2,4-Dimethyl-3-ethoxycarbonylpyrrole (III), m.p. 75.0–75.2° (lit.[10] m.p. 75–76°), was prepared by the hydrolysis of 2,4-dimethyl-3,5-diethoxycarbonylpyrrole and decarboxylation of the resulting carboxylic acid as described by Knorr.[10]

2,2′-(3,3′,5,5′-Tetramethyl-4,4′-diethoxycarbonyl)dipyrrylmethene (I) was synthesized through the condensation of 7.80 g. of 2-formyl-3,5-dimethyl-4-ethoxycarbonylpyrrole and 6.68 g. of 2,4-dimethyl-3-ethoxycarbonylpyrrole in the presence of 4.66 ml. of 48.3% hydrobromic acid in alcohol. A solution of the pyrrole in 50 ml. of absolute ethanol was added dropwise to a stirred, hot solution of the aldehyde and acid in 150 ml. of absolute alcohol during a period of 30 min. and the resulting mixture was refluxed for an additional 40 min. The mixture was cooled in an ice bath and 12.1 g. of the crude hydrobromide was collected. After two recrystallizations from a mixture of chloroform and cyclohexane 11.1 g. (65%) of the purified methene hydrobromide was obtained as red crystals, having a blue reflex, m.p. 212.0–213.5° dec. Portions of the purified methane hydrobromide in chloroform were shaken with an excess of ammonia in the same solvent. After filtering the resulting mixtures and evaporating the solvent, the residues were combined. The product was dissolved in a little chloroform and chromatographed on a column of Woelm alumina (nonalkaline, activity grade II). The middle fraction of the bright yellow ether eluate therefrom was collected, the solvent was evaporated, and the residue rechromatographed as before. Crystallization of the chromatographed product from acetone yielded beautiful, long, red needles of the methene (I), m.p. 186.8–188.1° dec. (lit.[11] m.p. 190°).

2,2′,2″-(3,3′,3″,5,5′,5″-Hexamethyl-4,4′,4″-triethoxycarbonyl)tripyrrylmethene (IV) was synthesized by the permanganate oxidation of the corresponding tripyrrylmethane[12] in different runs. In a typical case the methene, m.p. 215.0–216.5° dec. (lit.[12] m.p. 210.7–211.6°), was obtained in a yield of 63%.

Acknowledgment.—We are especially indebted to Dr. Norman E. Albert for suggestions and assistance with certain phases of this investigation.

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A New Synthesis of Methyl Aryl Sulfones

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Methyl aryl sulfones have been prepared by several methods[1-4] all of which have limitations. We have now found a new approach involving heating of an aromatic compound with methanesulfonic anhydride.

$$RH + (CH_3SO_2)_2O \longrightarrow RSO_2CH_3 + CH_3SO_3H$$

The data, summarized in Table I, indicate the scope of this procedure. It is evident that the CH_3SO_2 group enters primarily in the *para* position, although toluene also forms considerable *ortho* isomer. The structures indicated for new compounds were not proved, but for those derived from 1,4-xylene and from 1,2,4,5-tetramethylbenzene (compounds **3** and **6**), only one structure is possible if no rearrangement is assumed during reaction.

This procedure also has limitations under the conditions used. Use of pure reagents, especially with polymethylated benzenes, obviated tar formation, as did also use of fresh methanesulfonic anhydride, which deteriorates upon standing. Use of tetrachloroethylene as reaction solvent at reflux (b.p. 121°) generally gave a much cleaner reaction than employing an excess of the compound treated, as did also reduction of the standard reaction time of sixteen hours in a number of cases, as indicated in Table I. Less reactive and more volatile compounds, such as toluene and chlorobenzene, require longer periods of reaction. The following compounds did not react: 1,2-dichlorobenzene, phenyl benzoate, phenyl methanesulfonate, triphenyl phosphate, 2-nitroanisole, and 2-methoxybenzoic acid. Although anisole reacted normally, phenetole gave a good yield of phenyl methanesulfonate, as did also phenol and phenyl acetate. Intractable tars resulted from 1,2-xylene, 1,2,4-trimethylbenzene, pentamethylbenzene, phenoxyacetic acid, thioanisole, 2-methylanisole, and 3-methylanisole. Naphthalene, ethylbenzene, diphenyl oxide, and 2-phenylanisole appeared to react, but pure products could not be isolated. Infrared analysis of the product made from naphthalene showed it to comprise largely a mixture of the α- and β-methylsulfonyl derivatives. Where applicable, however, the present method appears simple and conveni-

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[1] C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 660 ff.

[2] A. Schoeberl and A. Wagner, "Houben-Weyl Methoden der Organischen Chemie," 4th Ed., Vol. IX, Thieme, Stuttgart, 1955, p. 227 ff.

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TABLE I. METHYL ARYL SULFONES

No.	Compound reacted	Substituted methanesulfonylbenzene formed	Reflux time, hr.	Yield, %[a]	M.p., °C.		% Sulfur	
					Lit.	Found[d]	Theor.	Found
1	Toluene	2- and 4-Methyl	20	53[b]	88[e]	88	18.8	18.8
2	1,3-Xylene	2,4-Dimethyl	16	75	55[f]	56	17.4	17.5
3	1,4-Xylene	2,5-Dimethyl	8	42	[g]	45	17.4	17.5
4	1,2,3-Trimethylbenzene	3,4,5-Trimethyl	16	82[c]	[g]	121	16.2	16.6
4a	1,2,3-Trimethylbenzene	2,3,4-Trimethyl			[g]	97	16.2	16.3
5	1,3,5-Trimethylbenzene	2,4,6-Trimethyl	8	75	130[f]	131	16.2	16.4
6	1,2,4,5-Tetramethylbenzene	2,3,5,6-Tetramethyl	4	60	[g]	133	15.1	15.1
7	Chlorobenzene	4-Chloro	24	10	98[f]	97	16.6	16.7
8	Biphenyl	4-Phenyl	16	40	145[h]	144	13.8	13.8
9	Anisole	4-Methoxy	16	70	120[i]	120	17.2	17.3
10	4-Methylanisole	2-Methoxy-5-methyl	16	20	87[j]	86	16.0	15.9
11	1,3-Dimethoxybenzene	2,4-Dimethoxy	8	50	[g]	105	14.8	15.1

[a] Average yields of fair quality crude. [b] Over half 2-isomer by infrared analysis. [c] Total for two isomers. [d] Uncorrected. [e] The 4-isomer of ref. 4. [f] J. Troeger and C. Budde, *J. prakt. Chem.*, (2) **66**, 149 (1902). [g] New compound. [h] A. Mangini, L. Ruzzier, and A. Tundo, *Bull. Sci. fac. chim. ind. Bologna*, **14**, 81 (1956); *Chem. Abstr.*, **52**, 19446 (1958). [i] Ref. 6. [j] D. T. Gibson and S. Smiles, *J. Chem. Soc.*, 2391 (1923).

ent and, in some cases, gives good yields where established methods give poor yields or no product at all. Thus, 1,3,5-trimethyl-benzene yields 10% or less of the methylsulfonyl compound by the Friedel–Crafts procedure[4] or by heating the hydrocarbon with methanesulfonic acid,[5] and anisole forms only phenyl methanesulfonate by the Friedel–Crafts approach.[4]

Experimental

Typical Procedure.—Anisole (6.0 g., 0.056 mole), methanesulfonic anhydride (9.0 g., 0.052 mole) (used as obtained from Distillation Products Industries) and tetrachloroethylene (50 ml.) were refluxed briskly for 16 hr. The reaction mixture was extracted with two 25-ml. portions of warm water to remove methanesulfonic acid and unchanged anhydride. The aqueous extracts were then combined, cooled, and extracted with ether to recover any dissolved product. The ether extract and the tetrachloroethylene solution of product were combined and evaporated to constant weight on a steam bath in a stream of air. The crude product solidified upon cooling and stirring. It was recrystallized from *n*-butyl alcohol or from hot water. A mixture melting point with material prepared by an alternative procedure[6] showed no depression.

The compounds in Table I have infrared spectra consistent with the structures indicated. The sulfone group showed absorption at 1160 to 1120 and at 1350 to 1300 cm.$^{-1}$ and the ether grouping at 1270 to 1230 cm.$^{-1}$.

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[5] M. S. Grant and W. J. Hickinbottom, *J. Chem. Soc.*, 2520, (1959).

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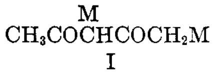
Communications TO THE EDITOR

Metallic Ion Effect in Mono- *vs.* Dialkylation of Dipotassio Acetylacetone with Alkyl Halides[1]

Sir:

Although dipotassio acetylacetone (I, M = K) previously has been alkylated with molecular equivalents of several alkyl halides to form the corresponding monoalkyl derivatives II,[2,3] the formation also of the dialkyl derivative III has been observed only with *n*-octyl bromide.[3]



$$\overset{M}{CH_3COCHCOCH_2M}$$

I

$CH_3COCH_2COCH_2R$

II

$RCH_2COCH_2COCH_2R$

III

A more thorough study of such reactions has now revealed that dialkylation generally accompanies monoalkylation of dipotassio I (M = K) and, more significantly, that disodio acetylacetone (I, M = Na) undergoes almost exclusively monoalkylation.

The dialkali salts I (M = K or Na), prepared from acetylacetone and two molecular equivalents of the corresponding alkali amide in liquid ammonia,[2,3] were treated during ten–twelve minutes with approximately molecular equivalents of methyl, *n*-butyl, and *n*-octyl halides.

Although the mono- and dibutylation products and especially the mono- and dimethylation products are difficult to separate by distillation, the mixtures were readily resolved by vapor phase chromatography. However, the mono- and dioctylation products were separated easily by distillation as described elsewhere.[3] The results are summarized in Table I, in which yields are given for duplicate runs. The dialkylation yields are calculated on the basis of the stoichiometry shown in Scheme A.

TABLE I

ALKYLATIONS OF DIALKALI SALTS I WITH ALKYL HALIDES TO FORM MONO- AND DIALKYLATION PRODUCTS OF II AND III

Dialkali salt I, M	Alkyl Halide	II Yield, %	III Yield,[a] %
Potassium	Methyl iodide	35, 46	26, 18
Sodium	Methyl iodide	59, 65	<1, <4
Potassium	*n*-Butyl bromide	43, 53	16, 14
Sodium	*n*-Butyl bromide	67, 73	<1, <1
Potassium	*n*-Octyl bromide	51, 57	14, 14
Sodium	*n*-Octyl bromide	66, 79	<2, <2

[a] Yield calculated based on the stoichiometry shown in Scheme A.

The identities of the monobutylation, monooctylation, and dioctylation products were established as described previously.[3] The identities of the monomethylation (from sodio experiment) and dibutylation products were established by comparison of their copper chelates with authentic samples.[4,5] The dimethylation product was compared by v.p.c. with authentic 3,5-heptanedione.[5] In all three cases monoalkylation had occurred at the 1-position and dialkylation at the 1,5-positions of 2,4-pentanedione. Incidentally, previous studies[3,6] of the alkylation of unsymmetrical β-diketones indicated that the isomeric 1,1- and 1,3-dialkylation products IV and V, respectively, would not be expected.

$R_2CHCOCH_2COCH_3$

IV

$$RCH_2CO\overset{R}{CH}COCH_3$$

V

Table I shows that a substantial amount of dialkylation was obtained in each example involving the dipotassio salt of I, while little or none was obtained when the disodio salt was employed. The significance of these results is twofold. First, the alkylation of the sodio salt must clearly be recommended for most

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[1] Supported in part by the National Science Foundation (NSF-G14527).

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[4] J. T. Adams and C. R. Hauser, *J. Am. Chem. Soc.*, **67**, 284 (1945).

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[6] T. M. Harris and C. R. Hauser, *ibid.*, **81**, 1160 (1959).

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