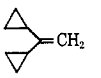
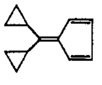
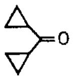
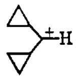
TABLE II

CHEMICAL SHIFTS OF CYCLOPROPYL PROTON MULTIPLETS (τ)

	α-H	β-H	Ref
	8.5–9.0	9.35–9.65	*a*
	8.08–8.60	9.08–9.41	This work
	7.69–8.18	8.92–9.33	This work
	6.5–7.1	7.2–7.7	*b*

[a] A. D. Ketley and J. L. McClanahan, *J. Org. Chem.*, **30**, 940 (1965). [b] N. Deno, *et al.*, *J. Am. Chem. Soc.*, **87**, 3000 (1965).

The most direct evidence of the enhanced contribution of the dipolar resonance form in Ia lies in the dipole moments of Ia and Ic. In dilute carbon tetrachloride solution at 20°, Ia has a dipole moment of 1.74 ± 0.05 D.; that of Ic is 1.52 ± 0.05 D.[11] This dipole moment is the highest reported for any fulvene containing only hydrocarbon groups. It unequivocally demonstrates the ability of the cyclopropyl ring to facilitate charge separation in a neutral molecule by stabilizing an electron-deficient center.

The stabilization of the fulvene molecule by the cyclopropyl groups, which is evident from the physical properties, is less evident from the chemical properties. Thus, Ia reacts readily with oxygen, as other fulvenes do, and reacts as a diene in the Diels–Alder reaction with maleic anhydride.[3] However, although reaction of Ic with maleic anhydride in refluxing benzene is essentially complete in 5 min as shown by loss of the yellow fulvene color, the reaction of Ia requires 2 to 3 hr under the same conditions.

Experimental Section

6,6-Dicyclopropylfulvene (Ia).—Freshly cut sodium metal (7.6 g, 0.33 g-atom) was dissolved in 125 ml of absolute ethanol, then 39.0 g (0.35 mole) of dicyclopropyl ketone (Aldrich Chemical Co.) was added. Freshly distilled cyclopentadiene was then added slowly in order to keep the temperature at or below 40°. After stirring overnight, the mixture was steam distilled until the distillate was nearly white. The nonaqueous layer was combined with methylene chloride washes of the aqueous layer, dried, and fractionated through a 12-in. spinning-band column. This yielded 7.0 g (13%) of dicyclopropylfulvene, bp 130–134° (18 mm), [lit.[3] bp 121–123° (13 mm)].[12] Samples for spectra and dipole moment studies were prepared by vpc, using a 10 ft × $^3/_8$ in. SF-96 on Chromosorb W column, in an Aerograph Model 700 Autoprep. Carbon–hydrogen analyses were invariably low, owing presumably to reaction with oxygen.[10]

The pure fulvene showed $n^{20}\text{D}$ 1.6005. On standing in air, the refractive index fell, and eventually a colorless precipitate formed, which showed broad bands at 3450 and 1720 cm^{-1} in the infrared (Nujol mull) and which did not melt below 200°.

6,6-Dimethylfulvene (Ic).—This compound was prepared by the method of Freiesleben[5] in 46% yield, bp 54–55.5° (17 mm), $n^{25}\text{D}$ 1.5416 [lit.[7] $n^{25}\text{D}$ 1.5404, bp 52° (10 mm)].

Attempts to make 6,6-diisopropylfulvene (Ib) by both the above methods failed. A preparation using diisopropyl ketone and cyclopentadiene in *t*-butyl alcohol containing potassium *t*-butoxide yielded on distillation a small amount of yellow material having an absorption maximum at 363 mμ in isooctane. No further work was done with this material.

Spectra.—Ultraviolet–visible spectra were obtained using a Perkin-Elmer Model 202 or a Carey Model 14 spectrophotometer. Infrared spectra were obtained in dilute carbon tetrachloride solutions, using a 0.1-mm cell in a Perkin-Elmer Infracord Model 137B, calibrated with a polystyrene film. Proton magnetic resonance spectra were obtained on a Varian A-60 spectrometer; chemical shifts are τ values relative to tetramethylsilane as internal standard (τ 10.00).

Dipole Moments.—These were determined from the dielectric constant of dilute carbon tetrachloride solutions at 20.0°, using a WTW dipolmeter, Model DM 01, obtained from Kahl Scientific Instrument Corp., El Cajon, Calif. The dipole moment was calculated by the method of Shoemaker and Garland,[13] using the following data: For Ia, $a(d\epsilon/dx_2)$ 3.944, $b(d\rho/dx_2)$ -1.824, $n^{20}\text{D}$ 1.6005, ρ_2 0.88 (assumed); for Ic a 2.930, b -1.034, $n^{20}\text{D}$ 1.5436, ρ_2 0.88.[14] These data yield for Ia $P_{2\text{m}^\circ} = 124.56$, $P_{2\mu^\circ} = 63.03$, $\mu = 1.74 \pm 0.05$ D; for Ic $P_{2\text{m}^\circ} = 86.20$, $P_{2\mu^\circ} = 48.13$, $\mu = 1.52 \pm 0.05$ D. All symbols are used as in ref 13.

Reactions with Maleic Anhydride.—Maleic anhydride (1.00 g, 10.2 mmoles) and 1.00 g of Ic (9.43 mmoles) were refluxed in 5 ml of benzene for 15 min (the yellow color was substantially discharged within 5 min), and the solution was evaporated. The residue was recrystallized from ether, then carbon tetrachloride–chloroform to give 0.80 g (40%) of white prisms, mp 137–138° (lit.[15] *exo* adduct mp 139–140°).

The same reaction, using 1.50 g (9.44 mmoles) of Ia for 3 hr gave a yellow residue from which a small amount of adduct, mp 120–122°, could be obtained by recrystallization from methanol (lit.[3] mp 120–122°).

Acknowledgments.—We wish to thank Mr. Norman Rapino for determining the dipole moment of Ic. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of the work, under Grant No. 562-Gl.

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[11] G. W. Wheland and D. E. Mann [*J. Chem. Phys.*, **17**, 264 (1949)] reported a value of 1.48 ± 0.03 D. in benzene.

[12] That this boiling point is somewhat higher than might be expected from those of closely related compounds [6,6-dipropylfulvene, bp 92–93° (10 mm): *cf.* B. A. Kazanskii and F. N. Gakhanov, *Dokl. Akad. Nauk SSSR*, **64**, 521 (1949); *Chem. Abstr.*, **43**, 5370 (1949)] [6,6-hexamethylenefulvene, bp 81–82° (4 mm): *cf.* S. I. Khromov, E. S. Balenkova, and E. G. Treshchova, *Vestn. Mosk. Univ.*, **14**, 143 (1959); *Chem. Abstr.*, **54**, 9798] probably reflects greater intermolecular association owing to more polar ground state of Ia.

[13] D. P. Shoemaker and C. W. Garland, "Experiments in Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 275–283.

[14] J. H. Day, *Chem. Rev.*, **53**, 167 (1953).

[15] D. Craig, *et al.*, *J. Am. Chem. Soc.*, **76**, 4573 (1954).

The Methylation of 1,2-Diarylethylenes by Dimethylsulfinyl Carbanion

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Recent reports of the ability of dimethylsulfinyl carbanion (DMSO$^-$) to methylate various unsaturated systems,[1-3] prompt us to disclose our findings which may be of relevance to the mechanism of these reactions. In the course of other studies we had occasion to treat certain 1,2-diarylethylenes with DMSO$^-$.

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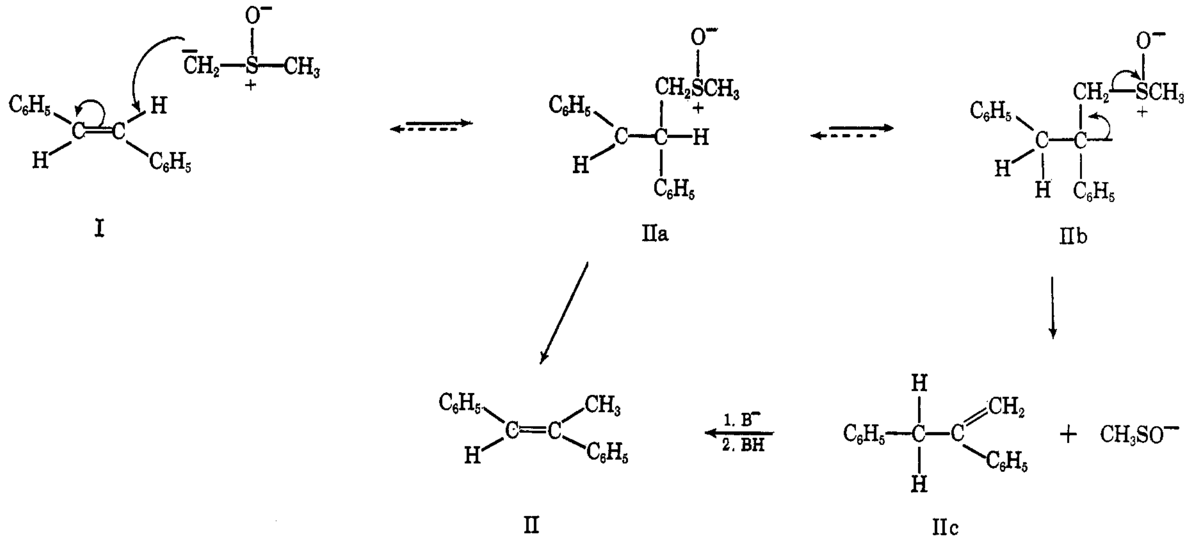
[1] P. A. Argabright, J. E. Hofmann, and A. Schriesheim, *J. Org. Chem.*, **30**, 3233 (1965).

[2] G. A. Russel and S. A. Weiner, *ibid.*, **31**, 248 (1966).

[3] H. Noyaki, Y. Yamamoto, and R. Noyori, *Tetrahedron Letters*, 1123 (1966).

SCHEME I



During the course of these studies it was noted that an allylic methyl group had been introduced.

When *trans*-stilbene (I) was added to a twofold molar excess of the methylsulfinyl anion[4,5] in DMSO at room temperature under nitrogen, a dark red color instantly appeared. After 15 min the reaction was quenched with water and upon work-up, a 60% yield of α-methyl-*trans*-stilbene (II) crystallized from the reaction mixture. Chromatography of the mother liquors afforded an additional 7% of this compound. The structural assignment rests on its melting point (77–80°, lit.[6] mp 81–82°) and infrared and nmr spectra. The latter exhibits signals ($\tau_{\mathrm{CCl_4}}$) at 2.4–3.0 (10) a multiplet, 3.2 (1) an unresolved quartet (J = 2 cps), 7.8 (3) a doublet (J = 2 cps) ppm. A proposed pathway for this reaction is shown in Scheme II.[7]

The formation of the methylated product (II) under these reaction conditions is in contrast to the results obtained by Walling and Bollyky[8] under similar conditions using 1,1-diphenylethylene (III) (Scheme II). These workers isolated as the principal product, 3,3-diphenyl-1-methylsulfinylpropane (IV) which upon subsequent pyrolysis afforded V. It will be noted that the stilbene case differs from the 1,1-diphenylethylene case, in that the proton-exchange step (IIa → IIb) invoked in the former instance, is not readily applicable to the latter case since the transformation IVa → IVb would be of high energy. This distinction is shown. We prefer the proton-exchange route (IIa ⇌ IIb → IIc) to the alternative hydride transfer possibility (IIa → II), of the type previously suggested[3] for elimination of methyl sulfenate IId in that it readily accounts for the difference between our results and those of Walling and Bollyky.[8] A related sequence has been postulated by Schriesheim and co-workers[1] in their studies of the methylation of conjugated dienes and can be invoked to account for the results of the reaction of DMSO⁻ with 1,2-diphenylacetylene reported by Iwai and Ide.[9]

Further insight into the nature of this type of reaction was gained by its application to the stilbazole series. Thus reaction of DMSO⁻ with 2-stilbazole (VI) afforded a 77% yield of an oil of the formula $C_{14}H_{13}N$. The assignment of structure VII to this compound is based on the following arguments. Its nmr spectrum [($\tau_{\mathrm{CCl_4}}$) 1.45 (1) doublet (J = 5 cps) with secondary unresolved structure, 2.4–3.4 (9) multiplet, 7.43 (3) doublet (J = 1.5 cps) ppm] in conjunction with that of its dihydro derivative [($\tau_{\mathrm{CCl_4}}$) 1.7 (1) doublet (J = 5 cps), 2.7–3.4 (8) multiplet, 6.5–7.4 (3) multiplet, 8.8 (3) doublet (J = 7 cps) ppm] obtained by reduction over palladized charcoal delineates two reasonable alternatives, VII and VIII. The decision between these alternatives in favor of VII is unambiguous in that authentic VIII was synthesized by the reaction of 2-ethylpyridine (IX) with benzaldehyde according to known procedures.[10,11] The compound thus obtained differed from that obtained from the DMSO⁻ reaction in its gas chromatographic retention properties in its infrared spectrum and its nmr spectrum [($\tau_{\mathrm{CCl_4}}$) 1.5 (1) doublet (J = 5 cps), 2.4–3.6 (9) multiplet, 7.74 (3) doublet (J = 1.5 cps) ppm]. The latter measurements exclude the possibility of

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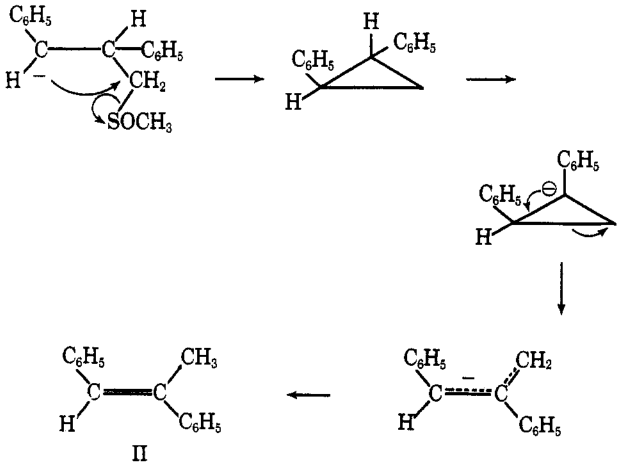
(4) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1345 (1965).

(5) M. Chaykovsky and E. J. Corey, *J. Org. Chem.*, **28**, 254 (1960).

(6) P. L. Écuyer and C. A. Olivier, *Can. J. Res.*, **28b**, 648 (1950).

(7) An alternative pathway would involve internal nucleophilic displacement of methyl sulfenate anion with formation of *cis*- or *trans*-1,2-diphenylcyclopropane which could undergo base-catalysed ring opening and subsequent protonolysis, affording the product, II.



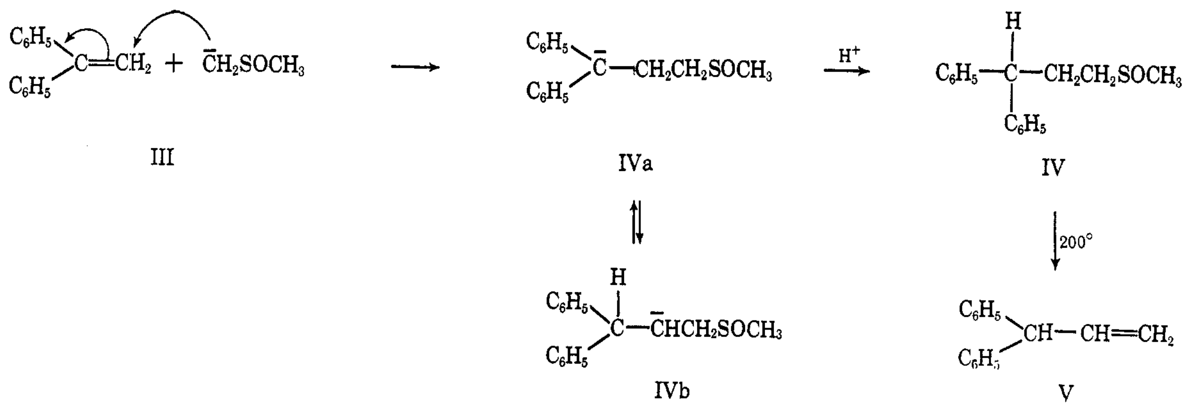
(8) C. Walling and L. Bollyky, *J. Org. Chem.*, **29**, 2699 (1964).

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

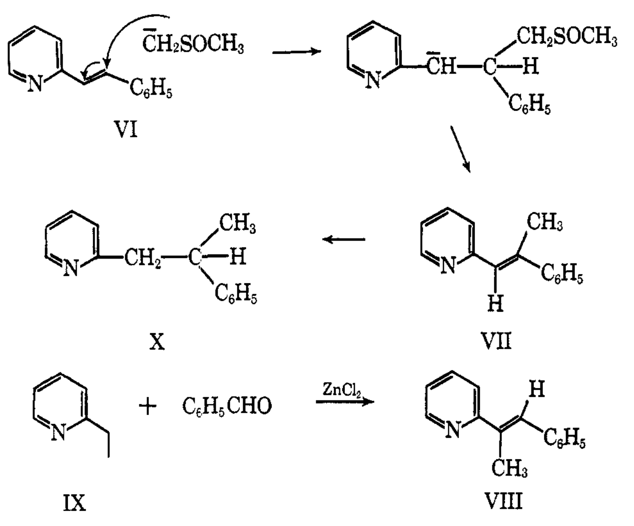
(10) A. P. Phillips, *J. Am. Chem. Soc.*, **76**, 3986 (1954).

(11) An attempt to prepare authentic VII by the reaction of α-picoline and acetophenone in the presence of anhydrous $ZnCl_2$ gave only triphenylbenzene.

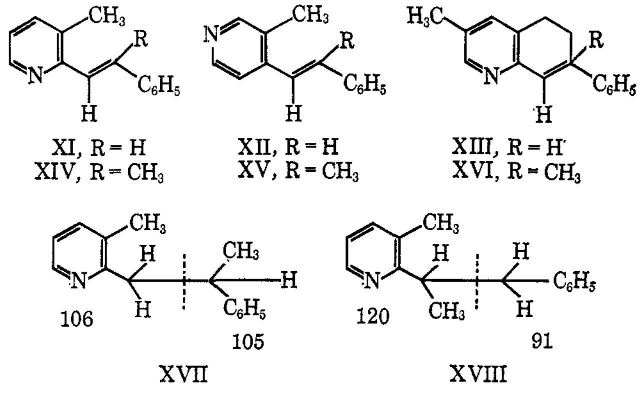
SCHEME II



the DMSO⁻ product being a mixture of VII and VIII. Structure VII is thus assigned to the DMSO⁻ product and X to its dihydro derivative. The formation of VII rather than VIII is presumably a consequence of the greater electrophilicity of 2-vinylpyridine relative to styrene. The over-all reaction is shown below.



Similarly, 3-methyl-2-stilbazole (XI), 3-methyl-4-stilbazole (XII), and 5-methyl-2-stilbazole (XIII) gave the corresponding methylated products XIV, XV, and XVI in moderate yields. The structural assignment of XIV follows from the mass spectrum of its dihydro derivative, XVII, which exhibits peaks at *m/e* 104, 105, 106, and 107. These are readily interpretable in terms of cleavage of the bibenzylic type bond of XVII followed by, or concerted with, hydrogen atom transfer. They can not be interpreted as arising from structure XVIII. The structural assignments of XV and XVI follow from their elemental analyses, spectral data, and analogy with the two established cases.



The formation of XIV and XV by this reaction was accompanied by the formation of dimers of XI and XII. Although the dimers were not obtained in crystalline form using the preformed methyl sulfinyl anion, they were so obtained using potassium *t*-butoxide as the base in DMSO. Utilization of KO-*t*-Bu-DMSO with VI and XIII led to diminished yields of methylated products but no dimer formation was noted. Apparently this type of dimerization requires an *ortho* relationship of the methyl and styryl functions. The structures of these complex dimers will be reported in a subsequent paper.

Attempted methylation of vinylpyridine *via* either KO-*t*-Bu-DMSO or the preformed DMSO⁻ led to resinous, polymeric products.

Experimental Section[12]

General Procedure for the Preparation of Stilbazoles. 3-Methyl-4-stilbazole (XII).—Under N_2, 9.24 g (0.086 mole) of 3,4-lutidine, 13.22 g (0.125 mole) of benzaldehyde, and 4.31 g (0.031 mole) of anhydrous zinc chloride were heated in a borosilicate glass pressure vessel at 195° for 20 hr. After cooling, the solution was made basic with 10% aqueous KOH and extracted with 100 ml of $CHCl_3$. The chloroform extract was dried and distillation of the chloroform left a residue, which upon distillation *in vacuo*, gave 8.55 g of material bp 134–145° (0.3 mm). This material crystallized on standing. Recrystallization from *n*-hexane gave white crystals: mp 89–91°; yield 44%; infrared $\lambda_{CCl_4}^{max}$ 6.14, 6.31 μ; ultraviolet λ_{EtOH}^{max} 303 mμ (ϵ 23,300); nmr τ_{CDCl_3} 1.51 (2) multiplet, 2.3–3.0 (8) multiplet, 7.67 (3) singlet ppm. *Anal.* Calcd for $C_{14}H_{13}N$: C, 86.11; H, 6.71; N, 7.17. Found: C, 86.37; H, 6.43; N, 7.13.

2-Stilbazole[13] (VI), mp 93.5°, 3-methyl-2-stilbazole[14] (XI), mp 55°, 5-methyl-2-stilbazole[15] (XIII), mp 70–71°, and α-methyl-2-stilbazole[8] (VIII), bp 144–145° (1 mm), were also prepared by this method.

α-Methyl-*trans*-stilbene (II).—To a solution containing the anion of dimethyl sulfoxide under N_2, made *via* the method of

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[12] Melting points were determined on a Fisher-Johns block and are uncorrected. Infrared, nmr, and ultraviolet spectra were taken on a Beckman IR-8 spectrophotometer, Varian A-60 spectrometer, and a Cary Model 14 spectrophotometer, respectively. Glpc was done on an Aerograph A-90-P3 chromatograph. Elemental analyses were performed by Galbraith Laboratories. DMSO was dried and distilled from calcium hydride. Sodium sulfate was used as a drying agent. We would like to thank Dr. F. E. Cislak of the Reilly Tar and Chemical Corp. for generously supplying us with the alkylpyridines.

[13] J. L. R. Williams, R. E. Adel, J. M. Carlson, G. A. Reynolds, D. G. Borden, and J. A. Ford, *J. Org. Chem.*, **28**, 387 (1963).

[14] A. Mustafa and M. K. Hilmy, *J. Chem. Soc.*, 1698 (1947).

[15] M. Häring, B. Prijs, and H. Erlenmeyer, *Helv. Chim. Acta*, **37**, 147 (1954).

Corey and Chaykovsky,[4,5] derived from 1.0 g (0.041 mole) of NaH and 40 ml of DMSO, was added 4.0 g (0.022 mole) of powdered *trans*-stilbene. The solution immediately turned deep red and heat was evolved. The solution, which was maintained at 25–35° with an ice bath, was stirred for 15 min, and was then added to 200 ml of water. Extraction with 100 ml of CH_2Cl_2, drying, and distillation of the solvent at the water pump left a residue which crystallized in part. The solid, 2.45 g, melted from 77 to 80° (lit.[5] mp 81–82°). The mother liquors chromatographed on neutral alumina and eluted with *n*-hexane, gave an additional 0.29 g of this material: mp 78–80°;[6] yield 67%; infrared $\lambda_{\mathrm{CHCl_3}}^{\max}$ 6.18, 6.29 μ; nmr ($\tau_{\mathrm{CCl_4}}$) 2.42–2.92 (10) multiplet, 3.2 (1) unresolved quartet (J = 2 cps), 7.83 (3) doublet (J = 2 cps) ppm.

General Procedure for the Methylation of Stilbazoles. β-Methyl-2-stilbazole (VII).—To a solution of DMSO anion prepared from 1.0 g (0.041 mole) of NaH and 40 ml of DMSO was added dropwise under N_2, a solution of 4.0 g (0.022 mole) of 2-stilbazole in 20 ml of DMSO. Total time for addition and stirring was 1 hr. The solution, which had turned dark brown, was added to 100 ml of water and extracted with 100 ml of CH_2Cl_2. Drying, followed by distillation of the solvent at the water pump left a residue which upon distillation *in vacuo* gave 3.28 g of material: bp 110–114° (0.4 mm); yield 77%; infrared $\lambda_{\mathrm{CHCl_3}}^{\max}$ 6.10, 6.28 μ. On a 5-ft column, packed with 20% SE 30 on Chromosorb W, column temperature 200°, flow rate 86 ml/min, this material had a retention time of 6.5 min. With equivalent conditions, VIII had a retention time of 7 min. *Anal.* Calcd for $C_{14}H_{13}N$: C, 86.12; H, 6.71. Found: C, 86.18; H, 6.84.

Also prepared in this manner was **β-methyl-3-methyl-2-stilbazole** (**XIV**): yield 67%; bp 100–107° (0.07 mm); infrared $\lambda_{\mathrm{CCl_4}}^{\max}$ 6.15, 6.33 μ; ultraviolet $\lambda_{\mathrm{EtOH}}^{\max}$ 312 mμ (ϵ 11,600), 272 mμ (ϵ 11,200); nmr ($\tau_{\mathrm{CCl_4}}$) 1.43 (1) doublet (J = 5 cps), 2.3–4.4 (8) multiplet, 7.46 (3) doublet (J = 1.5 cps), 7.9 (3) singlet ppm. *Anal.* Calcd for $C_{15}H_{15}N$: C, 86.08; H, 7.22; N, 6.69. Found: C, 86.03; H, 7.40; N, 6.52. **β-Methyl-3-methyl-4-stilbazole** (**XV**) was also prepared by this method: yield 51%; bp 107–108° (0.1 mm); infrared $\lambda_{\mathrm{CHCl_3}}^{\max}$ 6.18, 6.31 μ; ultraviolet $\lambda_{\mathrm{EtOH}}^{\max}$ 268 mμ (ϵ 13,000); nmr ($\tau_{\mathrm{CCl_4}}$) 1.50–1.85 (2) multiplet, 2.4–3.4 (7) multiplet, 7.96 (3) singlet, 8.05 (3) doublet (J = 1.5 cps) ppm., *Anal.* Calcd for $C_{15}H_{15}N$: C, 86.08; H, 7.22. Found: C, 85.74; H, 7.16. **β-Methyl-5-methyl-2-stilbazole** (**XVI**) was prepared in the same way: yield 37%; bp 126–128° (0.25 mm); mp 40–41°; infrared $\lambda_{\mathrm{CCl_4}}^{\max}$ 6.14, 6.25 μ; ultraviolet, $\lambda_{\mathrm{EtOH}}^{\max}$ 296 mμ (ϵ 15,400), 271 mμ (ϵ 14,800); nmr ($\tau_{\mathrm{CCl_4}}$) 1.67 (1) broad singlet, 2.45–3.40 (8) multiplet, 7.48 (3) doublet (J = 1.51 cps), 7.87 (3) singlet ppm. *Anal.* Calcd for $C_{15}H_{15}N$: C, 86.08; H, 7.22. Found: C, 85.85; H, 7.22.

General Procedure for the Hydrogenation of Stilbazoles. 1-(2-Pyridyl)-2-phenylpropane (**X**).—Hydrogenation of 3.22 g (0.017 mole) of VII was carried out at room temperature and atmospheric pressure, in 20 ml of absolute ethanol, using 0.5 g of Pd–C. The catalyst was filtered after 410 ml of H_2 had been absorbed (required 380 ml). Distillation of the ethanol at the water pump left a residue, which upon distillation *in vacuo* gave 2.91 g of material: bp 78–80° (0.07 mm); yield 86%; infrared $\lambda_{\mathrm{CCl_4}}^{\max}$ 6.30, 6.38 μ; nmr ($\tau_{\mathrm{CCl_4}}$) 1.72 (1) doublet (J = 5 cps), 2.68–3.42 (8) multiplet, 6.5–7.4 (3) multiplet, 8.8 (3) doublet (J = 8 cps) ppm. *Anal.* Calcd for $C_{14}H_{15}N$: C, 85.24; H, 7.66. Found: C, 85.37; H, 7.81.

Also prepared in this manner was **1-(3-methyl-2-pyridyl)-2-phenylpropane** (**XVII**): yield 90%; infrared $\lambda_{\mathrm{CCl_4}}^{\max}$ 6.36 μ; ultraviolet $\lambda_{\mathrm{EtOH}}^{\max}$ 267 mμ (ϵ = 4700); nmr ($\tau_{\mathrm{CCl_4}}$) 1.53 (1) doublet (J = 5 cps), 2.66–3.33 (7) multiplet, 6.2–7.1 (3) multiplet, 8.08 singlet, 8.70 (3) doublet (J = 7 cps) ppm. *Anal.* Calcd for $C_{15}H_{17}N$: C, 85.26; H, 8.11; N, 6.63. Found: C, 85.02; H, 8.29; N, 6.80. **1-(3-Methyl-4-pyridyl)-2-phenylpropane** (**XIX**) was prepared in this way: yield 70%; infrared, $\lambda_{\mathrm{KHCl_3}}^{\max}$ 6.29 μ; ultraviolet $\lambda_{\mathrm{EtOH}}^{\max}$ 264 mμ (ϵ 5800); nmr ($\tau_{\mathrm{CCl_4}}$) 1.6–1.9 (2) multiplet, 2.7–3.4 (6) multiplet, 6.3–7.2 (3), 8.24 (3) singlet, 8.9 (3) doublet (J = cps) ppm. *Anal.* Calcd for $C_{15}H_{16}N$: C, 85.26, H, 8.11. Found: C, 85.40; H, 8.25.

Acknowledgment.—The authors wish to thank the Amerian Cancer Society for their generous support of this work.

Condensation of Triethyl Phosphonoacetate with Aromatic Aldehydes

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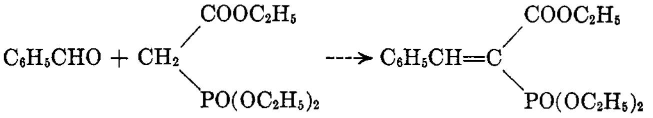
Received May 9, 1966

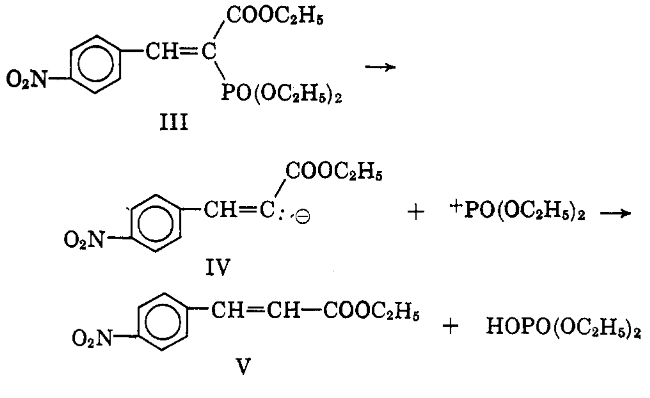
The condensation of triethyl phosphonoacetate (I) with benzaldehyde on heating at 160–170° with acetic anhydride was reported by Pudovik and Lebedeva[2] to give a 37–40% yield of triethyl benzylidenephosphonoacetate (II).



$$C_6H_5CHO + CH_2\begin{matrix}\diagup COOC_2H_5\\ \diagdown PO(OC_2H_5)_2\end{matrix} \dashrightarrow C_6H_5CH{=}C\begin{matrix}\diagup COOC_2H_5\\ \diagdown PO(OC_2H_5)_2\end{matrix}$$

I II

In a reinvestigation of this work, Patai and Schwartz[3] obtained lower yields (17%) of the ester (II) under the conditions used by the Russian authors but were able to obtain much better yields (70%) of the triester by using milder reaction conditions (refluxing benzene as a solvent, piperidine and acetic acid as catalysts) and longer reaction time. They also found that with *p*-nitrobenzaldehyde and triethyl phosphonoacetate in ethanol as the solvent and piperidine as the catalyst, very high yields (83%) of ethyl *p*-nitrocinnamate (V) were obtained, but that no phosphorus-containing ester (III) could be isolated. They believe that the dephosphonation in this case is due to the increased stabilization by the nitro group of the carbanion (IV) formed in the elimination.



III

IV

V

We have prepared a number of the triesters analogous to II with substituents on the aromatic ring which are electron donating or not so strongly electron withdrawing as the nitro group. The conditions used for the condensation reactions were analogous to the conditions used by Patai and Schwartz in which they obtained their best yield. Refluxing benzene was used as the solvent with a Dean–Stark trap so that the progress of the reaction could be followed as water

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