

The Reaction of Thiophthalic Anhydride with Trivalent Phosphorus

J. HODGE MARKGRAF, CHARLES I. HELLER,¹ AND NOYES L. AVERY, III¹

Department of Chemistry, Williams College, Williamstown, Massachusetts 01267

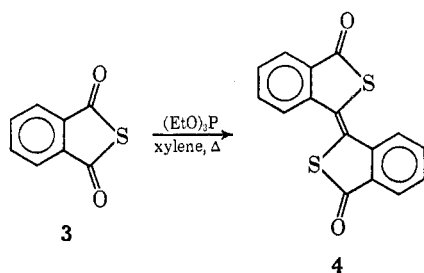
Received September 23, 1969

Thiophthalic anhydride (**3**) undergoes reductive dimerization with triethyl phosphite to yield *trans*-bithiophthalide (**4**), the structure of which was inferred from spectroscopic correlations and confirmed by X-ray analysis. A similar reaction of **3** with tris(dimethylamino)phosphine gives a novel mixture of products (**12** and **13**), the structures of which are assigned from extensive spectral data. The different products are rationalized in terms of the pathways available to a common phosphorane intermediate (**16**).

Among the extensive literature on the reactions of trivalent phosphorus species with carbonyl compounds,² cyclic anhydrides have received limited attention.³ Although it was reported a decade ago that phthalic anhydride (**1**) was converted by triethyl phosphite into 3,3'-bipthalide (**2**),⁴ no subsequent studies of this novel reductive dimerization appeared until very recently. The extension of this reaction to disubstituted maleic anhydrides and thiophthalic anhydride (**3**) was reported in a recent communication.⁵ We present here the results of a similar study of the reactions of **3** with several P(III) compounds. Our choice of the sulfur analog was based on the greater electrophilicity of sulfur than oxygen toward phosphorus. It was felt that a change in mechanism between **1** and **3**, as was observed with epoxides and episulfides,^{6,7} might afford a new process for constructing benzocyclobutenedione systems.⁸

Results

Treatment of **3** with triethyl phosphite (molar ratio 1:2) in refluxing xylene smoothly afforded *trans*-3,3'-bithiophthalide (**4**) in good yield. Despite the mention of **4** in the literature, the structure of the present



product was assigned with some care. 3,3'-Bithiophthalide was characterized in the previous reports⁹⁻¹¹

(1) Based in part on the Honors Theses, Williams College, of C. I. H. 1964, and N. L. A., 1966.

(2) For general reviews see (a) J. I. G. Cadogan, *Quart. Rev.* (London), **16**, 208 (1962); (b) R. F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry," Academic Press, New York, N. Y., 1965, Chapter 6; (c) A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus," Elsevier Publishing Co., Amsterdam, 1967, Chapter 3.

(3) We refer here to reactivity at the oxygen functions; maleic anhydride reacts at the vinyl carbon. Cf. R. F. Hudson and P. A. Chopard, *Helv. Chim. Acta*, **46**, 2178 (1963).

(4) (a) F. Ramirez, H. Yamanaka, and O. H. Basedow, *J. Org. Chem.*, **24**, 1838 (1959); (b) *J. Amer. Chem. Soc.*, **83**, 173 (1961).

(5) C. W. Bird and D. Y. Wong, *Chem. Commun.*, 932 (1969).

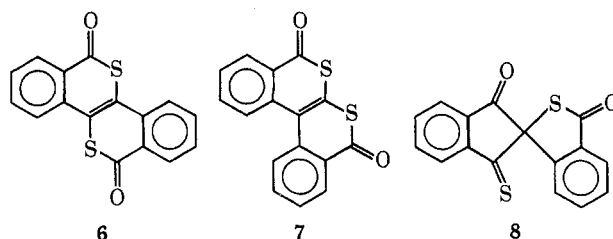
(6) N. P. Neureiter and F. G. Bordwell, *J. Amer. Chem. Soc.*, **81**, 578 (1959).

(7) D. B. Denney and M. J. Boskin, *ibid.*, **82**, 4736 (1960).

(8) The same objective, based on the photolysis of a phthaloyl dixanthate, was reported recently: cf. A. Shaw, S. N. Singh, and M. V. George, *Tetrahedron Lett.*, 3983 (1968).

(9) S. Gabriel and E. Leupold, *Ber.*, **31**, 2646 (1898).

as green-yellow needles, mp 335°, which sublimed to orange-yellow needles; no data on the sublimate were provided. The question of geometric isomerism received no comment. The earlier workers^{9,10} depicted only the *cis* isomer, while the contemporary groups^{5,11} have considered only the *trans* isomer. Unfortunately, no spectroscopic data were available from the recent reports. Finally, the limited degradative studies provided no clues to configuration.^{9,11} The literature was thus insufficient to assist in a definitive structural assignment. Our compound **4** was an orange-yellow substance, mp 351°, which elemental and mass spectrometric analyses confirmed to be C₁₆H₈O₂S₂. In addition to *trans*- (**4**) and *cis*-3,3'-bithiophthalide (**5**), it was necessary to consider the δ -thiolactones **6** and **7** and the spirothiolactone **8**. The infrared spectrum



contained a single carbonyl peak at 1700 cm⁻¹ and no double-bond absorption in the 1650-1670-cm⁻¹ region.¹² These data are inconsistent with **5**, **7**, and **8**.¹⁵ A decision between the remaining structures (**4** and **6**) was possible on the basis of the carbonyl absorption. The *trans*-3,3'-bithiophthalide formulation was consistent with the known variation of $\nu_{C=O}$ (cm⁻¹) with heteroatom and ring size: phthalide,¹⁶ 1761; thiophthalide,¹⁶ 1686; 3-phenylisocoumarin,¹⁷ 1721; and 3-phenylisothiocoumarin,¹⁸ 1635. An uncertainty, however, was introduced into this correlation. At the time that these deductions about **4** were in progress, there appeared a series of articles in which

(10) A. Reissert and H. Holle, *ibid.*, **44**, 3027 (1911).

(11) W. G. Toland and R. W. Campbell, *J. Org. Chem.*, **28**, 3124 (1963).

(12) The exocyclic double bonds of *cis*-bifurandione¹³ and *cis*-oxindigo¹⁴ absorb at 1668 and 1647 cm⁻¹, respectively.

(13) J. C. Sauer, R. D. Cramer, V. A. Engelhardt, T. A. Ford, H. E. Holmquist, and B. W. Howk, *J. Amer. Chem. Soc.*, **81**, 3677 (1959).

(14) H. Güsten, *Chem. Commun.*, 133 (1969).

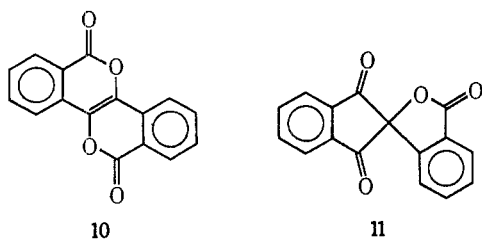
(15) The extremely low solubility of the compound precluded nmr and Raman spectra, which could have corroborated the absence of **5** and **7**.

(16) V. Prey, B. Kerres, and H. Berbalk, *Monatsh. Chem.*, **91**, 774 (1960).

(17) R. L. Letsinger, E. N. Oftedahl, and J. R. Nazy, *J. Amer. Chem. Soc.*, **87**, 742 (1965).

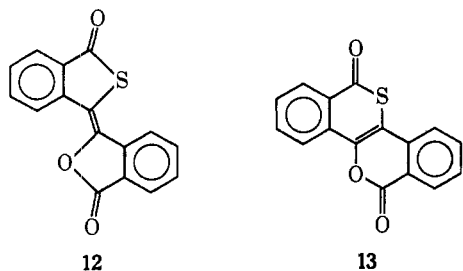
(18) L. Legrand and N. Lozac'h, *Bull. Soc. Chim. Fr.*, 1787 (1964).

trans- (2) and *cis*-3,3'-biphtalide (9) as well as 10 and 11 were reported.¹⁹⁻²¹ There was confusion



among the structural assignments, which cast doubt on the $\nu_{C=O}$ values for the γ - and δ -lactones.²² At this juncture we obtained independent confirmation of structure 4 by crystallographic methods.²⁴

Not only are there differences in the electrophilicity of bivalent oxygen and sulfur toward P(III), but also the reactivities of trivalent phosphorus compounds differ. The relative nucleophilicity of various phosphines has been correlated with their oxidation by sulfur dioxide²⁵ and dimethyl sulfoxide.²⁶ From the latter study, in which the data were best correlated by two series of P(III) compounds, it was inferred that two pathways were involved. Our attention was therefore directed to the reaction of 3 with other phosphines. Although triphenylphosphine showed no reactivity toward 3, the reaction with tris(dimethylamino)phosphine was of more interest. The yellow product, mp 340–341°, obtained in good yield, had the molecular formula $C_{16}H_8O_3S$; mass spectral data confirmed the elemental composition and further established the absence of $C_{16}H_8O_2S_2$ and $C_{18}H_8O_4$ molecular ions. The ir spectrum contained four carbonyl peaks at 1792, 1748, 1701, and 1656 cm^{-1} ; the Raman spectrum showed two strong carbon-carbon double bond stretching fundamentals at 1607 and 1552 cm^{-1} ; and the uv spectrum was indicative of extended conjugation. These data were consistent with a mixture of the γ - and δ -lactones and thiolactones 12 and 13.²⁷ The *trans* isomers were assumed on the basis of the preferred configurations in the biphtalide series.



(19) H.-D. Becker, *J. Org. Chem.*, **29**, 3070 (1964).

(20) R. F. C. Brown and R. K. Solly, *Tetrahedron Lett.*, 169 (1966).

(21) H. A. Staab and J. Ipaktschi, *ibid.*, 583 (1966).

(22) (a) The correct assignments were recently established: H. A. Staab and J. Ipaktschi, *Chem. Ber.*, **101**, 1457 (1968). (b) The biphtalide series, however, still contains inconsistencies; Sauer, *et al.*,¹³ as a structure proof for *trans*-bifurandione, converted it into 2 (*sic*), mp 331–334°, *vis-d-vis* authentic 2, mp 352–354°,⁸ and 10, mp 334–336°.²³

(23) M. P. Cava, D. R. Napier, and R. J. Pohl, *J. Amer. Chem. Soc.*, **85**, 2076 (1963).

(24) The X-ray diffraction analysis was conducted by Professor R. E. Davis, University of Texas; his results will be published separately.

(25) B. C. Smith and G. H. Smith, *J. Chem. Soc.*, 5516 (1965).

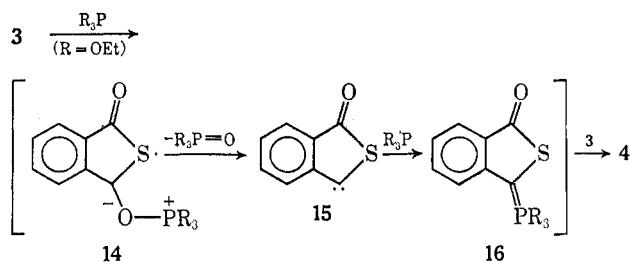
(26) E. H. Amoco-Neizer, S. K. Ray, R. A. Shaw, and B. C. Smith, *ibid.*, 4296 (1965).

(27) Bird and Wong⁵ postulated the previously unknown structure 12 for the product from the reaction of 3 with (EtO)₃P in the presence of 1; the structural assignment was not discussed.

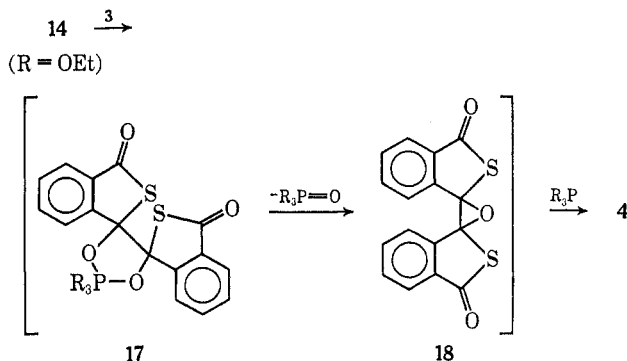
Both compounds are considered primary products, since control experiments established that no isomerization occurred under thermal or acidic conditions. In fact, the same mixture (12 to 13 ratio *ca.* 1:2) was obtained at room temperature. The carbonyl absorptions (in order of decreasing frequency) are consistent with a γ -lactone, δ -lactone, γ -thiolactone, and δ -thiolactone; the relative intensities of the four peaks support this interpretation. Although the force constants are the same for the exocyclic and endocyclic double bonds, the smaller angles (higher compression) of the bonds in a five-membered ring permit the assignment of the higher Raman frequency to 12. The extremely low solubility of the product precluded any chromatographic demonstration of a two-component mixture, and the above structural assignments remain tentative. Preliminary X-ray data, however, are consistent with the postulated structures.²⁸

Discussion

The conversion of 3 into 4 by triethyl phosphite was considered by Bird and Wong⁵ to involve carbene 15 and phosphorane 16, the latter intermediate proceeding to 4 *via* a Wittig reaction.²⁹ Although such



an interpretation has been suggested previously,³⁰ the supporting experiments of Bird and Wong⁵ do not appear to exclude an alternate pathway involving a five-membered cyclic oxyphosphorane intermediate (17)³¹ derived from 14. It is recognized that 17 may



(28) This analysis was conducted by Dr. K. J. Palmer, Western Utilization Research Laboratory, U. S. Department of Agriculture. The data exhibited regularity along the *a* and *c* axes, but irregularity along the *b* axis. The disordered arrangement along the *b* axis (perpendicular to the plane of the molecule) is indicative of irregular stacking; the regularity along the other two axes supports the same configuration for both planar compounds.

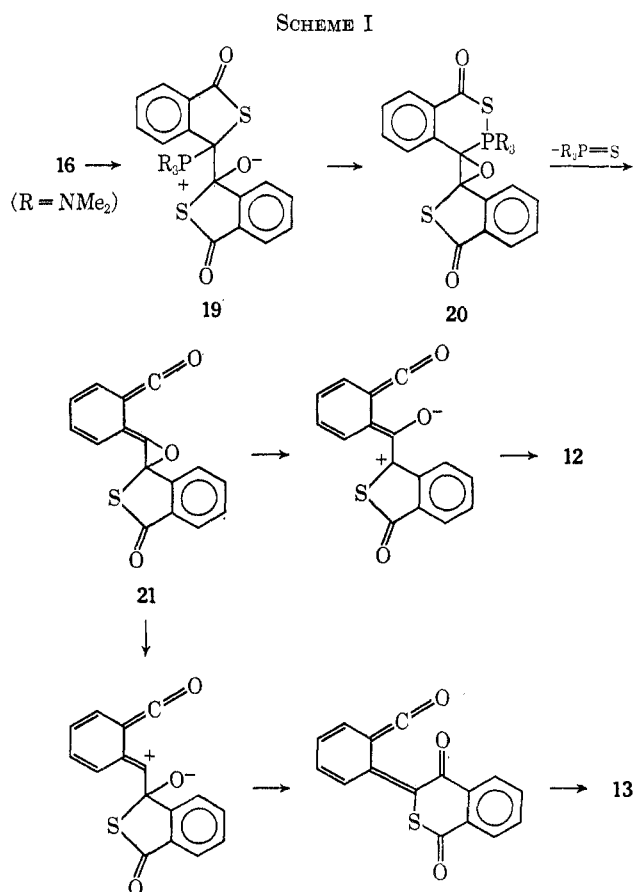
(29) These authors did not indicate the mode of generation of 15, which could result from nucleophilic attack of the phosphorus at either carbon or oxygen of the carbonyl group; species 14 represents the latter pathway.

(30) Reference 2b, p 185.

(31) For a recent review of oxyphosphoranes, see F. Ramirez, *Accounts Chem. Res.*, **1**, 168 (1968).

also exist as an open zwitterion,³² but the cyclic form is consistent with products isolated from similar reactions of triethyl phosphite with isatin,³³ indanetrione,³⁴ and fluorenone.³⁵

The reaction of **3** with tris(dimethylamino)phosphine requires a pathway not only different from the above routes to **4** but also one capable of generating the pair of isomeric C₁₆H₉O₃S products. Scheme I accommodates these requirements proceeding from **16** (R = NM₂). The ring expansion represented for **19** → **20** has been proposed for analogous systems.^{4a,36}



It was established that **13** was not derived from **12** and, therefore, species **21** is viewed as the precursor of both products *via* alternate modes of heterolysis of the epoxide ring. The precedent for ascribing different mechanistic involvement to triethyl phosphite and tris(dimethylamino)phosphine stems from earlier work of Ramirez³⁷ and others.²⁶

Experimental Section

Melting points and boiling points are uncorrected. Spectra were recorded on the following instruments: infrared, Perkin-Elmer 237B; ultraviolet, Cary 14; Raman, Perkin-Elmer laser

(32) F. Ramirez, A. V. Patwardhan, and C. P. Smith, *J. Amer. Chem. Soc.*, **87**, 4973 (1965).

(33) A. Mustafa, M. M. Sidky, and F. M. Soliman, *Tetrahedron*, **22**, 393 (1966).

(34) A. Mustafa, M. M. Sidky, S. M. A. D. Zayed, and M. R. Mahran, *Justus Liebigs Ann. Chem.*, **712**, 116 (1968).

(35) (a) F. Ramirez and C. P. Smith, *Chem. Commun.*, 662 (1967); (b) I. J. Borowitz and M. Anschel, *Tetrahedron Lett.*, 1517 (1967).

(36) W. Adam, R. J. Ramirez, and S.-C. Tsai, *J. Amer. Chem. Soc.*, **91**, 1254 (1969).

(37) F. Ramirez, A. S. Gulati, and C. P. Smith, *ibid.*, **89**, 6283 (1967).

Raman LR-1. Mass spectra were obtained with a CEC 21-110B spectrometer using direct introduction. All distillations and reactions were conducted under a nitrogen atmosphere. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. 11377.

Materials.—Triphenylphosphine³⁸ was purified by the method of Grisley, *et al.*,³⁹ mp 80–81° (EtOH) (lit.⁴⁰ mp 80°). Triethyl phosphite was treated repeatedly with sodium ribbon and the filtrate was distilled; a middle fraction was collected, bp 42.5–43.0° (6 mm) [lit.⁴¹ bp 46–47° (13 mm)]. Tris(dimethylamino)phosphine was prepared by the method of Burg and Slota;⁴² a middle fraction was collected, bp 40–41° (5 mm) [lit.⁴³ bp 49–51° (12 mm)]. Thiophthalic anhydride (**3**) was prepared by the method of Reissert and Holle;¹⁰ mp 111.2–112.2° (absolute EtOH) (lit.¹⁰ mp 114°); ir (KBr) 1792 (w), 1742 (w), 1695 (s), and 1658 cm⁻¹ (m); uv max (CH₃CN) 221 mμ (ε 2050), 231 (21,800), and 254 (8500). Biphthalide (**2**) was prepared by the method of Ramirez, *et al.*;^{4b} mp 350–351.5° (xylene) (lit.^{4b} mp 352–354°); ir (KBr) 1786 cm⁻¹; uv max⁴⁴ (CH₃CN) 219 mμ (ε 39,500), 225 (39,000), 256 (16,000), 291 (12,500), 303 (14,000), 357 (29,500) and 369 (sh, 24,500); Raman (solid) 1692 cm⁻¹. Xylene (bp 137.0–139.0°, Matheson Coleman and Bell A.C.S. analyzed reagent) was dried over sodium.

Reaction of Thiophthalic Anhydride (3) with P(III) Compounds.—The following general procedure was employed. A solution of **3** (*ca.* 3 mmol) and the phosphite or phosphine (*ca.* 6 mmol) in 10 ml of solvent was stirred at reflux for the periods indicated in Table I; the solid was collected from the cooled reaction mixture, washed with benzene, and dried. Recrystallization from xylene (charcoal treatment) afforded purified product.

TABLE I
REACTIONS OF THIOPHTHALIC ANHYDRIDE AND R₃P

R	Solvent ^a	Time, hr	Yield, %	Product
EtO	Benzene	24	9	4
EtO	Toluene	24	64	4
EtO	Xylene	24	82	4
EtO	Xylene	12	82	4
EtO	Xylene	6	68	4
EtO	Diglyme	24	64	4
Me ₂ N	Xylene	12	60	12 + 13
Me ₂ N	Xylene ^b	12	72	12 + 13
Ph	Xylene	12	0	

^a All runs conducted at reflux temperature, unless noted.

^b Room temperature.

From the reaction with (EtO)₃P was obtained *trans*-bithiophthalide (**4**): mp 350–351°; ir (KBr) 1700 cm⁻¹; uv max (CH₃CN) 213 mμ (ε 22,900), 243 (32,200), 300 (7800), and 401 (23,000); mass spectrum (70 eV) *m/e* 295.9960 (molecular ion).

Anal. Calcd for C₁₆H₉O₃S₂: C, 64.84; H, 2.72; S, 21.64; mol wt, 295.9966. Found: C, 64.98; H, 2.77; S, 21.69.

From the reaction with (Me₂N)₃P was obtained a mixture of **12** and **13**: mp 340–341° (vacuum sublimation); ir (KBr) 1792 (m), 1748 (s), 1701 (m), and 1656 cm⁻¹ (s); uv max (CH₃CN) 226 mμ (ε 56,200), 246 (sh, 29,800), 280 (7600), 315 (11,300), 367 (18,400), and 384 (15,600); Raman (solid) 1635 (w), 1607 (s), 1590 (w), 1552 (s), and 1484 cm⁻¹ (w); mass spectrum (70 eV) *m/e* 280.0190 (molecular ion).

Anal. Calcd for C₁₆H₉O₃S: C, 68.57; H, 2.86; S, 11.43; mol wt, 280.0194. Found: C, 68.14; H, 2.86; S, 11.60.

Attempted Isomerizations.¹⁸—The product (70 mg of **4** or **12** + **13**) was dissolved in 12 ml of hot, concentrated sulfuric acid, kept at 110° for 1 hr, and poured onto ice. The recovered product in each case exhibited no change in its melting point or ir and uv spectra.

(38) We thank the Metal & Thermit Corp. for a generous gift of this material.

(39) D. W. Grisley, Jr., J. C. Alm, and C. N. Matthews, *Tetrahedron*, **21**, 5 (1965).

(40) F. Ramirez, C. P. Smith, A. S. Gulati, and A. V. Patwardhan, *Tetrahedron Lett.*, 2151 (1966).

(41) T. R. Emerson and C. W. Rees, *J. Chem. Soc.*, 1917 (1962).

(42) A. B. Burg and P. J. Slota, Jr., *J. Amer. Chem. Soc.*, **80**, 1107 (1958).

(43) V. Mark, *Org. Syn.*, **46**, 42 (1966).

(44) H.-D. Becker, Report No. 64-RL-3631C, General Electric Co., 1964.

Registry No.—2, 19357-64-3; 3, 5698-59-9; 4, 23667-32-5; 12, 23667-33-6; 13, 23667-34-7.

Acknowledgments.—The authors are grateful to Dr. C. W. Koch, University of California, Berkeley, and Dr. J. R. Scherer, Western Utilization Research

Laboratory, USDA, for the mass spectral and Raman data, respectively. We are indebted to Professor R. E. Davis and Dr. K. J. Palmer for the X-ray analyses. We thank Dr. H.-D. Becker, General Electric Co., for helpful correspondence relating to the biphthalide structures.

Electronic Effects of the Substituents Containing the Thiocarbonyl Group

TAKESHI NISHIGUCHI AND YOSHIO IWAKURA

Department of Synthetic Chemistry, Faculty of Engineering, University of Tokyo, Tokyo, Japan

Received August 12, 1969

The Hammett substituent constants, σ_m and σ_p , of 3-ethylthioureido, 3-ethylureido, thioacetamido, acetamido, methylaminothiocarbonyl, and methylaminocarbonyl groups were obtained from the dissociation constants of the *meta*- and *para*-substituted benzoic acids for the discussion of the electronic effects of the thiocarbonyl and carbonyl group. Their σ_I and σ_R values were also calculated from the σ_m and σ_p values. The result shows that the thiocarbonyl group attracts electrons from the adjacent nitrogen atom more strongly by resonance and more weakly by induction than the carbonyl group. As a whole, the thiocarbonyl group has stronger electron-withdrawing power than the carbonyl group.

It has been reported by Luttringhaus and Grohmann¹ that the dipole moments of *para,para'*-substituted thiobenzophenones are larger than those of the corresponding benzophenones when the *para,para'* substituents are strongly electron releasing by resonance and smaller when the substituents are not so strongly electron releasing by resonance. The fact may suggest that the thiocarbonyl group is more strongly electron withdrawing by resonance and more weakly so by induction than the carbonyl group. The concept that the thiocarbonyl group of thioamides has stronger resonance interaction with the adjacent nitrogen atom than the carbonyl group of amides is supported by the fact that thioamides have larger dipole moments,^{1,2} higher rotational energy barriers³ about the C-N bond, larger ¹³C-H coupling constants^{3e} in the nmr spectra of NCH₃, and shorter C-N bond distances^{2a} than the amides. The above concept about thioamides and amides is also discussed with respect to the infrared^{2a,d} and ultraviolet spectroscopy,^{2a,d,4} the ability to form hydrogen bonds,^{2e,5} and LCAO-MO treatment.^{3f,4,6} Further, the presumption that the electron density on the nitrogen of thioamides is lower than that of the corresponding amides may be derived from the pK_a value of thioacetamide,⁷ the coupling constants described above,^{3e} and Janssen's observation that the dissociation constants of the thiocarbonyl compounds of the acids AC(=X)BCH₂COOH (X = O and S, A = Me, B =

S; A = Me₂N, B = O; A = Me₂N, B = S) are larger than those of the carbonyl analogs.⁸

In the course of the study of 1-substituted aziridines and azetidines,⁹ it was found that there existed a remarkable difference between the reaction mechanism of the isomerization of the 1-acyl and 1-thioacyl compounds and that the thiocarbonyl compounds had the proton signals of the ring methylenes at lower magnetic field in the nmr spectra than the corresponding carbonyl compounds. For example, 1-thiobenzoylazetidine shows peaks of methylene protons at τ 5.70 and 7.73, while 1-benzoylazetidine shows these peaks at τ 5.86 and 7.76. These phenomena may be rationalized by the assumption that the thiocarbonyl group of thioamides and thioureas attracts electrons more strongly from the adjacent nitrogen than the carbonyl group of amides and ureas. Electronic effects of substituents containing the thiocarbonyl group have not been elucidated sufficiently, and no σ parameters of such substituents seem to have been reported except for those of thioureido group obtained from ¹⁹F nmr measurement ($\sigma_m = 0.22$, $\sigma_p = 0.16$, $\sigma_I = 0.29$, and $\sigma_R = -0.13$).¹⁰ In order to clarify the electronic effects of thioamide and thiourea linkage quantitatively and to compare them with those of amide and urea linkage, the Hammett σ constants were determined from the dissociation constants of *meta*- or *para*-substituted benzoic acids.

Results

The substituted benzoic acids were prepared and purified as described in the Experimental Section and their physical properties and analyses are given in Table I.

The Hammett σ values obtained from the dissociation

- (1) V. A. Luttringhaus and J. Grohmann, *Z. Naturforsch.*, **10b**, 365 (1955).
- (2) (a) M. C. Lee and W. D. Kumler, *J. Org. Chem.*, **27**, 2052 (1962); (b) G. K. Kstok and S. P. Sood, *J. Phys. Chem.*, **66**, 1372 (1962); (c) M. H. Krackov, C. M. Lee, and H. G. Mautner, *J. Amer. Chem. Soc.*, **87**, 892 (1965); (d) H. G. Mautner and W. D. Kumler, *ibid.*, **78**, 97 (1956).
- (3) (a) G. Schwenker and H. Rosswag, *Tetrahedron Lett.*, 4237 (1967); (b) R. C. Neuman, Jr., D. N. Roark, and V. Jonas, *J. Amer. Chem. Soc.*, **89**, 3412 (1967); (c) A. Leowenstein, A. Melara, P. Ringnag, and W. Walter, *J. Phys. Chem.*, **68**, 1597 (1964); (d) R. C. Neuman, Jr., and L. B. Young, *ibid.*, **69**, 1777 (1965); (e) *ibid.*, **69**, 2570 (1965); (f) J. Sandström, *ibid.*, **71**, 2318 (1967).
- (4) U. Breg and J. Sandström, *Acta Chem. Scand.*, **20**, 689 (1966).
- (5) (a) N. Kulevsky, and P. M. Froehlich, *J. Amer. Chem. Soc.*, **89**, 4839 (1967); (b) E. P. Dudek and G. Dudek, *J. Org. Chem.*, **32**, 823 (1967).
- (6) (a) M. J. Janssen, *Rec. Trav. Chim. Pays-Bas*, **79**, 1066 (1960); (b) M. J. Janssen and J. Sandström, *Tetrahedron*, **20**, 2339 (1964).
- (7) J. T. Edward and T. C. Wang, *Can. J. Chem.*, **40**, 399 (1962).

- (8) M. J. Janssen, *Rec. Trav. Chim. Pays-Bas*, **82**, 931 (1963).
- (9) (a) T. Nishiguchi, H. Tochio, A. Nabeya, and Y. Iwakura, *J. Amer. Chem. Soc.*, **91**, 5835, 5841 (1969); (b) Y. Iwakura, A. Nabeya, and T. Nishiguchi, *J. Polym. Sci., Part A-1*, **6**, 2591 (1968); (c) Y. Iwakura, A. Nabeya, and T. Nishiguchi, *J. Org. Chem.*, **32**, 2362 (1967); (d) Y. Iwakura, A. Nabeya, T. Nishiguchi, and Y. Ichikawa, *ibid.*, **30**, 3410 (1965); (e) Y. Iwakura, A. Nabeya, T. Nishiguchi, and K. Ohkawa, *ibid.*, **31**, 3352 (1966); (f) Y. Iwakura, A. Nabeya, and T. Nishiguchi, *ibid.*, **31**, 1651 (1966).
- (10) J. C. Kauer and W. A. Sheppard, *J. Org. Chem.*, **32**, 3580 (1967).