*Tetrahedron.* Vol. 27, pp. 4003 to 4011. Pergamon Press 1971. Printed in Great Britain

# STUDIES ON 1,3-DITHIOLIUM CATIONS—IV[1,2]

## SYNTHESES, PHYSIOCHEMICAL PROPERTIES AND STABILITIES OF MONO-, DI-, AND TRIPHENYL- AND 2-*p*-SUBSTITUTED PHENYL-1,3-DITHIOLIUM CATIONS

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*Received in Japan* 13 *February* 1971 ; *Received in the UK for publication* 3 *May* 1971)

**Abstract**—In order to investigate the changes in the properties of 1,3-dithiolium cations when aryl groups are introduced into various positions, a number of 2-*p*-substituted phenyl-4-phenyl-1,3-dithiolium salts were prepared and their UV and NMR spectra and $pK_{R^+}$ values determined. Results showed that a phenyl group introduced to the C-2 position largely stabilized the 1,3-dithiolium cation by conjugation. Substituent effects in 2-*p*-substituted phenyl-4-phenyl-1,3-dithiolium cations indicated that the positive charge is largely localized on the S—C—S grouping in the 1,3-dithiolium ring.

## INTRODUCTION

THE 1,3-dithiolium cation (I) is a 5-membered ring having 6$\pi$ electrons; it is isoelectronic with tropylium cation (II). By replacement of the two sulfur atoms in I by C=C groups, II can be formally produced. Cation I is, therefore, expected to possess a potential "aromatic" sextet.[3]

I

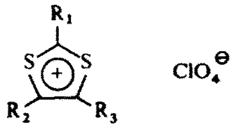
II

Our recent investigation of 4-*p*-substituted phenyl-1,3-dithiolium cations revealed that the C-2 position has the lowest $\pi$-electron density and that nucleophilic reagents exclusively attack this position giving covalently bonded 1,3-dithiole derivatives.[1,4] Our interest was then focused on the nature and extent of delocalization of the positive charge in the 1,3-dithiolium ring and the changes of physicochemical properties of this cation when aryl groups are introduced to various positions. In view of this it became of interest to investigate the substituent effect of 2-*p*-substituted phenyl-1,3-dithiolium cations. These cations are easily accessible as stable salts from the reactions described below.

## RESULTS

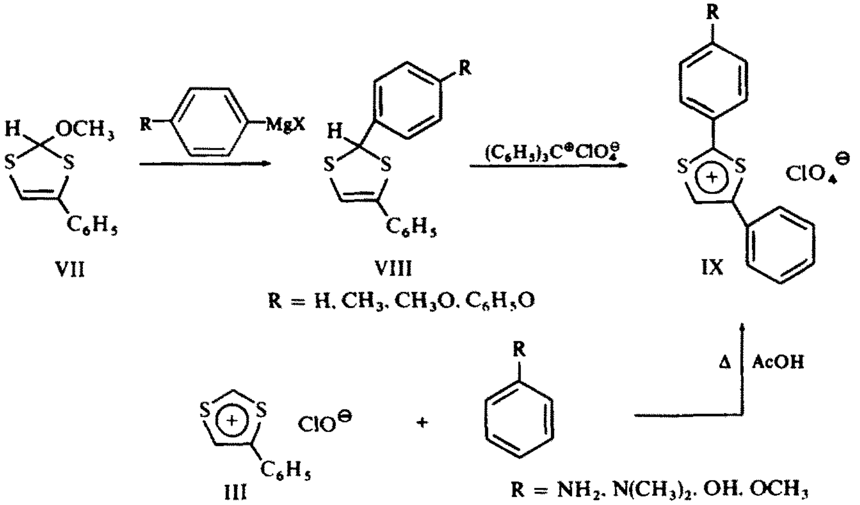
### *Synthesis and reaction*

4-Phenyl- (III), 4,5-diphenyl- (IV), 2,4-diphenyl- (V), and 2,4,5-triphenyl-1,3-dithiolium salts (VI) were prepared by the method previously reported.[4,5]



III: $R_1 = R_2 = H, R_3 = C_6H_5$
IV: $R_1 = H, R_2 = R_3 = C_6H_5$
V: $R_2 = H, R_1 = R_3 = C_6H_5$
VI: $R_1 = R_2 = R_3 = C_6H_5$

2-*p*-Substituted phenyl-4-phenyl-1,3-dithiolium perchlorates (IX) were prepared by the Grignard reaction of 2-methoxy-4-phenyl-1,3-dithiole (VII) with 2-*p*-substituted phenyl magnesium halide followed by hydride abstraction with trityl perchlorate. In this manner, 2-*p*-methyl, methoxy and phenoxy derivatives were obtained.

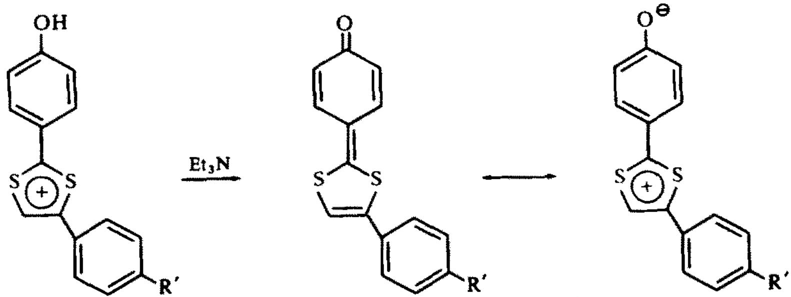


$R = H, CH_3, CH_3O, C_6H_5O$

$R = NH_2, N(CH_3)_2, OH, OCH_3$

On the other hand, heating III with aniline, dimethylaniline, phenol, or anisol in glacial AcOH gave directly the corresponding 2-*p*-substituted phenyl derivatives. These salts are yellow to red crystals and very stable at room temperature (Table 1).

Treatment of 2-(4-hydroxyphenyl)-4-phenyl-1,3-dithiolium perchlorate (IX: R = OH) with $Et_3N$ gave 2-quino-1,3-dithiole (X: R′ = H), m.p. 168–171° (decomp), as red crystals which showed strong UV absorption at a long wave-length, $\lambda_{max}^{EtOH}$ 247, 312, 484, 515 mμ (log ε 4·28, 3·50, 4·17, 4·49). Similarly, 2-(4-hydroxyphenyl)-4-(4-chlorophenyl)-1,3-dithiolium perchlorate (IX: R = OH, R′ = Cl) gave 2-quino-1,3-dithiole (X: R′ = Cl) by treatment with $Et_3N$.



IX: R = OH

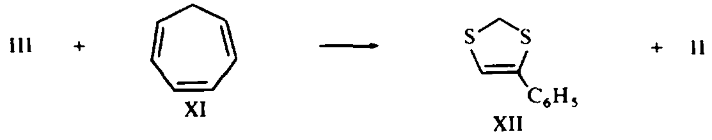
X: R′ = H, Cl

TABLE 1. ANALYTICAL DATA OF 2-*p*-SUBSTITUTED PHENYL-4-PHENYL-1,3-DITHIOLIUM PERCHLORATE (IX)

| R | M.p. (decomp) C° | Yield % | Formula | Calculated (%) |  |  |  | Found (%) |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  | C | H | S | Cl | C | H | S | Cl |
| $CH_3$ | 156–158° | 77[a] | $C_{16}H_{13}O_4S_2Cl$ | 52·09 | 3·59 | 17·39 | 9·61 | 52·26 | 3·55 | 17·21 | 9·32 |
| $CH_3O$ | 186–188° | 36[a] | $C_{16}H_{13}O_5S_2Cl$ | 49·92 | 3·40 | 16·66 | 9·21 | 49·53 | 3·40 | 16·48 | 9·30 |
| $C_6H_5O$ | 177–181° | 47[a] | $C_{21}H_{15}O_5S_2Cl$ | 56·43 | 3·38 | 7·93 | 14·35 | 56·74 | 3·49 | 7·79 | 14·60 |
| $NH_2$ | 246–248° | 25 | $C_{15}H_{12}O_4NS_2Cl$ | 48·72 | 3·27 | 17·33 | 9·58 | 48·84 | 3·37 | 17·09 | 9·96 |
| $N(CH_3)_2$ | 212–213°[b] | 23 | $C_{17}H_{16}O_4NS_2Cl \cdot H_2O$ | 49·08 | 4·36 |  | 8·52 | 49·80 | 4·42 |  | 7·93 |
| OH | 215–217° | 50 | $C_{15}H_{11}O_5S_2Cl$ | 48·59 | 2·99 | 17·30 | 9·56 | 48·60 | 3·04 | 17·36 | 9·66 |

[a] Grignard reaction. [b] Ref 6 reports m.p. 219–220° for anhyd. perchlorate.

4-Phenyl-1,3-dithiolium perchlorate (III) abstracted hydride anion from cycloheptatriene (XI) giving the thermodynamically more stable tropylium ion (II) as perchlorate and 1,3-dithiole (XII).



*UV spectra measurement*

The UV spectra of these cations were taken in $CH_3CN$ or in 50% $H_2SO_4$. Alcohol is not suitable as solvent because of the nucleophilic attack of the solvent to the C-2 position giving a covalently bonded product.[4]

As shown in Fig 1, III and IV showed maxima at about 340 mμ, but V and VI, having a phenyl group at the C-2 position, showed a strong absorption band at about 390 mμ.

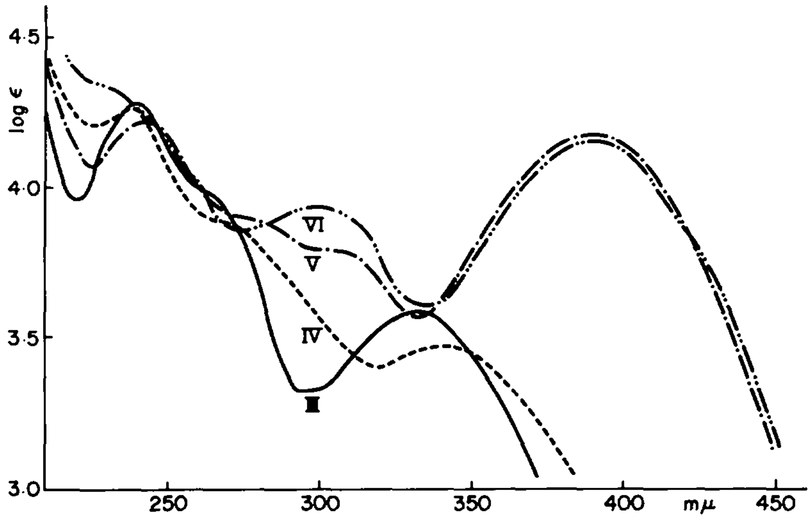


FIG 1. UV spectra of III, IV, V and VI in $CH_3CN$

The UV spectra of 2-*p*-substituted phenyl derivatives (IX) in $CH_3CN$ showed a marked red shift by electron donating groups (Table 2). There is a linear correlation between intensities and wave-numbers (Fig 2). The UV spectra of H, $CH_3$, $C_6H_5O$, $CH_3O$ and OH substituted compounds showed maxima at the same position both in 50% $H_2SO_4$ and in $CH_3CN$. However, $NH_2$ and $N(CH_3)_2$ compounds showed a blue shift in 50% $H_2SO_4$. This can be ascribed to protonation of the amino nitrogen giving quaternary bases which have electron withdrawing character (Table 2).

When the wave-number of the longest wave-length bands are plotted against Hammett $\sigma_p$ values,[7] a straight line is obtained (Fig 3), giving equation 1.

$$\nu(\text{cm}^{-1} \times 10^{-3}) = 8{\cdot}8\,\sigma_p + 26{\cdot}1 \qquad (1)$$

TABLE 2. SPECTRAL DATA OF 2-*p*-SUBSTITUTED PHENYL-4-PHENYL-1,3-DITHIOLIUM PERCHLORATE (IX)

| R | UV | | NMR (C-5-H) | |
|---|---|---|---|---|
| | $\lambda_{max}^{CH_3CN}$ mμ (log ε) | $\lambda_{max}^{50\%\ H_2SO_4}$ mμ (log ε) | τ ($CF_3COOD$) | τ ($CD_3CN$) |
| H | 242·5, 278 (sh), 307, 390<br>(4·24, 3·90, 3·80, 4·19) | 243, 310, 394<br>(4·38, 3·95, 4·35) | 1·22 | 1·06 |
| $CH_3$ | 242, 282 (sh), 317, 402<br>(4·32, 3·84, 3·77, 4·36) | 244, 283 (sh), 321, 408<br>(4·27, 3·80, 3·73, 4·35) | 1·35 | 1·18 |
| $CH_3O$ | 245, 292 (sh), 333, 432<br>(4·45, 3·65, 3·50, 4·49) | 245, 292 (sh), 335, 434<br>(4·35, 3·67, 3·57, 4·47) | 1·48 | 1·32 |
| $C_6H_5O$ | 244, 290 (sh), 334, 423<br>(4·39, 3·75, 3·66, 4·46) | 245, 290 (sh), 336, 430<br>(4·37, 3·80, 3·66, 4·46) | 1·48 | 1·27 |
| $NH_2$ | 248, 337 (sh), 499<br>(4·27, 3·40, 4·78) | 243, 277, 307, 392<br>(4·20, 3·99, 3·91, 4·13) | 1·20 | 1·68 |
| $N(CH_3)_2$[a] | 246, 258·5 (sh), 536<br>(4·26, 4·18, 4·82) | 243, 278, 306 (sh), 392[a]<br>(4·17, 4·01, 3·94, 4·11) | 1·05[b] | 1·93 |
| OH | 244, 294 (sh), 336, 428<br>(4·29, 3·62, 3·49, 4·44) | 245, 293 (sh), 333, 424<br>(4·26, 3·63, 3·58, 4·42) | 1·50 | 1·38 |

[a] Ref 6 reports $\lambda_{max}^{70\%\ HClO_4}$ 243, 278, 390 mμ (log ε 4·19, 4·01, 4·08) and $\lambda_{max}^{CF_3COOH}$ 275, 300, 298, 535 mμ (log ε 4·09, 4·03, 4·08, 3·70).

[b] Ref 6 reports τ 1·00 for C-5 proton in $CF_3COOH$.

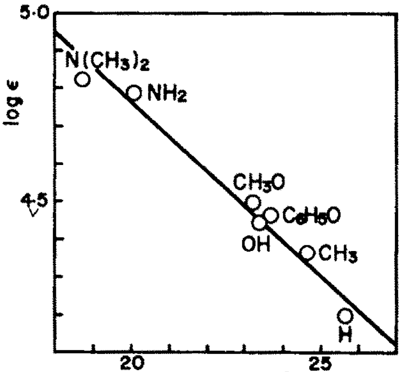


FIG 2. Wavenumber (ν) vs. intensity (log ε) of the longest wavelength UV absorption band of IX in $CH_3CN$

*NMR spectra measurements*

The NMR spectra of IX were taken in $CD_3CN$ or in $CF_3COOD$ and the chemical shifts of the C-5 proton in 1,3-dithiolium ring were obtained as shown in Table 2. With 2-*p*-substituted phenyl derivatives, the C-5 proton signal in $CD_3CN$ appeared at higher fields than in the spectra of the unsubstituted compound (V). However, in $CF_3COOD$, $NH_2$ and $N(CH_3)_2$ compounds showed C-5 proton signals at lower fields than that for the unsubstituted compound (V). This must be due to protonation of the amino nitrogens. This point has been discussed previously by Campaigne and Hamilton.[6]

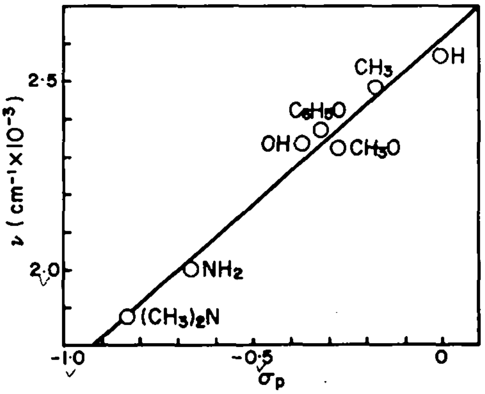


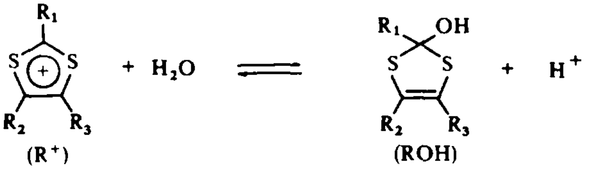
FIG 3. Correlation of wavenumber (ν) of the longest wave length band with Hammett $\sigma_p$ constant (in $CH_3CN$)

When the C-5 proton chemical shifts are plotted against Hammett $\sigma_p$, a straight line presenting equation 2 was obtained (Fig 4).

$$\tau = -1{\cdot}05\,\sigma_p + 1{\cdot}02 \qquad (2)$$

*p*$K_{R^+}$ *value measurement*

A good criterion for the stability of the carbonium ion is the p$K_{R^+}$ value for the carbonium ion-carbinol equilibrium (eq. 3) (p$K$ presents the pH at which the concentration of $R^+$ and ROH are equal).[8] p$K_{R^+}$ measurement has been carried out by a



(3)

spectroscopic method in 50% EtOH or in 10% DMF and the results are in Tables 3 and 4. The media used are not standard ones for p$K_{R^+}$ determination, so these figures are relative not absolute values.

TABLE 3. APPARENT p$K_{R^+}$-VALUES OF VARIOUSLY SUBSTITUTED PHENYL 1,3-DITHIOLIUM IONS

| | p$K_{R^+}$ in 10% DMF | p$K_{R^+}$ in 50% EtOH |
|---|---|---|
| 4-Phenyl (III) | 2·2 | 0·7 |
| 4,5-Diphenyl (IV) | 1·8 | 0·3 |
| 2,4-Diphenyl (V) | 4·4 | 3·3 |
| 2,4,5-Triphenyl (VI) | | 2·6 |

With 2-*p*-substituted phenyl derivatives (IX), electron releasing groups raised the p$K_{R^+}$ values compared to that of the unsubstituted compound (Table 4). When the p$K_{R^+}$ values were plotted against Brown–Okamoto's $\sigma^+$ values,[9] a straight line was obtained which is represented by equation 4.

$$pK_{R^+} = -1{\cdot}0\,\sigma^+ + 3{\cdot}33 \tag{4}$$

When Deno's $\sigma^+$ parameter[10] was used, a straight line was also obtained and the $\rho$ value was shown to be $-1{\cdot}2$ (Fig 5).

TABLE 4. APPARENT $pK_{R^+}$-VALUES OF 2-*p*-SUBSTITUTED PHENYL-4-PHENYL-1,3-DITHIOLIUM PERCHLORATE (IX) IN 50% EtOH

| R | H | $CH_3$ | $C_6H_5O$ | $CH_3O$ |
|---|---|---|---|---|
| $pK_{R^+}$ | 3·32 | 3·67 | 3·79 | 4·11 |

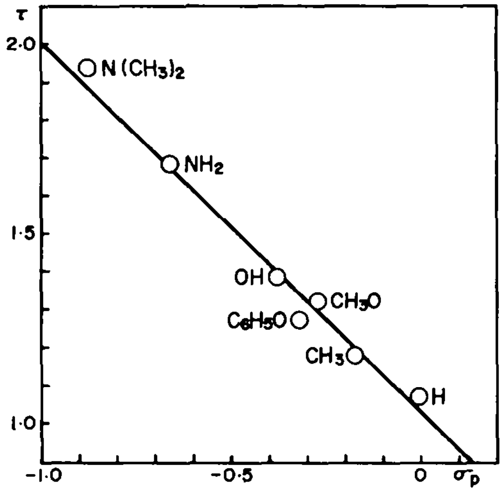


FIG 4. Correlation of Hammett $\sigma_p$ with C-5-H chemical shift of IX (in $CD_3CN$)

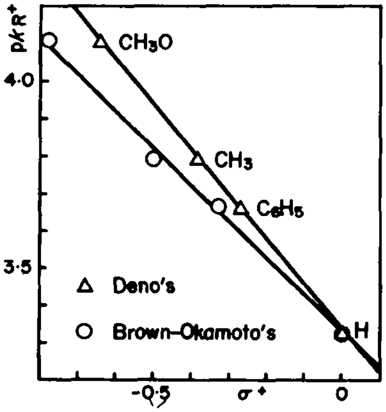


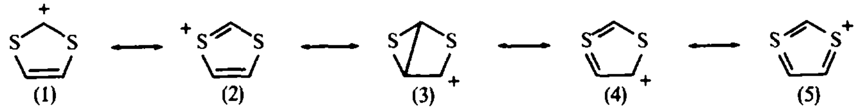
FIG 5. Correlation of $pK_{R^+}$ with $\sigma^+$ values

## DISCUSSION

It has been shown that substituting phenyl for hydrogen at the C-2 position of the 1,3-dithiolium ring caused a marked shift in the UV spectra. This could be expected from the phenyl conjugation with the positively charged 1,3-dithiolium ring as for simple carbonium ions. The thermodynamic stability of these ions was demonstrated by p$K_{R^+}$ measurement. Table 3 shows that introduction of a phenyl group to the C-2 position of the 1,3-dithiolium ring increased the stability of the ion by approximately 2·4 p$K$ units. On the other hand, introduction of a phenyl group to the C-5 position destabilized the ion by approximately 0·4 p$K$ units. This destabilization is probably due to coplanarity interference or inductive effect by the phenyl group.

LCAO–MO theory predicts that the greatest positive-charge density is at the C-2 position of the 1,3-dithiolium cation,[1,3] and the NMR resonance for a proton of this position is at the lowest field[1,5] supporting this prediction.

The effect of replacing C-2 phenyl substituents with anisyl, phenoxyphenyl, and tolyl groups in 4-phenyl-1,3-dithiolium cation is to increase the stability of the ion (Table 4), and a linear correlation of the p$K_{R^+}$ values with Brown–Okamoto's $\sigma^+$ or Deno's $\sigma^+$ parameter (Fig 5) is obtained. This contrasts with the linear correlation between p$K_{R^+}$ and Hammett $\sigma_p$ constant in 4-*p*-substituted phenyl-1,3-dithiolium cations.[1] Brown–Okamoto's $\sigma^+$ was derived from the solvolysis of t-cummyl chloride and Deno's $\sigma^+$ was derived from the p$K_{R^+}$ of trityl alcohol. Therefore, the reaction mechanism is the same in these cases, involving the direct attachment of the *p*-substituted phenyl group to the carbonium ion. However, our $\rho$ value ($-1·0$, $-1·2$) is rather small compared to those of Brown–Okamoto or Deno, their $\rho$ values being $-4·5$ and $-4·0$, respectively. This means that the contribution of the substituent effect to the reaction center in the 2-*p*-substituted phenyl-4-phenyl-1,3-dithiolium cation is relatively small compared to those of t-cummyl or trityl cations, and this may be ascribed to cation stabilization by the 1,3-dithiolium ring. Thus, it can be concluded that the positive charge is largely localized on the S–C–S grouping and that the most important limiting structures in resonance are the carbonium-sulfonium structures (I (1) and (2)) as Prinzbach and Futterer had suggested in their review.[3] The contribution of other structures will be estimated in a subsequent paper.



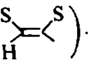
I (1) (2) (3) (4) (5)

## EXPERIMENTAL

M.ps were determined in a capillary on a Yamato Apparatus MP-1 and were uncorrected. The NMR spectra were recorded on a Varian A-60 (TMS as an internal reference), and UV spectra on a Hitachi EPS-3 spectrophotometer. p$K_{R^+}$ values were determined by the spectrometric method described in the preceding paper.[1]

*General procedure for the preparation of* 2-p-*substituted phenyl-4-phenyl*-1,3-*dithiolium perchlorate* (IX). (a) To a suspension of 0·0036 mole metallic Mg in ether (25 ml), 0·0032 mole of *p*-substituted bromobenzene and a small amount of $I_2$ were added and the suspension was stirred under reflux for 2 hr to give *p*-substituted PhMgBr solution. To this solution, 0·0013 mole of 2-methoxy-4-phenyl-1,3-dithiole (VII) was added and stirred under reflux for 1·5 hr. Saturated $NH_4Cl$ solution was added to the mixture and the ether layer decanted, washed with $H_2O$, dried over anhyd. $MgSO_4$, and evaporated to give an oil. To a solution of this oil in 2 ml of AcOH. trityl perchlorate (prepared from 0·3 g of triphenyl carbinol. 3 ml of $Ac_2O$. and 0·3 ml of 70% $HClO_4$) was added and the solution warmed for 2 min on a steam bath. Ether was added and crystals (IX: R = $CH_3$. $CH_3O$. $C_6H_5O$) were obtained. When an oil separated. it was dissolved in MeOH and 10% $Na_2CO_3$ added to convert the product into 2-methoxy-2-*p*-substituted phenyl-4-phenyl-1.3-dithiole. The solution was concentrated and the residue was added to $H_2O$. and ether extracted. After extract concentration. 70% $HClO_4$ was added dropwise to give crystal separation (IX). Tables 1 and 2 show the properties of these perchlorates.

(b) A mixture of 0·0011 mole of 4-phenyl-1.3-dithiolium perchlorate (III) and 0·0032 mole of substituted benzene in 5 ml of glacial AcOH was refluxed for 8 hr. After being cooled separated crystals were collected and washed with cold AcOH to give IX (R = $NH_2$. $N(CH_3)_2$. OH. $OCH_3$).

*2-(4-Oxocyclohexa-2.5-dienylidene)-4-phenyl-1.3-dithiole* (X: R′ = H). To a suspension of 0·01 g 2-(4-hydroxyphenyl)-4-phenyl-1.3-dithiolium perchlorate (IX: R = OH) triethylamine was added dropwise to give dark red solution. $CHCl_3$ was added and the solution washed with $H_2O$. The $CHCl_3$ layer was dried and evaporated. The residue was dissolved in EtOH and $H_2O$ added causing a red ppt. (X: R′ = H) m.p. 160° (decomp). (Found: C. 66·23; H. 3·83; S. 24·10. $C_{15}H_{10}OS_2$ requires: C. 66·64; H. 3·73; S. 23·72%). UV (EtOH): $\lambda_{max}$ 247. 312. 484 and 515 mμ (log ε. 4·28. 3·50. 4·17. and 4·49). NMR ($CDCl_3$): τ 3·02 ().

*2-(4-Oxocyclohexa-2.5-dienylidene)-4-(4-chlorophenyl)-1.3-dithiole X: R′ = Cl.* To a suspension of 0·18 g of 2-(4-hydroxyphenyl)-4-(4-chlorophenyl)-1.3-dithiolium perchlorate in 2 ml of $CHCl_3$ 0·4 g of triethylamine was added dropwise to give dark red precipitate. It was collected and washed with hot EtOH to give 0·1 g red crystals (X: R′ = Cl). m.p. 210–213° (decomp). (Found: C. 58·49; H. 2·97; S. 20·94; Cl. 12·04. $C_{15}H_9OS_2Cl$ requires: C. 59·10; H. 2·97; S. 21·04; Cl. 11·65%). UV (EtOH): $\lambda_{max}$ 249. 265 (sh). 315. 485 and 516 mμ (log ε 4·29. 4·21. 4·40. 4·79).

*Reaction of* 4-*phenyl*-1.3-*dithiolium perchlorate* III *with cycloheptatriene* XI. A mixture of 0·05 g cycloheptatriene (XI) and 0·13 g 4-phenyl-1.3-dithiolium perchlorate (III) in 3 ml of AcOH was heated at 90° for 1 hr. cooled and crystals which separated were found to be a mixture of tropylium perchlorate (II) and 4-phenyl-1.3-dithiolium perchlorate (III) by IR and NMR. AcOH filtrate was added to $H_2O$ and extracted with $Et_2O$. dried and evaporated to leave oil found to be identical with 4-phenyl-1.3-dithiole (XII) by TLC ($SiO_2$. $Et_2O$-n-Hexane. 1:1. $R_f$ 0·62).

*Acknowledgements*—The author is much indebted to Prof. P. von R. Schleyer of Princeton University for helpful discussion. The author is also grateful to Prof. Emeritus E. Ochiai of Tokyo University and to Dr. K. Takeda. Director of this laboratory. for their encouragement and to Dr. H. Tanida of this laboratory for stimulating discussion and kind interest in this investigation.

## REFERENCES

[1] Part III: A Takamizawa and K. Hirai. *Chem. Pharm. Bull.. Tokyo* **18**. 865 (1970)

[2] A part of this report was presented at the International Symposium on the Chemistry of Nonbenzenoid Aromatic Compounds. Sendai. Aug. 1970. Abstracts of papers. p. 39

[3] H. Prinzbach and E. Futterer. "*Advances in Heterocyclic Chemistry.*" Vol. 7. p. 39. Ed by A. R. Katritzky and A. J. Boulton. Academic Press: New York and London (1966)

[4] A. Takamizawa and K. Hirai. *Chem. Pharm. Bull.. Tokyo* **17**. 1931 (1969)

[5] A. Takamizawa and K. Hirai. *Ibid.* **17**. 1924 (1969)

[6] E. Campaigne and R. D. Hamilton. *J. Org. Chem.* **29**. 1711 (1964)

[7] D. H. McDaniel and H. C. Brown. *Ibid.* **23**. 420 (1958)

[8] [a] R. Breslow. "*Organic Reaction Mechanisms.*" p. 23; W. A. Benjamin, Inc.: New York and Amsterdam (1966);

[b] R. Breslow. H. Hover and H. W. Chang, *J. Am. Chem. Soc.* **84**. 3168 (1962);

[c] A. Streitwieser. Jr.. "*Molecular Orbital Theory for Organic Chemists.*" p. 363; John Wiley and Sons: New York (1961);

[d] M. A. Battiste and T. J. Barton. *Tetrahedron Letters* 2951 (1968);

[e] R. G. Turnbo. D. L. Sullivan and R. Pettit. *J. Am. Chem. Soc.* **86**. 5630 (1964);

[f] H. A. Olah. C. U. Pittman. Jr. and M. C. R. Symons. "*Carbonium Ions.*" Vol. 1. p. 153. Ed. by G. A. Olah and P. von R. Schleyer: John Wiley and Sons. Inc.: New York (1968)

[9] H. C. Brown and Y. Okamoto. *J. Am. Chem. Soc.* **79**. 1913 (1957); *Ibid.* **80**. 4977 (1958); *J. Org. Chem.* **22**. 485 (1957)

[10] N. C. Deno. J. J. Jaruzelski and A. Schriesheim. *J. Am. Chem. Soc.* **77**. 3044 (1955)