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Sulfoxonium Ylide Chemistry. II.[1] Reaction of Stable Sulfoxonium Ylides with Base

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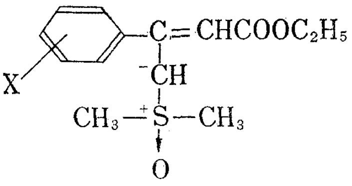
Ethyl 3-phenyl-1,3-butadiene-2-carboxylate derivatives (IIa–d) were prepared from dimethylsulfoxonium 3-ethoxycarbonyl-2-phenylallylide by the treatment with triethylamine. These structures were determined by nuclear magnetic resonance spectra, Diels–Alder reaction with tetracyanoethylene and other chemical evidence. The mechanistic assumption for the formation of the butadiene derivatives from sulfoxonium ylides was given. Dimethylsulfoxonium N,4-diphenyl-3,4-dehydropiperidino-3,6-dion-5-ylide derivatives (XIa—c) were obtained from dimethylsulfoxonium 1-phenylcarbamoyl-3-ethoxycarbonyl-2-phenylallylide (Xa—c) by the treatment with sodium ethoxide.

In the preceding paper,[1] we reported first on the formation of a series of stable sulfoxonium ylides (I) by the reactions of ethyl phenylpropiolate derivatives with dimethylsulfoxonium methylide[3,4] and secondly on the formtaion of various stable ylides by the reactions of the ylides (I), thus obtained, with acetylenic carboxylic acid esters and some other electrophiles.

In the continuation and the extension of our studies on ylide chemistry, we attempted to conduct some reactions of sulfoxonium ylides with amines and alkoxides.[5]



X=p-CH$_3$-, p-CH$_3$O-, o,m,p-Cl

I

Chart 1

There have been some reports about the rearrangement of N-, S-, and P- ylides. Stevens and Sommelet–Hauser[6] rearrangements can be explained as rearrangement reactions involving plausible N-ylide intermediates derived from quarternary ammonium salts and base. Sulfonium salts also undergo the same type rearrangements to afford sulfide derivatives reported by Stevens and Thompson.[7]

Triphenylchloromethylphosphonium chloride underwent the migration of the phenyl group by the treatment with excess butyl lithium to afford diphenyl butylphosphonium benzylylides.[8]

Recently, Corey and Chaykovsky have found photoinduced Arndt–Eistert or Wolff type rearrangement of dimethylsulfoxonium ylides[9] which may be assumed to involve the keto-carbene intermediate.

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[1] Part I: *Chem. Pharm. Bull.* (Tokyo), **16**, 784 (1968).

[2] Location: *Hiromachi, Shinagawa-ku, Tokyo.*

[3] E.J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 867 (1962).

[4] E.J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1353 (1965).

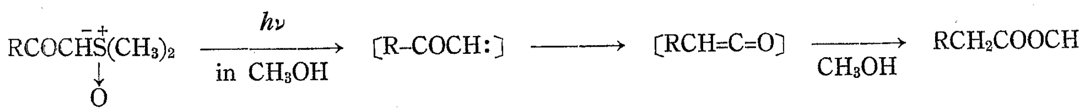
[5] A part of this work has been reported in a preliminary form. J. Ide and Y. Kishida, *Tetrahedron Letters*, 1787 (1966).

[6] P. de Mayo, "Molecular Rearrangements," Part I, Interscience Publishers, N.Y., 1963, p. 345. E.S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Company, N.Y., 1959, p. 640.

[7] A.W. Thompson and B.R. Stevens, *J. Chem. Soc.*, **1932**, 69.

[8] M. Schlosser, *Angew. Chem.*, **74**, 291 (1962).

[9] E.J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **86**, 1640 (1964).



$$\underset{\underset{O}{\downarrow}}{RCO\overset{-}{C}H\overset{+}{S}(CH_3)_2} \xrightarrow[\text{in } CH_3OH]{h\nu} [R\text{-}COCH:] \longrightarrow [RCH{=}C{=}O] \xrightarrow[CH_3OH]{} RCH_2COOCH_3$$

However, there have been found no base-catalyzed rearrangement of sulfoxonium ylides.

Treatment of dimethylsulfoxonium 3-ethoxycarbonyl-2-phenylallylide (I-a) with triethylamine in anhydrous benzene followed by alumina chromatography afforded ethyl-3-phenyl-1,3-butadiene-2-carboxylate (II-a) in 85% yield. II-a polymerizes easily and can not be distilled even under diminished pressure (0.1 mmHg) (Chart 2).

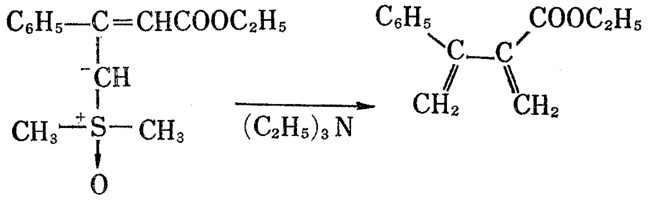


Chart 2

Generally, this type of butadiene derivatives which possess the substituents such as carboethoxy and phenyl groups at 2 and 3-positions, respectively, have not been easily available. However, Blanchard, Jr. and Cairncross[10] have recently reported this type of butadiene derivative, 3-methyl-1,3-butadiene-2-carbonitrile which has been prepared from 3-methylbicyclo[1.1.0]butanecarbonitrile by pyrolysis in gas-phase at 200—340°, but this compound is very unstable as to dimerize and polymerize on storage at room temperature. Similarly our butadiene (II-a) is also unstable and polymerizes on storage at room temperature for a few days but in refrigerator it can be stored for a few weeks. The analytical sample of the butadiene was prepared by the purification of alumina column chromatography. The structural assignment of II-a was based on the following facts. The infrared spectrum of II-a showed absorption bands at 900 (terminal methylene group), 1613 (conjugated double bond with ester), and 1733 cm^{-1} (α,β-unsaturated ester), and an absorption maximum in the ultraviolet spectrum appeared at 240 mμ (ε=9620). The nuclear magnetic resonance spectrum[11] consists of a triplet at 1.06 and a quartet at 4.10 for the ethyl ester and two sets of AB type patterns with small coupling constants at 5.39 and 5.49 (two protons, J_{AB}=1.1 cps) and at 5.78 and 6.30 ppm (two protons, J_{AB}=2.0 cps) for the two characteristic terminal methylene groups.[12]

The authors should recall an earlier paper,[13] in which one of the present authors has reported the formation of 2,3-diphenyl-1,3-butadiene (IV)[14] by the reaction of diphenylacetylene (III) with methylsulfinyl carbanion.[15] The AB type patterns in the nuclear

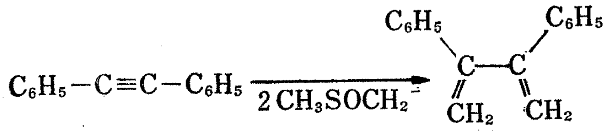


Chart 3

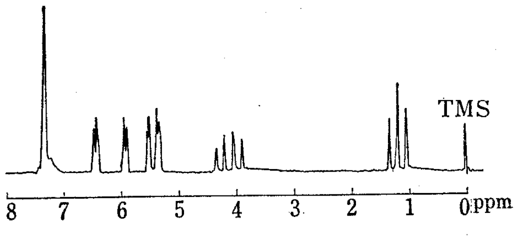


Fig. 1. Nuclear Magnetic Resonance Spectra (60 Mc) of 2-Ethoxycarbonyl-3-phenyl-1,3-butadiene in $CDCl_3$ using Tetramethylsilane as Internal Standard

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[10] E.P. Blanchard, Jr. and A. Cairncross, *J. Am. Chem. Soc.*, **88**, 487 (1966).

[11] The nuclear magnetic resonance spectra were measured using Varian A-60 spectrometer and the chemical shifts were expressed in ppm unit from the internal standard of tetramethylsilane in deuterochloroform solution.

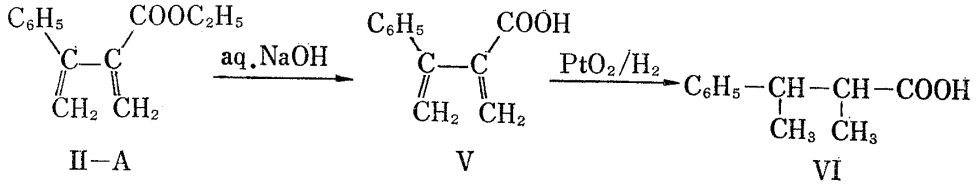
[12] L.M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p. 85.

[13] I. Iwai and J. Ide, *Chem. Pharm. Bull.* (Tokyo), **13**, 663 (1965).

[14] W. Thorner and Th. Zincke, *Chem Ber.*, 13, 645 (1880). J.M. Johlin, *J. Am. Chem. Soc.*, **39**, 291 (1917). C.F.H. Allen, C.G. Eliot, and A. Bell, *Can. J. Res.*, **B17**, 75, 80, 81 (1939). Yu. S. Zal'kind and P. Mosunov, *J. Gen. Chem. USSR*, **10**, 517, 519 (1940). K. Alder and J. Haydn, *Ann.*, **570**, 201, 208 (1950).

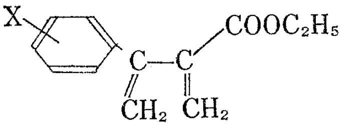
magnetic resonance spectrum of IV are very similar to those of II–a: 5.26 and 5.48 ppm (J_{AB} =3.0 cps) (Fig. 1).

II–a was hydrolyzed in a sodium hydroxide solution to give the corresponding acid (V), mp 106—107°. The absorption maximum in the ultraviolet spectrum appeared at 240 mμ (ε=12390) and the nuclear magnetic resonance spectrum showed a pair of AB type patterns with small coupling constants at 5.38 and 5.52 ppm (two protons, J_{AB}=1.3 cps), and 5.88 and 6.44 (two protons, J_{AB}=1.7 cps) assignable to two characteristic terminal methylene groups, and a slightly broadening singlet at 10.22 ppm for carboxylic proton. The acid (V) was catalytically hydrogenated, in the presence of platinum, to 2–methyl–3–phenylbutylic acid (VI), mp 132—133,[16,17] uptaking two moles of hydrogen.



Butadiene derivatives having a substituent on the phenyl group were synthesized from the corresponding sulfoxonium ylides by the treatment with triethylamine. The results are summarized in Table I.

Table I.



IIa−d

	Substituents (X)	Yield (%)	UV λ_{max}^{EtOH} mμ (ε)	Analysis (%)			
				Calcd.		Found	
				C	H	C	H
II-a	H	85	240(9620)	77.20	6.98	77.03	6.91
II-b	p-CH_3	57	244(11300)	77.75	7.46	77.31	7.29
II-c	p-OCH_3	74	253(12600)	72.39	6.94	73.07	6.58
II-d	p-Cl	70	245(12100)	65.96	5.53	65.91	5.34

Another support for the structure of IIa was obtained from the Diels–Alder adducts with tetracyanoethylene[18] in ethyl acetate.

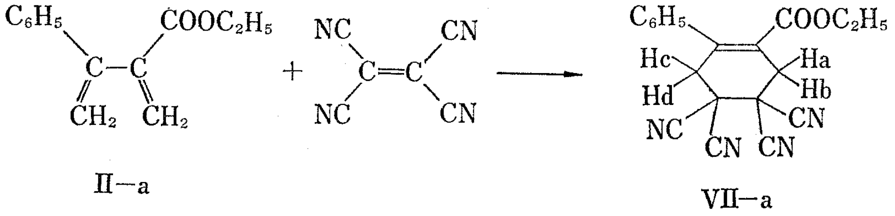


Chart 4

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15) E.J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962). *Idem, ibid.*, **87**, 1345 (1965).

16) H. Rupe, H. Steiger, and F. Fiedler, *Chem. Ber.*, 47, 63 (1914).

17) M.C. Kloetzel, *J. Am. Chem. Soc.*, **62**, 1708 (1940).

18) T.L. Cairns, R.A. Carboni, D.D. Coffman, V.A. Engelhardt, R.E. Heckert, E.L. Little, E.G. McGeer, B.C. McKusick, W.J. Middleton, R.M. Scribner, C.W. Theobald, and H.E. Winberg, *J. Am. Chem. Soc.*, **80**, 2775 (1958).

Thus, IIa was converted to ethyl 1–phenyl–4,4,5,5–tetracyano–1–cyclohexene–2–carboxylate (VII–a), mp 152—153°, which in the NMR showed no vinyl protons but two sets of AB type signals overlapping each other at about 3.5 ppm due to four protons, as shown in Fig. 2. The infrared spectrum showed an absorption at 2257 cm^{-1} for the nitrile group and the ultraviolet spectrum of VII–a showed an absorption maximum at 246 mμ (ε=5600) (Chart 4).

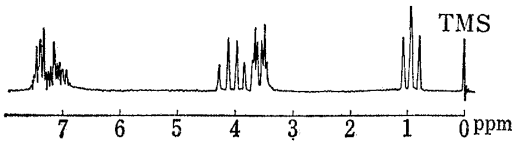
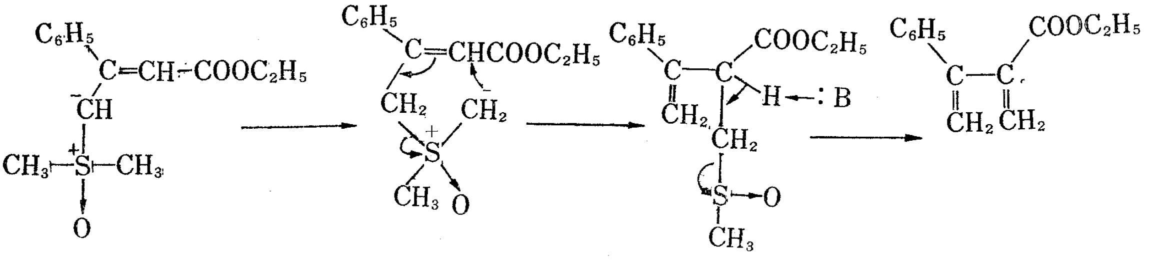


Fig. 2. Nuclear Magnetic Resonance Spectra (60 Mc) of 1–Phenyl 2–ethoxycarbonyl–4,4,5,5–tetracyano–1–cyclohexene in $CDCl_3$ using Tetramethylsilane as Internal Standard

Likewise, ethyl 3–(*p*–methylphenyl)–1,3–butadiene–2–carboxylate (IIb) also reacted with tetracyanoethylene to afford ethyl 1–(*p*–methylphenyl)-4,4,5,5-tetracyano-1-cyclohexene-2–carboxylate (VII–b), mp 145—146°.

A mechanistic assumption for the formation of the butadiene derivatives (II) from ylides (I) would be expressed as follow. The ylide–carbanion was initially transferred into one of the dimethyl groups, forming an unstable ylide (VIII). Then the attack of the anion to the 2–carbon of *α,β*–unsaturated ester *via* a five–membered ring sulfoxide transition state followed by double bond migration and C–S bond fission gives an intermediate (IX). Then the base attacks the *α*–hydrogen to cause the elimination of methyl sulfenic acid forming the butadiene, II. The mode of attacking of the ylide–carbanion to the *α*–carbon of *α,β*–unsaturated ester opposes to the usual Michael type addition, but in this case the ease of the formation of the five–membered ring transition state and the product stability of IX would be operative as a driving force in detemining the reaction course (Chart 5).

This type of reaction pass way will be reported in the reaction of the ylide (I) with 1,3–dipolar reagents in the near future.



Ia VIII IX II–a

Chart 5

When dimethylsulfoxonium 1–phenylcarbamoyl–3–ethoxycarbonyl–2–phenylallylide[1] (X) was treated with triethylamine in benzene, no reaction occurred and the starting material recovered unchanged. However, treatment of X with sodium ethoxide in ethanol at room temperature gave colorless prisms, mp 205—206° in 95% yield. The ultraviolet absorption spectrum showed absorption maxima at 248 (ε=16370) and 320 mμ (ε=14520), and the nuclear magnetic resonance spectrum exhibited the signals at 3.5 (six protons, singlet) due to two methyl groups on sulfoxonium ion, 5.54 (one proton, singlet) due to vinyl proton and at about 7.2 ppm (ten protons, multiplet) for the two phenyl groups. The infrared absorption spectrum showed absorptions at 1042 (sulfoxide), and 1650, and 1603 cm^{-1} (an *α,β*–unsaturated cyclic imido), the latter of which seemed to be abnormally low frequencies comparing with those of the normal *α,β*–unsaturated six–membered ring imido compounds (1730 and 1670 cm^{-1}).[19] The lowering in the frequencies would be the results from that the C–5 is the ylide carbon possessing sp^2 hybridized orbital. From these spectroscopic evidence and the elemental analysis, this compound was concluded to be cyclized ylide derivative, dimethylsulfoxonium N,4–diphenyl–3,4–dehydropiperidino–3,6–dion–5–ylide (XI–a) (Chart 6).

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19) K. Nakanishi, "IR Absorption Spectroscopy," Nankodo, Tokyo, 1960, p. 52.

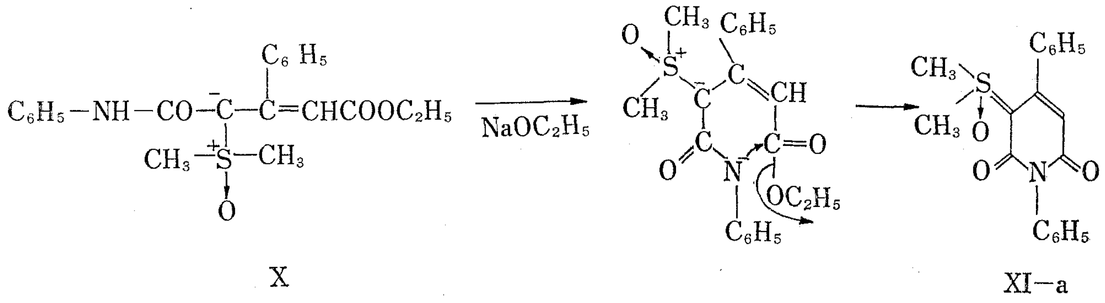
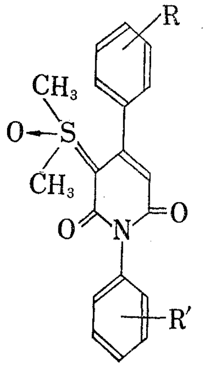


Chart 6

Other carbamoyl ylide derivatives also furnished cyclic ylides in good yields in a similar way and the results are summarized in Table II.

Table II. Yields and Ultraviolet Spectrum Data of the Reactions of the Carbamoyl Ylides with Sodium Ethoxide



	R	R'	Yield (%)	mp (°C)	UV $\lambda_{\max}^{\mathrm{EtOH}}$ mμ (ε)
XI-a	H	H	87.5	205—206 (decomp.)	248 (16370) 320 (14520)
XI-b	*p*-CH_3	H	85	197—198 (decomp.)	254 (16770) 320 (13320)
XI-c	H	*p*-Cl	66	217—218 (decomp.)	238 (18850)[a] 320 (12700)

[a] measured in acetonitrile

Experimental[20]

General Procedure of Ethyl-3-phenyl-1,3-butadiene-2-carboxylate Derivatives——A solution of 0.02 mole of dimethylsulfoxonium 3-ethoxycarbonyl-2-phenylallylide derivatives and 0.02 mole of triethylamine in 90 ml of anhyd. C_6H_6 was refluxed for 1 hr and then the solvent was evaporated under reduced pressure at 30°. The oily residue was chromatographed on 250 g of Al_2O_3 (Woelm, neutral, grade II) and eluted with *n*-hexane-benzene (3:1) to afford colorless oil (70—90% yield), which was satisfactorily used for further reaction. Further chromatography on silica gel with eluting solvent of *n*-hexane-benzene (3:1) gave an analytically pure sample. These butadiene derivatives are so sensitive to heat that vacuum distillation even under 0.1 mmHg pressure at 90° is impossible but in refrigerator one can store it in a few weeks.

Ethyl 3-Phenyl-1,3-butadiene-2-carboxylate (II-a)——A solution of 5.2 g (0.019 mole) of dimethylsulfoxonium 3-ethoxycarbonyl-2-phenylallylide (I-a) and 1.98 g (0.019 mole) of triethylamine in 90 ml of anhyd. C_6H_6 was refluxed for 1 hr, then the solvent was evaporated under diminished pressure at 20°. The oily residue was chromatographed on 250 g of Al_2O_3 (Woelm, neutral, grade II) and eluted with *n*-hexane-

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[20] All melting points were uncorrected. The dimethylsulfoxonium ylide derivatives which were used and described as a starting material in this experimental part, were prepared according to the manner described in the previous paper.[1]

benzene (3:1) to give colorless oil, 3.58 g (90.5%), a small porton of which was rechromatographed on silica gel eluting with *n*–hexane–benzene (3:1) to give an analitically pure sample. *Anal.* Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.16; H, 6.91.

3-Phenyl-1,3-butadiene-2-carboxylic Acid (V)——A suspension of 500 mg of ethyl 3–phenyl–1,3–butadiene–2–carboxylate (II–a) in 10 ml of 10% KOH solution had been warmed at 70° for 15 hr under stirring in nitrogen gas until the reaction mixture became homogeneous. The cold reaction mixture was extracted with ether twice and the aqueous layer was acidified with 5% HCl solution until pH 2 under ice–water cooling. The precipitate was filtered to give the crude acid, 270 mg (62.8% yield). Recrystallization from CCl_4 gave colorless prisms, mp 106—107°. *Anal.* Calcd. for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.80; H, 5.66.

2-Methyl-3-phenylbutylic Acid (VI)——A solution of 86 mg of 3–phenyl–1,3–butadiene–2–carboxylic acid (V) in 12 ml of ethanol was hydrogenated with 18 mg of platinum oxide in hydrogen gas at an atmospheric pressure. The uptake of 24 ml of hydrogen was observed (100.1% of theoretical amount at 21°) during 1.5 hr. After removal of the catalyst, solvent was evaporated under reduced pressure and the residue was recrystallized from petr. ether (bp 75—120°) to furnish colorless prisms 12 mg, mp 132—133. *Anal.* Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.98; H, 7.51.

Ethyl 1-Phenyl-4,4,5,5-tetracyano-1-cyclohexene-2-carboxylate (VII-a)——To a solution of ethyl 3–phenyl–1,3–butadiene–2–carboxylate 2.66 g (0.01 mole) in 30 ml of ethyl acetate was added dropwsie a solution of tetracyanoethylene 1.28 g (0.01 mole) in 20 ml of ethyl acetate at room temperature. During the addition the color of reaction mixture developed to orange–brown but no heat evolution was observed. The reaction mixture was allowed to stand for 48 hr at room temperature. The solvent was removed under reduced pressure to leave a solid. Recrystallization from 99% EtOH gave colorless prisms, 3.01 g, mp 152—153° (77% yield). *Anal.* Calcd. for $C_{19}H_{14}O_2N_4$: C, 69.08; H, 4.27; N, 16.96. Found: C, 69.14; H, 4.18; N, 16.91.

Ethyl 1-(*p*-Methylphenyl)-4,4,5,5-tetracyano-1-cyclohexene-2-carboxylate (VII-b)——To a solution of ethyl 3–(*p*–methylphenyl)–1,3–butadiene–2–carboxylate 370 mg (1.71 mmole) in 7 ml of ethyl acetate was added dropwise a solution of tetracyanoethylene 219 mg (1.71 mmole) in 5 ml of ethyl acetate at room temperature with stirring. During the addition the color of reaction mixture developed to orange–brown but no heat evolution was observed. The reaction mixture was allowed to stand for 48 hr at room temeperature. The solvent was removed under reduced pressure to leave a solid. Recrystallization from 99% EtOH gave colorless needles, 315 mg (53.6% yield), mp 145—146°. *Anal.* Calcd. for $C_{20}H_{16}O_2N_4$: C, 69.75; H, 4.68; N, 16.27. Found: C, 69.96; H, 4.60; N, 16.37.

Dimethylsulfoxonium N,4-Diphenyl-3,4-dehydropiperidino-3,6-dion-5-ylide (XI-a)——To a solution of sodium ethoxide prepared from 50 mg of sodium and 3 ml of abs. EtOH was added dropwise a solution of 100 mg of dimethylsulfoxonium 1–phenylcarbamoyl–3–ethoxycarbonyl–2–phenylallylide (X–a) in 2 ml of abs. EtOH with stirring at room temperature. After stirring for 10 min white solid began to appear. After additional stirring for 1 hr the precipitate was filtered and recrystallized from EtOH to give 77 mg of colorless prisms, mp 205—206° (87.5% yield). *Anal.* Calcd. for $C_{19}H_{17}O_3NS$: C, 67.23; H, 5.05; N, 4.13; S, 9.44. Found: C, 67.40; H, 5.13; N, 4.24; S, 9.19.

Dimethylsulfoxonium 1-Phenyl-4-(*p*-methylphenyl)-3,4-dehydropiperidino-3,6-dion-5-ylide (XI-b)——To a stirred solution of sodium ethoxide prepared from 50 mg of sodium and 3 ml of abs. EtOH was added 200 mg of powdered dimethylsulfoxonium 1–phenylcarbamoyl–3–ethoxycarbonyl–2–(*p*–methylphenyl)allylide (X–b) in portion at room temperature. After five min the color of the reaction mixture was changed into colorless from yellow and white precipitate appeared. After additional stirring for 1 hr, the precitpiate was filtered and recrystallized from EtOH to afford 150 mg of colorless prisms, mp 197—198° (decomp.) (85% yield). *Anal.* Calcd. for $C_{20}H_{19}O_3NS$: C, 69.96; H, 5.41; N, 3.96; S, 9.07. Found: C, 69.87; H, 5.55; N, 4.03; S, 9.47.

Dimethylsulfoxonium N-(*p*-chlorophenyl)-4-phenyl-3,4-dehydropiperidino-3,6-dion-5-ylide (XI-c)——To a stirred solution of sodium ethoxide prepared from 50 mg of sodium and 3 ml of abs. EtOH was added 200 mg of powdered dimethylsulfoxonium 1–(*p*–chlorophenyl)carbamoyl–3–ethoxycarbonyl–2–phenylallylide (X–c) in portionwise at room temperature. After usual processing as described above, 177 mg of colorless prisms, mp 217—218° (decomp.) (66% yield) was obtained. *Anal.* Calcd. for $C_{19}H_{16}O_3NSCl$: C, 61.03; H, 4.31; N, 3.73; S, 8.57; Cl, 9.48. Found: C, 61.28; H, 4.22; N, 3.59; S, 8.81; Cl, 9.23.

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