the pH is further increased up to 13.0. In 0.1 M sodium hydroxide the first wave is only about 13% higher than the second.

TABLE I

$E_{1/2}$ *vs.* THE SATURATED CALOMEL ELECTRODE (ALL $E_{1/2}$ VALUES ARE NEGATIVE)

pH (aq.)	pH (alc.)	$E^{1}_{1/2}$	$E^{2}_{1/2}$	$E^{12}_{1/2}$[a]	$E^{2}_{1/2}$	Curr., μa. 1st wave	Curr., μa. 2nd wave
		Phenyl 2-Thienyl Ketone[b]					
1.0	1.4	0.80	..	..	..	0.60	..
2.4	2.8	.89	..	..	..	.58	..
3.2	3.8	.97	1.21	..	..	.50	0.64
4.1	4.6	1.01	1.20	..	..	.64	.66
5.1	5.7	..	..	1.16	..	1.23	..
6.0	6.6	..	..	1.18	..	1.38	..
7.0	7.5	..	..	1.18	..	1.27	..
8.1	8.8	..	..	1.29	..	1.18	..
9.1	9.8	..	..	1.30	..	1.27	..
10.1	10.6	..	..	1.32	1.79	1.14	.20
11.0	11.6	..	..	1.33	1.69	0.86	.30
12.0	12.1	..	..	1.36	1.77	.75	.44
13.0	13.0	..	..	1.36	1.68	.68	.52
		2,2′-Dithienyl Ketone[b]					
1.0	1.4	0.75	..	..	..	0.73	..
2.4	2.8	.85	1.18	..	..	.76	0.92
3.2	3.8	.90	1.21	..	..	.78	.73
4.1	4.6	.94	1.21	..	..	.80	.80
5.1	5.7	1.00	1.21	..	..	.74	.68
6.0	6.6	1.03	1.20	..	..	.69	.74
7.0	7.5	1.06	1.21	..	..	.68	.73
7.7	8.3	1.10	1.23	..	..	.80	.80
8.1	8.8	1.16	1.32	..	..	.64	.70
9.1	9.8	..	..	1.25	1.79	1.24	.24
10.1	10.6	..	..	1.26	1.71	1.00	.42
11.0	11.6	..	..	1.26	1.65	1.04	.44
12.0	12.1	..	..	1.28	1.71	.68	.64
13.0	13.0	..	..	1.28	1.63	.84	.60

[a] Indicates $E_{1/2}$ of wave formed by merging waves 1 and 2. [b] Concentration of each ketone 0.000250 M.

The behavior of 2,2′-dithienyl ketone is strikingly similar to that of the ketone fluorenone in its tendency to form double waves.[1] At pH 1.0 the second wave is masked by discharge of hydrogen, but at pH 2.4 both acid waves are observed. These two waves are not merged until the pH is increased to 9.1. In this solution another small wave is present. As the pH is further increased this second wave increases in height at the expense of the first and in 0.1 M sodium hydroxide the waves are about equal in height. In other words two waves are observed over the entire pH range as with fluorenone. The waves are not as sharply separated as those of fluorenone in the pH range 6 to 8 but are easily recognized.

Both calcium and tetramethylammonium ions in basic media tend to shift the half-wave potential of the second wave to more positive values. In a calcium hydroxide–calcium chloride buffer of pH 12.0 and in 0.01 M tetramethylammonium hydroxide the two waves of both ketones are merged. This is in accord with the effect of these cations found by Ashworth.[3]

Experimental

The current–voltage curves were determined with a Leeds and Northrup Electro-Chemograph Type E. The instrument was normally operated at a damping of 3, the half-wave potentials being corrected for lag at this damping. The electrolysis cell, buffer solutions and experimental procedure were the same as previously described.[1]

A single capillary of Corning Marine barometer tubing was used. Its characteristics were: drop-time 6.0 sec., m = 1.291 mg./sec., determined in 25% ethanol, citrate–phosphate buffer of pH 5.5 with an open circuit. Half-wave potentials were corrected for IR drop when this amounted to as much as 0.01 v.

All cell solutions were 25% by volume of 95% ethanol. The concentration of ketone was 0.00025 M in all cases. All electrolyses were carried out in a constant temperature bath at 25.0 ± 0.1°. A Beckman model H-2 pH meter with a glass electrode was used for pH measurements.

Phenyl 2-thienyl ketone was prepared according to directions in "Organic Syntheses."[5] After several recrystallizations from petroleum ether the melting point was 54–55° (uncor.). The directions of Blicke and Zienty[6] were used for the preparation of thiophene-2-carboxylic acid. The acid was treated with thionyl chloride to form 2-thenoyl chloride. The latter compound was treated with thiophene-2-magnesium bromide to form 2,2′-dithienyl ketone. After two recrystallizations from ethanol the ketone had a melting point of 86–88° (uncor.). The melting point reported in the literature is 87–88°.[7]

(5) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 520.

(6) F. F. Blicke and M. F. Zienty, THIS JOURNAL, **63**, 2945 (1941).

(7) L. Gattermann, *Ber.*, **18**, 3013 (1885).

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Aromatic Compound and Complex Formation[1]

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In recent years, considerable attention has been given to the stability and absorption spectra of aromatic complexes and one popular classification of them has grouped them into so-called σ- and π-complexes. The nature of the π-complexes is not well understood yet. For instance, the contributions to their stability from such effects as polarization, resonance, van der Waals forces, and acid–base interactions have not been clearly defined. It has been said that the relative stability of π-complexes of the alkylbenzenes is due primarily to polarization.[3] According to one prominent school of thought,[4] molecular addition compounds (MAC's) arise through a polarization of one molecule by a second and then the two moieties are held together by dipole-induced dipole forces. Hence, it was thought that a knowledge of the relative tendencies of benzene derivatives to form MAC's[5] might shed some light upon the importance of po-

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(2) (a) Guggenheim Fellow, Cytochemical Department, Carlsberg Laboratorium, Copenhagen, Denmark; (b) American Philosophical Society Predoctoral Fellow, Pennsylvania State College.

(3) H. C. Brown and J. D. Brady, THIS JOURNAL, **74**, 3570 (1952).

(4) G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 68; D. L. Hammick and R. B. M. Yule, *J. Chem. Soc.*, 1539 (1940); G. Briegleb, "Zwischenmolekulare Kraft und Molekulstructure," F. Enke, Stuttgart, 1937. An extension of this viewpoint has been given by R. S. Mulliken in terms of acid–base interactions (R. S. Mulliken, *J. Chem. Phys.*, **19**, 514 (1951); *J. Phys. Chem.*, **56**, 801 (1952); J. Landauer and H. McConnell, THIS JOURNAL, **74**, 1221 (1952).

(5) T. S. Moore, F. Shepherd and E. Goodall, *J. Chem. Soc.*, **1447** (1931).

larization toward π-complex stability. For this purpose, a spectroscopic study of complexes between *sym*-trinitrobenzene (TNB) and substituted benzenes was begun.

In chloroform solutions sufficiently dilute for spectroscopic measurements, the complexes are completely dissociated, for when chloroform solutions of TNB were added to chloroform solutions of the second compound, the absorbencies of the mixtures were exactly the sums of the absorbencies of the respective separate components.[6] With solutions of TNB dissolved in the pure compounds studied, Beer's law was observed. It was believed therefore, that all of the TNB was converted into the MAC and that dissociation did not occur under the prevailing conditions. In comparison with a chloroform solution, solutions of TNB in all of the aromatic compounds studied showed a marked increase in absorption in the range 280 to 340 mμ. It was assumed, therefore, that the greater the absorption in this region, the greater the polarization of the aromatic component of the MAC and possibly the greater is its stability. Inasmuch as several spectroscopic studies,[7] as well as other types,[8] already have established the fact that the components of these MAC's combine in a one-to-one molar ratio primarily, this note reports measurements made at a single wave length. It was decided to work at 330 mμ because some of the solutions have a maximum in the range 280–315 mμ and some do not.

TABLE I

MOLAR ABSORBENCIES OF SOLUTIONS OF TNB

Solvent	a_{330} mμ	a/a C_6H_6
Chloroform	273	0.26
Fluorobenzene	610	.57
Chlorobenzene	894	.84
Benzene	1069	1.00
Bromobenzene	1225	1.15
Toluene	2090	1.96
Ethylbenzene	1996	1.87
Isopropylbenzene	1896	1.78
t-Butylbenzene	2400	2.25
o-Xylene	2867	2.69
m-Xylene	2528	2.37
p-Xylene	2725	2.55
Pseudocumene	2765	2.59
Mesitylene	3680	3.45

In Table I are listed the molar absorption indexes, a, of TNB in the respective compounds at 330 mμ; in column five are the ratios of these values to that of benzene at 330 mμ. It is seen that the order of increasing absorption with respect to the substituents in the monosubstituted benzenes is

$C(CH_3)_3 > CH_3 > CH_2CH_3 > CH(CH_3)_2 > Br > H > Cl > F$

This order is not that expected originally and the *t*-butyl group appears to be anomalous at first glance. It is noticeable from Table II that the order of decreasing basicity of these compounds toward HCl corresponds to the order of decreasing dipole moments[9] and it was anticipated that a similar series would be obtained in the present work. On the contrary, with the exception of hydrogen, the trend of decreasing absorption of the MAC's is identical to that of increasing electronegativity of the substituents as determined by their effects on the dissociation constant of acetic acid (see Table II). This correlation is not strange from the view that MAC's owe their stability to dipole-induced dipole forces. The order is only tentative until equilibrium constants have been determined, but the two correlations drawn suggest that π-complex stability varies with the original permanent polarization (dipole moment) in the donor component while the stabilities of MAC's chiefly depend upon the polarizabilities of the polarized components.

TABLE II

SEQUENCES OF EFFECTS FROM SUBSTITUENTS ON THE PROPERTIES OF MONOSUBSTITUTED BENZENES

Absorption of TNB complex at 330 mμ:[10]

$C(CH_3)_3 > CH_3 > CH_2CH_3 > CH(CH_3)_2 > Br > H > Cl > F$

Electronegativity:[11]

$10^5 K_a$ of XCH_2COOH =	0.89	1.34	1.51	1.55	1.75	138	140	213
X =	$C(CH_3)_3$	$< CH_3$	$< CH_2CH_3$	$< CH(CH_3)_2$	$< H$	$< Br$	$< Cl$	$< F$

π-Complex formation:

Toward ICl, SO_2, etc.: $C(CH_3)_3 > CH_3 > H > Br > Cl$[12]

Toward HCl: $C(CH_3)_3 > CH(CH_3)_2 > CH_2CH_3 > CH_3 > H > F > Cl > Br > I$[3]

Dipole moments:[9] (positive value indicates negative pole directed away from ring)

Moment =	$-0.70D$	-0.65	-0.58	-0.4	0	1.44	1.64	1.65	1.69
	$C(CH_3)_3$	$< CH(CH_3)_2$	$< CH_2CH_3$	$< CH_3$	$< H$	$< F$	$< Cl$	$< Br$	$< I$

Ionization potentials:[13]

$C(CH_3)_3 < CH(CH_3)_2 < CH_2CH_3 < Cl < CH_3 < F < H$

Experimental

The *sym*-trinitrobenzene was recrystallized from ethanol, m.p. 123°. The compounds studied were from "high grade" commercial stocks and fractionated. Absorption

(6) This effect has been reported for other MAC's by R. C. Jones and M. B. Neuworth, THIS JOURNAL, **66**, 1497 (1944).

(7) K. H. Takamura, M. D. Cameron and M. S. Newman, *ibid.*, **75**, 3280 (1953); D. M. G. Lawrey and H. McConnell, *ibid.*, **74**, 6175 (1952); J. Landauer and H. McConnell, *ibid.*, **74**, 1221 (1952).

(8) See references cited in L. N. Ferguson, "Electron Structures of Organic Molecules," Prentice-Hall, Inc., New York, N. Y., 1952, p. 47ff.

(9) This is on the basis of acceptance of the solvent and other corrections suggested by L. G. Groves and S. Sugden (*J. Chem. Soc.*, 1992 (1937)) and by A. Audsley and F. R. Goss (*ibid.*, **358**, 497 (1942)).

(10) This study.

(11) Reference 8, p. 76.

(12) L. K. Andrews and R. M. Keefer, THIS JOURNAL, **73**, 4169 (1951); **72**, 5170 (1950), and earlier papers.

(13) W. C. Price, *Chem. Revs.*, **41**, 257 (1947).

spectra were taken with a Beckman spectrophotometer, model DU, on at least two different samples. All measurements were made at room temperature, approximately 30°.

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An Improved Synthesis of Tin Tetramethyl[1]

BY WALTER F. EDGELL AND C. H. WARD[2]

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During the course of studies employing various organotin compounds, it was necessary to prepare quantities of tin tetramethyl. Of the several preparative methods reported,[3-6] those employing the Grignard reagent[5-6] were considered more feasible. Although a yield of 80–85% has been reported,[5] the yields obtained in this Laboratory by this method have approximated 35%. These methods have the disadvantages of being time consuming, of requiring a very large excess of methyl Grignard reagent, and of yielding a product which can be isolated only after fractional[7] distillation of large quantities of ethyl ether.

The low-boiling reaction media employed by previous workers (ethyl ether or ethyl ether–hydrocarbon mixtures) appear to be responsible for these difficulties. Di-*n*-butyl ether has been used successfully with Grignard reagents where a higher boiling solvent was desired.[8] We have found that the Grignard method gives superior results when *n*-butyl ether is used as the reaction medium. The tin tetramethyl is readily isolated from the *n*-butyl ether in high yield. Smaller excesses of methyl Grignard reagent have been employed with equal success[9] and the over-all time requirements are much lower. Pertinent data for three preparations are given in Table I.

TABLE I

TIN TETRAMETHYL PREPARATION DATA

$SnCl_4$ used, mole	CH_3MgI in excess, mole	Yield of $Sn(CH_3)_4$ (based on $SnCl_4$), %
0.20	0.80	90
.23	.68	85
.29	.44	91

Experimental

Fifty grams (2.06 g. atoms) of magnesium turnings and about 600 ml. of *n*-butyl ether were placed in a 1-liter three-necked round-bottom flask fitted with a mercury-sealed stirrer of the Hershberg type, an Allihn reflux condenser with a thermometer and drying tube, and a dropping funnel. The *n*-butyl ether was prepared for use according to the procedure described by Vogel.[10] A solution of 225 g. (1.59 moles) of freshly distilled methyl iodide in an equal volume of *n*-butyl ether was placed in the dropping funnel and then, after the addition of a few crystals of iodine to the magnesium suspension, a 3–5 ml. portion of this methyl iodide solution was added with stirring to the reaction flask. Formation of the Grignard reagent usually occurs immediately, but gentle heating was sometimes required. The remaining methyl iodide solution was added dropwise at a rate sufficient to cause only gentle refluxing. About three hours was required for this step. After allowing the reaction mixture to cool to room temperature, 50–75 g. (0.19–0.29 mole) of anhydrous stannic chloride was added dropwise. Only gentle refluxing should occur during this step which requires 2–2.5 hr. to complete. The reaction mixture was heated under steady reflux (85–95°) for one hour and then allowed to stand for several hours. After replacing the Allihn condenser with a Claisen head and West condenser, the crude product was distilled from the reaction mixture. A mixture of tin tetramethyl and *n*-butyl ether, distilling at 85–95°, is obtained. The tin tetramethyl was isolated by fractional distillation using a Todd column (35–40 plates). The main fraction of tin tetramethyl distils at 76.6°, uncor. (748 mm.). The refractive index and the infrared spectrum were used in establishing the purity of the fractionated product.[11,12]

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(1) Abstracted from the Ph.D. thesis of C. H. Ward.

(2) Purdue Research Foundation Fellow, 1950–1952, and Allied Chemical and Dye Corporation Fellow, 1952–1953.

(3) J. Schmidt, "Organo-Metallverbindungen," II Teil, Edward Brothers, Inc., Ann Arbor, 1943, p. 242.

(4) (a) C. A. Krause and C. C. Callis, U. S. Patent 1,639,947 (1927); (b) R. H. Bullard and W. B. Robinson, THIS JOURNAL, **49**, 1368 (1927).

(5) S. N. Naumov and Z. M. Manulkin, *J. Gen. Chem.* (*U.S.S.R.*), **5**, 281 (1935).

(6) (a) C. E. Waring and W. S. Horton, THIS JOURNAL, **67**, 540 (1945); (b) H. Korsching, *Z. Naturforsch.*, **1**, 219 (1946).

(7) The marked affinity of tin tetramethyl for ethyl ether precludes simple distillation.

(8) C. S. Marvel, A. T. Blomquist and L. E. Vaughn, THIS JOURNAL, **50**, 2810 (1928), and many others.

(9) No effort was made to determine the minimum amount of Grignard reagent which might be employed.

(10) A. I. Vogel, "A Textbook of Practical Organic Chemistry," 2nd Ed., Longmans, Green and Co., London, 1951, p. 254.

(11) Infrared spectrum to be published soon.

(12) Tin tetramethyl is an excellent solvent for Silicone stopcock greases and the presence of extremely small amounts of these lubricants gives rise to strong spurious infrared bands in the 8–10 μ region.

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A Hydrocarbostyril Derivative with a Two-Carbon *Peri* Bridge

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The literature describes no derivative of hydrocarbostyril containing a two-carbon *peri* bridge. We have been able to prepare an example of this tricyclic system in two ways, β-(*o*-nitrophenyl)-glutaric acid (II) being the starting material in both syntheses. In the first of these, the chloride of the nitro acid was converted to 4-nitroindan-1-one-3-acetic acid (I) by the Friedel–Crafts reaction. The ring closure had been effected earlier by Manske[1] on the unnitrated acid, and a similar closure was realized by Hoyer[2] with *o*-nitrohydrocinnamic acid. The heterocycle was then closed by subjecting the keto acid I to hydrogenation over Raney nickel, the tricyclic compound being produced in 90% yield.

In the second method, the heterocycle was formed first by the reductive cyclization of β-(*o*-nitrophenyl)-glutaric acid by essentially the method used by Blout and Silvermann[3] on *o*-nitrocinnamic acid, and the product, hydrocarbostyril-4-acetic acid (III), was converted to the tricyclic compound V by the Friedel–Crafts method. The identity of the two tricyclic products serves to establish the structure.

(1) R. H. Manske, THIS JOURNAL, **53**, 1104 (1931).

(2) H. Hoyer, *J. prakt. Chem.*, **139**, 94 (1934).

(3) E. R. Blout and D. C. Silvermann, THIS JOURNAL, **66**, 1442 (1944).