Thermal Rearrangement of Arylazotribenzoylmethanes in the Solid State. Examination with Differential Thermal Analysis[1]

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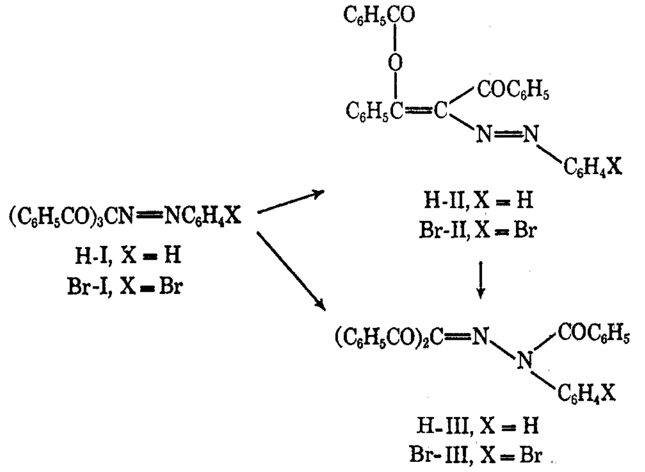
The rearrangements of phenylazotribenzoylmethane (H-I) to the corresponding enol benzoate (H-II) and the hydrazone (H-III), as well as the following rearrangement of the H-II first formed to H-III, have been studied with the aid of differential thermal analysis. The similar set of reactions of *p*-bromophenylazotribenzoylmethane (Br-I) and its relatives Br-II and Br-III have also been studied. The various thermal changes associated with melting and rearrangement evident from the thermograms have been correlated with chemical analysis of interrupted reaction mixtures. Examination of mixtures of these compounds (H-I, H-II, and H-III or Br-I, Br-II, and Br-III) has shown that their eutectic points are at 115–120°, well above the temperatures required for convenient study of the rearrangements. It is shown that the relative areas corresponding to the various thermal changes in a thermogram are quite reproducible from one experiment to another. A method is described for determining approximate values of the enthalpy changes associated with the processes evident from the thermograms.

Although intramolecular rearrangements of organic compounds have been considered in a number of instances to occur in the solid state,[3,4] it is impossible, with the evidence available in most cases, to decide to what extent disordering of the crystal precedes the reaction; in an extreme situation, reaction can appear to occur in the solid state but actually occur in microscopic pockets of liquid[5] or even in the vapor in equilibrium with the solid.[6]

Our previous study[4] of the thermal rearrangement of benzeneazotribenzoylmethane (H-I) or its *p*-bromo derivative (Br-I) to a mixture of enol benzoate (H-II or Br-II) and hydrazone (H-III or Br-III) had led us to conclude that these reactions can occur in the solid state; differential thermal analysis[7] (DTA) has now been found to provide valuable new insight into the nature of such reactions. In addition, a modification of the DTA method has been introduced in order to obtain an estimate of the magnitudes of the ΔH's of the observed changes.



In dioxane or benzene solution, the yellow azo ketones I had been found[4b] to rearrange at temperatures near 55° to nearly equimolar mixtures of II and III; crystalline H-I and Br-I at 70–90° undergo a similar pair of rearrangements with preservation of the crystal faces and no visible indication of melting.[4a] At considerably higher temperatures (95° in solution or 140° in the solid state), a third reaction, conversion of the red enol benzoate II to the white benzoylhydrazone III, was observed, again with no indication of melting.[4a]

In approaching the question of whether these are solid-state reactions, it would be most desirable to have melting-point diagrams of the three-component systems involved. This is rendered impossible by the rapidity of the rearrangements in the vicinity of the melting points of the compounds, which makes equilibrium studies out of the question. It was believed that differential thermal analysis might be of help in attacking this problem.

Thermogram obtained on heating the azotriketones H-I and Br-I are shown in Figure 1. To identify the chemical changes associated with the various features of the thermograms, the experiment (heating rate 10°/min) was interrupted at various times by rapid cooling of the sample with Dry Ice and analysis of the reaction mixture by ultraviolet–visible spectroscopy. At a heating rate of 5°/min, H-I showed an initial endotherm at about 124° associated with partial melting.[8] This changed suddenly to a substantial exotherm, which was shown by interruption of the reaction and chemical analysis to be accompanied by rearrangement of H-I to an approximately equimolar mixture of H-II and H-III. A second broad exotherm, completed by the time the temperature reached 190°, was due to the slower rearrangement of H-II to H-III, as shown by interruption and analysis at that point. The final endotherm at 200° was due to melting of H-III in agreement with the previously reported[11] mp 199–

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[1] We are very much indebted to the National Science Foundation for grant supporting part of this work.

[2] Sinclair Oil Corp. Fellow, 1967–1968.

[3] See, for example, H. Morawetz, *Science*, **152**, 705 (1966); H. Morawetz "Physics and Chemistry of the Organic Solid State," Vol. 1, D. Fox, M. M. Labes, and A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1963, Chapter 4; Vol. 2, 1965, pp 853 ff.

[4] (a) R. T. Puckett, C. E. Pfluger, and D. Y. Curtin, *J. Amer. Chem. Soc.*, **88**, 4637 (1966); (b) D. Y. Curtin and M. L. Poutsma, *ibid.*, **84**, 4892 (1962).

[5] See R. E. Pincock, K. R. Wilson, and T. E. Klovsky, *ibid.*, **89**, 6890 (1967), and references cited therein.

[6] J. D. Cosgrove and A. J. Owen, *Chem. Commun.*, 286 (1968).

[7] W. J. Smothers and Y. Chiang, "Handbook of Differential Thermal Analysis," Chemical Publishing Co., Inc., New York, N. Y., 1966; P. D. Garn, "Thermoanalytical Methods of Investigation," Academic Press Inc., New York, N. Y., 1965; W. W. Wendlandt, "Thermal Methods of Analysis," Interscience Publishers, New York, N. Y., 1964.

[8] The melting of this compound (which is accompanied by rearrangement) has been reported to occur at 125 or 121–123°.[9,10] (The structure was incorrectly assigned at that time.)[11]

[9] O. Dimroth and M. Hartmann, *Chem. Ber.*, **41**, 4012 (1908).

[10] C. S. Russell, Ph.D. Thesis, Columbia University, 1950, p 23.

[11] D. Y. Curtin and M. L. Poutsma, *J. Amer. Chem. Soc.*, **84**, 4887 (1962).

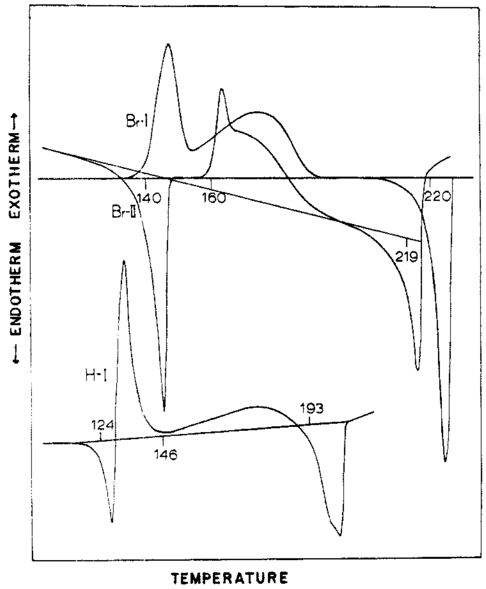

Figure 1.—Thermograms of phenylazotribenzoylmethane (H-I) (heating rate 5°/min), *p*-bromobenzeneazotribenzoylmethane (Br-I) (heating rate 10°/min), and enol benzoate Br-II (heating rate 10°/min). The baseline is indicated for each curve together with the temperature calibration at the onset of each thermal change.

200.5°. At higher heating rates, the size of the first endotherm increased relative to the exotherm which followed it.

The thermogram of the bromo compound Br-I differed from that of H-I in that no initial endotherm was visible at heating rates of 5–20°/min. At 40°/min, a small initial endotherm at 142° is attributed to melting of Br-I, which was obscured by the rapid rearrangement to Br-II and Br-III at lower heating rates.[12] The behavior of Br-I paralleled that of H-I, as shown by quenching a reaction heated at 10°/min and chemical analysis after the first exotherm, at which point the ratio of II/III was 54:46, and after the second exotherm, when the analysis showed 98% III. The onset temperature of the final endotherm agreed with the melting point previously reported[3] of 228°. These data are summarized in Table I.

Consistency of these results with earlier rate studies of the rearrangement of H-I in solution[13] was shown by extrapolation of the solution rate to the temperature range being considered here. The extrapolated rate is quite fast enough to allow the reaction to be completed in the times available in the DTA experiment.[14]

The great variation in the positions of the melting endotherms of H-I, H-II, and Br-II with changes in heating rate indicates that the apparent melting points measured by conventional methods even with "rapid heating" are seriously influenced by the occurrence of rearrangement; the true melting points are probably near the values obtained at a heating rate of 40°/min.

In order to gain an understanding of the melting point characteristics of mixtures of H-I, H-II, and H-III, DTA curves measured at the very high rate of 40°/min provided a means of minimizing the amount of rearrangement before melting. There was chosen for study a series of mixtures whose compositions were those to be expected as the reaction of H-I progressed first to an equimolar mixture of H-II and H-III and finally to H-III. Mixing was accomplished by grinding the components together with a mortar and pestle. The points where melting endotherms were observed are shown in Table II. The fast heating rates required to avoid rearrangement introduce possible inaccuracy due to incomplete thermal and chemical equilibrium. For this reason, a mixture of acetanilide and 2,4-dinitrophenol previously studied by microscopic methods[15] was examined with the DTA. At a heating rate of 40°/min, onset temperatures of melting both of the two pure compounds and of the eutetic mixture were within 4° of the carefully determined[15] literature values. As a further check on the method, a product mixture produced by partial rearrangement of a large number of crystals of H-I and shown by analysis to have the composition 75% H-I, 12.5% H-II, and 12.5% H-III was found by DTA to begin melting at 116.5° in good agreement with the result obtained with a mixture of similar composition mixed by grinding the pure constituents. It seems clear from these results that 110° is a conservative lower limit for the eutectic temperature for mixtures of H-I, H-II, and H-III and that reactions carried out at 70–105° where they can be conveniently studied do not involve any liquid phase.

Similar studies of mixtures of the bromo derivatives Br-I, Br-II, and Br-III suggested that the eutectic temperature is about 120°.[16]

A more detailed interpretation of the shapes of the thermograms of H-I and Br-I can be made by considering more fully the changes in physical state which occur during the heating process. As Br-I is heated, it is clear that, at all but the highest heating rates, any heat absorbed in melting is more than compensated by heat evolved by the reaction and by recrystallization of reaction products. Since Br-II is being formed near or above its melting point of 148°, it is unlikely that it crystallizes to an appreciable extent. Br-III, is first formed some 70° below its melting point. It would seem likely then, that at the minimum point between the first and second exotherms there is solid Br-III and a melt of Br-II saturated with Br-III. During the second exotherm, Br-II rearranges and the Br-III so formed crystallizes, so that by the end of that exotherm there is essentially crystalline Br-III. This description is in agreement with the results of visual observation of a crystal of Br-I heated on a microscope hot stage at 10–15°/min.[17] The behavior of the enol

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[12] Although melting is accompanied by considerable rearrangement, a melting point of 130–135° "with rapid heating" has been reported.[9]

[13] D. Y. Curtin and M. L. Poutsma, *J. Amer. Chem. Soc.*, **84**, 4892 (1962); D. Y. Curtin and L. L. Miller, *ibid.*, **89**, 637 (1967).

[14] For example, times for 90% reaction (in minutes) are 1.35 at 130°, 0.63 at 140°, and 0.31 at 150°. (The reaction was quite insensitive to the nature of the solvent.) Reaction of the solid was less than 1/100th as fast.[4]

[15] G. Tammann and A. A. Botschwar, *Z. Anorg. Chem.*, **157**, 27 (1926).

[16] A puzzling phenomenon was observed in the DTA's of mixtures of the three bromo compounds. There was a consistent change in the slope of the baseline at about 69° (behavior which might be indicative of an imbalance introduced by a change in the heat capacity of thermal conductivity of the sample). No such behavior was ever noted with the pure components nor with any unbrominated mixtures. No change could be observed at that temperature by careful visual observation of mixtures on a microscope hot stage.

[17] At 127° there was a change of color from yellow to yellow-orange, followed at 140–145° by what appeared to be some internal melting as regions of the crystal turned red. By the time the temperature was 163°, the entire crystal was red, after which it became pale yellow-orange and faded to white just before melting at 230°. (These are uncorrected temperatures recorded from a thermometer in the heating stage of the Kofler block and are probably only roughly indicative of the temperature of the sample because of the high heating rate.)

TABLE I

THERMAL CHANGES ON HEATING SOLID BENZENEAZOTRIBENZOYLMETHANES H-I AND Br-I AND THEIR REACTION PRODUCTS II AND III

	Temp of transition onset, °C[a]				% of total area[b]		
	Heating rate, deg/min				Results separated according to method	Combined results and standard deviation	ΔH, kcal/mol
Transition	5	10	20	40			
			Benzeneazotribenzoylmethane H-I[c]				
A_1	123	127	131	138	15.5[d] 14.1[e]	14.8 ± 1.7	5
A_2	128	132	140	149	−36.7[d] −34.2[e]	−35.5 ± 3.8	−11
A[f] = $A_1 + A_2$						(−20.7)	(−6)
B[g,h]	146	150	157	173	−17.5[d] −24.0[e]	−20.8 ± 4.8	−7
C	195	200	199	...[i]	30.3[d] 28.7[e]	29.5 ± 3.9	9
			p-Bromobenzeneazotribenzoylmethane Br-I[j]				
A[k,l]	136	141	145	151	−22.4[m] −19.8[e]	−21.3 ± 1.8	−6
B[g,n]	149	153	162	165	−43.4[m] −41.0[e]	−42.4 ± 1.8	−13
C	218	219	222	222	34.2[m] 39.2[e]	36.3 ± 3.1	11
			Enol Benzoate H-II[o]				
	163	163	170	173			
			Enol Benzoate Br-II[p]				
	142	142	148	148			
			Benzoylhydrazone H-III[q]				
	204	200	201	206			12[r]
			Benzoylhydrazone Br-III[s]				
	217	220	224	226			8[r]

[a] Extrapolated onset temperatures obtained as the intersection with the base line of the linear portion of the low-temperature side of the transition curve. [b] A positive value refers to an endotherm, a negative value to an exotherm. [c] Conventional "mp" 121–123°.[8] [d] Average of five measurements with the thermocouple in the sample tube at a heating rate of 10°/min. [e] Average of five values from weighed samples and with the thermocouple in an external oil bath. [f] The composition of the mixture immediately after this transition was H-I/H-II/H-III = 5.3?:47:47. The value for H-I is the maximum possible; it seems likely that a by-product of the reaction may have given rise to a false indication of the presence of H-I in certain cases. [g] Temperature at the minimum between exotherms A and B. [h] The composition of the mixture at the end of the transition was H-I/H-II/H-III = 4?:0:96. (See note *f*.) [i] The exotherm B was too close to endotherm C to permit a meaningful value. [j] Conventional "mp" 130–135°.[12] [k] At a heating rate of 40°/min, an endotherm corresponding to the A_1 of H-I was apparent with an onset temperature of 144°, but with its area only 0.8% of the total. [l] The composition at the end of this transition was Br-I/Br-II/Br-III = 0:54:56. [m] Average of seven values measured with the thermocouple in the sample tube and at heating rates of 5–40°/min. [n] The composition at the end of this transition was Br-I/Br-II/Br-III = 1.6?:0:98. The value for Br-III is probably a maximum and may be due to interference with the analytical method by a small amount of an impurity [o] Conventional "mp" (this work) 162.5–163°.[11] Samples obtained by interrupting the reaction before the first endotherm (154°) contained 93% of enol benzoate and 7% of what was either H-I or a by-product. Immediately after the exotherm, analysis showed 50% enol benzoate H-II, 45% hydrazone H-III, and 5% what was H-I or a by-product. When the reaction was interrupted just before the last melting endotherm, analysis showed 94% hydrazone H-III and no enol benzoate H-II. [p] Conventional "mp" 146–148° (present work). [q] Conventional "mp" 204–205° (this work), 199–200.5°.[11] [r] Average of two values from weighed samples and with the thermocouple in an external oil bath. [s] Conventional "mp" 228–229° (this work), 227–228°.[4] This compound, at a heating rate of 40°/min, showed a broad endotherm between 100 and 177° estimated to correspond to a ΔH of less than 2 kcal/mol. This may be associated with the phase transition noted earlier.[4]

TABLE II

DIFFERENTIAL THERMAL ANALYSIS MEASUREMENTS OF MIXTURES OF H-I, H-II, AND H-III AT A HEATING RATE OF 40°/MIN[a]

% H-I	79.7	71.5	34.1	0	0	0
% H-II	11.8	14.3	35.8	50	25	0
% H-III	8.5	14.3	30.1	50	75	100
$T_{\text{endotherm}}$, °C	120	117[b]	119	153	153	206

[a] Extrapolated onset temperatures obtained as the intersection with the base line of the linear portion of the low-temperature side of the curve describing the endotherm. A measurement with a heating rate of 5°/min gave a value of 118°. [b] A mixture of H-I/H-II (50:50) also had mp 117°.

benzoate Br-II was quite different from that of Br-I. At all heating rates, it underwent extensive melting before rearrangement became dominant, as shown by the large endotherm followed by a sharp exotherm superimposed on a broader exotherm (Figure 1). The sharp exotherm is attributed to the relatively rapid crystallization of Br-III formed by rearrangement of Br-II in the melt and superimposed on the broader exotherm associated with further rearrangement of Br-II and crystallization of the product Br-III.

Although DTA is not a highly accurate method for the determination of heats of transition, it has been found that the area under a maximum or minimum corresponding to a reaction or transition is approximately proportional to the enthalpy change involved.[7] As is shown in Table I, it was found in the present work that the areas under the peaks of the DTA curves expressed as per cents of the total of all such areas measured in a single curve were quite consistent. In order to obtain an approximate calibration of these areas, a modification of the DTA method was used, whereby the thermocouples were placed in external baths of silicone oil into which were placed microtubes containing carefully weighed amounts of the sample and reference substance. More detail is supplied in the Experimental Section. The apparatus was calibrated by measuring areas of melting endotherms of known amounts of a number of substances with known heats of fusion. The results, reported in Table I, although not highly accurate, have some interesting features. It will be seen that the sum of the enthalpies associated with the first endotherm and the following exotherm of H-I is -6 kcal/mol, which is the same as the enthalpy of the first exotherm of Br-I. This suggests that, although the initial melting is apparent in the thermogram of H-I, the net change by the end of the first exotherm is about the same in each system, and that at that point in each there is a mixture of crystallized hydrazone III and liquid II saturated with III. A second point of interest is that the enthalpy change of the final melting endotherm (9 kcal/mol) is rather close to the enthalpy change of melting observed with the thermogram of H-III; this suggests that the hydrazone H-III which has been formed in the reaction of H-I has become largely or completely ordered by the time its melting point has been reached. The same thing seems to be true with the bromo compounds Br-I and Br-III, but the measurements here are less reliable because there is evidence that the hydrazone undergoes sublimation[4a] and decomposition in the region where it melts, as shown by the fact that the thermogram shows no return to the base line at the end of the melting thermogram. It is hoped that more refined thermochemical data obtained from both solid and solution studies may make it possible to sort out thermal changes due to chemical reaction from those associated with crystallization and melting.

Experimental Section

Those melting points described in the footnotes of Table I as "conventional" and which were determined in the course of this investigation were obtained with a Kofler hot stage. Differential thermal analyses were made with a Du Pont Thermograph. Visible spectra were measured with a Bausch and Lomb Model 505 spectrophotometer.

Syntheses and Purification of the Compounds.—H-I, H-III, Br-I, and Br-III were carried out by methods previously described.[4,11] The enol benzoates H-II and Br-II were prepared by partial rearrangement[4] of H-I and Br-I or, more conveniently, by benzoylation of the appropriate diphenyl triketone *sym*-phenylhydrazone[9] (5.0 g) in 50 ml of dry pyridine with 7.5 ml of benzoyl chloride for 50 min at room temperature, a method patterned after that employed by Russell and Weisleder[18] for the preparation of α-phenylazo-β-benzoyloxystilbenes. Isolation of the enol benzoate H-II was carried out by treatment of the reaction mixture with 300 ml of ether and repeated washing with water. A small amount (0.3 g) of hydrazone H-III which precipitated at that point was removed by filtration. After being dried over magnesium sulfate, the resulting red oil was allowed to stand with a small amount of ethanol to promote crystallization of the product. Recrystallization from acetone gave 3 g of H-II, mp 162° (lit.[11] mp 162–163°). The ir spectra agreed with those obtained previously.[11] The bromo derivative Br-II was obtained similarly in 61% yield, accompanied by the hydrazone Br-III, mp 228–229° (lit.[4] mp 227–228°), in 13% yield. The ir spectra agreed with those of previous investigators.[4] The thermograms of certain samples of Br-I showed a small endotherm followed by a sharp exotherm (less than 1 kcal/mol) at about 80° which, however, was never observed with later, more carefully purified, samples. Samples of H-I which crystallize from diethyl ether with two molecules of ether per four of H-I showed a broad intense endotherm below 100° associated with the loss of the ether. Even traces of ether remaining in crystals which had stood for many days could be detected. When the ether had been allowed to escape completely, these crystals showed thermograms identical with those of the compound crystallized from xylene.

Differential Thermal Analyses. Method A.—With the thermocouple in the sample tube, samples of about 5 mg were employed, with tubes 2 mm in diameter and with ground glass in the reference tube. The reference thermocouple was immersed in an ice–water bath. Initial tests in a nitrogen atmosphere showed that the same results were obtained as in air, so that the studies reported here were carried out in air. The values for the extrapolated onsets in Table I were corrected for thermocouple error using the data provided by the manufacturer and are based in almost all cases on averages of from two to eight determinations. The reproducibility was estimated conservatively to be ±3°. Determinations carried out with compounds stable at their melting points agreed with conventional melting point determinations to within these limits. Areas were measured with a polar planimeter, each curve being measured two or three times. Since pairs of exotherms A and B were not completely resolved, the overlap area was divided by extending the linear portion of the B curve to the base line, although separation of the two curves by other methods seemed to make no significant difference in the results.

Method B.—Glass tubes 2 mm in diameter, selected such that their weights were 62 ± 4 mg, were employed for the sample, weighed with an accuracy of about 2% (*ca.* 7 mg), and for the reference tube (containing a weight of powdered glass equal to the weight of the sample). The samples were powdered and the tubes were packed by dropping through a glass tube. These tubes were sealed and placed in macro tubes (4 mm in diameter) chosen to weigh 215 ± 0.5 mg, and silicone oil was added to the outer tube until the total weight of both containers was 344.0 ±0.5 mg. After the tubes were inserted in the heating block, thermocouples were inserted in the silicone oil, care being taken to position the inner tube and the thermocouple as nearly the same each time as possible. Areas of curves were measured as with method B. Calibration was carried out using the equation[19]

$$\Delta H = KAT_s\Delta T_s/ma$$

where

K = an instrument constant (mcal/°C min) to be determined
m = mass of the sample, mg
a = heating rate, 10°/min
A = area, in^2
T_s = T scale setting, deg/min
ΔT_s = ΔT scale setting, deg/min

K was determined from the thermograms of a set of substances, including naphthalene, mp 81°; benzoic acid, mp 122°; *p*-toluic acid, mp 188°; and *p*-nitrobenzoic acid, mp 243°; whose heats of fusion were known.[20] The average value of K and the standard deviation from 16 determinations were $4.31 \pm 0.79 \times 10^{-3}$. The values of K showed no trend with changes of transition temperature or with heating rate (10–20°/min).

Method of Analysis.—The compositions of mixtures were determined from uv spectra in methylene chloride and spectra of the three known components, I, II and III, in the region between 410 and 475 mμ. Spectra were determined within 5 min after solution to insure that negligible reaction occurred at this point. For analysis of the data, the absorbance at each of 14 wavelengths was expressed as a function of the known extinction

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[18] C. S. Russell and D. Weisleder, *J. Org. Chem.*, **29**, 2959 (1964).

[19] J. K. Guillory, *J. Pharm. Sci.*, **56**, 72 (1967).

[20] D. H. Andrews, G. Lynn, and J. Johnston, *J. Amer. Chem. Soc.*, **48**, 1274 (1926).

coefficients of the pure compounds at that wavelength and of the unknown concentrations of each of the three components. This set of 14 equations in 3 unknowns was solved by an IBM model 1800 computer by a method of least squares.[21] Results are given in the footnotes to Table I. Use of the method with known mixtures gave results accurate to better than 1%.

Registry No.—H-I, 14373-36-5; H-II, 21317-39-5; H-III, 21317-40-8; Br-I, 13025-90-6; Br-II, 21317-43-1; Br-III, 21317-42-0.

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[21] We are indebted to Professor D. H. Secrest for the suggestion of a generalized solution to this problem by matrix algebra.

Complex Metal Hydride Reduction of *t*-Alkynyl-1-phosphine Sulfides

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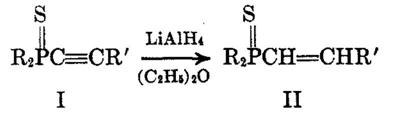
Reduction of a variety of diaryl- and dialkyl-1-alkynylphosphine sulfides to *trans*-β-substituted vinylphosphine sulfides employing lithium aluminum hydride is described. Support for a mechanistic path involving the β addition of a hydride ion is presented. Similar reduction of the corresponding alkynyl-1-phosphine oxides employing sodium borohydride is also described. A discussion of the 100-MHz proton nmr of α- and β-deuterated dimethyl-1-butenylphosphine sulfides is also included.

Desulfurization of *t*-phosphine sulfides has been accomplished with a variety of reagents including lithium aluminum hydride,[1a–d] iron,[1e] Raney nickel,[1a] sodium,[1f] and tributylphosphine.[1g] Reduction of α,β-unsaturated *t*-phosphine sulfides has not been investigated. We wish to report the results of our investigation into the use of complex metal hydrides as reagents in the reduction of *t*-α,β-unsaturated phosphine sulfides and oxides.

It was found that, when dimethyl-1-butynylphosphine sulfide (Ia, $R = CH_3$, $R' = C_2H_5$) is treated with excess lithium aluminum hydride for 30 min in ether at room temperature, dimethyl-1-butenylphosphine sulfide (IIa, $R = CH_3$, $R' = C_2H_5$) is obtained (eq 1).



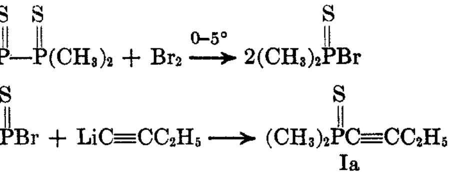
$$\underset{\text{I}}{R_2\overset{S}{\overset{\|}{P}}C{\equiv}CR'} \xrightarrow[(C_2H_5)_2O]{LiAlH_4} \underset{\text{II}}{R_2\overset{S}{\overset{\|}{P}}CH{=}CHR'} \qquad (1)$$

This is a direct analogy to the sodium borohydride reduction of acetylenic aromatic sulfide acids.[2]

The starting alkynyl sulfide (Ia) was prepared by bromination of tetramethylbiphosphine sulfide[3] followed by treatment with butynyllithium (Scheme I).

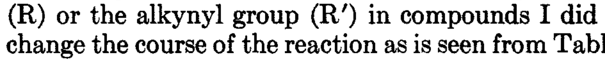
Comparison of the phosphorus–vinyl proton coupling constant in the proton nmr spectrum of IIa with the values for the same coupling in vinylphosphines and their oxides[4,5] leads to the tentative assignment of a *trans* configuration to this vinylphosphine sulfide. This assignment is supported by the fact that identical treatment of phenylethynyldiphenylphosphine sulfide[6] (Ib, $R = R' = C_6H_5$) leads to the known *trans*-β-styryldiphenylphosphine sulfide[4] (IIb, $R = R' = C_6H_5$). The heretofore unreported *cis*-β-styryldiphenylphosphine sulfide was prepared for comparison and found to be different as expected. Both the *cis*- and *trans*-β-styryldiphenylphosphine sulfides were independently prepared by treatment of the respective phosphine with sulfur in hot benzene[4,6] (eq 2). Compound Ib was obtained in the same fashion (eq 3).

SCHEME I

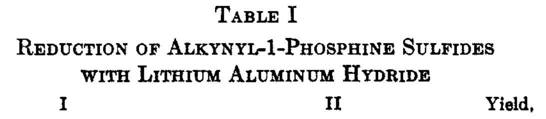


$$(CH_3)_2\overset{S}{\overset{\|}{P}}{-}\overset{S}{\overset{\|}{P}}(CH_3)_2 + Br_2 \xrightarrow{0\text{–}5^\circ} 2(CH_3)_2\overset{S}{\overset{\|}{P}}Br$$

$$(CH_3)_2\overset{S}{\overset{\|}{P}}Br + LiC{\equiv}CC_2H_5 \longrightarrow \underset{\text{Ia}}{(CH_3)_2\overset{S}{\overset{\|}{P}}C{\equiv}CC_2H_5}$$



$$(C_6H_5)_2PCH{=}CHC_6H_5 + S \xrightarrow[\Delta]{C_6H_6} (C_6H_5)_2\overset{S}{\overset{\|}{P}}CH{=}CHC_6H_5 \qquad (2)$$



$$(C_6H_5)_2PC{\equiv}CC_6H_5 + S \xrightarrow[\Delta]{C_6H_6} (C_6H_5)_2\overset{S}{\overset{\|}{P}}C{\equiv}CC_6H_5 \qquad (3)$$

No polymerization problem was encountered in the preparation of these unsaturated phosphine sulfides employing sulfurization.

Varying the substituents on either the phosphorus (R) or the alkynyl group (R′) in compounds I did not change the course of the reaction as is seen from Table I.

TABLE I

REDUCTION OF ALKYNYL-1-PHOSPHINE SULFIDES WITH LITHIUM ALUMINUM HYDRIDE

	I	II	Yield, %
a	$(CH_3)_2P(S)C{\equiv}CC_2H_5$	$(CH_3)_2P(S)CH{=}CHC_2H_5$	92
b	$(C_6H_5)_2P(S)C{\equiv}CC_6H_5$	$(C_6H_5)_2P(S)CH{=}CHC_6H_5$	100
c	$(C_6H_5)_2P(S)C{\equiv}CCH_3$	$(C_6H_5)_2P(S)CH{=}CHCH_3$	94.5
d	$(CH_3)_2P(S)C{\equiv}CC_6H_5$	$(CH_3)_2P(S)CH{=}CHC_6H_5$	85

Reduction of *t*-alkynyl-1-phosphine sulfides to the corresponding *trans*-vinylphosphine sulfides employing

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