temperature rose to 24°, the mixture was hydrolyzed and worked up as described in the previous preparations. Distillation data are given in Table IV.

Fraction 4 corresponds to a 45% yield (based on the Grignard reagent) of ethylene diisoamylborinate. For analysis the fraction was redistilled to give 27.30 g. of material boiling at 147° (0.48 mm.) to 151° (0.65 mm.), $n^{25}{}_D$ 1.4378, $d^{25}{}_4$ 0.8267.

Anal. Calcd. for $C_{22}H_{48}O_2B_2$: C, 72.14; H, 13.21; equiv. wt., 183. Found: C, 72.06; H, 12.72; equiv. wt., 181 ± 4

Hydrolysis of fraction 1 yielded 3.53 g. (3.4% yield of 3-methylbutaneboronic acid based on the Grignard reagent) of a white, solid, boronic acid, which after two recrystallizations from toluene and drying over 65% sulfuric acid in a nitrogen atmosphere melted at 64–69°. The equivalent weight of this material determined by titration in the presence of mannitol was 115, that calculated for 3-methylbutaneboronic acid, 116. Reported values for the melting point of this acid are in disagreement. Krause and Nitsche claimed the melting point to be 169°,[12] and Khotinsky and Melamed reported a value of 101°.[13]

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[12] E. Krause and R. Nitsche, *Ber.*, **54**, 2784 (1921).

[13] E. Khotinsky and M. Melamed, *ibid.*, **42**, 3090 (1909).

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC COMPANY]

Molecular Compounds. IV. The Effect of Substituents on the Equilibrium Constant for Complex Formation

BY SIDNEY D. ROSS, MORTON BASSIN AND IRVING KUNTZ

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The equilibrium constants for complex formation between anthracene and a series of 1-substituted-2,4,6-trinitrobenzenes in chloroform at 23.8 ± 0.1° and between 1,3,5-trinitrobenzene and a series of substituted anilines in absolute ethanol at 25.0 ± 0.1° have been determined spectroscopically. Data available in the literature have been used to calculate the equilibrium constants for complexing between 2,4-dinitrochlorobenzene and a series of substituted anilines in absolute ethanol at both 35.0 and 45.0°. The magnitudes of the equilibrium constants within each series cannot be explained by considerations of potential energy alone, and estimation of the thermodynamic constants for the 2,4-dinitrochlorobenzene–substituted aniline equilibria shows that kinetic energy changes accompanying complex formation are not uniformly the same in this series of compounds.

In the previous papers in this series[1] measurements of the extent of molecular compound formation by the spectroscopic method were self-consistent and adequately encompassed by the Mulliken theory.[2] In accord with this theory, molecular compound formation results from donor–acceptor interaction, resulting in the formation of a charge-transfer type intermolecular bond. The specific interaction may be represented as

$$A + B \rightleftharpoons (A\ B) \longleftrightarrow (A\cdot^{-} - \cdot B^{+})$$

the intermolecular bonding in the complex being due to the resonance indicated above, although the contribution of the ionic structure is undoubtedly small.

On the basis of this theory it would be anticipated that complex formation would be favored by electron-donating substituents in the donor molecule and electron-withdrawing substituents in the acceptor molecule. In the present paper we wish to report the effect of systematic substitution of both the donor and acceptor molecules on the equilibrium constant for complex formation.

The most successful correlation of structure and reactivity is due to Hammett[3] and applies to a large number of side chain reactions of *meta* and *para* substituted aromatic compounds. For such reactions

$$\log (k/k^0) = \sigma\rho$$

where k^0 and k are the rate or equilibrium constants for the unsubstituted and substituted aromatic compound, respectively, ρ is a constant characteristic of the reaction and the conditions under which it occurs, and σ depends only on the substituent group and its position. This equation holds only for the special cases where the effect of a change in structure on rate or equilibrium can be explained in terms of internal electron displacements, in terms that is of potential energies alone, and only when there is a cancellation of other effects due to the internal kinetic energies of the reactants.

The σ-constants reflect the changes in electron density on the different carbon atoms of the aromatic ring, and Jaffe[4] has shown that it is possible to correlate Hammett's σ-values with electron densities in mono-substituted benzenes as calculated by the MO method. The Hammett σ-constants thus apply to *side chain* reactions in *meta* and *para* substituted benzenes and would not apply to molecular complex formation where the electron density of the aromatic ring as a whole is presumably involved. However, it is still possible that a similar treatment, with new σ-constants reflecting the electron density of the aromatic ring as a whole, will hold for molecular compound formation provided, of course, that the other limiting conditions are met.

Results

The first system studied was complexing between anthracene and 1-substituted-2,4,6-trinitrobenzenes in chloroform at 23.8 ± 0.1°. The equilibrium constants were determined spectroscopically by methods previously described.[1a,b,5] The results are given in Table I.

In this first system the substitution was in the acceptor moiety. Table II presents the results for complexing between trinitrobenzene and a series of *meta* and *para* substituted anilines in absolute alco-

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[1] (a) S. D. Ross, M. Bassin, M. Finkelstein and W. A. Leach, THIS JOURNAL, **76**, 69 (1954); (b) S. D. Ross and I. Kuntz, *ibid.*, **76**, 74 (1954); (c) S. D. Ross and I. Kuntz, *ibid.*, **76**, 3000 (1954).

[2] R. S. Mulliken, *ibid.*, **72**, 600 (1950); **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).

[3] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, Chapter VII.

[4] H. H. Jaffe, *J. Chem. Phys.*, **20**, 279 (1952).

[5] R. M. Keefer and L. J. Andrews, THIS JOURNAL, **74**, 1891 (1952).

TABLE I

EQUILIBRIUM CONSTANTS FOR COMPLEXING BETWEEN ANTHRACENE AND 1-SUBSTITUTED-2,4,6-TRINITROBENZENES IN CHLOROFORM AT 23.8 ± 0.1°

1-Substituent	K, liters × moles^{-1}
H	3.6 ± 0.2
OH	2.53 ± .07
OCH_3	2.32 ± .05
CH_3	1.75 ± .15
Cl	1.26 ± .08
I	1.0 ± .2

hol at 23.8 ± 0.1°. In this series of measurements the substitution is in the donor molecule. In this case, too, the equilibrium constants were determined spectroscopically.

TABLE II

EQUILIBRIUM CONSTANTS FOR COMPLEXING BETWEEN 1,3,5-TRINITROBENZENE AND *meta* AND *para* SUBSTITUTED ANILINES IN ABSOLUTE ETHANOL AT 25.0 ± 0.1°

Substituent	K, liters × moles^{-1}
m-CH_3	0.740 ± 0.005
m-COOH	.69 ± .02
p-COOH	.605 ± .005
p-OC_2H_5	.458 ± .004
p-$COCH_3$	.44 ± .02
H	.397 ± .008
p-Cl	.35 ± .01
p-CN	.22 ± .02
m-CF_3	.17 ± .01

Perhaps the most significant results were obtained by calculations based on data already in the literature. We have shown previously[1c] that the decrease in the bimolecular rate constant, observd when the rate of reaction of 2,4-dinitrochlorobenzene and aniline is measured at constant 2,4-dinitrochlorobenzene concentration and increasing aniline concentration, is due to molecular compound formation and that it is possible to determine the equilibrium constant for complex formation from such rate data. Moreover, we were able to show that the equilibrium constant obtained in this manner was in agreement with the equilibrium constant measured spectroscopically.

Since Singh and Peacock[6] have made careful measurements of the rate of reaction of 2,4-dinitrochlorobenzene with a series of substituted anilines and have reported results at two aniline concentrations and at both 25 and 35°, we can obtain from their data, by the method previously described,[1c] the equilibrium constants for complexing between 2,4-dinitrochlorobenzene and the substituted anilines. In addition, by using the expressions

$$\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R} \frac{T_2 - T_1}{T_2T_1} \qquad (1)$$

$$\Delta F^0 = -2.303\,RT \log K \qquad (2)$$

$$\Delta F^0 = \Delta H - T\Delta S^0 \qquad (3)$$

we can estimate the thermodynamic constants for these equilibria. The results for 35° are given in Table III, and Table IV presents the results for 45°.

TABLE III

EQUILIBRIUM CONSTANTS AND THERMODYNAMIC CONSTANTS FOR COMPLEXING BETWEEN 2,4-DINITROCHLOROBENZENE AND SUBSTITUTED ANILINES IN ABSOLUTE ETHANOL AT 35.0°

Substituent	K, liter × moles^{-1}	ΔH^0, kcal. × mole^{-1}	ΔF^0, cal. × mole^{-1}	ΔS^0, cal. × deg.$^{-1}$	k, liter × moles^{-1} × hr.$^{-1}$
m-OCH_3	0.99	− 9.4	+5.5	−30.4	0.44
o-OCH_3	.73	−18.0	+193	−59.1	.21
o-CH_3	.62	−11.1	+293	−37.0	.031
m-Cl	.52	−3.5	+404	−12.5	.031
p-OCH_3	.51	−9.3	+413	−31.5	5.0
m-Br	.45	−4.9	+492	−17.3	0.033
p-CH_3	.36	−10.4	+627	−35.6	1.5
p-Br	.34	−2.7	+668	−11.0	0.076
p-Cl	.32	−4.2	+692	−15.7	.10
m-CH_3	.23	−6.1	+895	−22.6	.65
H	.19	−12.1	+1010	−42.6	.46

TABLE IV

EQUILIBRIUM CONSTANTS AND THERMODYNAMIC CONSTANTS FOR COMPLEXING BETWEEN 2,4-DINITROCHLOROBENZENE AND SUBSTITUTED ANILINES IN ABSOLUTE ETHANOL AT 45.0°

Substituent	K, liter × moles^{-1}	ΔH^0, kcal. × moles^{-1}	ΔF^0, cal. × moles^{-1}	ΔS^0, cal. × deg.$^{-1}$	k, liters × moles^{-1} × hr.$^{-1}$
m-OCH_3	0.61	−9.4	+309	−30.4	0.64
m-Cl	.43	−3.5	+529	−12.5	.065
o-CH_3	.35	−11.1	+663	−37.0	.058
m-Br	.35	−4.9	+665	−17.4	.066
p-OCH_3	.32	−9.3	+728	−31.5	7.7
p-Br	.29	−2.7	+778	−11.0	0.16
o-OCH_3	.29	−18.0	+782	−59.1	.34
p-Cl	.26	−4.2	+849	−15.7	.19
p-CH_3	.21	−10.4	+984	−35.6	2.4
m-CH_3	.17	−6.1	+1120	−22.6	1.2
H	.10	−12.1	+1437	−42.6	0.77

The method of calculation[1c] which results in the K's reported in Tables III and IV also leads to revised values for k, the rate of reaction between 2,4-dinitrochlorobenzene and the substituted anilines to form the substituted 2,4-dinitrodiphenylamines and the substituted aniline hydrochlorides. A Hammett plot of these data is linear, with all the points on the line. Treatment of the data by the method of least squares leads to ρ-values of −3.187 and −3.033 at 35° and 45°, respectively.[7] This value is in excellent agreement with the value previously reported for this reaction in the literature,[3] and this adds further confidence to the validity of our mathematical treatment and the resultant equilibrium constants. The revised bimolecular rate constants have been included in the last column of Tables III and IV.

Experimental

A Beckman model DU spectrophotometer was used in making all of the absorption spectra measurements. Stoppered absorption cells were used, and the cell housing was maintained at constant temperature by means of two Beckman thermospacers, through which water from a constant temperature bath was circulated. The solutions for

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(6) A. Singh and D. H. Peacock, *J. Phys. Chem.*, **40**, 669 (1936).

(7) In applying the Hammett equation we have assumed that the final products result from a rate-determining reaction between the aniline and 2,4-dinitrochlorobenzene. This was done to make our value for ρ comparable with the value already in the literature. As we have shown previously (S. D. Ross and I. Kuntz, THIS JOURNAL, **76**, 3000 (1954)), the question of whether the final products result from the above bimolecular reaction or a unimolecular decomposition of the complex is still unresolved. It is possible to calculate the unimolecular rate constants for this latter possibility, and a Hammett plot using these rate constants is also linear.

TABLE V

RANGES OF CONCENTRATION EMPLOYED IN MEASUREMENT OF THE ANTHRACENE–SUBSTITUTED TRINITROBENZENE COMPLEXES

Complex, anthracene–	Anthracene concentrations, *M*	Substituted trinitrobenzene concentrations, *M*
1,3,5-Trinitrobenzene	6.24×10^{-3}–1.00×10^{-2}	7.26×10^{-3}–1.90×10^{-2}
Picric acid	7.50×10^{-3}–2.00×10^{-2}	7.65×10^{-3}–1.76×10^{-2}
2,4,6-Trinitroanisole	2.00×10^{-2}–6.25×10^{-2}	2.67×10^{-3}–3.00×10^{-2}
2,4,6-Trinitrotoluene	1.00×10^{-2}–3.02×10^{-2}	1.21×10^{-2}–4.28×10^{-2}
Picryl chloride	1.00×10^{-2}–4.12×10^{-2}	1.22×10^{-2}–2.99×10^{-2}
Picryl iodide	2.45×10^{-2}–5.94×10^{-2}	4.99×10^{-3}–1.01×10^{-2}

TABLE VI

RANGES OF CONCENTRATION EMPLOYED IN MEASUREMENT OF THE 1,3,5-TRINITROBENZENE–SUBSTITUTED ANILINE COMPLEXES

Complex, trinitrobenzene–	1,3,5-Trinitrobenzene concentrations, *M*	Substituted aniline concentrations, *M*
m-Toluidine	5.12×10^{-3}–1.02×10^{-2}	9.88×10^{-2}–4.46×10^{-1}
m-Aminobenzoic acid	6.51×10^{-3}–1.19×10^{-2}	8.03×10^{-2}–2.34×10^{-1}
p-Aminobenzoic acid	3.10×10^{-3}–9.50×10^{-3}	1.82×10^{-1}–4.68×10^{-1}
p-Phenetidine	2.18×10^{-3}–8.20×10^{-3}	2.03×10^{-1}–4.99×10^{-1}
p-Aminoacetophenone	5.86×10^{-3}–1.79×10^{-2}	1.51×10^{-1}–4.50×10^{-1}
Aniline	5.14×10^{-3}–1.49×10^{-2}	1.03×10^{-1}–4.51×10^{-1}
p-Chloroaniline	9.97×10^{-3}–3.99×10^{-2}	5.96×10^{-2}–2.33×10^{-1}
p-Cyanoaniline	1.33×10^{-3}–2.31×10^{-2}	3.34×10^{-2}–1.03
m-Aminobenzonitrile	5.69×10^{-3}–1.59×10^{-2}	9.88×10^{-2}–6.85×10^{-1}

measurement were prepared by weighing specific quantities of the requisite reagents directly into a volumetric flask and making it up to volume with solvent at 25.0 ± 0.1°.

For each equilibrium constant measurements were made at at least six different sets of concentrations of the donor and acceptor, and readings of absorption were taken at 10 mμ intervals from 400–500 mμ. The method of calculation was that described in the first paper of this series.[1a] The method of least squares was used in every case. The first value of *K* obtained was used to obtain estimates of donor, acceptor and complex concentrations, and these concentrations were then used to obtain the final value of *K*, again using the method of least squares. The calculations were made for data at at least two wave lengths and frequently for data at four wave lengths.

The solvents were both C.P. reagents, used without further purification. The other reagents were all Eastman Kodak white label materials and were distilled or crystallized prior to use. The physical constants for the materials are:

Anthracene, m.p. 217° from benzene
1,3,5-Trinitrobenzene, m.p. 121° from abs. ethanol
Picric acid, m.p. 120.3–121.5° from methanol
p-Aminoacetophenone, m.p. 106–107° from water
2,4,6-Trinitroanisole, m.p. 68–68.5° from methanol
Picryl chloride, m.p. 83–84° from ethanol
Picryl iodide, m.p. 164–165° from benzene
2,4,6-Trinitrotoluene, m.p. 81–82° from ethanol
m-Toluidine, b.p. 80° (12 mm.)
m-Aminobenzoic acid, m.p. 174° from water
p-Aminobenzoic acid, m.p. 187° from ethanol
p-Phenetidine, b.p. 125° (12 mm.)
Aniline, b.p. 63–65° (8 mm.)
p-Chloroaniline, m.p. 70–71° from methanol
p-Cyanoaniline, m.p. 85–87° from water
m-Aminobenzotrifluoride, b.p. 186° (740 mm.)

The ranges of concentration employed in the spectroscopic measurements are given in Tables V and VI.

Discussion

It is apparent from even a casual inspection of Table I that the results are contrary to our *a priori* expectations. For complexing between anthracene, the donor in this case, and 1-substituted-2,4,6-trinitrobenzenes, the acceptors, we would expect that electron-withdrawing substituents would increase the extent of complexing and that electron-donating substituents would decrease it. The 1-substituent in the substituted 2,4,6-trinitrobenzenes would be expected to affect the acceptor ability of these compounds almost entirely through an inductive effect, since the nitro groups at the 2- and 6-positions would inhibit resonance interaction of the 1-substituent with the benzene ring.[8] The relative magnitudes for the inductive effects of these substituents can be estimated from the ionization constants of the α-substituted acetic acids. On this basis we would expect that complexing would decrease in the order: Cl, I, OCH_3, H, CH_3. The measured equilibria constants in this series, however, are in the order of the size of the 1-substituents, with the smallest substituent giving the largest equilibrium constant and the largest substituent resulting in the smallest equilibrium constant. This suggests that, for this system, steric factors are controlling and that the ease of approach of the donor to the acceptor determines the amount of complexing.[9]

The results reported in Table II are in accord with our preconceptions to some extent but not completely. In this case the donor is substituted, and we would, therefore, expect electron acceptors to decrease complexing. Experimentally we find that the *p*-Cl group, the *p*-CN group and the *m*-CF_3 all lower the equilibrium constant for complex formation. However, the *m*-COOH group, the *p*-COOH group and the *p*-$COCH_3$ group all increase the extent of complexing in spite of the fact that these are all electron-withdrawing groups. The two electron-donating groups both increase complexing as expected, but *m*-CH_3 is more effective than *p*-OC_2H_5 in spite of the fact that we would normally classify the *p*-OC_2H_5 group as a much stronger electron donor.

Consideration of the thermodynamic functions listed in Tables III and IV makes it clear why our expectations were met so poorly. Our over-simplified prediction of the effect of substituents on the extent of complexing carries the tacit assumption

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[8] R. H. Birtles and G. C. Hampson, *J. Chem. Soc.*, 10 (1937).

[9] M. Orchin, *J. Org. Chem.*, **16**, 1165 (1951).

that the magnitudes of the equilibria constants are determined by considerations of potential energy alone. It is clear from the observed large variations in ΔS^0 that this is not the case and that, in fact, the kinetic energy changes accompanying complex formation are not uniformly the same throughout this series. Under these conditions it becomes hopeless to attempt to correlate structure and reactivity toward complex formation in terms of potential energy considerations alone. The changes in equilibrium constant resulting from a particular substituent could stem from a whole series of effects amongst which we might list polar or inductive effects, resonance effects, steric hindrance effects, polarizability effects and solvent effects.

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NOTES

A New Preparation of Bis-cyclopentadienyl–Metal Compounds

By J. M. Birmingham, D. Seyferth and G. Wilkinson

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Three major types of reactions have been used to prepare bis-cyclopentadienyl-iron(II) and other bis-cyclopentadienyl-metal compounds: (a) the reaction of a cyclopentadienyl organometallic reagent: C_5H_5MgBr in benzene[1] or C_5H_5Na in tetrahydrofuran[2] with transitional metal halides or acetylacetonates, or C_5H_5K in liquid ammonia with a metal thiocyanate.[3] Bis-indenyl derivatives of Fe and Co also have been prepared by similar reactions[4]; (b) the reaction of cyclopentadiene vapor with a metallic iron catalyst[5a] or ferrous oxide at 350°,[5b] and (c) the reaction of cyclopentadiene vapor with a metal carbonyl.[6]

Method a depends upon the acidic character of the methylene hydrogen of cyclopentadiene which enables the formation of an organometallic derivative with the evolution of hydrogen in the reaction with Na or K, or in the case of the Grignard reagent, where cyclopentadiene reacts with C_2H_5MgBr, of ethane. The dissociation constant of the acidic hydrogen of cyclopentadiene is very small; the pK value for indene has been estimated to have a minimum value of 21[7] and the minimum pK value for cyclopentadiene should be slightly lower.[8] Consideration of this slight acidity of cyclopentadiene suggested that a reaction of cyclopentadiene with a metal halide in the presence of a hydrogen halide acceptor might be an alternate route for the preparation of bis-cyclopentadienyl-metal compounds, *e.g.*

$$2C_5H_6 + FeCl_2 + 2\ Base = (C_5H_5)_2Fe + 2\ Base{\cdot}HCl$$

We have found that such reactions do indeed give small yields of ferrocene and of bis-cyclopentadienyltitanium(IV) chloride,[9] $(C_5H_5)_2TiCl_2$. As hydrogen halide acceptors, triethylamine, diethylamine, pyridine and sodium methoxide have been used. The formation of $FeCl_2$–amine addition compounds that are insoluble in the solvents tried is a competing reaction that has thus far prevented good yields. Sodium methoxide seems to cause polymerization of the cyclopentadiene. It is, however, significant that bis-cyclopentadienyl-metal compounds are formed under these conditions; in the absence of a hydrogen halide acceptor, none of the desired product could be detected.

Experimental

(1) An equimolar mixture of $(C_2H_5)_3N$ and C_5H_6 was slowly added to anhydrous $FeCl_2$ with rapid stirring under a nitrogen atmosphere. Benzene was then added and the mixture was stirred overnight. The reaction mixture was filtered and the yellow filtrate was allowed to evaporate slowly. The yellow acicular crystals that separated were identified as ferrocene by infrared spectrum and melting point. A yield of about 4% was thus obtained. Variation of the base—$(C_2H_5)_2NH$, C_5H_5N, $NaOCH_3$—also gave similar yields. The use of ferrous acetate in place of the chloride with the above bases gave ferrocene but did not improve the yield.

(2) A benzene solution of $TiCl_4$ was added slowly with vigorous stirring to an equimolar mixture of $(C_2H_5)_3N$ and C_5H_6. The mixture was stirred overnight. Removal of the solvent from the red reaction mixture, extraction of the resulting residue with chloroform, and slow evaporation of the extracts yielded red crystals. Recrystallization from toluene gave pure $(C_5H_5)_2TiCl_2$, identified by its infrared spectrum. Yields of about 3% were obtained with triethylamine, diethylamine or pyridine. Again, serious competing reactions were the formation of insoluble $TiCl_4$–amine complexes and polymerization of the cyclopentadiene.

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(1) T. J. Kealy and P. L. Pauson, *Nature*, **168**, 1039 (1951).

(2) G. Wilkinson and F. A. Cotton, *Chemistry and Industry*, 307 (1954).

(3) E. O. Fischer and R. Jira, *Z. Naturforsch.*, **8b**, 217 (1953).

(4) (a) P. L. Pauson and G. Wilkinson, This Journal, **76**, 2024 (1954); (b) E. O. Fisher, *et al.*, *Z. Naturforsch.*, **8b**, 692, 694 (1953).

(5) (a) S. A. Miller, J. A. Tebboth and J. F. Tremaine, *J. Chem. Soc.*, 632 (1952); (b) G. Wilkinson, unpublished observation.

(6) (a) G. Wilkinson, This Journal, **76**, 209 (1954); G. Wilkinson, P. L. Pauson and F. A. Cotton, *ibid.*, **76**, 1970 (1954).

(7) W. K. McEwen, *ibid.*, **58**, 1124 (1936).

(8) G. W. Wheland, *J. Chem. Phys.*, **2**, 474 (1934).

(9) G. Wilkinson and J. M. Birmingham, This Journal, **76**, in press (1954).

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The Pyrolysis of Methyl Ethyl Ketone Cyanohydrin Acetate

By Earl C. Chapin and Richard F. Smith

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The pyrolysis of unsymmetrical aliphatic acetates has been reported[1] to yield the olefin with the least number of alkyl groups attached to it.

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(1) W. J. Bailey and C. King, Abstracts of the 122nd Meeting of the American Chemical Society, 1952 p. 3M.