Debromination of *N*,*N*-Diethylcinnamamide Dibromide

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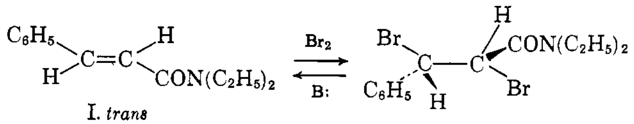
Attempts to prepare *trans*-*N*,*N*-diethyl-3-phenylglycidamide from the corresponding *erythro*-*N*,*N*-diethylcinnamamide dibromide (II) and bases gave unexpectedly the debromination product, *trans*-*N*,*N*-diethylcinnamamide (I). The debromination of *erythro*-ethyl *p*-nitrocinnamate dibromide (VIIa) and *erythro*-ethyl cinnamate dibromide (VIIb) to the corresponding *trans* olefins occurred with highly nucleophilic reagents such as triphenylphosphine and pyridinium thiolacetate. However, when VIIa,b were treated with alcoholic sodium acetate, *trans* elimination of hydrogen bromide became the only reaction. These results are explicable on the basis of the preferred conformation in the transition state of the respective dibromides for the debromination and the dehydrohalogenation reactions and the nucleophilicity of the base in its attack on "positive" α-halogen or α-hydrogen.

The reaction of branched vicinal dibromides with sodium thiophenolate was reported[1,2] to yield olefins. However, with ethylene and propylene dibromides, only substitution products were isolated.[1,3] The formation of olefins from vicinal dibromides with iodide ion is well known.[4] The reaction is second order and proceeds by a *trans* elimination mechanism.[4e,5-7] Thus, *meso*-stilbene dibromide and *meso*-2,3-dibromobutane yield *trans* olefins whereas the corresponding *threo* dibromides give *cis* olefins.[8] The debromination of acyclic dibromides with metals, *e.g.*, zinc, magnesium, and sodium is also well known.[4d,9]

Bickel[10] reported the debromination of chalcone dibromide with bases in the presence of alcohol-free acetone or aqueous acetone. However, Abell,[11] Bickel,[12] and Lutz, *et al.*,[13] noted that the chalcone dibromide on treatment with potassium acetate in 95% ethanol or triethylamine in acetone gave only α-bromochalcone. The debromination of vicinal dibromides adjacent to a carbonyl group by trialkylphosphite has also been reported.[14,15]

Our attempt to prepare *trans*-*N*,*N*-diethyl-3-phenylglycidamide from the corresponding *erythro* dibromide (II)[16] with sodium carbonate in aqueous acetone gave unexpectedly *trans*-*N*,*N*-diethylcinnamamide (I) as the only product. This finding prompted us to investigate further the results of the treatment of this dibromide with other bases.



I. *trans*

II. *erythro* dibromide

The debromination of the *erythro*-dibromide (II) under the conditions studied (Table I) led only to *trans*-cinnamamide.

TABLE I

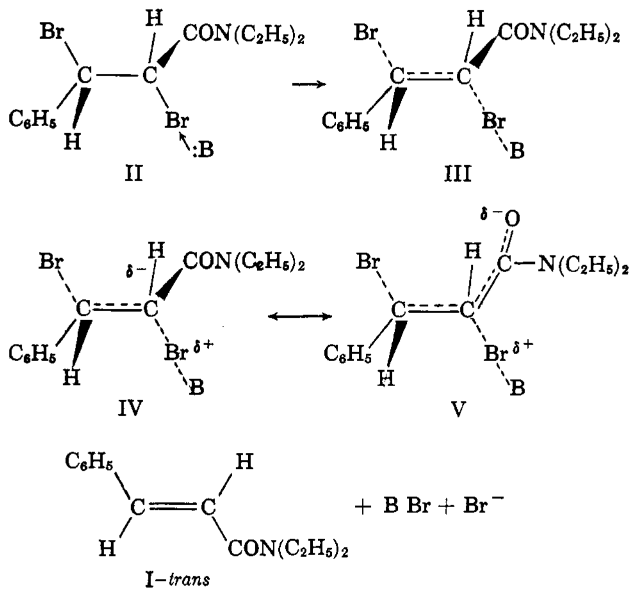
DEBROMINATION OF II BY BASES

Base	% Yield of I
Na_2CO_3, H_2O	97.0
KOH, H_2O	96.0
CH_3COONa, C_2H_5OH	51.3[a]
$(C_6H_5)_3P$, $CHCl_3$	95.5
C_5H_5N, CH_3COSH, C_6H_6	90.0

[a] Quantitative yield based on 48.7% recovered II.

Two alternate competitive reactions of II with base, *trans* elimination of hydrogen bromide and S_N2 displacement of either or both bromine atoms, were not observed.

The stereospecific elimination of bromine undoubtedly proceeds *via* a concerted E2 mechanism which is facilitated by the favored *trans* coplanar transition state (III). The partial accumulation of negative



II III

IV V

I-*trans*

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(1) R. Otto, *J. prakt. Chem.*, [2] **51**, 299 (1895).

(2) E. Eliel and R. G. Haber, *J. Org. Chem.*, **24**, 143 (1959).

(3) J. Hine and W. H. Brader, Jr., *J. Am. Chem. Soc.*, **75**, 3964 (1953).

(4) (a) R. T. Dillon, W. G. Young, and H. J. Lucas, *ibid.*, **52**, 1953 (1930); (b) R. T. Dillon, *ibid.*, **54**, 952 (1932); (c) W. G. Young and S. Winstein, *ibid.*, **58**, 102 (1936); (d) W. G. Young, Z. Jasaitis, and L. Levanas, *ibid.*, **59**, 403 (1937); (e) S. Winstein, D. Pressman, and W. G. Young, *ibid.*, **61**, 1645 (1939); (f) W. G. Young, S. J. Cristol, and T. S. Skei, *ibid.*, **65**, 2099 (1943); (g) J. Weinstock, S. N. Lewis, and F. G. Bordwell, *ibid.*, **78**, 6072 (1956).

(5) W. G. Young, D. Pressman, and C. D. Coryell, *ibid.*, **61**, 1640 (1939); **65**, 2099 (1943).

(6) (a) D. H. R. Barton and E. Miller, *ibid.*, **72**, 1066 (1950); (b) D. H. R. Barton and W. J. Rosenfelder, *J. Chem. Soc.*, 1048 (1951); (c) G. H. Alt and D. H. R. Barton, *ibid.*, 4284 (1954).

(7) W. M. Schubert, H. Steahly, and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **77**, 5755 (1955).

(8) When ethanolic potassium hydroxide was used instead of iodide, *meso*-stilbene dibromide yielded *cis*-bromostilbene, and *threo*-stilbene dibromide yielded *trans*-bromostilbene [P. Pfeiffer, *Z. physik. Chem.*, **48**, 40 (1904)].

(9) W. M. Schubert, B. S. Rabinovitch, N. R. Larson, and V. A. Sims, *J. Am. Chem. Soc.*, **74**, 4590 (1950).

(10) C. L. Bickel, *ibid.*, **72**, 349 (1950).

(11) R. D. Abell, *J. Chem. Soc.*, **101**, 1000 (1912).

(12) C. L. Bickel, *J. Am. Chem. Soc.*, **68**, 865 (1946).

(13) R. E. Lutz, D. F. Hinkley, and R. H. Jordan, *ibid.*, **73**, 4647 (1951).

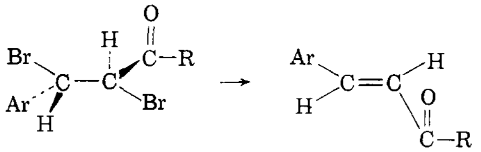
(14) V. S. Abramov and N. A. Ilyina, *J. Gen. Chem., USSR*, **26**, 2245-2249 (1956).

(15) S. Dershowitz and S. Proskauer, *J. Org. Chem.*, **26**, 3595 (1961).

(16) The transformation of a dibromide to an epoxide with base proceeds through the bromohydrin [D. Y. Curtin, A. Bradley, and Y. G. Hendrickson, *J. Am. Chem. Soc.*, **78**, 4064 (1956)].

TABLE II

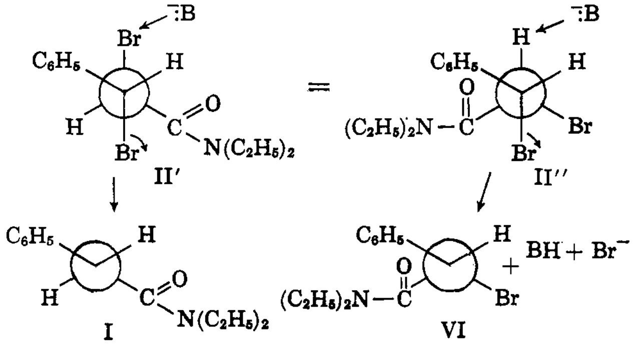
DEBROMINATION OF *erythro*-DIBROMIDES WITH TRIPHENYLPHOSPHINE AND THIOLACETATE ION



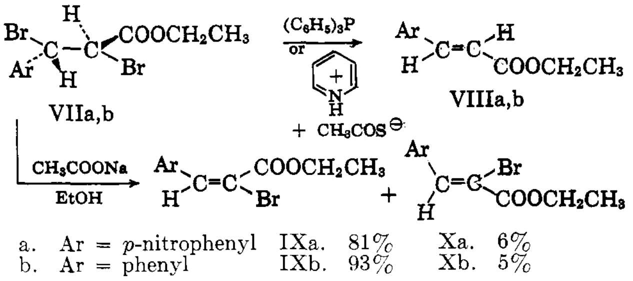
	Ar	R	α,β-Unsat., %	$(C_6H_5)_3PBr_2$, %	$(CH_3C(=O)—S)_2$, %	$C_5H_5\overset{+}{N}HBr^-$, %
II	C_6H_5	$N(C_2H_5)_2$	96	86	. .	
II	C_6H_5	$N(C_2H_5)_2$	90	. .	87	Theory
VIIa	$4-NO_2C_6H_4$	OC_2H_5	87	99	. .	
VIIa	$4-NO_2C_6H_4$	OC_2H_5	95	. .	89	Theory
VIIb	C_6H_5	OC_2H_5	92	93	. .	
VIIb	C_6H_5	OC_2H_5	84	. .	85	96.5
XIa	$3,4-Cl_2C_6H_3$	$N(C_2H_5)_2$	80	. .	78	98.5
XIb	C_6H_5	OH	82	. .	74	91.5

charge on the α-carbon atom would also be stabilized by resonance forms IV ↔ V.

The *trans* elimination of hydrogen bromide from II to from *cis* α-bromoölefin (VI) would be sterically unfavored because of the repulsion associated with eclipsing a phenyl and a diethylamido group (as in II″). However, *trans* debromination of II would involve the more favored conformer II′ (eclipsed phenyl and hydrogen). The SN2 displacement of bromine atoms is also sterically hindered in either II′ or II″.



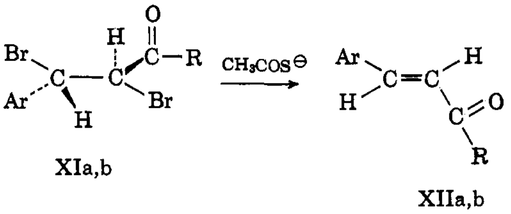
The debromination of *erythro*-ethyl *p*-nitrocinnamate dibromide (VIIa) and *erythro*-ethyl cinnamate dibromide (VIIb) with highly nucleophilic reagents (triphenylphosphine or pyridinium thioacetate) gave the corresponding *trans* olefins (VIIIa,b).



a. Ar = *p*-nitrophenyl IXa. 81% Xa. 6%
b. Ar = phenyl IXb. 93% Xb. 5%

However, when VIIa,b were treated with alcoholic sodium acetate, *trans* elimination of hydrogen bromide became the only reaction. Thus, VIIa,b were converted to the *cis*-α-bromoölefins (IXa,b) with 5–7% of *trans*-α-bromoölefins (Xa,b).[17] Even though the preferred conformation of VIIa,b is that depicted by II′ [$N(C_2H_5)_2$=OC_2H_5], debromination did not occur. A plausible explanation for these results is that since acetate ion is a poor nucleophile, abstraction of a proton from the less favored conformation II″ [$N(C_2H_5)_2$=OC_2H_5] is preferred. The difference in behavior of the bromo amides and bromo esters may be due to the fact that the α-hydrogen atom of the amide is considerably less acidic than that of the ester.[18] Because the debromination of II by acetate ion proceeded to only 51.3% in twelve hours (Table I) and dehydrobromination of VIIa and VIIb proceeded to 89.9% and 97.5% in six hours, it is suggested that the acidities (or positive character) are in the following orders: αH in VIIa,b > αBr in II > αH in II.

Treatment of *erythro*-dibromides (XIa,b) with pyridinium thiolacetate also gave the debromination products, XIIa,b.



a. Ar = 3,4-dichlorophenyl; R = $N(C_2H_5)_2$
b. Ar = phenyl; R = OH

The mechanism proposed for the debromination of the *erythro*-dibromides involves the attack by base on a positive bromine atom. (The one occupying the α-position is the most reasonable.) Although no attempt was made to isolate hypobromite or acetyl hypobromite from the reaction of I with carbonate, hydroxide, or acetate ions, the reactions of triphenylphosphine and thioacetate ion with II, VIIa,b, and XIa,b were investigated in some detail. The results are tabulated in Table II.

The *erythro*-dibromides (II, VIIa,b, and XIa,b) with triphenylphosphine gave high yields of triphenylphosphine dibromide. Its infrared spectrum was identical with an authentic sample prepared from triphenyl-

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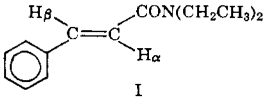
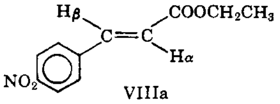
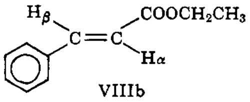
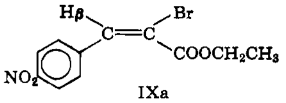
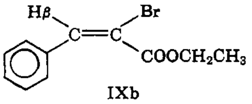
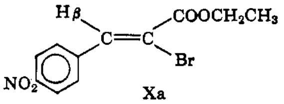
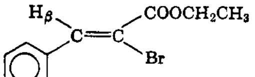
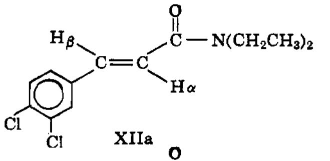
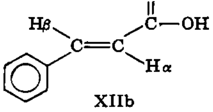
[17] Since the formation of *trans* α-bromoölefins does not arise from the isomerization of the corresponding *cis* olefins,[13] *trans* α-bromoölefins Xa,b, could result either (a) from the *trans* elimination of hydrogen bromide from traces of the *threo* dibromides which could be formed during the preparation of *erythro* dibromides, or (b) from the *cis* elimination of hydrogen bromide from the *erythro* dibromides. Although *cis* eliminations of this type are unsatisfactory, they, however, are derived in this case from the favored conformer (II′).

[18] A. J. Speziale and H. W. Frazier, *J. Org. Chem.*, **26**, 3176 (1961).

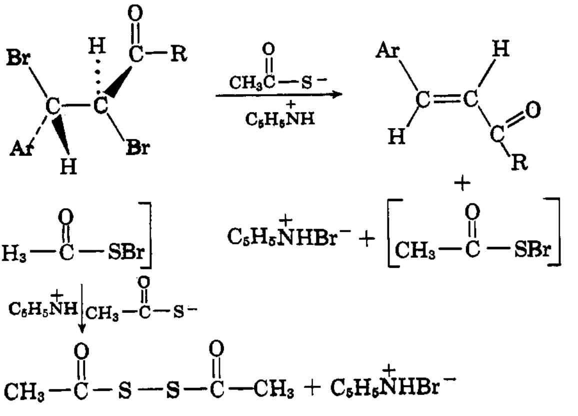
Table III

Chemical Shifts[a] and Spin–Spin Coupling Constants of Cinnamamide and Cinnamates

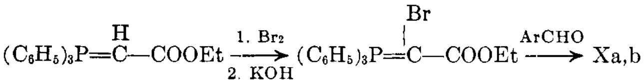
Compound	Chemical shifts, τ				Coupling constants, c.p.s.		
	CH_3 triplet	CH_2 quartet	Hα doublet	Hβ doublet	J_{CH_3}	J_{CH_2}	$J_{H\alpha H\beta}$[b]
 I	8.78	6.50	3.18	2.25	7.5	7.5	16.0
 VIIIa	8.67	5.75	3.40	2.20	8.0	8.0	16.5
 VIIIb	8.67	5.72	3.56	2.30	8.0	8.0	16.0
 IXa	8.80	5.75	..	1.83[c]	8.0	8.0	..
 IXb	8.82	5.77	..	1.83[c]	7.5	7.5	..
 Xa	8.63	5.60	..	1.84[c]	7.5	7.5	..
 Xb	8.70	5.71	..	1.83[c]	7.5	7.5	..
 XIIa	8.85	6.68	3.45	2.52	7.0	7.0	15.0
 XIIb	..	..	3.52	2.15	..	..	16.0

[a] N.m.r. spectra were measured at 60 Mc./sec. on a modified Varian Model A-60 spectrometer. The samples contained tetramethylsilane (TMS) as internal reference. [b] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., 1959, p. 238. [c] Singlet.

phosphine and bromine. The triphenylphosphine dibromide was further identified by its quantitative conversion to triphenylphosphine oxide by stirring in water. With thiolacetic acid in pyridine, II, VIIa,b, and XIa,b gave high yields of diacetyl disulfide. The disulfide would arise from the reaction of acetylsulfur bromide with thioacetate ion as shown.



The *trans*-α-bromoölefins (Xa,b) were identical with authentic samples prepared from the ylid (XIV)[19] and the corresponding aldehydes (XVa,b).[20]



$$(C_6H_5)_3P{=}\overset{H}{C}{-}COOEt \xrightarrow[2.\ KOH]{1.\ Br_2} (C_6H_5)_3P{=}\overset{Br}{C}{-}COOEt \xrightarrow{ArCHO} Xa,b$$

XIII XIV XVa,b

a. Ar = *p*-nitrophenyl
b. Ar = phenyl

The assignment of *trans* configuration for I, VIIIa,b, IXa,b, Xa,b, and XIIa,b was confirmed by n.m.r. spectra (Table III). Their coupling constants (JH_α, H_β) are in full agreement with known data.

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(19) The conversion of ylids of the type XI to XII and reaction of XII with aldehydes is based on the unpublished work of K. W. Ratts.

(20) For the stereoselective synthesis of an α,β-unsaturated ester from an ylid see [H. O. House and G. H. Rasmusson, *J. Org. Chem.*, **26**, 4278 (1961)].

Experimental

trans-**N,N-Diethylcinnamamide** (I) (m.p. 71–72°) was prepared in 95.0% yield from cinnamoyl chloride and diethylamine *via* the procedure employed by Cromwell and Coughlan.[21]

trans-**N,N-Diethyl-3',4'-dichlorocinnamamide (XIIa)** (m.p. 65.5–66.2°) was prepared in 83% yield (recrystallized from hexane) from 3,4-dichlorocinnamoyl chloride (m.p. 57.8–58.2) and diethylamine.

Anal. Calcd. for $C_{13}H_{15}Cl_2NO$: C, 57.40; H, 5.55; N, 5.14; Cl, 26.02. Found: C, 57.52; H, 5.74; N, 5.03; Cl, 26.22.

erythro-**N,N-Diethylcinnamamide dibromide**[22] **(II)** (m.p. 129.8–130.5°) was prepared in 96.8% yield (recrystallized from hexane–benzene) from bromination of I in carbon tetrachloride solution.

erythro-**Ethyl** *p*-**nitrocinnamate dibromide**[23] **(VIIa)** (m.p. 116–117°) (recrystallized from hexane), was obtained in quantitative yield from bromination of *trans*-ethyl *p*-nitrocinnamate (Eastman Distillation Products).

Anal. Calcd. for $C_{11}H_{11}Br_2NO_4$: Br, 41.95. Found: Br, 42.40.

erythro-**Ethyl Cinnamate Dibromide**[24] **(VIIb)**.—The bromination of *trans*-ethyl cinnamate (Eastman Distillation Products) in chloroform gave 97.0% yield of VIIb, m.p. 77–78° (recrystallized from hexane–benzene).

erythro-**N,N-Diethyl-3',4'-dichlorocinnamamide dibromide (XIa)** (m.p. 142.9–143.6) (recrystallized from hexane–benzene) was obtained in 77% yield from bromination of *trans*-XIIa in carbon tetrachloride solution.

Anal. Calcd. for $C_{13}H_{15}Br_2Cl_2NO$: C, 36.20; H, 3.51; Br, 37.10; Cl, 16.48; N, 3.24. Found: C, 36.22; H, 3.60; Br, 37.18; Cl, 16.38; N, 3.14.

erythro-**Cinnamic acid dibromide (XIb)** (m.p. 205–206°) was prepared from *trans*-cinnamic acid (Eastman Distillation Products) and bromine in carbon tetrachloride solution.

Debromination of *erythro*-**N,N-Diethylcinnamamide Dibromide (II). (a) With Sodium Carbonate in Aqueous Acetone.**—A solution of 5.0 g. (0.0137 mole) of *erythro*-dibromide II in 150 ml. of acetone and 150 ml. of 7% aqueous sodium carbonate was heated at reflux temperature for 7 hr. After removal of the acetone by evaporation, the oil was extracted with ether. The ether solution was then washed with water and dried over magnesium sulfate. Removal of the ether gave 2.9 g. of colorless solid, m.p. 69–70°. One recrystallization from hexane gave 2.7 g. (97.0% yield) of *trans*-*N*,*N*-diethylcinnamamide (I), m.p. 71–72°, identified by infrared data and mixture melting point.

(b) **With Potassium Hydroxide in Aqueous Acetone.**—A solution of 3.0 g. (0.00826 mole) of *erythro*-dibromide II in 80 ml. of acetone and 6.6 g. of potassium hydroxide in 200 ml. of water was heated at reflux temperature for 0.5 hr. The product was worked up as described in method a to obtain 1.7 g. of solid, m.p. 68–70°. One recrystallization from hexane gave 1.6 g. (96.0% yield) of *trans*-*N*,*N*-diethylcinnamamide (I).

(c) **With Anhydrous Sodium Acetate in Ethanol.**—A mixture of 11.7 g. (0.032 mole) of *erythro*-dibromide II, 13.2 g. (0.16 mole) of anhydrous sodium acetate and 400 ml. of 99.5% ethanol was heated at reflux temperature (80°) for 12 hr. The ethanol solution was evaporated to dryness under reduced pressure and the residue was washed repeatedly with water. The solid, air-dried, weighed 9.3 g. The infrared data indicated the solid to be a mixture of unchanged *erythro*-dibromide II and *trans*-*N*,*N*-diethylcinnamamide (I). It was chromatographed on alumina to give 5.7 g. (48.7%) recovery of *erythro*-dibromide II (m.p. 128–129°) and 3.4 g. (theoretical yield based on used II) of *trans*-*N*,*N*-diethylcinnamide (I) (m.p. 70–71°).

(d) **With Triphenylphosphine.**—To a stirred solution (24°) of 18.2 g. (0.050 mole) of *erythro*-dibromide II in 120 ml. of chloroform was added, in one portion, 13.1 g. (0.050 mole) of triphenylphosphine. The reaction was exothermic and the temperature rose to 58°. After the reaction mixture was allowed to cool to room temperature, it was heated at reflux temperature for 1 hr. The triphenylphosphine dibromide, 13.9 g. (0.033 mole) was removed by filtration. The triphenylphosphine dibromide was hygroscopic and fumed when exposed to the air. Its infrared spectrum was identical with an authentic sample prepared from triphenylphosphine and bromine in chloroform solution. The triphenylphosphine dibromide was further identified by its quantitative conversion to triphenylphosphine oxide by stirring in water. The chloroform filtrate was evaporated to dryness under reduced pressure to give 22.4 g. of viscous oil which was found to consist of a mixture of *trans*-*N*,*N*-diethylcinnamamide I and triphenylphosphine dibromide by infrared analysis. The viscous oil was then stirred with 300 ml. of water and a solid precipitated. The solid material was triturated with 200 ml. of boiling hexane and filtered. The hexane insoluble solid weighed 2.8 g. (0.0101 mole) and was identified as triphenylphosphine oxide. The hexane filtrate, upon evaporation, gave 9.7 g. (0.0477 mole, 95.5% yield) of *trans*-*N*,*N*-diethylcinnamamide (I). The yield of triphenylphosphine dibromide based upon the recovered triphenylphosphine oxide was 86.2%.

(e) **With Pyridine and Thiolacetic Acid.**—To a stirred solution of 18.2 g. (0.05 mole) of *erythro*-dibromide II and 11.4 g. (0.15 mole) of distilled thiolacetic acid in 50 ml. of benzene was added dropwise 11.9 g. (0.15 mole) of pyridine over 15 min. Temperature of the reaction mixture rose from 24 to 40° and pyridine hydrobromide was precipitated immediately. The mixture was stirred at room temperature for 3 hr. The hydrobromide salt, 16.0 g. (theory), was removed by filtration. The mother liquor was evaporated to dryness and dissolved in ether. The ethereal solution was washed thoroughly to remove excess of pyridine and thiolacetic acid and dried over magnesium sulfate. The solvent was removed under reduced pressure and the residual oil was chromatographed over silica gel to give 6.9 g. (86.5%) of diacetyl disulfide[25] and 9.1 g. (90.0%) of *trans*-*N*,*N*-diethylcinnamamide (I).

The diacetyl disulfide, b.p. 41–42° (0.3 mm.), n^{25}_{D} 1.5363, solidified at 18° and exhibited infrared absorption at 1750 cm.$^{-1}$ (acetyl C=O str.), 1125 cm.$^{-1}$ (C—S str.), and 945 cm.$^{-1}$ (S—S str.).

Anal. Calcd. for $C_4H_6O_2S_2$: C, 31.98; H, 4.02; S, 42.70. Found: C, 31.63; H, 4.43; S, 42.90.

Debromination of *erythro*-**Ethyl** *p*-**Nitrocinnamate Dibromide (VIIa). (a) With Triphenylphosphine.**—To a stirred solution of 19.1 g. (0.05 mole) of dibromide VIIa in 50 ml. of benzene was added a solution of 13.1 g. (0.05 mole) of triphenylphosphine in 70 ml. of benzene over 5 min. Temperature of the reaction mixture rose to 52° and triphenylphosphine dibromide was immediately precipitated. An additional 50 ml. of benzene was added to facilitate stirring and the reaction mixture was heated at reflux temperature for 1 hr. After cooling to room temperature, the triphenylphosphine dibromide was collected by filtration, washed with 50 ml. of benzene, and dried under vacuum at room temperature. The weight of triphenylphosphine dibromide was 20.8 g. (98.6%) and was converted to 13.2 g. (94.6%) of triphenylphosphine oxide by hydrolysis in water. The benzene filtrate was evaporated to dryness to give 10.4 g. of colorless solid which after one recrystallization from benzene gave 9.6 g. (86.8%) of *trans*-ethyl *p*-nitrocinnamate (VIIIa).

(b) **With Pyridine and Thiolacetic Acid.**—To a stirred solution of 50.0 g. (0.131 mole) of *erythro*-dibromide VIIa and 30.0 g. (0.393 mole) of thiolacetic acid in 150 ml. of benzene, was added 32.0 g. (0.40 mole) of pyridine. The solution was stirred at room temperature for a period of 4 hr. and then at 40° for 7 hr. The mixture was cooled to room temperature and pyridine hydrobromide, 42.0 g. (theory), was separated by filtration. The filtrate was evaporated to dryness to give a straw colored semisolid. The semisolid was triturated with hot hexane and cooled to room temperature. The hexane insoluble solid was collected by filtration. The solid weighed 27.5 g. (94.6% yield), m.p. 135–136°, and was identified as *trans*-ethyl *p*-nitrocinnamate (VIIIa) by infrared and mixture melting point determination. The hexane mother liquor was evaporated to dryness and the residue dissolved in ether. The ethereal extract was washed with water, dried over magnesium sulfate and evaporated to dryness to give 17.4 g. (88.6%) of diacetyl disulfide, n^{25}_{D} 1.5362.

Debromination of *erythro*-**Ethyl Cinnamate Dibromide (VIIb). (a) With Triphenylphosphine.**—To a stirred solution (22°) of 16.8 g. (0.050 mole) of *erythro*-dibromide VIIb in 80 ml. of chloroform and 80 ml. of hexane was added in one portion, 13.1 g. (0.050

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[21] N. H. Cromwell and L. A. Coughlan, *J. Am. Chem. Soc.*, **67**, 903 (1945).

[22] P. Herrmann and D. Vorlander, *Chem. Zent.*, I, 730 (1899), reported m.p. 127°.

[23] (a) C. L. Muller, *Ann.*, **212**, 129 (1882); (b) V. B. Drewsen, *ibid.*, **212**, 153 (1882), reported m.p. 110–111°.

[24] "Organic Synthesis", Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y. 1943, p. 270.

[25] Kekule, E. Linnemann, *Ann.*, **123**, 278 (1862).

mole) of triphenylphosphine. The temperature of the reaction mixture rose to 48°. After being cooled to room temperature, the reaction mixture was heated to reflux temperature for 1 hr. To the reaction mixture 200 ml. of hexane was added and the triphenylphosphine dibromide, 19.6 g. (92.8% yield), was removed by filtration. The mother liquor was concentrated and the residue (9.1 g.) was distilled to give 8.1 g. (92% yield) of *trans*-ethyl cinnamate (VIIIb).

(b) **With Pyridine and Thiolacetic Acid.**—To a stirred solution of 11.9 g. (0.0354 mole) of *erythro*-dibromide VIIb and 11.4 g. (0.15 mole) of distilled thiolacetic acid in 50 ml. of benzene was added dropwise over 15 min., 11.9 g. (0.15 mole) of pyridine. The reaction mixture was stirred at room temperature for 3 hr. and pyridine hydrobromide 10.8 g. (96.5% yield) was removed by filtration. The mother liquor, treated as above, afforded 4.5 g. (84.8% yield) of diacetyl disulfide, and 5.2 g. (84.0%) of *trans*-ethyl cinnamate (VIIIb).

Dehydrobromination of *erythro*-Ethyl *p*-Nitrocinnamate Dibromide (VIIa). (a) With Sodium Acetate in Ethanol.—A solution of 18.7 g. (0.049 mole) of dibromide VIIa and 18.4 g. (0.224 mole) of anhydrous sodium acetate in 390 ml. of 99.5% ethanol was heated at reflux temperature for 6 hr. After removal of the solvent, the residual crystalline mass was stirred with 150 ml. of water to give 13.2 g. (89.9%) of cream colored solid, m.p. 42–46°. The solid, 3.0 g., was chromatographed on alumina from which was obtained 2.7 g. (90%) of solid, m.p. 60.4–61.2° and 0.2 g. (6.8%) of solid, m.p. 93.0–94.1°. The low melting solid was reported as *cis*-ethyl α-bromo-*p*-nitrocinnamate (IXa)[26] and the high melting solid as *trans* isomer Xa.[27] The infrared data of the high melting solid was identical with an authentic sample of *trans*-ethyl α-bromo-*p*-nitrocinnamate (Xa) from ylid XII. The mixture melting point showed no depression.

The yield of *cis* isomer was 80.8% and *trans* isomer 6.1%.

The *trans* isomer had infrared absorption (in carbon tetrachloride solution) at 1725 cm.$^{-1}$, 1730 cm.$^{-1}$ (doublet for *trans* conj. ester C=O), 1260 cm.$^{-1}$ (ester$-OC_2H_5$), and 1600 cm.$^{-1}$ (conj. C=C).

Anal. Calcd. for $C_{11}H_{10}BrNO_4$: C, 44.10; H, 3.34; N, 4.77; Br, 26.67. Found: *cis* isomer: C, 44.29; H, 3.40; N, 4.65; Br, 26.60. *trans* isomer: C, 44.50; H, 3.14; N, 4.54; Br, 27.06.

The *cis* isomer had infrared absorptions (in carbon tetrachloride solution) at 1725 cm.$^{-1}$ (conj. ester C=O), 1220 cm.$^{-1}$ (ester $-OC_2H_5$), and 1600 cm.$^{-1}$ (conj. C=C).

Dehydrobromination of *erythro*-Ethyl Cinnamate Dibromide (VIIb). (a) With Sodium Acetate in Ethanol.—A solution of 15.1 g. (0.045 mole) of dibromide VIIb and 18.5 g. (0.225 mole) of anhydrous sodium acetate in 400 ml. of 99.5% ethanol was heated at reflux temperature for 6 hr. The solvent was removed under reduced pressure and the residue was dissolved in 150 ml. of water. The oil was extracted with four 150-ml portions of ether and the combined ethereal extract was dried over magnesium sulfate. Removal of the solvent gave 11.2 g. (97.5% yield) of ethyl α-bromocinnamate as a light yellow oil, $n^{25}\mathrm{D}$ 1.5654 (reported[28] for *cis*-ethyl α-bromocinnamate $n^{25}\mathrm{D}$ 1.5657). The gas chromatogram[29] showed two peaks: a major peak corresponding to 95.3% and small peak with longer retention time corresponding to 4.7%. The small peak was assigned to the *trans* isomer since its retention time was the same as that of the authentic sample of *trans*-ethyl α-bromocinnamate from the ylid XII and benzaldehyde. The major peak was assigned as *cis*-ethyl α-bromocinnamate IXb which had a boiling point of 115° (2 mm.), and $n^{25}\mathrm{D}$ 1.5697.

Debromination of *erythro*-*N*,*N*-Diethyl-3′,4′-Dichlorocinnamamide Dibromide (XIa) with Pyridine and Thiolacetic Acid.—Same procedure as described for the debromination of II was employed. The yields were as follows: pyridine hydrobromide (98.5% yield), diacetyl disulfide (78.0% yield), and *trans*-*N*,*N*-diethyl-3′,4′-dichlorocinnamamide (80.1% yield).

Debromination of *erythro*-Cinnamic Acid Dibromide (XIb).—Same procedure as described for the debromination of II was used. The yields were as follows: pyridine hydrobromide (91.5% yield), diacetyl disulfide (73.8% yield), and *trans*-cinnamic acid (81.7% yield).

***trans*-Ethyl α-Bromo-*p*-nitrocinnamate Xa from Ylid XIII[30].**—Bromination of 22.2 g. (0.0638 mole) of ylid XIII in chloroform at 0° yielded 33.6 g. (quantitative yield) of the crude phosphonium salt which upon neutralization with aqueous potassium hydroxide gave 19.7 g. of crude ylid XIV. Two recrystallizations from chloroform–pentane gave 15.3 g. (54.3% yield) of XIV, m.p. 155.2–156.0°.

Anal. Calcd. for $C_{22}H_{20}BrO_2P$: C, 61.80; H, 4.68; Br, 18.75; P, 7.27. Found: C, 61.98; H, 4.65; Br, 19.02; P, 7.41.

To a stirred solution at 22° of 8.55 g. (0.020 mole) of ylid XIV in 50 ml. of methylene chloride was added 3.02 g. (0.020 mole) of *p*-nitrobenzaldehyde in one portion. The reaction was exothermic and the temperature rose to 39°. The mixture then was heated at reflux for 3.5 hr., followed by evaporation of the solvent to dryness under reduced pressure. The yellow residue was extracted with three 150-ml. portions of pentane and the combined extract was evaporated to dryness to give 1.92 g. of colorless solid, m.p. 91–92.5°. One recrystallization from hexane gave 1.78 g. (29.7%) of pure *trans*-ethyl α-bromo-*p*-nitrocinnamate (Xa), m.p. 93.1–94.2°.[27]

***trans*-Ethyl α-Bromocinnamate Xb from Ylid XIV.**—A solution of 3.50 g. (0.0082 mole) of ylid XIV and 0.85 g. (0.0082 mole) of benzaldehyde in 40 ml. of methylene chloride was heated at reflux temperature for 3.5 hr. The solvent was evaporated to dryness and the resulting solid was extracted with three 50-ml. portions of heptane. Removal of the solvent yielded 2.00 g. of light yellow oil. The gas chromatogram[29] showed one major peak corresponding to 92.0% of *trans*-ethyl α-bromocinnamate (Xb) and two small peaks corresponding to 2.1% of benzaldehyde and 5.9% of *cis*-ethyl α-bromocinnamate (same retention time as the major peak from dehydrobromination of *erythro*-ethyl cinnamate dibromide with sodium acetate in ethanol). The yields based on benzaldehyde consumed were 96.9% for *trans*-ethyl α-bromocinnamate (Xb) and 3.1% for the *cis* isomer IXb.

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(26) (a) C. L. Mullen, *Ann.*, **212**, 137 (1882); (b) S. Reich and N. Y. Chang, *Helv. Chim. Acta*, **3**, 235 (1920), reported m.p. 63°.

(27) (a) C. L. Müller, *Ann.*, **212**, 133, 136 (1882); (b) S. Reich and N. Y. Chang, *Helv. Chim. Acta*, **3**, 235 (1920), reported m.p. 93°.

(28) K. V. Auwers and E. Schmellenkamp, *Ber.*, **54**, 626 (1921).

(29) A column packed with silicon rubber on ground firebrick was used.

(30) O. Isler, *Helv. Chim. Acta*, **40**, 1242 (1957).