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- (6) The high ratios of hydrogen loss to deuterium loss observed for IIb and IIIb are due to the operation of an isotope effect; photolysis of *trans*-4-*tert*-butylcyclohexyl phenylacetate-2,2,6,6-*d*<sub>4</sub> proceeded with >98% elimination of phenylacetic acid-*d*<sub>1</sub>.
- (7) A referee has suggested that this conclusion is contradicted by the data reported by Saunders et al. (ref 5a) for photoelimination from *cis*- and *trans*-2-methylcyclohexyl phenylacetate. Actually, however, Saunders' data permit no conclusions concerning the preferred stereochemistry of elimination from *trans*-4-*tert*-butylcyclohexyl phenylacetate. For example, *cis*-2-methylcyclohexyl phenylacetate photoeliminates to give ca. 10% 1-methylcyclohexene (*trans* elimination) and ca. 90% 3-methylcyclohexene (*cis* and *trans* elimination). However, since this compound exists largely (80–85%) in the conformer in which the phenylacetate group is axial,<sup>5a</sup> and since the quantum yield for elimination from certain axial phenylacetates is ca. three times greater than that from the corresponding equatorial phenylacetates,<sup>5a</sup> this result has little relevance to the stereochemistry of elimination from an equatorial phenylacetate. *trans*-2-Methylcyclohexyl phenylacetate exists very predominantly in the conformer with an equatorial phenylacetate; photoelimination gives roughly equal amounts of 1-methylcyclohexene (*trans* elimination) and 3-methylcyclohexene (*cis* and *trans* elimination). However, since the relative reactivities of secondary and tertiary hydrogens in this reaction are unknown, conclusions concerning the preferred stereochemistry of elimination from *trans*-4-*tert*-butylcyclohexyl phenylacetate are hazardous. Nevertheless, the relatively large amount of 1-methylcyclohexene observed is indicative of appreciable *trans* elimination from this system, and fully consistent with the results in this paper.
- (8) Alternatively, if alkene formation and/or reverse hydrogen transfer occur from isomeric biradicals, the overall stereochemistry will depend on the relative rates of axial and equatorial hydrogen abstraction, and on the relative rates of reverse hydrogen transfer and alkene formation from each biradical.
- (9) K. Dawes, J. C. Dalton, and N. J. Turro, *Mol. Photochem.*, **3**, 71 (1971); N. J. Turro and D. S. Weiss, *J. Am. Chem. Soc.*, **90**, 2185 (1968).
- (10) See, for example, L. M. Stephenson, P. R. Cavigli, and J. L. Partlett, *J. Am. Chem. Soc.*, **93**, 1984 (1971); P. J. Wagner and R. G. Zepp, *ibid.*, **94**, 287 (1972); F. D. Lewis, *ibid.*, **92**, 5602 (1970).

### Methoxycarbonylation of Substituted Benzenes. Effect of the Electronic Configuration of Carbon Radicals in Homolytic Substitutions

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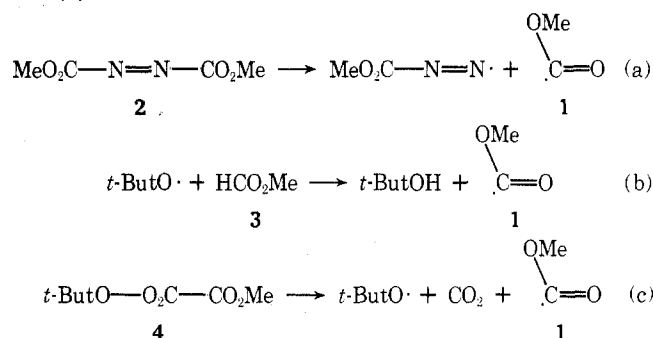
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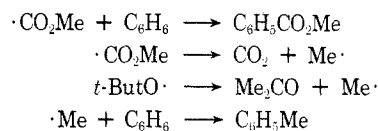
From studies of relative rates and isomer distributions in homolytic substitutions it emerged that one of the factors affecting the polar nature of carbon-centered radicals is the hybridization of the orbital carrying the unpaired electron; because the *s* orbital has higher electronegativity than the *p* orbital, it can be expected that the greater the *s* character of an orbital, the greater will be its electronegativity and hence the lower will be the nucleophilicity of the corresponding radical. Thus for carbon radicals the nucleophilicity should decrease along the series  $p > sp^3 > sp^2 > sp$ ; substituents linked to the radical carbon atom will modify the polar character and it can be expected that this effect should be more pronounced with  $\pi$  than with  $\sigma$  radicals. Simple alkyl and bridgehead polycyclic alkyl radicals present various degrees of nucleophilicity depending upon their structure, while acetylenic radicals are slightly electrophilic.<sup>1</sup> Radicals produced on carbon having an  $sp^2$  configuration, like phenyl,<sup>2</sup> vinyl,<sup>3</sup> and cyclopropyl,<sup>4</sup> present substantially similar neutral properties; only in the case in which they react with strongly deactivated substrates, like the protonated pyridines, some degree of nucleophilicity

can be evidenced, which, however, is much less pronounced than that of simple alkyl radicals.<sup>5</sup> The effect of substituents on  $\sigma$  radicals having an  $sp^2$  configuration has been studied in the case of the phenyl radical; the presence of electron-withdrawing or electron-donating groups makes the resulting aryl radical respectively more electrophilic or more nucleophilic than the phenyl radical.<sup>2</sup>

We report in this paper the results of a study on the methoxycarbonyl radical,  $\cdot CO_2Me$ , carried out with the aim of investigating the effect of the oxygen functions on the electronic nature of this radical, where the unpaired electron still occupies an  $sp^2$  orbital.<sup>6</sup> Alkoxy-carbonyl radicals have been formulated as reaction intermediates<sup>7–11</sup> and have been spectroscopically detected and studied;<sup>12,13</sup> indications that these radicals can effect homolytic substitutions on aromatic<sup>8</sup> and heteroaromatic<sup>14</sup> compounds have also been obtained. In the present investigation methoxycarbonyl radicals, **1**, have been produced in three different ways: (a) the thermal decomposition, at 130°C, of dimethyl azodicarboxylate (**2**); (b) the hydrogen abstraction from methyl formate (**3**) by *tert*-butoxy radicals, photolytically generated at room temperature,<sup>12</sup> and (c) the thermal decomposition,<sup>7</sup> at 65°C, of the methyl *tert*-butylperoxyoxalate (**4**).



Experiments carried out in benzene showed that the substitution product, the methyl benzoate, was formed in every case. Small quantities of toluene were also detected indicating that the radical **1** suffers fragmentation to  $\text{CO}_2$  and methyl radicals; in the cases b and c the methyl radicals can obviously be produced also from the *tert*-butoxy radicals.



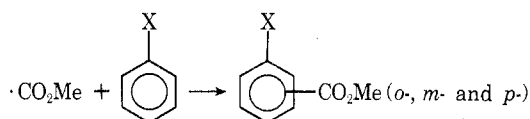
Diphenyl was also formed as a by-product in the reactions b and c, but not from the decomposition of **2**; the formation of this compound has already been reported from the decomposition of the ethyl *tert*-butylperoxyoxalate<sup>7</sup> and of the di-*tert*-butyl peroxide<sup>15</sup> in benzene and has been attributed to the production of phenyl radicals from the reaction of *t*-ButO $\cdot$  with benzene.<sup>16</sup> Finally, from the reactions b and c in benzene traces of dibenzyl were also detected as a result of the dimerization of the benzyl radicals produced from toluene; the dibenzyl obviously constituted the major reaction product when toluene was used as solvent for the studies on the relative reactivities described below. In the thermolysis of dimethyl azodicarboxylate (**2**), other unidentified products were also present and this reaction was therefore not employed for further studies.

In order to evaluate the polar character of methoxycarbonyl radicals, reactions were carried out in several differently substituted benzenes and in an equimolecular mixture of substituted benzenes and benzene; these experiments allowed the reactivity of the various nuclear posi-

Table I  
Distribution of Positional Isomers and Relative Reactivities<sup>a</sup> in Aromatic Substitutions of Benzene Derivatives by the Methoxycarbonyl<sup>b</sup> and the Phenyl Radicals

Registry no.	Substrate	·CO <sub>2</sub> Me				Yield, <sup>c</sup> %	C <sub>6</sub> H <sub>5</sub> ·			
		<i>o</i> -	<i>m</i> -	<i>p</i> -	<i>K</i>		<i>o</i> -	<i>m</i> -	<i>p</i> -	<i>K</i>
108-88-3	C <sub>6</sub> H <sub>5</sub> Me	56.0	26.9	17.1	1.45	10	60.9	25.1	14.0	1.58 <sup>d</sup>
98-06-6	C <sub>6</sub> H <sub>5</sub> CMe <sub>3</sub>		64.7	35.3	0.73	13	23.3	51.2	25.5	0.72 <sup>d</sup>
108-90-7	C <sub>6</sub> H <sub>5</sub> Cl	46.8	34.2	19.0	0.85	11	50.0	32.0	18.0 <sup>e</sup>	1.0 <sup>f</sup>
108-86-1	C <sub>6</sub> H <sub>5</sub> Br	45.1	37.3	17.6	0.86	10	53.5	31.5	15.0	1.39
93-58-3	C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> Me	35.1	17.9	47.0	2.2	16	57.0	17.5	25.5	1.77 <sup>g</sup>
98-86-2	C <sub>6</sub> H <sub>5</sub> COMe	40.0		60.0	2.3	15	58.0	13.1	28.9	2.2 <sup>h</sup>
100-47-0	C <sub>6</sub> H <sub>5</sub> CN	38.5	13.5	48.0	2.6	20	61.0	12.0	27.0	2.4 <sup>h,i</sup>
98-95-3	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	77.4		22.6	3.8	21	63.0	10.0	27.0	2.94 <sup>f</sup>

<sup>a</sup> Determined by GLC (see ref 18). <sup>b</sup> The data in the table refer to the ·CO<sub>2</sub>Me radical produced from methyl *tert*-butylperoxyoxalate, at 65°C. The following results were obtained from the photolysis of di-*tert*-butyl peroxide in the presence of HCO<sub>2</sub>Me, at room temperature (% ortho, meta, para, and *K* are given in order): C<sub>6</sub>H<sub>5</sub>CMe<sub>3</sub>, 0, 64.7, 35.3, 0.73; C<sub>6</sub>H<sub>5</sub>Cl, 45.8, 54.2 (*m* + *p*), 0.88; C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>Me, 37.0, 15.9, 47.1, not determined; C<sub>6</sub>H<sub>5</sub>CN, 41.6, 12.1, 46.3, 2.3. <sup>c</sup> Determined from reactions carried out on a preparative scale, as described for benzene. <sup>d</sup> G. Martelli, P. Spagnolo, and M. Tiecco, *J. Chem. Soc. B*, 1413 (1970). <sup>e</sup> C. Shih, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 2600 (1958). <sup>f</sup> D. H. Hey, S. Orman, and G. H. Williams, *ibid.*, 565 (1961). <sup>g</sup> D. H. Hey, F. C. Saunders, and G. H. Williams, *ibid.*, 3409 (1964). <sup>h</sup> This work. The phenylations of C<sub>6</sub>H<sub>5</sub>COMe and C<sub>6</sub>H<sub>5</sub>CN have been carried out by aprotic diazotization of aniline. <sup>i</sup> R. Dannley and E. Gregg, *J. Am. Chem. Soc.*, 76, 2997 (1954), reported 60.0, 10.0, 30.0, 3.7. <sup>j</sup> R. A. McClelland, R. O. C. Norman, and C. B. Thomas, *J. Chem. Soc., Perkin Trans. 1*, 578 (1972), reported the isomer ratio of 66, 3, 31 for the methoxycarbonylation of C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> from the reaction of lead tetraacetate with monomethyl oxalate.

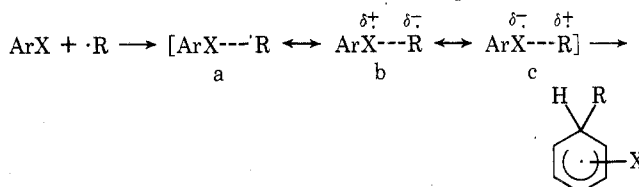


X = Me, CMe<sub>3</sub>, Cl, Br, CO<sub>2</sub>Me, COMe, CN, NO<sub>2</sub>

tions and the total reactivity of a given substrate relative to benzene to be easily determined by gas chromatography from the ratio of substituted methyl benzoates and methyl benzoate. The results are collected in Table I, where the available corresponding values for phenylation are also reported for comparison. The methoxycarbonylbenzenes were obtained in 10–20% yields, depending upon the nature of the aromatic substrate employed. These low yields of conversion are due to concurrent reactions given by the ·CO<sub>2</sub>Me radical in this system; one of the most important of these reactions is the above-mentioned fragmentation into carbon dioxide and methyl radicals.

The first characteristic of homolytic methoxycarbonylation which can be revealed from these results is that the degree of ortho substitution results in every case considerably lower than that observed with phenyl radicals; this is particularly evident with *tert*-butylbenzene, where the methyl *o*-*tert*-butylbenzoate is not formed at all, but is also observed with all the other substituents (with the exception of the nitro group) and is independent from their electronic properties. It can be assumed therefore that steric effects play an important role which can probably be attributed to unfavorable interactions between the substituents and the oxygen atoms linked to the entering carbon radical. This decrease of ortho substitution in respect to phenylation is accompanied by an increase in reactivity of both the meta and para positions in *tert*-butylbenzene; with the other substrates holding electron-withdrawing substituents, however, the meta substitution remains practically unaffected and an increase of the para isomer is observed in every case. With acetophenone and nitrobenzene the meta isomers were not formed at all. These results could be taken as an indication of the preference of the methoxycarbonyl radical for relatively electropositive nuclear positions as a result of a low nucleophilicity. As a matter of fact, over the range of aromatics listed in Table I, the values of the relative reactivities vary only by a factor of 4–5 but it seems indicative that all the substrates holding electron-withdrawing substituents present a slightly greater reactivity toward

the ·CO<sub>2</sub>Me than the phenyl radicals. It can be assumed that, in the transition state leading to the intermediate cyclohexadienyl radical, some charge transfer from the radical to the substrate or vice versa can take place.



Structure b will contribute with electrophilic radicals, while structure c will assume some importance with nucleophilic radicals. In the latter case the importance of the contribution of polar forms will depend upon the capability of substituents to stabilize the incipient positive charge, and it can be expected that with radicals having an sp<sup>2</sup> configuration, like the ·CO<sub>2</sub>Me, the charge separation will play a minor role and will occur only with benzene derivatives holding strongly electron-withdrawing substituents, being completely negligible with the others. It is interesting in this respect to note that in a recent investigation<sup>17</sup> on the polar properties of ethoxy carbonyl radicals, Minisci and co-workers have used protonated pyridines as substrates and have found that the 4-cyano- and 4-acetylpyridines have a reactivity of 18.7 and 6.7 relative to the 4-methylpyridine; owing to the greater electron affinity of these protonated heteroaromatic bases with respect to the benzene derivatives, the charge development in the transition state will assume a greater importance and, as a consequence, the nucleophilic properties of the carbon radicals will be more clearly evidenced.

The results here reported with benzene derivatives show that no substantial changes are produced on the electronic properties of the ·CO<sub>2</sub>Me radical by the presence of the oxygen functions; although a certain degree of nucleophilicity can be observed for this radical, its essential behavior does not significantly differ from those of other carbon radicals with similar hybridization, like phenyl, vinyl, and cyclopropyl.

### Experimental Section<sup>18</sup>

Monosubstituted benzenes used as substrates, methyl formate and di-*tert*-butyl peroxide, and several substituted methyl benzoates were commercial products; dimethyl azodicarboxylate<sup>19</sup> and

some substituted methyl benzoates were prepared as described in the literature. Methyl *tert*-butylperoxyoxalate was prepared according to the procedure reported<sup>7</sup> for the synthesis of the corresponding ethyl derivative.

**Decomposition of Dimethyl Azodicarboxylate in Benzene.** A solution of **2** (1 g) in benzene (20 ml) was heated in a sealed tube at 130° for 3 days. The GLC analysis of the reaction mixture showed the presence of toluene in small quantities, and methyl benzoate and other unidentified products in much higher quantities. The solvent was evaporated and the residue was chromatographed through a silica gel column using a mixture of pentane and ether (9:1) as eluent; methyl benzoate (0.25 g) was identified by comparison of its infrared spectrum with that of an authentic sample.

**Photolysis of Di-*tert*-butyl Peroxide in Benzene in the Presence of Methyl Formate.** A solution of di-*tert*-butyl peroxide (7.3 g) and methyl formate (12 ml) in benzene (200 ml) was put in a cylindrical vessel, surrounded by a water jacket, with a central neck from which the lamp (Hanau P.L. 368) was immersed in the solution. The mixture was magnetically stirred and irradiated for 48 hr and then analyzed by GLC; the main reaction product was methyl benzoate, which was accompanied by small quantities of diphenyl and dibenzyl. The residue after evaporation of benzene was chromatographed under the conditions described above; diphenyl and dibenzyl were eluted first and were identified by comparison with authentic samples. The following fractions contained methyl benzoate (1.3 g).

**Decomposition of Methyl *tert*-Butylperoxyoxalate in Benzene.** A solution of **4** (3.9 g) in benzene (100 ml) was kept at 65° for 48 hr; analysis by GLC showed the presence of methyl benzoate, diphenyl, and traces of dibenzyl. The solvent was evaporated and the residue chromatographed as described above; diphenyl, dibenzyl, and methyl benzoate (0.5 g) were identified by comparison with authentic samples.<sup>20</sup>

**Determination of Isomer Distributions and Relative Reactivities for the Methoxycarbonylation.** A. Solutions (0.1 M) of **4** in an equimolecular mixture of benzene and monosubstituted benzenes were put in a sealed 2-ml glass tube and kept at 65° for 72 hr and then directly analyzed by GLC without manipulation. Three independent experiments were carried out in every case; the results were reproducible in every case and the averaged values are collected in Table I.

B. Solutions of di-*tert*-butyl peroxide (0.01 mol) and methyl formate (0.01 mol) in equimolecular mixtures of benzene and monosubstituted benzenes (4 ml) were put in a stoppered 5-ml quartz conical flask and irradiated for 72 hr. The reaction mixtures were analyzed as in A. The results are reported in Table I.

When toluene was used as solvent the main reaction product was dibenzyl in both cases. Competitive experiments between benzene and methyl benzoate could not be carried out directly and the relative reactivity of the C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>Me was therefore determined indirectly using equimolecular mixtures of C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>Me and C<sub>6</sub>H<sub>5</sub>CN. The relative reactivity of C<sub>6</sub>H<sub>5</sub>CN was obtained from the direct competition with benzene and confirmed from the determination of its reactivity relative to acetophenone.

The substituted methyl benzoates formed were also isolated by a combination of column chromatography and preparative GLC from reactions carried out on preparative scale and identified by comparison with authentic samples.

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**Registry No.**—**1**, 16481-04-2; **2**, 2446-84-6; **4**, 57031-51-3; di-*tert*-butyl peroxide, 110-05-4.

## References and Notes

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- (16) The rather unfavorable process of hydrogen abstraction from benzene may induce suggestion of an alternative way of formation of biphenyl through the addition of the *tert*-butoxy radical to the benzene followed by dimerization of the resulting cyclohexadienyl radical and nonradical fragmentation of the dimers to *tert*-butyl alcohol and diphenyl; a similar mechanism has already been postulated to explain the formation of diaryls in reactions involving oxygen-centered radicals.<sup>1a,b</sup>
- (17) A. Clerici, F. Minisci, and O. Porta, *J. Chem. Soc., Perkin Trans. 2*, 1699 (1974).
- (18) Gas chromatographic analyses were performed on a Hewlett-Packard 5700 instrument equipped with a flame ionization detector. Calibrations for area response differences between methyl benzoate and isomeric monosubstituted methyl benzoates were effected for each reaction using the pure samples. The columns used, all on Aeropak 30 (100–120 mesh), follow: 10% Silicone GE XE-60 for the methyl derivatives, 5% Bentone 34 for the halogeno derivatives, and 10% LAC 728 for all the other substituted methyl benzoates; in several cases the results were confirmed using 5% FFAP and 5% SE-30 columns.
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