms p and q. The following k values were employed: C-C bond, -17.484, C-O bond, -12.129, and C=O bond, -8.809. The (p^2,q^2) integrals were calculated using the method of uniformly charged spheres.

The reactivity indices for free-radical substitution for coumarin and benzo[*b*]furan calculated by the above two methods are given in Table IV. These results can be summarized as follows: (a) In the case of benzo[*b*]furan, all the HMO and SCF-MO reactivity indices show that the position 2 should be most reactive in free-radical substitutions, whereas the positions 5 and 6 should exhibit decreased reactivity. However, these reactivity indices generally overestimate the reactivity of the position 3. This is especially true in the case of the SCF-MO free valences which give the best agreement with the experimental results: $2 \gg 4 > 7 > 6 \geqslant 5 > 3$. Similar results were obtained with the HMO radical delocalization energies, A_r. (b) In the case of coumarin, the HMO indices (F, S_r, and A_r), overestimate the reactivity of the position 4, similarly as the data published in the literature (6). The SCF-MO free valences correctly predict the experimental reactivity, i.e., the position 3 is found to be most reactive. The HMO A_r values for the positions 3 and 4 are practically identical.

In conclusion, one can say that the present study has permitted us to confirm, experimentally and theoretically, the preferred reactivity of position 3 in coumarin and, to a lesser extent, position 2 in benzo[*b*]furan in free-radical arylations.

As mentioned before, because of the similarity of the mass spectra of the isomeric arylbenzo[*b*]furans, mass spectrometry cannot be used to identify the individual isomers. However, the pmr spectroscopy makes the identification possible.

Finally, we have shown that 1,3-diaryltrizenes can be used as a convenient source of aryl (or heteroaryl) radicals for homolytic arylation of various substrates.

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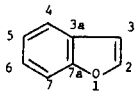
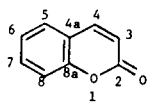
Table IV

Free Radical Reactivity Indices for Benzo[*b*]furan and Coumarin (a)

Compound	Position	SCF-MO F	HMO F	HMO S_r	HMO A_r
Benzo[*b*]furan	2	*0.585*	*0.539*	*1.102*	*2.041*
	3	0.443	0.423	0.916	2.473
	4	0.434	0.447	0.951	2.350
	5	0.395	0.396	0.832	2.547
	6	0.405	0.410	0.892	2.458
	7	0.411	0.417	0.878	2.463
Coumarin	3	*0.730*	0.441	1.006	*2.294*
	4	0.459	*0.484*	*1.214*	*2.296*
	5	0.428	0.453	1.012	2.311
	6	0.396	0.398	0.838	2.534
	7	0.407	0.416	0.951	2.416
	8	0.405	0.416	0.882	2.654

(a) q = π-electron density, F = free valence. S_r = radical superdelocalizability (Fukui), A_r = radical localization energy (Wheland). The values for the most reactive positions are in italics.

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(11) The procedure employed was as follows. Arylamine (0.5 g.) or the corresponding triazene (1.0 g.) was placed in 10 ml. of benzo[*b*]furan in the presence of 2 ml. of isoamyl nitrite. In the case of coumarin, the reaction was carried out with 2 g. of coumarin without a solvent or in the presence of 10 ml. of acetonitrile. The mixture was stirred for about 1 hour at 110-120°. The decomposition of the triazene was followed by thin-layer chromatography. The excess benzo[*b*]furan was distilled off under reduced pressure and the residue was analyzed by gas chromatography. Then the residue was dissolved in 15 ml. of benzene and the solution was quickly chromatographed on an alumina column (20 g.), activity I, using ligroin with 10% of benzene as the eluent (500 ml.). This procedure removed colored azo compounds and other polar products formed during the reaction. The solvent was distilled off and the mixture of isomers was analyzed by gas chromatography on OV-1 and SE-30 columns.

(12) Gas chromatographic analyses were performed on an Intersmat IGC 15 gas chromatograph equipped with a flame ionization detector and hooked up to a Vidar Autolab integrator. The following columns were used: (a) A silicone SE-30 column (5%) on Chromosorb W AW HMDS (60/80 mesh), 2 m long; (b) An OV-1 column (5%) on the same support and of the same length. The separations were carried out at constant temperature (220, 240 or 260°C) or, in some cases, using programmed temperature from 180 to 250° (15°/min).

(13) Coupled VPC-MS was performed using Varian Aerograph Model 1400 and Varian MAT 111 instruments at 80 eV. The column used was SE-30 (3%), 2 m long, at 220°.

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