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).

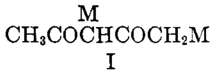
[6] C. M. Suter and H. L. Hansen, *J. Am. Chem. Soc.*, **54**, 4101 (1932).

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]


$CH_3CO\overset{M}{C}HCOCH_2M$

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


$RCH_2CO\overset{R}{C}HCOCH_3$

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).

[2] C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **80**, 6360 (1958).

[3] R. B. Meyer and C. R. Hauser, *J. Org. Chem.*, **25**, 158 (1960).

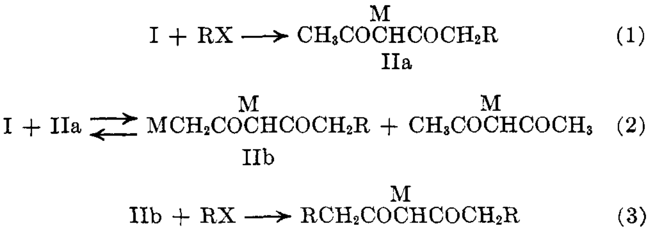
[4] J. T. Adams and C. R. Hauser, *J. Am. Chem. Soc.*, **67**, 284 (1945).

[5] J. T. Adams and C. R. Hauser, *ibid.*, **66**, 1220 (1944).

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

[7] S. D. Work and C. R. Hauser, *J. Org. Chem.*, **28**, 725 (1963).

synthetic purposes. Second, these observations have considerable theoretical significance. Although metallic cation effects have been observed before in the acylation[7] and aldol-type condensation[8] of β-diketone dianions, this represents the first observation of such an effect in alkylation reactions. The previously observed[7,8] cation effects involved ionization of the carbonyl reagent by the dianion. The present effect appears to involve a proton transfer between dianion I and alkylation product IIa (Scheme A).



$$\text{I} + \text{RX} \longrightarrow \underset{\text{IIa}}{\text{CH}_3\text{CO}\overset{\text{M}}{\text{C}}\text{HCOCH}_2\text{R}} \qquad (1)$$

$$\text{I} + \text{IIa} \rightleftharpoons \underset{\text{IIb}}{\text{MCH}_2\text{CO}\overset{\text{M}}{\text{C}}\text{HCOCH}_2\text{R}} + \text{CH}_3\text{CO}\overset{\text{M}}{\text{C}}\text{HCOCH}_3 \qquad (2)$$

$$\text{IIb} + \text{RX} \longrightarrow \text{RCH}_2\text{CO}\overset{\text{M}}{\text{C}}\text{HCOCH}_2\text{R} \qquad (3)$$

SCHEME A

The difference in the results obtained with potassium and with sodium might be explained on the basis that the ratio of the rates of alkylation (step 1) to proton exchange (step 2) is somewhat less with the potassio salts (M = K) than with the sodio salts (M = Na). This permits a significant build up of potassio IIb, which undergoes alkylation (step 3). This hypothesis is supported by the observation that with potassium, but not with sodium, the rate of addition of the alkyl halide affects the ratio of mono- and dialkylation observed. Thus, when *n*-butyl bromide was added to I (M = K) over a few seconds, considerably less dialkylation was observed than when the halide was added over two hours. In contrast, with disodio acetylacetone (I, M = Na) no more than a trace of the dialkylation product could be observed even when the *n*-butyl bromide was added over a two-hour period. Further study of this effect is in progress.

(8) R. J. Light and C. R. Hauser, *J. Org. Chem.* **26**, 1716 (1961).

(9) National Science Foundation Cooperative Fellow, 1961–1962; James B. Duke Fellow, 1962–1963.

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RECEIVED APRIL 10, 1963

Hydrogenation of Aromatics with Complex Metal Catalysts

Sir:

The preparation of hydrogenation catalysts by the borohydride reduction of transition metal salts[1] or by the aluminum trialkyl reduction of organic soluble metal salts[2] has been described recently. Both of these catalyst systems are effective for the hydrogenation of olefins, the latter presumably by addition of transition metal hydrides to the double bond followed by hydrogenolysis of the resultant transition metal alkyl. We now wish to report the facile hydrogenation of aromatic nuclei by transition metal complex catalysts. For such systems, the hydride addition mechanism is probably not valid.

TABLE I

HYDROGENATION OF AROMATICS WITH COMPLEX NICKEL CATALYSTS[a]

	Temp., °C.	Time, hr.	Products	Yield, %
Benzene	150–190	0.2	Cyclohexane	100
o-Xylene	150	3.7	*cis*-1,2-Dimethylcyclohexane	65.5
			trans-1,2-Dimethylcyclohexane	34.5
Phenol	150–160	0.2	Cyclohexanol	92.1
			Cyclohexanone	5.2
Pyridine	150–174	3	Piperidine	98
Dimethyl terephthalate	200	3.5	Dimethyl hexahydroterephthalate	100
Dimethyl phthalate	150	0.4	Dimethyl hexahydrophthalate	100
Naphthalene	210	18	Tetralin	84
			Decalin	13

[a] Initial pressure, 1000 p.s.i., 0.3–5.0 mole % nickel.

When triethyl aluminum is added to nickel(II) 2-ethylhexanoate dissolved in a noncomplexing organic solvent such as heptane or benzene, an exothermic reaction occurs with the evolution of a gas which is greater than 95% ethane. The ultimate amount of gas evolution and the highest catalytic activity occurs at aluminum:nickel ratios of 3–4:1. The black reaction mixture is not separated by ultracentrifugation and is neither pyrophoric nor paramagnetic. This solution is an extremely effective catalyst for the hydrogenation of aromatics. For example, addition of 1000 p.s.i. of hydrogen to a benzene solution containing 0.3 mole % nickel gave complete hydrogenation in one-fifth hour, temperature increasing from 150–190°. In comparison, hydrogenation of benzene with a like amount of nickel as 49% nickel on kieselguhr required eight hours under the same conditions. The hydrogenation of other aromatics is given in Table I. In general, the hydrogenations (Table I) proceed more readily than the reported[3] hydrogenations with Raney nickel or other supported nickel catalysts. Surprisingly, nitrobenzene or *p*-nitrophenol, so readily reduced by Raney or supported nickel catalysts, are relatively inert to hydrogenation with the present complex nickel catalysts. Other transition metal complex catalysts can be prepared similarly. Catalytic activity toward benzene hydrogenation decreases in the order Ni ≥ Co > Fe > Cr > Cu.

Catalytic activity is very dependent on the associated anion or other electron donors present. While any carboxylate salt gives active catalysts, it is most convenient to use the soluble 2-ethylhexanoates or commercially available naphthenates. Halides give poor catalysts and the hydrogenation of benzene is

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(1) (a) R. Paul, P. Buisson, and N. Joseph, *Compt. rend.*, **232**, 627 (1951); (b) H. C Brown and C. A. Brown, *J. Am. Chem. Soc.*, **84**, 1493–1495 (1962).

(2) M. F. Sloan, A. S. Matlack, and D. S. Breslow, reported at 14th Delaware Science Symposium, Delaware Section of the American Chemical Society, University of Delaware, Newark, Del., February 23, 1963.

(3) (a) H. Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, Wis., 1937; (b) H. A. Smith, in "Catalysis," Vol. V, P. H. Emmett, Ed., Reinhold Publishing Co., New York, N. Y., 1957, p. 175.

poisoned by triphenylphosphine. A similar sensitivity to electron donors has been reported in the oligomerization behavior of dienes with soluble nickel(0) catalysts.[4]

We do not believe the active catalyst is the free metal, but rather the metal hydride whose existence would be fleeting at the temperatures employed or a zero-valent metal π-complex solubilized by organic ligands. In support of the latter, Wilke[5] has reported that reaction of nickel acetylacetonate and aluminum trialkyls in the presence of 1,5-cyclooctadiene gives the stable crystalline complex, *bis*-1,5-cyclooctadiene nickel(0).

(4) G. Wilke, *Angew. Chem.*, **75**, 10 (1963).

(5) G. Wilke, B. Bogdanovic, P. Heimbach, M. Kroner, and E. Muller, *Advan. Chem. Ser.*, **34**, 137 (1962).

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RECEIVED APRIL 29, 1963