3. In the nitration of nitramine anions by nitronium tetrafluoroborate, the opposite effect is observed with respect to the influence of the salt cation on the outcome of the reaction, i.e., bulky, soft cations favor O-nitration.

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RADICAL REACTION OF ACETONE WITH AROMATIC COMPOUNDS

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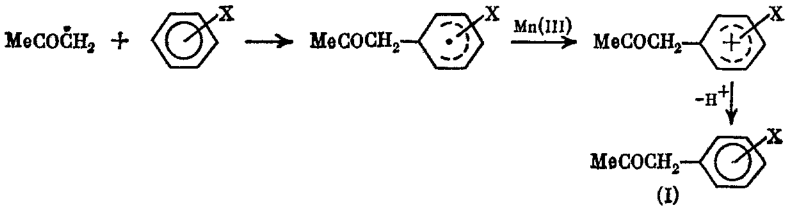
Substitution of the aromatic nucleus by alkyl radicals has been extensively investigated [1-3]. The reaction of aromatic compounds with functionally substituted alkyl radicals has been investigated only in the cases of $\dot{C}H_2COMe$ [4], $\dot{C}H_2COOH$ [5-8], $\dot{C}H_2COOEt$ [9], $\dot{C}H_2NO$ [10], and the isomeric composition of the products has been examined quantitatively only in the carboxymethylation of toluene [5, 6] and anisole [7, 8].

We have examined the reaction of anisole, toluene, chlorobenzene, ethyl benzoate, benzonitrile, and thiophene with $\dot{C}H_2COMe$ radicals, generated in the redox system acetone–Mn(OAc)$_3$–AcOH at 70°:

$$MeCOMe + Mn(OAc)_3 \rightarrow MeCO\dot{C}H_2 + Mn(OAc)_2 + AcOH$$

Reaction of $\dot{C}H_2COMe$ with benzene derivatives affords benzyl ketones (I) in yields of 30-80% based on Mn(III).



X = CH_3O (a), CH_3 (b), Cl (c), COOEt (d), CN (e)

2,5-Hexanedione, formed by the recombination of $\dot{C}H_2COMe$ radicals, is obtained in yields of only 3-4% based on Mn(III). The yield of (I) decreases regularly with decreasing electronegativity of the substituents in the benzene ring (Table 1) owing to the electrophilic character of the $\dot{C}H_2COCH_3$ radical. Similar behavior has been observed in the radical carboxymethylation and nitromethylation of monosubstituted benzenes [7, 10].

The benzyl ketones (I) are thermally stable except for the o isomer (Id), which under GLC conditions undergoes partial conversion to 3-methylisocoumarin. This was allowed for in

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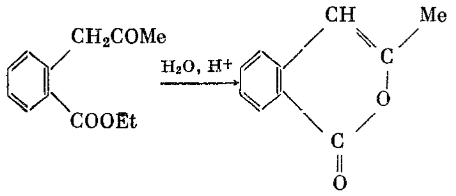
analyzing the products of the reaction of acetone with PhCOOEt. 3-Methylisocoumarin is also obtained by hydrolysis of (Id):

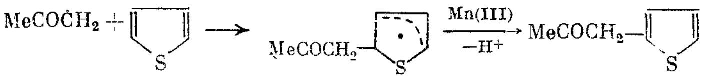


Alkylation of substituted benzenes with the $\dot{C}H_2COMe$ radical affords predominantly the o isomer (cf. Table 1), behavior which is typical of the homolytic substitution of benzenoid compounds either by unsubstituted alkyl radicals, or by $\dot{O}R$, $\dot{O}COR$, $\dot{C}H_2COOH$, $\dot{C}H_2NO_2$ [1-10]. The ratios of the m and p isomers formed are highly dependent upon the polar properties of the radical.

Reaction of $\dot{C}H_2COCH_3$ with anisole, toluene, or chlorobenzene gives a m/p isomer ratio of 0.5-1 in the cases of (Ia-c) (cf. Table 1), which is substantially lower than that for the radical methylation of these compounds (1.6-3, [3]), but differs little from the isomer ratio for the radical carboxymethylation of [5-8] and hydroxylation [2] of these monosubstituted benzenes, i.e., $\dot{C}H_2COCH_3$ is similar in electrophilicity to the radicals $\dot{C}H_2CO_2H$ and $\dot{O}H$. This behavior is not seen with ethyl benzoate and benzonitrile, for which the products (Id) and (Ie), like the products of the radical methylation of benzonitrile [11, 12], possess the same m/p ratio (0.2-0.4). In these compounds, the orientation of homolytic substitution is determined primarily by the stabilizing effect of the CO_2Et and CN groups in the formation of the σ complex of the radical with the aromatic nucleus [1-3].

The electrophilic character of the $\dot{C}H_2COMe$ radical is apparent from the fact that it does not react with protonated bases (pyridine, methylpyridines, and quinoline, in AcOH), in contrast to the nucleophilic alkyl and acyl radicals and the $\dot{C}O_2Me$ radical [13, 14].

The Mn(III) acetate-initiated reaction of acetone with thiophene affords exclusively 1-(2-thienyl)propan-2-one



In this case, the site of reaction (the α carbon atom of the ring) is the same as that in the thiiylation and phenylation of thiophene [15].

EXPERIMENTAL

PMR spectra were recorded in CCl_4 on a Varian DA-60-IL or a Tesla BS-487C spectrometer. IR spectra were obtained as thin layers on a UR-20 instrument. GLC was carried out on a LKhM-8MD/5 instrument, using a flame-ionization detector and 200 × 0.3 mm columns containing 15% PEG on Chromosorb W, 10% XE-60 on Chromaton N-AW HMDS, and on a glass capillary column (70 × 0.6 mm) with PEG-40M.

The $Mn(OAc)_3 \cdot 2H_2O$ was obtained as in [16]. The content of Mn(III), according to cerimetric analysis, was 19.6% (calculated 20.5%).

The aromatic starting materials were purified by distillation. The ratios of the isomeric 1-arylpropan-2-ones were determined by GLC and PMR, using as standards samples of m- and p-(I) synthesized from the substituted benzaldehydes according to [17] (Table 2).

Reaction of Acetone with Aromatic Compounds (general method). Acetone (1 mole), 0.25 mole of the aromatic compound, 0.05 mole of $Mn(OAc)_3 \cdot 2H_2O$, and 50 ml of AcOH were shaken in a sealed ampul at 70° until the brown color of the Mn(III) had disappeared (1-5 h). The reaction mixture was analyzed by GLC. For the preparative isolation of the products, the mixture was filtered, the excess of starting materials distilled off, and the residue poured into water and extracted with ether. The extract was washed with water, dried, and distilled.

TABLE 1. Homolytic Substitution in the Aromatic Ring of Monosubstituted Benzenes, C_6H_5X, by $\dot{C}H_2COCH_3$ Radicals Generated in the Redox System Acetone–$Mn(OAc)_3$–AcOH at 70°

X	Yield of (I), %*	Isomeric composition of the homolytic substitution products (I), %		
		ortho	meta	para
OMe	80	85	5	10
Me†	65	55	21	24
Cl	55	74	9	17
CO_2Et	45	52	14	34
CN	30	74	8	18

*Based on Mn(III).

†In the reaction with toluene, the 2-oxopropyl radicals attack the methyl group to some extent (20%), and the resulting benzyl radicals are oxidized by Mn(III) acetate to benzyl acetate [4].

TABLE 2. 1-Arylpropan-2-ones $XC_6H_4CH_2COMe$

X	bp of the mixed isomers (p, mm Hg)	PMR spectrum (δ, ppm)				
		CH_3CO		CH_2CO		X(H)
		ortho	meta + para	ortho	meta + para	
OMe	128–130(15)	1,87	1,87	3,40	3.33	3,55
Me	104–105(13)	2,18	2,09	3,45*	3,38†	1,88
Cl	67–68(1)	2,05	2.05	3,70	3.52	–
CO_2Et	128–130(1)	2,04	1,90	3,88	3,50	1,2(CH_3) 4,1(CH_2)
CN	118–120(1)	2.10	2,05	3,88	3,68	–

*ortho + meta.

†para.

1-(2-Thienyl)propan-2-one. This was obtained from acetone and thiophene by the method given above, yield 20% on Mn(III), bp 82° (5 mm) [18]. PMR spectrum (δ, ppm): 2.2 s (CH_3), 3.57 s (CH_2), 6.67 (H^3), 6.7 (H^4), 6.98 (H^5), J_{3-4} = 3.5, J_{4-5} = 5.1, J_{3-5} = 0.9 Hz. IR spectrum (ν, cm^{-1}): 860 (ring), 1360 (CH_3CO), 1425 (CH_2–CO), 1725 (C=O).

Hydrolysis of Mixtures of Isomers of 1-(Ethoxycarbonylphenyl)propan-2-ones. The mixture of o-, m-, and p-1-(ethoxycarbonylphenyl)propan-2-ones (4.2 g), obtained by the method given above (composition, cf. Table 1) was hydrolyzed [19], and the reaction mixture was diluted with water and shaken with ether. The aqueous layer, containing the sodium salts of the 1-(ethoxycarbonylphenyl)propan-2-ones, was separated, and the ether extract was dried and distilled to give 1.4 g (80%) of 3-methylisocoumarin [20], bp 135° (1 mm); mp 70° (from hexane). PMR spectrum (δ, ppm): 2.13 s (CH_3), 5.98 d (C=CH), 7.65 m (C_6H_4). IR spectrum (ν, ppm): 760 (aromatic ring), 1485,1570, 1610, 1075, 1245 (OC=), 1350 (CH_3), 835, 1660 (C=CH), 1725 (C=O).

CONCLUSIONS

1. Anisole, toluene, chlorobenzene, ethyl benzoate, and benzonitrile have been substituted in the aromatic nucleus by the $CH_3CO\dot{C}H_2$ radical, generated in the redox system acetone–$Mn(OAc)_3$–AcOH at 70°. The acetonyl radical displays electrophilic properties in this reaction.

2. The radical reaction of acetone with thiophene proceeds selectively at the α-carbon atom of the thiophene ring to form 1-(2-thienyl)propan-2-one.

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