141. *Mechanism of Aromatic Side-chain Reactions, with Special Reference to the Polar Effects of Substituents. Part X. Physical and Chemical Evidence relating to the Polar Effect of* o-*Methyl Substituents in Derivatives of the Type* $C_6H_2Me_3 \cdot CO \cdot CH_2R$.

By JOHN W. BAKER and WILLIAM T. TWEED.

The heat of combustion of 2 : 4 : 6-trimethylacetophenone is 0·17 volt-electron per molecule lower than that of the 2 : 4 : 5-isomeride. This indicates a slightly larger resonance energy in the former molecule and supports the earlier suggestion (Baker, J., 1938, 445) that resonance occurs between the electrons of the C–H bonds of the methyl substituents and those of the carbonyl group. Further support is derived from a comparison of the molecular refractivities and of the basic character of the carbonyl oxygen of the two isomerides and of the corresponding 2 : 4 : 6- and 2 : 4 : 5-*trichloro-acetophenones*, in which the chlorine substituents, although approximately isosteric with methyl, are of a different polar type. The velocities of interaction of 2 : 4 : 5-*trimethyl-*, p-chloro-, 2 : 4 : 5- and 2 : 4 : 6-*trichloro-phenacyl bromides* with pyridine in dry acetone have also been determined. The combined data suggest that the large inhibitory effect of the two ortho-substituents in this reaction is due largely, but not entirely, to purely spatial factors.

IN Part IX (Baker, J., 1938, 445) it was suggested that the very large inhibiting effect of the methyl substituents on the reaction of 2 : 4 : 6-trimethylphenacyl bromide with pyridine arose, at least partly, from the existence of resonance involving the electrons of the C–H bonds in the methyl substituents and those of the carbonyl group.* Such

* Conjugation between C–H bonds and an attached unsaturated system, postulated by Baker and Nathan (J., 1935, 1844; Baker, J., 1939, 1150) on a qualitative basis, has now been computed on a quantitative basis by Mulliken, Rieke, and Brown (*J. Amer. Chem. Soc.*, 1941, **63**, 41), using the method of molecular orbitals. These authors classify such conjugation as " second-order conjugation " or " first-order hyperconjugation." This would seem to be equivalent to the permanent conjugation to which the term " mesomeric effect " of alkyl groups has been applied by one of us on the basis of the
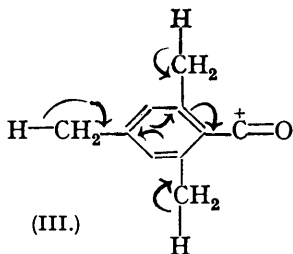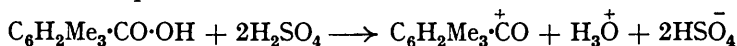
acetophenone derivatives were regarded as resonance hybrids of structures of the types (I) and (II).
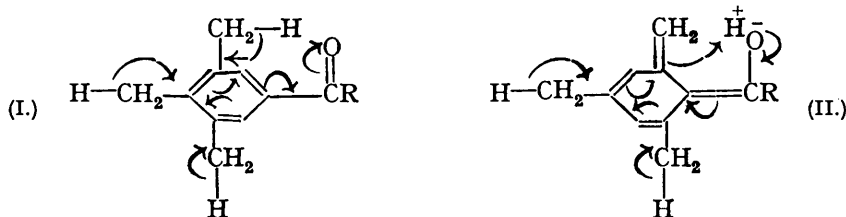
This conclusion was, of necessity, rather tentative, since it was not possible to exclude purely spatial effects of the two *o*-methyl groups if the mechanism involves the direct attack of the base at the carbonyl carbon (cf. Part IX, *loc. cit.*, p. 446; also this communication, p. 799), *e.g.*,
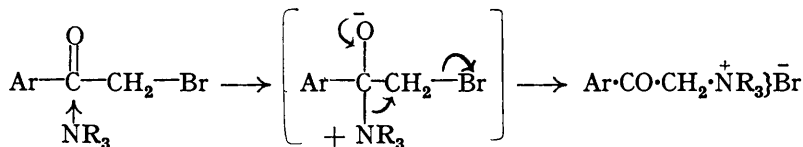
The effect of such methyl substitution on the carbonyl activity is also revealed in other published data. For instance, Reich, Salzmann, and Kawa (*Bull. Soc. chim.*, 1917, **21**, 217) found that 2 : 4 : 6-trimethylbenzaldehyde would not undergo the Perkin reaction, the first stage of which is generally regarded as an aldol type of condensation at the carbonyl group. Hammett and Treffers (*J. Amer. Chem. Soc.*, 1937, **59**, 1708) demonstrated by cryoscopic measurements the abnormal ionisation of 2 : 4 : 6-trimethylbenzoic acid as a base in concentrated sulphuric acid :

$$C_6H_2Me_3 \cdot CO \cdot OH + 2H_2SO_4 \longrightarrow C_6H_2Me_3 \cdot \overset{+}{C}O + H_3\overset{+}{O} + 2HS\overset{-}{O_4}$$

The stabilising influence of the above mesomeric electron release on the anomalous cation is obvious, since it makes possible the distribution of the positive charge between all nine hydrogen atoms of the methyl groups, in addition to the usual distribution within the benzene nuclus itself (see III). On the other hand, Hammett and Zucker (*ibid.*, 1939, **61**, 2779) found no inhibition of the iodination of 2 : 4 : 6-trimethylaceto-phenone, a reaction which depends essentially on the ionis-ation of hydrogen from the side-chain methyl group and should therefore be unaffected by spatial effects arising from ortho-substitution (cf. p. 799, and Baker, paper shortly to be published in *Trans. Faraday Soc.*).

Various attempts have been made to substantiate the polar as distinct from the purely spatial effects (which are almost certainly operative) of the *o*-methyl substituents. The existence of a mesomeric effect of the type postulated, giving rise to the inclusion of structures of type (II) in the resonance hybrid, should be detected by a comparison of certain physical properties of 2 : 4 : 6- and 2 : 4 : 5-trimethylacetophenones and by similar comparison of suitable equilibria, in which only the ground states of the initial and final products are involved. Evidence of increased conjugation in 2 : 4 : 6-trimethylacetophenone is provided by the fact that its molecular refractivity exhibits a greater exaltation (2·4 units) than does

nomenclature of Professor C. K. Ingold. An electromeric effect, of similar origin, but operating only in the activated transition complex of a suitable substitution, was also envisaged and has since been conclusively established by Hughes, Ingold, and Taher (*J.*, 1940, 949). Mulliken *et al.* extend the principle to " second-order hyperconjugation " in saturated molecules of the type of ethane $H_3 \equiv C-C \equiv H_3$, in which they claim that the C–C bond has, as a result, about 11% of double-bond character.

that of 2 : 4 : 5-trimethylacetophenone. The values (von Auwers, *Annalen*, 1919, **419**, 120) as follows :

	$n_a^{14.9°}$.	$d^{14°}$.	$[M]_a$.
2 : 4 : 5-$C_6H_2Me_3 \cdot CO \cdot CH_3$	1·5357	1·001	50·3
2 : 4 : 6-$C_6H_2Me_3 \cdot CO \cdot CH_3$	1·5148	0·9854	52·7

The calculated value is $[M]_a$ 49·1.

Although it was expected that the contribution of structures of type (II) (R = H) to the resonance hybrid representing the ground state of the 2 : 4 : 6-trimethylacetophenone molecule would be very small, it was thought that the possibility that nine C–H bonds could take part in the resonance of this molecule, whereas only six could be operative in the 2 : 4 : 5-trimethyl isomeride, might be revealed in a small, but definite, increase in the resonance energy of the former molecule. Accordingly, the heats of combustion of carefully purified specimens of the two liquid ketones were determined for us by Dr. W. A. Roth at Freiburg. In agreement with expectation, it was found that the 2 : 4 : 6-trimethylacetophenone has a slightly lower heat of combustion (8925 $\pm$ 4 cals./g.) than the 2 : 4 : 5-compound (8947 $\pm$ 6 cals./g.). These data correspond to values of 63·16 $\pm$ 0·021 and 63·33 $\pm$ 0·042 volt-electrons per molecule of vapour, respectively.* The difference, $+$ 0·17 volt-electron per molecule, in the resonance energies of 2 : 4 : 6- and 2 : 4 : 5-trimethylacetophenone thus indicated is small, but is significant when compared with the resonance energies of the corresponding substituted hydrocarbons mesitylene and ψ-cumene : their heats of combustion in the vapour state are 54·23 and 54·15 volt-electrons per molecule, respectively, a difference of only $-$ 0·08 volt-electron. The difference in the resonance energy arising from the transfer of the 5-methyl substituent to the 6-position in the case of the ketones ($+$ 0·17 volt-electron) is appreciably greater than the probable experimental error ($\pm$ 0·042 volt-electron) and, moreover, is in the opposite sense to the much smaller difference ($-$ 0·08 volt-electron) in the corresponding hydrocarbons where, of course, the absence of a carbonyl group makes the postulated extra resonance energy impossible. These data thus give considerable support to the theoretical deduction that 2 : 4 : 6-trimethylacetophenone has a greater resonance energy than the 2 : 4 : 5-isomeride.

Another expected effect of the incursion of structures of type (II) into the ground state of 2 : 4 : 6-trimethylacetophenone would be a diminution in the basic character of the carbonyl oxygen. A qualitative comparison of the relative basic strengths of 2 : 4 : 6- and 2 : 4 : 5-trimethylacetophenone was made by using the partition method between ligroin and concentrated sulphuric acid (Baker, J., 1931, 307). For purposes of comparison the corresponding 2 : 4 : 6- and 2 : 4 : 5-trichloroacetophenones were also examined, since chlorine is approximately isosteric with methyl but is of different polar type. The methyl substituents would normally be expected to increase the basic character of acetophenone whereas chlorine substitution should decrease it. The data are in Table I.

TABLE I.

Partition of derivatives of the type $C_6H_2X_3 \cdot CO \cdot CH_3$ *between ligroin and sulphuric acid at 18°.*

X.	H$_2$SO$_4$ = 100%.	90%.	80%.
	Percentage of ketone in the ligroin layer.		
H	0	0	8
2 : 4 : 5-Me	0	0	3
2 : 4 : 6-Me	33	80	90
2 : 4 : 5-Cl	14	56	70
2 : 4 : 6-Cl	32	80	92

The basic strengths of the two trichloro-isomerides are of the same order of magnitude, but whereas 2 : 4 : 5-trimethylacetophenone has a basic strength closely similar to (or

* It is recognised that these values include the heats of vaporisation, the values of which have been computed by a method detailed on p. 801. Since the density of 2 : 4 : 6-trimethylacetophenone is lower than that of the 2 : 4 : 5-isomeride, it is extremely improbable that the former compound would have a higher heat of vaporisation. Moreover, in order to account for the observed differences in heats of combustion of the two ketones on this basis alone, it would be necessary to assume a *ca.* 50% increase in the postulated heat of vaporisation, an assumption which is regarded as highly improbable.

slightly greater than) that of the parent acetophenone, the 2 : 4 : 6-trimethyl compound, in spite of the more favourable orientation of the methyl groups, is as weak a base as the corresponding trichloro-compound. It is difficult to escape the conclusion that the equilibrium

$$\text{Ar·CO·CH}_3 + \text{H}_2\text{SO}_4 \rightleftharpoons \text{Ar·C(CH}_3)\text{:}\overset{+}{\text{O}}\text{H} + \text{H}\overset{-}{\text{S}}\text{O}_4$$
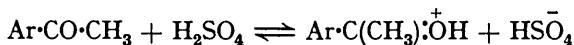
is displaced abnormally to the left in the case of 2 : 4 : 6-trimethylacetophenone. Therefore, deductions from the energy content of the molecule, from its molecular refractivity, and from the base–salt equilibrium all support the postulated interaction between the *o*-methyl groups and the adjacent carbonyl group.

Although less likely to be conclusive, since the energy levels of activated, transition complexes in a bimolecular, nucleophilic substitution are also involved, an examination was made of the relative velocities of interaction of the two isomeric *trimethyl-* and *trichloro-phenacyl bromides* with pyridine under the standard conditions of Baker and Nathan (J., 1935, 1840). The results are in Table II.

TABLE II.

Interaction of $C_6H_2X_3\text{·CO·CH}_2\text{Br}$ *with* C_5H_5N, *both* 0·025M *in dry acetone at* 20°.

(k in g.-mol.$^{-1}$ litre sec.$^{-1}$.)

X.	10^3k.	Ref.	X.	10^3k.	Ref.
H	0·79	(1)	2 : 4 : 6-Cl	∼10^{-4} *	(2)
2 : 4 : 5-Me	0·54	(2)	2 : 4 : 5-Cl	0·72	(2)
2 : 4 : 6-Me	∼10^{-3} to 10^{-4} *	(1)	(*p*-Cl)	1·29	(2)

(1) Baker, J., 1938, 445. (2) This communication.

* Too slow for accurate measurement.

The large difference in magnitude between the reaction velocities of the 2 : 4 : 5- and the 2 : 4 : 6-trichloro-compound is similar to that observed in the corresponding trimethyl-phenacyl halides. Conjugation of the unshared chlorine electrons, giving rise to structures of the type (IV) is theoretically possible, but the increased velocity observed with *p*-chlorophenacyl bromide (due largely to the inductive electron-attraction of the halogen substituent), taken in conjunction with the comparable order of basic strengths of the 2 : 4 : 5- and 2 : 4 : 6-trichloroacetophenones, suggests that such structures are of minor importance and that the greatly reduced velocity of interaction between pyridine and 2 : 4 : 6-trichlorophenacyl bromide is due, to a very large extent, to purely spatial inhibition. It would thus appear probable that such spatial effects are largely, although not entirely, responsible for the lack of reactivity of the side chain situated between two ortho-substituents and, as a necessary corollary if this be accepted, that the attack of the base molecule occurs initially at the carbonyl carbon and not at the side-chain methylene carbon atom or bromine atom.
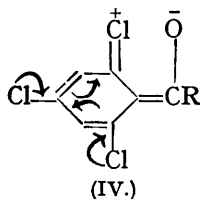
(IV.)

EXPERIMENTAL.

(All analyses, except those marked with an asterisk, are by Dr. G. Weiler of Oxford.)

Preparation of Materials.—2 : 4 : 5-Trimethylacetophenone, prepared from *ψ*-cumene and acetyl chloride (Claus, *J. pr. Chem.*, 1890, **41**, 109), had b. p. 110°/7 mm. after repeated purification. It was converted by the action of 1 mol. of bromine, without solvent, into 2 : 4 : 5-*trimethylphenacyl bromide*, m. p. 57° after repeated crystallisation from ligroin (b. p. 40—60°) (Found : C, 54·7; H, 5·55; Br, 35·5. $C_{11}H_{13}$OBr requires C, 54·8; H, 5·4; Br, 33·2%).

2 : 4 : 6-*Trichloroacetophenone.* The method of Lock and Bock (*Ber.*, 1937, **70**, 916) was first tried : aceto-*m*-toluidide was converted into 2 : 4 : 6-trichlorobenzaldehyde, but this could not be converted into the methylcarbinol, the aldehyde being recovered unchanged from treatment with methylmagnesium iodide. Chlorination of *m*-acetamidobenzoic acid with sodium chlorate in acetic–hydrochloric acid solution to give the trichloro-acid, hydrolysis of the product, and removal of the amino-group by diazotisation gave only (?) pentachlorobenzoic acid (Found :

C, 29·8; H, 0·34; Cl, 58·2. Calc. for $C_7HO_2Cl_5$: C, 28·5; H, 0·34; Cl, 57·9%). The required ketone was eventually obtained by the method of Fuson and Ross (*J. Amer. Chem. Soc.*, 1932, **54**, 4300; 1937, **59**, 1508). The action of 2 : 4 : 6-trichlorobenzoyl chloride with an excess of methylmagnesium iodide in boiling ether gave the ketone, b. p. 110°/1 mm., m. p. 50° after crystallisation from ligroin (Found : C, 43·0; H, 2·2. Calc. for $C_8H_5OCl_3$: C, 43·15; H, 2·4%), and a *compound*, which crystallised from alcohol in yellow needles, m. p. 192°. From its analysis it may be either 2 : 4 : 6-trichlorophenacyl-2 : 4 : 6-trichlorophenylmethylcarbinol or the isomeric β-2 : 4 : 6-trichlorophenyl*iso*propyl 2 : 4 : 6-trichlorobenzoate (Found : Cl, 47·5. $C_{16}H_{10}O_2Cl_6$ requires Cl, 47·6%).

2 : 4 : 6-*Trichlorophenacyl bromide* was obtained by the action of the theoretical quantity of dry bromine on the ketone without solvent. When evolution of hydrogen bromide had ceased, the product was diluted with ether, washed with water and sodium hydrogen carbonate solution, and dried over sodium sulphate. The residue from the dried ethereal solution crystallised. Repeated crystallisation from ice-cold ligroin (b. p. 40—60°) gave the bromide, m. p. 81° (Found : C, 31·9; H, 1·5; Br*, 26·3. $C_8H_4OCl_3Br$ requires C, 31·8; H, 1·3; Br, 26·5%).

2 : 4 : 5-*Trichloroacetophenone.* Great difficulty was experienced in the synthesis of this compound. The following methods were investigated.

(1) Aceto-*m*-toluidide was converted *via* its 4 : 6-dichloro-derivative and 4 : 6-dichloro-*m*-toluidine into 2 : 4 : 5-trichlorotoluene, m. p. 80·5°, identical with the original specimen prepared by Cohen and Dakin (J., 1902, **81**, 1336). This, however, was unchanged by refluxing with potassium permanganate solution for 48 hours, and the corresponding 2 : 4 : 5-trichloro-benzotrichloride obtained from it (Beilstein and Kuhlberg, *Annalen*, 1869, **150**, 313; **152**, 224) was similarly inert.

(2) 1 : 2 : 4-Trichlorobenzene was converted into 2 : 4 : 5-trichloronitrobenzene, m. p. 57°, and thence into 2 : 4 : 5-trichloroaniline, m. p. 95° (Lesimple, *Annalen*, 1866, **137**, 123). This was converted into the nitrile by diazotisation in concentrated hydrochloric acid with solid sodium nitrite, addition of cuprous cyanide solution, and steam distillation. Crystallisation of the product from ligroin (b. p. 40—60°) gave 2 : 4 : 5-*trichlorobenzonitrile*, m. p. 104° (Found : C, 38·5, 39·2; H, 1·1, 1·3; Cl, 52·0. $C_7H_2NCl_3$ requires C, 40·7; H, 1·0; Cl, 51·6%). This was, however, contaminated by 1 : 2 : 4 : 5-tetrachlorobenzene, which is also steam-volatile and crystallises from the same solvents as the nitrile.

The nitrile (46 g.) was hydrolysed to the amide by treating it with 600 c.c. of 80% (by weight) sulphuric acid for 12 hours at room temperature, followed by 6 hours' heating on the steam-bath and finally 1 hour's refluxing over a free flame (during which 1 : 2 : 4 : 5-tetra-chlorobenzene, m. p. 139°, sublimed into the condenser). The reaction mixture was cooled, slightly diluted with water, and 17 g. of powdered sodium nitrite were added to the cooled solution. The precipitate was extracted several times with warm sodium carbonate solution; the insoluble tetrachlorobenzene was filtered off, and the 2 : 4 : 5-trichlorobenzoic acid, m. p. 168°, was precipitated by slow addition of concentrated hydrochloric acid to the cold filtrate.

2 : 4 : 5-*Trichlorobenzoyl chloride.* The acid (22 g.) was converted by means of thionyl chloride into its chloride, which was purified by distillation under reduced pressure; it had b. p. 125°/2 mm. and crystallised from cold ligroin (in the refrigerator), m. p. ∼28°. Yield, 25 g. The orientation of this compound was checked by its conversion into 2 : 4 : 5-trichlorobenzamide, m. p. 168°, and into ethyl 2 : 4 : 5-trichlorobenzoate, m. p. 65°, both m. p.'s agreeing with those recorded in the literature.

2 : 4 : 5-*Trichloroacetophenone.* The products obtained by the action of methylzinc iodide on the acid chloride depend greatly on the experimental conditions. In one experiment the main product was a white solid, m. p. 228°, which, from its analysis (Found : C, 43·6; H, 2·3. $C_{16}H_{10}O_2Cl_6$ requires C, 42·8; H, 2·3%), would seem to be the *analogue* of the compound, m. p. 192°, obtained from the 2 : 4 : 6-trichlorobenzoyl chloride (see above). In another experiment in which 0·075 g.-mol. of the acid chloride was added to methylzinc iodide (0·1 g.-mol.) in ice, the reaction mixture refluxed for 3 hours, and then worked up in the usual manner, the product, on distillation, gave a small amount of a compound, b. p. 130°/1·5—2 mm., m. p. 64°, which was not the ketone, and much high-boiling residue which decomposed extensively during distillation. The required ketone was finally obtained as follows. The acid chloride (0·1 g.-mol.), dissolved in its own volume of dry benzene, was added slowly to 0·1 g.-mol. of methylzinc iodide cooled in a freezing mixture. No apparent action occurred until the mixture was gently warmed on a steam-bath, whereupon a brisk reaction, necessitating some cooling, set in. After this reaction had ceased, the mixture was left for ¾ hour and then cooled in a freezing mixture and decomposed by ice, followed by cold, dilute hydrochloric acid. The product was extracted with ether, and

the extract washed several times with sodium carbonate solution, and dried over sodium sulphate. The solvents were distilled off through a column, and the product fractionated in a vacuum. The first fraction, b. p. 128—132°/1·5 mm., was the required ketone and crystallised on cooling. After draining on porous porcelain 2 : 4 : 5-*trichloroacetophenone*, m. p. 47°, was purified by repeated crystallisation from ligroin (b. p. 40—60°) (Found : C, 43·1; H, 2·6; Cl, 47·0. $C_8H_5OCl_3$ requires C, 43·0; H, 2·2; Cl, 47·65%). The residue in the distilling flask crystallised, and by fractional crystallisation from various solvents it afforded (1) a ligroin-soluble portion (not further investigated); (2) a fraction readily soluble in ether, probably 2 : 4 : 5-trichloro-benzoic acid, m. p. 166°, which had escaped removal; and (3) a non-acidic portion, difficultly soluble in ether, which after repeated crystallisation from acetone was obtained in fine needles, m. p. 130°. This has not been identified (Found : C, 37·6; H, 1·2; Cl, 50·0%).

2 : 4 : 5-*Trichlorophenacyl bromide.* The ketone (2·5 g.), dissolved in a little ligroin (b. p. 40—60°), was warmed on a steam-bath, and 1·8 g. of dry bromine added dropwise. Instant decolorisation of the bromine and rapid evolution of hydrogen bromide occurred. The mixture was cooled, largely diluted with ether, washed repeatedly with water and dilute aqueous sodium bicarbonate, and dried over sodium sulphate. The residue from the dried ethereal solution crystallised in a vacuum desiccator. After being washed on porous porcelain with a little cold ligroin (b. p. 40—60°) and repeatedly crystallised from this solvent, 2 : 4 : 5-*trichlorophenacyl bromide* was obtained in burr-like clusters of needles, m. p. 60° [Found : C, 32·2; H, 1·5; Br* (by pyridine method), 26·1. $C_8H_4OCl_3Br$ requires C, 31·8; H, 1·3; Br, 26·5%]. When this was warmed with a little pyridine, 2 : 4 : 5-*trichlorophenacylpyridinium bromide*, m. p. 227° (decomp.), rapidly crystallised from the reaction mixture (Found* : Br', by microtitration, 21·2. $C_{13}H_7ONCl_3Br$ requires Br', 21·1%). Addition of dilute nitric acid to an aqueous solution of this bromide caused rapid crystallisation of the nitrate.

Heats of Combustion of 2 : 4 : 5- *and* 2 : 4 : 6-*Trimethylacetophenone.*—The following determinations were carried out by Dr. W. A. Roth, of Freiburg. Two methods of ignition of the ketone in the bomb-calorimeter were employed, (1) naphthalene and (2) cellulose acetate being used. The former gave rather higher and less consistent results, but the mean values obtained for the two ketones differed in the same direction as those obtained by the second method, which are regarded by Dr. Roth as the more reliable. They are summarised in the following table.

Heats of combustion of liquid 2 : 4 : 5- *and* 2 : 4 : 6-*trimethylacetophenone.*

(Water equivalent of the calorimeter : 2454 ± 0·9 cals./degree.)

Compound.	Wt. used (g.).	Temp. rise, corr.	Cals., net.	Cals./g.	
2 : 4 : 5-	0·38950	1·5100°	3483·2	8943	Mean : 8947 ± 6 cals./g., *i.e.*, 62·87
	0·42525	1·6370	3801·8	8940	± 0·042 volt-electrons/mol.
	0·29795	1·1730	2669·3	8959	
2 : 4 : 6-	0·15765	0·6630	1407·5	8928	
	0·37250	1·4380	3322·6	8920	Mean : 8925 ± 4 cals./g., *i.e.*, 62·71
	0·37330	1·4470	3336·0	8937	± 0·021 volt-electrons/mol.
	0·39780	1·5320	3547·1	8917	
	0·37865	1·4670	3378·2	8922	

The heats of vaporisation of the two ketones have not been determined directly but may be closely estimated from the following data (Landolt–Börnstein) :

Heat of vaporisation of C_6H_6 = 7·31 kg.-cals./g.-mol. Heat of vaporisation of 2 : 4 : 6-$C_6H_3Me_3$ = 8·62 kg.-cals./g.-mol. Heat of vaporisation of 2 : 4 : 5-$C_6H_3Me_3$ = 8·76 kg.-cals./g.-mol. Difference for 2 : 4 : 6-Me_3 = 1·31 kg.-cals./g.-mol. Difference for 2 : 4 : 5-Me_3 = 1·44 kg.-cals./g.-mol. Heat of vaporisation of $C_6H_5 \cdot CO \cdot CH_3$ = 9·27 kg.-cals./g.-mol. Whence, heat of vaporisation of 2 : 4 : 6-$C_6H_2Me_3 \cdot CO \cdot CH_3$ = 9·27 + 1·31 = 10·58 kg.-cals./g.-mol. = 0·45 volt-electron/molecule. Heat of vaporisation of 2 : 4 : 5-$C_6H_2Me_3 \cdot CO \cdot CH_3$ = 9·27 + 1·44 = 10·71 kg.-cals./g.-mol. = 0·46 volt-electron/molecule.

Partition Data.—Baker's method (*loc. cit.*) was used except that the concentration of the ketone in the ligroin layer was found by determination of the refractive index of the solution, sodium light being used. It was shown that the value of $n_D^{20°}$ plotted against the concentration of the ketone gave a straight-line relationship, and that large dilution of the sulphuric acid regenerated the whole of the ketone, the ligroin extract having the same $n_D^{20°}$ value as that of the

original solution. 20 C.c. of a 0·1092M-solution * of the ketone were shaken at 18° with 5 c.c. of 100% sulphuric acid (by titration), 5·63 c.c. of 90%, or 6·62 c.c. of 80% sulphuric acid, so that the molecular ratio, ketone/H_2SO_4, was maintained constant throughout. The data are in the following table.

Partition of $C_6H_2R_3 \cdot CO \cdot CH_3$ between ligroin ($n_D^{20°}$ 1·4110) and sulphuric acid at 18°.

R_3.	H_2SO_4, %.	$n_D^{20°}$ of ligroin layer.	Ketone, %, in ligroin layer.	R_3.	H_2SO_4, %.	$n_D^{20°}$ of ligroin layer.	Ketone, %, in ligroin layer.
2 : 4 : 6-Cl_3	100	1·4118	32	2 : 4 : 6-Me_3	100	1·4121	33
	90	1·4130	80		90	1·4136	80
	80	1·4133	92		80	1·4140	90
	0	1·4135	(100)		0	1·4141	(100)
2 : 4 : 5-Cl_3	100	1·4115	14	2 : 4 : 5-Me_3	100	1·4110	0
	90	1·4122	56		90	1·4110	0
	80	1·4125	70		80	1·4111	3
	0	1·4132	(100)		0	1·4140	(100)

Velocity of Formation of the Phenacylpyridinium Bromide in Dry Acetone.—The velocity measurements were carried out at 20° in 0·025M-concentrations of both reactants by the micro-technique of Baker and Nathan (J., 1935, 1840), the same sample of dry acetone being used as in the earlier work. The new data are in Table II, the value of k being obtained, as before, from the plot of $x/(a-x)$ against t, which gave a good straight-line relationship in all cases. With 2 : 4 : 5-trichlorophenacyl bromide, crystallisation of the quaternary salt occurred after 2 hours.