diacetate showed 17β -proton absorption as a singlet at 288 c.p.s. with a half-height width of 1.5 c.p.s.

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Carbonyl-Stabilized Sulfonium Ylids. Reaction with Schiff Bases

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Carbonyl-stabilized sulfur ylids have been prepared via treatment of the corresponding sulfonium salts with sodium hydride. These ylids react with Schiff bases to produce 3-arylaminocinnamate derivatives demonstrating the synthetic potential of this ylid series.

Discussion

The stabilization of carbanions by the inductive and p-d overlap effects of an adjacent phosphorus atom has provided a class of P-ylids which have been shown to provide one of the most useful carbon-carbon bond forming reactions.¹ In the same manner as phosphorus, sulfur may also expand its valence shell utilizing 3d orbitals to stabilize an adjacent carbanion.² The synthetic utility of S-ylids has not been as fully explored as the P-ylids. S-Ylids, however, appear to react with carbonyl compounds by initial nucleophilic attack with the elimination of a sulfide whereas the Pylids eliminate phosphine oxides.³

S-Ylids were known as early as 1930,⁴ although their reactivity has been studied only recently.³ Corey⁵ has demonstrated that dimethyl sulfonium methylide generated in situ provides a valuable synthesis of epoxides via reaction with aldehydes and ketones. S-Ylids which are resonance stabilized are known in only one reported instance.³ Dimethyl sulfonium fluorenylides, generated by the action of base on the corresponding sulfonium salt, are stable, isolable, and undergo reaction with carbonyl compounds. In our continuing study of ylid chemistry⁶ we have prepared some sulfonium methylides wherein the carbanion is stabilized by a carbonyl group, a type of ylid which in the phosphorus series is isolable yet reacts with electrophiles.

Treatment of sulfonium salts (I) with sodium hydride in tetrahydrofuran resulted in the evolution of 1

(1) See "Methoden der Organische Chemie," Vol. 12, Part 1, Houben-Weyl, Ed., Georg Thieme Verlag, Stuttgart, 1963, p. 112, for leading references

- (2) G. Cilento, Chem. Rev., 60, 147 (1960).
 (3) (a) A. W. Johnson and R. B. LaCount, J. Am. Chem. Soc., 83, 417 (1961); (b) A. W. Johnson, V. J. Hruley, and J. L. Williams, ibid., 86, 918 (1964).
- (4) C. K. Ingold and J. A. Jessop, J. Chem. Soc., 713 (1930).

(5) (a) E. J. Corey and M. Chaykovsky, J. Am. Chem. Soc., 84,

3782 (1962); (b), Tetrahedron Letters, No. 4, 169 (1963). (6) See A. J. Speziale and D. E. Bissing, J. Am. Chem. Soc., 85, 3878 (1963), for leading reference.

equiv. of hydrogen. Addition of Schiff bases to the ylid in situ, followed by a short reflux period, gave 3arylaminocinnamates and -cinnamamides II in generally good yields. (See Table I.)

$$\begin{array}{cccc} X^{-} & O & Ar'NH & O \\ (CH_3)_2 \overset{+}{S} & -CH_2 CR + ArCH = NAr' & \overset{NaH}{\xrightarrow{}} & ArC = CHCR' \\ I & II & II \end{array}$$

The assignment of structure II is made on the basis of elemental and spectral analysis and upon hydrolysis experiments. The n.m.r. values are given in Table II. The presence of a singlet (area = 1) at low field suggests an N-H intramolecularly chelated with a carbonyl oxygen.⁷ This is inferred from the large paramagnetic shift of the N-H proton observed in similar β -amino unsaturated carbonyl compounds in comparison to dimedone Schiff bases in which such hydrogen bonding is precluded. The cis isomer (IIIa) of 3-methyl-4methylamino-3-buten-2-one exhibits an N-H singlet at τ 0.5 whereas the *trans* isomer (IIIb) (incapable of N-H hydrogen bonding) shows this proton at 5.0.8 Consequently, II possesses an N-H proton chelated to



(7) G. Dudek and R. H. Holm, ibid., 84, 2691 (1962) (8) G. Dudek and G. P. Volpp, *ibid.*, 85, 2697 (1963).

	NHAr'
Table I.	ArC=CHCOR

R	Ar	Ar'	M.p., °C.	Yield,		Calcd. H	— Ana	l., % — C	- Found H	
$\begin{array}{c} OC_{2}H_{5} \\ N(C_{2}H_{3})_{2} \\ N(CH_{2}CH=\!\!\!\!CH_{2})_{2} \\ N(CH_{2}CH_{3})_{2} \\ N(CH_{2}CH_{3})_{2} \\ \end{array}$	C ₆ H ₅ C ₆ H ₅ C ₆ H ₅ <i>p</i> -CH ₃ OC ₆ H ₅ <i>p</i> -O ₂ NC ₆ H ₅	C ₆ H ₆ C ₆ H ₅ C ₆ H ₅ C ₆ H ₅ 2,3-Cl ₂ C ₆ H ₁	67–68 91–92 91–92 108–110 178–181	33 81 36 74 45	76.38 77.51 79.31 74.04 55.89	6.41 7.53 6.97 7.46 4.69 (CL 17.37	5.24 9.52 8.80 8.64 10.29	76.35 77.64 78.90 74.29 56.02	6.64 7.63 7.00 7.61 4.55 (C) 17.42	5.19 9.31 8.60 8.81 10.13

Table II. Chemical Shifts (τ) for ArC(NHAr')=CHCOR^a

R	Аг	Ar'	ArH ^b	CH ₂ ^e	CH³c	Vinyl H	NH
$\begin{array}{c} OC_{2}H_{5} \\ N(C_{2}H_{5})_{2} \\ N(CH_{2}CH=CH_{2})_{2} \\ N(CH_{2}CH=CH_{2})_{2} \\ N(CH_{2}CH_{3})_{2} \\ N(CH_{2}CH_{3})_{2} \end{array}$	C ₆ H ₅ C ₆ H ₅ C ₆ H ₅ 4-CH ₂ OC ₆ H ₅ 4-NO ₂ C ₆ H ₅	$\begin{array}{c} C_6H_5\\ C_6H_5\\ C_6H_5\\ C_6H_5\\ 2,3\text{-}Cl_2C_6H_2 \end{array}$	2.67-3.22(10) 2.67-3.32(10) 2.65-3.55 2.60-3.42(10) 1.76-3.96	5.77 (2) 6.57 (4) 6.07-7.25 6.25 (4) 6.53	8.74 (3) 8.80 (6) 6.58 (3); 8.81 (6) 8.77	4.97 (1) 4.90 (1) 4.24 ^d -4.89 4.95 (1) 4.62	$\begin{array}{r} -0.43(1) \\ -1.66(1) \\ -0.60 \\ -1.51(1) \\ -1.60 \end{array}$

^a N.m.r. spectra were measured at 60 Mc./sec. on a modified Varian Model A-60 spectrometer. The samples contained tetramethylsilane as internal reference. Relative areas are given in parentheses. ^b Multiplet range given. ^c J values for the CH_2 quartet and CH_3 triplets are 7.0–7.5 c.p.s. The values given are the center of the multiple peaks. ^d Overlapping of the vinyl protons of the allyl groups precludes identification of the single vinyl proton.

Table III. (CH₃)₂S⁺CH₂COR Cl⁻

			Anal., %											
	M.p.,	Yield,	N.m	.r., τ^a			Calcd					Found -		
R	°Ĉ.	%	CH₃S	SCH ₂ CO	С	Н	Cl	Ν	S	С	Н	Cl	Ν	S
$OC_2H_5^b$	85-87	60	6.50	5.74	31.45	5.72	34.87		13.99	31.60	5.69	35.08		14.22
$N(C_2H_5)_2$	146-147.5	58	6.56	4.80	45.37	8.57	16.74	6.62	15.14	45.10	8.40	16.69	6.03	15.25
$N(CH_2CH=CH_2)_2$	121-122	66	6.60	4.59	50.94	7.69	15.04	5.94	13.60	50.74	7.63	14.95	6.08	13.33

^a Area ratio $CH_3/CH_2 = 6/2$. ^b Bromide salt.

the carbonyl oxygen. The vinyl proton of II (τ 4.90, A = 1) corresponds more closely to that observed in ethyl 3-benzylaminocrotonate (IV) and 4-benzylamino-3-penten-2-one (V) (τ 5.52 and 4.99, respectively) than in 3-methyl-4-methylamino-3-buten-2-one (III) (τ 3.45).⁸ Also 4-alkylamino-3-buten-2-ones (VI) exhibit the 3-vinyl proton in the range τ 4.62–5.08 and 4-vinyl proton at 2.93–3.93.⁸ These n.m.r. results, coupled with the fact that complete hydrolysis of II (Ar = Ar' = C₆H₆; R = N(C₂H₅)₂) gives a high yield of acetophenone, indicate that the amino group is attached to the 3- rather than 2-position. Hydrolysis of the corresponding 2-aminocinnamamide would lead to phenylacetic acid rather than acetophenone.

The α -sulfonium-substituted amides and esters (I) were prepared by direct reaction of dimethyl sulfide and the corresponding halocarbonyl compound. The

$$(CH_3)_2S + XCH_2COR \longrightarrow I$$

characteristics and yields of these compounds are given in Table III.

The formation of II may occur by several pathways, all of which involve an initial nucleophilic attack of the ylid upon the Schiff base to yield a betaine (VII). Several alternative pathways are available: (a) a hydride shift to nitrogen followed by the elimination of dimethyl sulfide; (b) a hydride shift to carbon with elimination of dimethyl sulfide followed by rearrangement of the resulting ketimine; (c) alternately VII may undergo ring closure to an aziridine (VIII) which subsequently opens to yield II.



Copper-catalyzed reaction of ethyl diazoacetate with benzalaniline at 40–50° gave only II (Ar = Ar' = C_6H_5 ; R = OC₂H₅). A carbene addition to the C=N bond is presumed. Since no reaction occurred without catalysis, the possibility of nucleophilic attack by

ethyl diazoacetate is eliminated. The aziridine VIII $(Ar = Ar' = C_6H_5; R = OC_2H_5)$ which presumably was initially formed opened to give the 3-anilinocinnamate.

The aziridine pathway c is chosen as more likely than a or b since: (1) the aziridine opens under mild conditions to give the observed products II and, (2) this mechanism is in accord with other known reactions of S-ylids.9

The reaction of carbonyl-stabilized sulfonium ylids as nucleophilic species provides a useful class of sulfur ylids for synthetic purposes. Further exploration will indicate the extent of their value.

Experimental¹⁰

Sulfonium Salts (I). The procedure used is illustrated with ethyl bromoacetate and dimethyl sulfide. Dimethyl sulfide (62.1 g., 1.0 mole) and ethyl bromoacetate (167.0 g., 1.0 mole) were added to benzene (500 ml.) and stirred at room temperature for 18 hr. The precipitate was filtered and dried under dry N₂ to give 138.0 g. (60%) of sulfonium salt. When necessary the solution was refluxed overnight, or alternately the reaction was carried out with no solvent.

Arylaminocinnamates and -amides (II). The general procedure used is illustrated by the reaction between benzalaniline and dimethyl (N,N-diethylcarbamoylmethyl)sulfonium chloride. To a stirred suspension of dimethyl (N'N-diethylcarbamoylmethyl)sulfonium chloride (12.0 g., 0.05 mole) in tetrahydrofuran¹¹ (previously dried over Fisher molecular sieve 4A, 250 ml.) under nitrogen atmosphere, was added in one portion sodium hydride (2.3 g., 0.05 mole, 53% in mineral oil). The system was immediately connected to a gas meter and the evolution of hydrogen was noted. The mixture was stirred at room temperature for 2 hr. (or until the amount of hydrogen evolved was quantitative or until no more hydrogen could be evolved). Hydrogen (1.4 l.) was evolved (theory 1.12 l. at STP). Benzalaniline (9.1 g., 0.05 mole) was added in one portion (to the stirred suspension) under nitrogen. After stirring for 1 hr. at room temperature, the mixture was heated to 60°, then cooled to room temperature and filtered to remove sodium chloride. The filtrate was concentrated to a brown oil which was distilled at 190-194° (0.7 mm.) to give a yellow oil (5.5 g., 37%). The vellow oil was treated with petroleum ether (b.p. 30- 75°) and crystallized to give a light yellow solid, m.p. 70-73°. Recrystallization of the solid from petroleum ether (with charcoal treatment) gave colorless needles which were dried at 56° in vacuo, m.p. 91-92°. A higher yield (81%) was obtained by allowing the yellow

(11) In order to procure 100% release of H₂ in this reaction, the solvent had to be air exposed for a short period.

oil to stand and crystallize rather than distilling. Crystallization requires a period of 1 week in some instances.

Hydrolysis of 3-Anilino-N,N-diethylcinnamamide. 3-Anilino-N,N-diethylcinnamamide (4.0 g., 0.17 mole) was dissolved in 50% aqueous hydrochloric acid (60 ml.) and refluxed for 2-3 days. A few drops of dark oil separated. The solution was cooled and extracted several times with ether. The ether extract was then dried and evaporated to give 1.75 g. (85%) of yellow oil with an odor of acetophenone. The infrared and n.m.r. spectra and the 2,4-dinitrophenylhydrazone derivative were identical with those of acetophenone. The aqueous portion, after ether extraction, was neutralized with aqueous potassium hydroxide solution and evaporated to dryness. The white solid salt was repeatedly extracted with ether and the ether extract was dried and evaporated to dryness to give 1.07 g. (68% yield) of aniline.

Reaction of Ethyl Diazoacetate with Benzalaniline. A. Heat Catalyzed. To a freshly prepared ethyl diazoacetate solution¹² (35 ml., 4.67 g., based on 80%yield) was added benzalaniline (4.5 g., 0.025 mole). The yellow solution was stirred for 16 hr. at room temperature. The methylene chloride was evaporated from the above mixture and the remaining oil was heated for 2 days at 110°. After this time the infrared spectrum of the oil showed no diazo band. The material was chromatographed on neutral alumina to give recovered Schiff base and an oil whose infrared spectrum was essentially identical with that of ethyl 3-anilinocinnamate.

B. Copper Catalyzed. Ethyl diazoacetate (17.5 ml.) in methylene chloride was added with ice-bath cooling to a solution of benzalaniline (4.5 g., 0.025 mole) in methylene chloride (3 ml.). The solution was stirred for 20 min. at 0° and at room temperature for 17 hr. Infrared analysis at this point and after the mixture was allowed to stand for 2 months indicated no appreciable diminution of the diazo band although the methylene chloride evaporated. Activated copper powder (0.1 g.)¹³ was added to this reaction mixture in benzene (25 ml.) and heated to 60-70° for 30 min. After the gas evolution ceased, the mixture was heated for an additional 2 hr. and stirred overnight at room temperature. After filtration of the copper powder, the infrared spectrum of the resulting solution indicated the presence of no diazo compound but showed bands characteristic of benzalaniline and ethyl 3-anilinocinnamate. Chromatography of the mixture on Woelm neutral alumina gave only benzalaniline and an oil characterized as ethyl 3-anilinocinnamate by proton resonance spectra. Dry Ice-acetone cooling of the latter oil induced crystallization of a product identical in all respects with ethyl 3-anilinocinnamate.

⁽⁹⁾ The major reported product from the reaction of dimethylsulfonium methylide and Schiff bases is the corresponding aziridine. ref. 5a and V. Franzen and H. E. Driesen, Chem. Ber., 96, 1881 (1963). Reference 5a reports the product of dimethylsulfoxonium methylide and benzalaniline to be a 2:1 mixture of 1,2-diphenylaziridine and acetophenone anil

⁽¹⁰⁾ All melting points are uncorrected. Microanalyses were per-formed by Galbraith Laboratories, Knoxville, Tenn.

⁽¹²⁾ N. E. Searle, "Organic Synthesis," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p. 424.
(13) R. Q. Brewster and T. Groenig, "Organic Synthesis," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 446.