prepared by means of acetic anhydride in the presence of 1 *M* hydrochloric acid and was recrystallized from benzene–methanol. The monobenzenesulfonyl derivative **4c**, mp 214–216°, was recrystallized from methanol.

**B.**—A solution of **2** (550 mg) in pyridine (50 ml) was stirred and cooled in an ice bath. A mixture of piperidine (2 g) and pyridine (20 ml) was saturated with $H_2S$ to give a precipitate, which was added to the former solution. The reaction mixture was stirred for 6 hr to give a dark red solution. The bulk of solvent was removed under vacuum and the residue was diluted with water (350 ml). The precipitate was taken up in methanol (150 ml) and the filtered solution was aerated overnight in the presence of a few drops of sodium hydroxide solution (10%). The mixture was diluted with water to give a red solid (230 mg), which was extracted with cold 20% hydrochloric acid. The free base was liberated by addition of aqueous sodium hydroxide and was recrystallized from methanol to give orange crystals of **5a**, mp 271–273° (transition to red crystals at 250°). The orange-colored phthalyl derivative **5d**, mp 305–306°, was prepared by heating **5a** with phthalic anhydride in acetic acid and was recrystallized from acetic acid.

**Synthesis of 6. A.**—*N*,*N'*-Bis(dimethylaminosulfonyl-*p*-benzoquinonediimide) was prepared from bis(dimethylsulfonyl-*p*-phenylenediamine).[18] The crude bisdiimide, 10.4 g, was added in several portions to a solution of *o*-nitrobenzenesulfinic acid[19] (7.7 g) in glacial acetic acid (156 ml) containing 8 drops of sulfuric acid. The reaction mixture was stirred overnight and then poured into water. The precipitate was collected on a cooled Büchner funnel. This precipitate was treated with hydrogen peroxide (30%, 5 ml) in acetic acid for 0.5 hr and reprecipitated again by pouring into water. The precipitate was refluxed in concentrated hydrobromic acid (50 ml) for 10 min. The resulting solution was diluted with water to 600 ml and was treated with charcoal. The filtrate was neutralized with 10% sodium hydroxide solution to give a dark red solid. Recrystallization from methanol gave red needles of **6a** (4.65 g, mp 143–144°). The monobenzenesulfonyl derivative **6c**, mp 144–146°, was recrystallized from methanol.

A solution of **6a** (1.82 g), phthalic anhydride (940 mg), and glacial acetic acid (50 ml) was kept at room temperature overnight and then at 60° for 10 hr. The precipitate (2.6 g) was recrystallized to afford the yellow monophthalyl derivative **6d**, mp 289–292°.

The red needles of **6a** dissolved in dilute hydrochloric acid to give a colorless solution from which white needles of the hydrochloride, mp 148–153°, were obtained. The free base is regenerated with 10% aqueous sodium hydroxide solution.

**B.**—Alternatively, **6a** was prepared by the following sequence of reactions. Condensation of *p*-benzoquinonedibenzimide[12] with o-nitrobenzenethiol gave 2,5-dibenzamido-2'-nitrodiphenyl sulfide (86%), mp 230–234°. This sulfide was oxidized with hydrogen peroxide in glacial acetic acid to give 2,5-dibenzamido-2'-nitrodiphenyl sulfone (90%), mp 232–233°. The sulfone was hydrolyzed quantitatively with hot concentrated sulfuric acid (water bath) to give **6a**.

**Reduction of the Derivatives of 2,5-Diamino-2'-nitrodiphenyl Sulfone (6). A.**—A solution of **6a** (490 mg) was reduced with stannous chloride (5 g) by the method described above. The liberated base (340 mg) was recrystallized from aqueous methanol to give yellow cubes of **4a**, mp and mmp 167–168°.

**B.**—A solution of **6c** (1.3 g) in ethanol (100 ml) was hydrogenated (60 psi) in the presence of Raney nickel. The product was crystallized from ethanol to give white prisms of **4c**, mp and mmp 214–216°.

**C.**—A solution of **6d** (2.2 g) in dioxane (150 ml) and acetic acid (10 ml) was hydrogenated in the presence of Raney nickel for 15 hr. The greenish precipitate was recrystallized from aqueous dioxane to give white crystals of **4d**, mp 225–227°.

**Oxidative Cyclization of 4d.**—A solution of **4d** (1.1 g) and phenyliodoso acetate (1.8 g) in toluene (300 ml) was agitated overnight. The reaction mixture was warmed to dissolve the orange crystals and was then filtered to remove a red residue (85 mg). The filtrate was concentrated to a volume of 80 ml and was cooled to afford orange crystals, 854 mg, mp 294–300°. Recrystallizations from acetone gave **5d**, mp and mmp 305–307°. The reaction of **5d** with hydrazine solution in ethanol gave **5a**, mp and mmp 271–273°.

Compound **5d** (110 mg) was refluxed in a mixture of acetic acid (70 ml) and peracetic acid (7 ml) for 30 min. The solution was diluted with water to give a pale yellow precipitate (113 mg). This solid was recrystallized from acetic acid to give **7**, mp 307–309°. Compound **7** was also obtained when **4d** was oxidized with peracetic acid at room temperature. The reaction of **7** with hydrazine gave a poor yield of **5a**.

**Reduction of 3.**—The dinitro compound **3** (150 mg) was reduced with stannous chloride and concentrate hydrochloric acid to give a crude tetraamino compound, mp 149–153°. This crude product was treated with acetic anhydride in the presence of 1 *M* hydrochloric acid to give a precipitate (980 mg) which upon recrystallizations from isopropyl alcohol gave the analytically pure diacetyl derivative (**10**), mp 249–251°.

**Registry No.**—**2**, 30388-08-0; **3**, 30453-05-5; **4a**, 30388-09-1; **4b**, 30388-10-4; **4c**, 30388-11-5; **4d**, 30388-12-6; **5a**, 30388-13-7; **5d**, 30388-14-8; **6a**, 30388-15-9; **6c**, 30388-16-0; **6d**, 30388-17-1; **7**, 30388-18-2; **10**, 30388-19-3.

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[19] T. Zincke and F. Farr, *Justus Liebigs Ann. Chem.*, **391**, 73 (1912).

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# Stabilized Sulfonium Ylides. II.[1] Ethyl Dimethylsulfuranylidene-2,4,6-trinitrophenylacetate

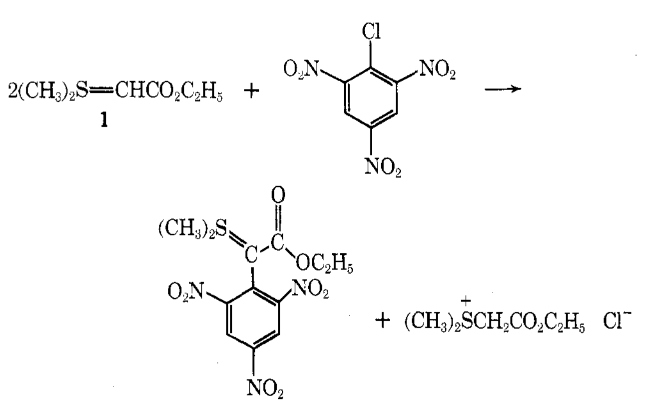
J. CASANOVA*[2] AND R. A. LOEWE

*Department of Chemistry, California State College, Los Angeles, Los Angeles, California 90032*

*Received December 3, 1970*

Although the nucleophilic properties and synthetic potential of carbonyl-stabilized sulfonium ylides have been the object of numerous studies in the past few years,[1,3] the behavior of these ylides as nucleophiles in nucleophilic aromatic substitution has not been explored. We report herein a case in which such substitution occurs with facility to produce a novel ylide with interesting properties.

When ethyl dimethylsulfuranylidenylacetate (**1**)[1,3i] and picryl chloride are mixed in a variety of solvents, either in the presence or absence of a tertiary amine, a



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[1] Paper I: J. Casanova, Jr., and D. A. Rutolo, *Chem. Commun.*, 1224 (1967).

[2] Department of Organic Chemistry, University of Lund, Sweden.

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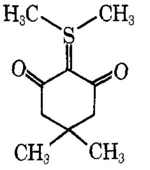
deep red color is produced immediately. A wine-red crystalline compound, formulated as **2** from analytical evidence (*vide infra*), can be isolated from the mixture in moderate yield. The formation of **2** can be regarded as proceeding by nucleophilic addition of the ylide to picryl chloride, followed by elimination of hydrogen chloride. For the elimination step, either the tertiary amine or a second equivalent of ylide can serve as the base. Compound **2** is stable in air and in aqueous solution and can be protonated by dilute mineral acids to produce the colorless conjugate acid **3** of **2**. The p$K_a$ of **3** is 1.8, qualifying it as an unusually strong organic acid. The color change can be reversed by the addition of base to an acidified solution of **2**. The formation of a very stable "anion" in which charge is delocalized over the entire aromatic ring as well as over the sulfuranylidene skeleton is undoubtedly responsible for the acid strength of **3**.

$$2H^+X^- \rightleftharpoons 2 + HX$$

**3**



**4**

A similar color is produced when **1** is mixed with *sym*-trinitrobenzene or with trinitrotoluene. Systematic study of these colored complexes[4] is hampered by their propensity toward decomposition and by their apparent lack of simple stoichiometry. Aromatic solvents in general, and nitroaromatic solvents in particular, produce a large downfield shift in the methinyl proton resonance signal of **1**, suggesting that a weak charge transfer interaction may be operating in these cases as well.[5] However, no color was produced when 2-dimethylsulfuranylidene-5,5-dimethylcyclohexane-1,3-dione (**4**)[6] was mixed with *sym*-trinitrobenzene. Beyond these observations, the scope of the substitution reaction remains to be explored, as does the possibility of a parallel reaction in ylides of other elements.

### Experimental Section

**Ethyl Dimethylsulfuranylidene-2,4,6-trinitrophenylacetate** (**2**).—Ethyl dimethylsulfuranylidenylacetate[3a] (2.25 g, 15 mmol), dissolved in 10 ml of acetone, was mixed with a solution of picryl chloride (1.88 g, 7.6 mmol) in 15 ml of acetone under a nitrogen atmosphere. An intense red color developed immediately. The mixture was refluxed for 90 min, cooled, and evaporated to a small volume. Chromatography in benzene on 300 g of alumina (grade II) caused the product to separate into three colored bands. The first band, eluted rapidly by ether, was evaporated to give a deep red semisolid, 1.41 g. Recrystallization of this material from benzene, ether–petroleum ether, or ethanol–water (best) afforded small deep red prisms: 0.76 g (28%); mp 176° dec (Koeffler block; the melting point varied with heating rate); ir ($CHCl_3$) 1639 (C=C aliphatic), 1600, 1522 (C=C arom), 1515 ($CNO_2$ asym), 1319 $cm^{-1}$ ($CNO_2$ sym); nmr ($CDCl_3$) $\delta$ 8.73 (s, 2, arom H), 4.07 (q, 2, $J$ = 7.8 Hz, $OCH_2CH_3$), 3.08 (s, 6, $S^+(CH_3)_2$), 1.19 (t, 3, $J$ = 7.8 Hz, $OCH_2CH_3$); uv max ($CH_3CN$) 234 nm ($\epsilon$ 10,200), 380 sh (2460), 474 (5240); uv max (95% $C_2H_5OH$) 230 sh nm ($\epsilon$ 29,900), 368 (4410), 469 (8500); p$K_a$[7] (50% $C_2H_5OH$) = 1.8.

*Anal.* Calcd for $C_{12}H_{13}O_8N_3S$: C, 40.11; H, 3.65; N, 11.70; S, 8.93. Found: C, 40.1; H, 3.68; N, 11.7; S, 9.14.

**Complex of Ethyl Dimethylsulfuranylidenylacetate with *sym*-Trinitrobenzene.**—Equimolar solutions of ylide **1** and *sym*-trinitrobenzene in either cyclohexane, benzene, chloroform, ether, acetonitrile, dioxane, or alcohol gave a deep red color immediately upon mixing, detectable below $5 \times 10^{-5}$ *M*: uv max ($CH_3CN$) 220 nm ($\epsilon$ 23,600), 438 (13,900), 557 (9110), which changed slowly over 1 hr. No isosbestic point was apparent. A plot of molar absorptivity *vs.* molar concentrations of donor/donor + acceptor for the two longer wavelength maxima showed no maximum between 0.25 and 0.80. An equimolar mixture of ylide **1** and *sym*-trinitrobenzene, 2 *M* in CDCl , displayed a proton resonance spectrum with very broad, undistinguishable signals which changed slowly with time. The spectrum was not sharpened noticeably upon cooling the sample to −35°. No electron spin resonance spectrum could be detected. After 1 hr a sharp proton resonance signal due to dimethyl sulfide became apparent, as did the odor of this compound.

**Registry No.**—**2**, 29765-36-4.

**Acknowledgment.**—The authors are indebted to the Department of Organic Chemistry, University of Lund, for elemental analysis.

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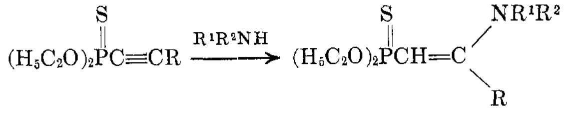
## Organophosphorus Enamines. IV.[1] Enamine Thiophosphonates: Preparation and Their Attempted Use in the Synthesis of α,β-Ethylenic Ketones

Mohinder S. Chattha[2] and Adam M. Aguiar*

*Department of Chemistry, Tulane University,*
*New Orleans, Louisiana 70118*

*Received January 26, 1971*

Recently we reported a general synthesis of dialkyl alkynyl-1-thiophosphonates (**1**) which in themselves constitute a new class of phosphorus(V) esters.[3] We now wish to report that addition of amines to the carbon–carbon triple bond in **1** is rather facile, giving enamine thiophosphonates **2** in essentially quantitative yields (eq 1).

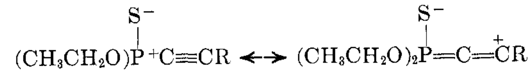


$$(H_5C_2O)_2\overset{S}{\overset{\|}{P}}C{\equiv}CR \xrightarrow{R^1R^2NH} (H_5C_2O)_2\overset{S}{\overset{\|}{P}}CH{=}C(NR^1R^2)R \qquad (1)$$

**1** **2**

R = alkyl, phenyl
R¹ = alkyl, cycloalkyl
R² = alkyl, H

No doubt there is some contribution of phosphine–methylene to the transition state of the addition.



$$(CH_3CH_2O)\overset{S^-}{\overset{|}{P}}{}^+C{\equiv}CR \longleftrightarrow (CH_3CH_2O)_2\overset{S^-}{\overset{|}{P}}{=}C{=}\overset{+}{C}R$$

Enamine thiophosphonates **2** produced in this manner are listed in Table I together with their boiling points, yields and chemical analyses.

Enamines **2** ($R^1$ = alkyl; $R^2$ = H) have been found to react with NaH to give anions **3** which, when treated

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[5] J. Casanova and R. A. Felix, unpublished observations.

[6] A. F. Cook and J. G. Moffatt, *J. Amer. Chem. Soc.*, **90**, 740 (1968).

[7] C. N. R. Rao, "Ultraviolet and Visible Spectroscopy," Butterworths, London, 1967, p 77.

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[2] Awarded Cities Service Award for Excellence in Teaching, 1969.

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