TABLE IV
PER CENT YIELDS BASED ON AMOUNT OF CARBON DIOXIDE PRODUCED[a]

Acid	Yield, % Benzene	Nitrobenzene	Bromobenzene	Chlorobenzene	C_2Cl_4-F_2	C_2Cl_3-F_3	Hexane
Palmitic	69	82	76	67	71	58	40
Phthalic	0	0	32				
Terephthalic		26					
Propionic			79		61	2	40
Benzoic	6			48	41		0
Stearic						81	
2-Ethylbutyric					60	43	

[a] Using red mercuric oxide and different solvents.

using silver oxide and the acid chloride. The Cristol–Firth method is simpler than the original Hunsdiecker method in that it does not require the preparation of the dry silver salt. In many cases higher yields were obtained with tetrachloroethane as solvent than with carbon tetrachloride. This probably was due to the higher boiling point of the tetrachloroethane which permitted a higher reaction temperature. Bromobenzene and tetrachlorodifluoroethane seem to offer some promise as other solvents for this reaction. Yellow mercuric oxide was found to be almost as effective as red mercuric oxide. As a general rule aromatic and dicarboxylic acids underwent less bromodecarboxylation than did aliphatic monocarboxylic acids.

Experimental

For the preparation and isolation of the organic bromides, 0.1 mole of bromine was slowly added to a warm, stirred mixture of 0.1 mole of acid and 0.1 mole of red mercuric oxide in 150 to 200 ml. of solvent. The reaction mixture was then refluxed for at least 1 hr., then filtered, washed, and dried, and the organic bromide was separated by fractional distillation. The preparation of 1-bromohexane is typical of the method used.

Preparation of 1-Bromohexane from Heptanoic Acid.—A few drops of a solution containing 16 g. (0.1 mole) of bromine in 50 ml. of dry carbon tetrachloride produced an immediate reaction when added to a warm, stirred mixture of 13.0 g. (0.1 mole) of heptanoic acid and 22 g. of red mercuric oxide in 150 ml. of dry carbon tetrachloride. The remainder of the bromine solution was added slowly and the reaction mixture was refluxed for 1 hr. The mixture was then filtered, washed with 5% sodium hydroxide solution and then with water, and dried with anhydrous magnesium sulfate. Careful fractional distillation of the solution gave 6 g. of 1-bromohexane, b.p. 150–159°, $n^{28}D$ 1.4470.

To determine the per cent yield based on the amount of carbon dioxide produced, 2 ml. of bromine was slowly added to a warm, stirred mixture containing 50 ml. of solvent, 0.01 mole of acid, and 5 g. of red mercuric oxide in a 500-ml., three-neck flask. The flask was fitted with a dry nitrogen inlet, separatory funnel for addition of the bromine, and a reflux condenser. The carbon dioxide produced was swept out of the flask by nitrogen and passed through three Dry Ice traps to remove all bromine vapor and then absorbed in standard barium hydroxide solution. The barium carbonate precipitate was filtered off and the excess barium hydroxide was titrated with standard acid. The following is typical of the method used.

Bromodecarboxylation of Palmitic Acid.—Bromine (2 ml.) was added slowly to a warm, stirred mixture containing 50 ml. of carbon tetrachloride, 2.564 g. (0.01 mole) of palmitic acid, and 5 g. of red mercuric oxide. The carbon dioxide produced was swept out of the flask by nitrogen and absorbed in 125.0 ml. of standard 0.2 N barium hydroxide solution. The barium carbonate precipitate was filtered off and the excess barium hydroxide titrated with standard hydrochloric acid, yielding 0.0090 (90%) mole of carbon dioxide.

Acknowledgment.—Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research and to the E. I. du Pont de Nemours and Company for furnishing samples of tetrachlorodifluoroethane and trichlorotrifluoroethane.

Synthesis and Reactions of Some Triphenylphosphazines. The Use of Long-Range P^{31}–H^1 Coupling for Structure Determination

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Some β-N-alkylidene- and -arylidenehydrazinotriphenylphosphonium bromides have been synthetized by reacting triphenylphosphine dibromide with appropriate hydrazones. Dehydrobromination of these phosphonium bromides with sodamide in liquid ammonia led to the corresponding triphenylphosphazines. These triphenylphosphazines are nucleophiles as is shown by their reactions with methyl and ethyl iodides to yield α-N-alkyl-β-N-alkylidene- and -arylidenehydrazinotriphenylphosphonium iodides. Thes tructures of these phosphonium iodides have been verified through n.m.r. spectroscopy. The ultraviolet and visible absorption data of triphenylphosphazines are compared with those of the corresponding hydrazones.

Recently we became interested in the synthesis and reactions of organophosphorus compounds containing a $-N=P<$ linkage, such as triphenylphosphinalkylimines[2] and triphenylphosphin- and disubstituted aminoimines.[3,4] These compounds reacted readily with methyl and ethyl iodides to give dialkylaminotriphenylphosphonium iodides[2] and α-N-alkylhydrazino- and α-N-alkyl-β-N-disubstituted hydrazinotriphenylphosphonium iodides,[4] respectively. Hydrolysis of dialkylaminotriphenylphosphonium iodides and α-N-alkyl-β-N-disubstituted hydrazinotriphenylphosphonium iodides furnished the corresponding secondary amines and 1,1,2-trisubstituted hydrazines, respectively, in excellent yields. Thus, these compounds, containing a phosphorus–nitrogen double bond, represent a convenient tool for the synthesis of certain, especially sterically hindered, secondary amines and 1,1,2-trisubstituted hydrazines.

The structures of all organophosphorus compounds, mentioned above, were proved by elemental analyses, chemical behavior, and ultraviolet and n.m.r. spectroscopic studies. The latter method proved to be of

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TABLE I

β-N-ALKYLIDENE- AND -ARYLIDENEHYDRAZINOTRIPHENYLPHOSPHONIUM BROMIDES

$(Ph_3P—NH—N{=}CRR')^+Br^-$

No.	=CRR'	Formula	Color	M.p., °C.	Yield, %	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
1	Benzylidene	$C_{25}H_{22}BrN_2P$	White	225	93.2	65.08	65.41	4.80	4.84	..	..
2	*p*-Nitrobenzylidene	$C_{25}H_{21}BrN_3O_2P$	Yellow	162	88.4	59.29	59.55	4.15	4.26	8.30	7.88
3	Furfurylidene	$C_{23}H_{20}BrN_2OP$	Brownish	189–190 dec.	74.4	61.20	61.12	4.43	4.63	6.21	6.23
4	Diphenylmethylene	$C_{31}H_{26}BrN_2P$	White	200–201	94.0	69.28	68.74	4.87	4.97	..	..
5	Fluorenylidene	$C_{31}H_{24}BrN_2P$	Yellow	226–228	98.0	69.54	68.91	4.52	4.71	5.23	5.32
6	Camphorylidene	$C_{28}H_{32}BrN_2P$	White	173–174	98.6	66.25	66.10	6.31	6.02	5.52	5.72
7	Fenchonylidene	$C_{28}H_{32}BrN_2P$	White	167–168	73.5	...	...	..	..	5.52	5.71

TABLE II

TRIPHENYLPHOSPHAZINES

$Ph_3P{=}N—N{=}CRR'$

No.	=CRR'	Formula	Color	M.p., °C.	Yield, %	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
8	Benzylidene	$C_{25}H_{21}N_2P$	Yellowish	129–130[a]	90.0	78.94	78.92	5.56	5.60	7.36	7.37
9	*p*-Chlorobenzylidene	$C_{25}H_{20}ClN_2P$[b]	Yellowish	158.5	81.9	72.38	71.87	5.06	5.10	6.76	6.88
10	*p*-Nitrobenzylidene	$C_{25}H_{20}N_3O_2P$	Red	162	94.0	70.59	70.21	4.70	4.96	9.41	9.51
11	Furfurylidene	$C_{23}H_{19}N_2OP$	Pinkish	129-130 dec.	60.0	74.59	74.86	5.17	5.24	7.56	7.54
12	Diphenylmethylene	$C_{31}H_{25}N_2P$	Yellowish	165 dec.[c]	76.8	81.56	81.26	5.48	5.66	6.14	6.33
13	Fluorenylidene	$C_{31}H_{23}N_2P$	Yellow	205 dec.[d,e]	96.4	81.92	81.94	5.10	5.02	6.16	6.39
14	Camphorylidene	$C_{28}H_{31}N_2P$	Yellowish	161–162	80.2	78.87	79.08	7.28	7.33	6.57	6.69
15	Fenchonylidene	$C_{28}H_{31}N_2P$	Yellowish	144–145	68.0	78.87	79.32	7.28	7.34	6.57	6.39

[a] Lit.[11] m.p. 65°. [b] Prepared according to eq. 2. [c] Lit.[5,11] m.p. 173°. [d] Lit.[5] m.p. 209–210° dec. [e] Lit.[11] m.p. 203°.

special value particularly for the determination of the position of alkylation during the reaction of alkyl halides with triphenylphosphinaminoimines.[4] Invariably, the alkylation occurred at the α-nitrogen.

In further pursuit of the interest developed with the investigation of the chemistry of $—N{=}P<$ bond containing systems, attention was directed towards the synthesis, and chemical and spectroscopical behavior of triphenylphosphazines, another class of compounds containing phosphorus–nitrogen double bonds. This report deals with the synthesis and elucidation of some chemical properties of certain triphenylphosphazines.

Triphenylphosphazines (I) were first prepared by Staudinger and co-workers[5,6] by treating triphenylphosphine with diazo compounds (eq. 1). Recently, the preparation of triphenylphosphazines was reported by several authors.[7–9] All of them used Staudinger's method for the synthesis of these compounds.

$$Ph_3P + N_2CRR' \longrightarrow \underset{\text{I}}{Ph_3P{=}N—N{=}CRR'} \qquad (1)$$

When this work was in progress,[10] Bestmann, *et al.*,[11,12] probably also guided by Horner's method of preparing triphenylphosphinimines,[13] reported the synthesis of triphenylphosphazines. These authors allowed hydrazones to react with triphenylphosphine dibromide in the presence of triethylamine to get phosphazines (eq. 2).

$$Ph_3PBr_2 + H_2N—N{=}CRR' \xrightarrow{2Et_3N} Ph_3P{=}N—N{=}CRR' + 2(Et_3NH)^+Br^- \qquad (2)$$

Results and Discussion

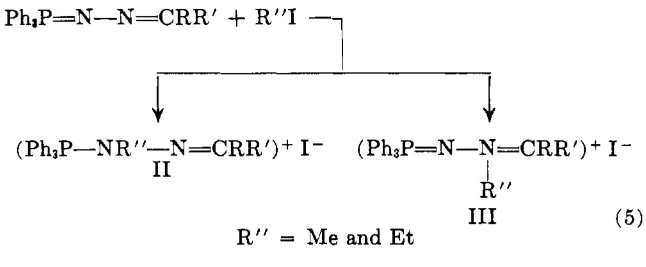
In this study triphenylphosphine dibromide was treated with hydrazones in the presence of equimolar amount of triethylamine. β-N-Alkylidene- and -arylidenetriphenylphosphonium bromides were isolated in good to excellent yields (eq. 3, Table I.). The phosphonium bromides reported here were stable, high-melting solids.

$$Ph_3PBr_2 + H_2N—N{=}CRR' \xrightarrow{Et_3N} (Ph_3P—NH—N{=}CRR')^+Br^- + (Et_3NH)^+Br^- \qquad (3)$$

The dehydrobromination of β-N-alkylidene- and -arylidenehydrazinotriphenylphosphonium bromides to the corresponding triphenylphosphazines was again readily effected with sodamide in liquid ammonia[2] (eq. 4). The relevant data about the triphenylphosphazines are listed in Table II.

$$(Ph_3P—NH—N{=}CRR')^+Br^- \xrightarrow[\text{liq. }NH_3]{NaNH_2} Ph_3P{=}N—N{=}CRR' + NaBr + NH_3 \qquad (4)$$

The triphenylphosphazines reported in this paper were stable under ambient conditions. They reacted with methyl and ethyl iodides to give 1:1 addition reaction products as shown by the elemental analyses. That the products obtained from the reactions of triphenylphosphazines and the alkyl halides were α-N-alkyl-β-N-alkylidene- and -arylidenetriphenylphosphonium iodides (II) and not compounds of structure III was confirmed by n.m.r. studies (Table III).



$$Ph_3P{=}N—N{=}CRR' + R''I \longrightarrow \underset{\text{II}}{(Ph_3P—NR''—N{=}CRR')^+I^-} \quad \text{and} \quad \underset{\text{III}}{(Ph_3P{=}N—\underset{R''}{\underset{|}{N}}{=}CRR')^+I^-} \qquad (5)$$

R'' = Me and Et

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TABLE III

α-N-ALKYL-β-N-ALKYLIDENE- AND -ARYLIDENEHYDRAZINOTRIPHENYLPHOSPHONIUM IODIDES

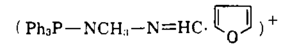
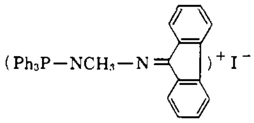
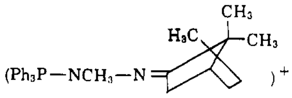
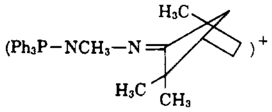
$(Ph_3P—NR''—N=CRR')^+ I^-$

No.	=CRR'	R''	Formula	Color	Refluxing period, hr.	M.p., °C.	Yield, %	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
16	Benzylidene	CH_3	$C_{26}H_{24}IN_2P$	White	3	229–230 dec.[a]	100.0	59.77	58.55[b]	4.60	4.65	5.32	5.25
17		C_2H_5	$C_{27}H_{26}IN_2P$	White	3	210 dec.	93.3	60.45	60.39	4.85	5.01	5.22	4.95
18	*p*-Chlorobenzylidene	CH_3	$C_{26}H_{23}ClIN_2P$	White	2	204 dec.	75.7	56.06	55.33	4.13	4.27	5.03	5.07
19	*p*-Nitrobenzylidene	CH_3	$C_{26}H_{23}IN_3O_2P$	Yellow	1	223	93.2	55.03	54.97	4.06	4.30	7.41	7.20
20		C_2H_5	$C_{27}H_{25}IN_3O_2P$	Yellow	2	193	90.0	55.77	55.62	4.30	4.57	7.23	7.00
21	Furfurylidene	CH_3	$C_{24}H_{22}IN_2OP$	Brownish	3	215–217 dec.	93.0	56.25	55.76	4.30	4.19	5.47	5.43
22		C_2H_5	$C_{25}H_{24}IN_2OP$	Brownish	3	219–220 dec.	90.0	57.03	56.07[b]	4.57	4.81	5.32	5.13
23	Diphenylmethylene	CH_3	$C_{32}H_{28}IN_2P$	White	2	195–196 dec.[c]	90.3	64.23	63.78	4.68	4.70	4.68	4.83
24		C_2H_5	$C_{33}H_{30}IN_2P$	White	3	190–191 dec.	85.0	64.71	64.31	4.90	4.91	4.58	4.93
25	Fluorenylidene	CH_3	$C_{32}H_{26}IN_2P$	Yellow	5	180–181 dec.[d]	84.6	64.42	63.13[b]	4.36	4.60	4.70	4.68
26		C_2H_5	$C_{33}H_{28}IN_2P$	Yellow	12	209–210 dec.	57.6	...	...	..	..	4.57	4.44
27	Camphorylidene	CH_3	$C_{29}H_{34}IN_2P$	White	3	199	71.5	61.27	60.71	6.00	6.02	4.95	4.80
28		C_2H_5	$C_{30}H_{36}IN_2P$	White	3	192–194	62.1	61.86	61.57	6.18	6.37	4.81	5.00
29	Fenchonylidene	CH_3	$C_{29}H_{34}IN_2P$	White	3	238–239	93.0	61.27	60.74	6.00	6.02	4.95	4.57
30		C_2H_5	$C_{30}H_{36}IN_2P$	White	3	248 dec.	87.5	61.86	61.70	6.18	5.96	4.81	4.70

[a] Lit.[12] m.p. 230–231°. [b] Owing to incomplete combustion, carbon analysis was slightly low; see also ref. 12. [c] Lit.[12] m.p. 199–200°. [d] Lit.[12] m.p. 175–178°.

TABLE IV

N.M.R. DATA[a] OF α-N-METHYL-β-N-ALKYLIDENE- AND -ARYLIDENEHYDRAZINOTRIPHENYLPHOSPHONIUM IODIDES

No.	Compd.	P-N-CH₃ δ_{CH_3}[b]	P-N-CH₃ $J_{P,H}$, c.p.s.
16	$(Ph_3P—NCH_3—N=HC·C_6H_5)^+ I^-$	3.52	9.4
18	$(Ph_3P—NCH_3—N=HC·C_6H_4·Cl\text{-}p)^+ I^-$	3.52	9.0
19	$(Ph_3P—NCH_3—N=HC·C_6H_4·NO_2\text{-}p)^+ I^-$	3.65	9.0
21		3.46	9.3
23	$(Ph_3P—NCH_3—N=C(C_6H_5)_2)^+ I^-$	2.91	12.0
25		3.36	14.0
27		2.25	13.4
29		3.19	15.5

[a] Spectra were obtained in deuteriochloroform, using a Varian A-60 spectrometer. [b] Chemical shifts are in parts per million downfield from an internal reference of tetramethylsilane.

N.m.r. investigations were conducted on compounds obtained from the reactions of triphenylphosphazines with methyl iodide (eq. 5).[14] Recently, we reported[3,4] the occurrence of long-range P^{31}–H^1 coupling in systems such as P—N—C—H and P—N—C—C—H. But the long-range coupling between phosphorus and the protons was not detectable in compounds containing the P=N—N—C—H (or P—N—N—C—H) system. As is evident from Table IV, a rather strong spin–spin coupling between phosphorus and the methyl protons was observed in the case of compounds in question. Thus, long-range P^{31}–H^1 spin–spin coupling supported the structure II over structure III, because the latter possessed a noncoupling system, *i.e.*, P=N—N—C—H.

Ultraviolet and Visible Absorption Spectra of Triphenylphosphazines.—The ultraviolet and visible absorption spectra of triphenylphosphazines were compared with those of the corresponding hydrazones (Table V). The spectra of triphenylphosphazines were very much different from the simple addition spectra of triphenylphosphine[2] and the corresponding hydrazones. For example, *p*-nitrobenzaldehydetriphenylphosphazine exhibited a high intensity absorption at 419 mμ, whereas *p*-nitrobenzaldehyde hydrazone absorbed at 332 mμ. Similar absorption shifts were observed in the case of other triphenylphosphazines, especially those derived from aromatic aldehydes. Whether these large bathochromic shifts in the case of triphenylphosphazines as compared with the hydrazones are due to the difference in the azinyl group (=N—N—CRR') and the hydrazone, or due to resonance between the phenyl groups and the azinyl group through the d-orbitals of phosphorus, could not be decided from the data reported here. However, synthesis of additional phosphazines, better suited to shed light on this problem, is underway in this laboratory, and will be the subject of a later communication.

Experimental[15]

Preparation of Hydrazones.—The hydrazones of benzaldehyde,[16] *p*-nitrobenzaldehyde,[17] *p*-chlorobenzaldehyde,[16] furfural,[18] benzophenone,[19] fluorenone,[20] *d*-camphor,[21] and *dl*-fenchone[21] were prepared according to the methods reported in the literature. *p*-Chlorobenzaldehyde and *dl*-fenchone hydrazones, prepared for the first time, melted at 57–58° and 56°, respectively. Owing to the extreme hygroscopicity of *d*-camphor and *dl*-fenchone hydrazones they were used immediately for further reaction.

β-N-Alkylidene- and -arylidenehydrazinotriphenylphosphonium Bromides (Table I).—The appropriate hydrazone (0.1 mole) and triethylamine (10.1 g., 0.1 mole) were added simultaneously, with stirring, to freshly prepared triphenylphosphine dibromide[13] (42.2 g., 0.1 mole) in dry benzene (200 ml.) over a period of 0.5 hr. The stirring was continued for an additional hour; then dry

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[14] Methyl iodide reaction products were selected for n.m.r. study because of the simplicity of their spectra.

[15] Melting points are uncorrected. Microanalyses were by A. Bernhardt, Mikroanalytisches Laboratorium im Max Planck Institut, Mülheim/Ruhr, Germany, and by Galbraith Laboratories, Knoxville, Tenn.

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[19] T. Curtius and F. Rauterberg, *J. prakt. Chem.*, [2] **44**, 192 (1891).

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TABLE V

ULTRAVIOLET AND VISIBLE ABSORPTION SPECTRA[a] OF TRIPHENYLPHOSPHAZINES AND HYDRAZONES

=CRR′	Triphenylphosphazine, $Ph_3P=N-N=CRR'$ λ_{max}, mμ ($\epsilon_{max} \times 10^{-4}$)	Hydrazone, $H_2N-N=CRR'$ λ_{max}, mμ ($\epsilon_{max} \times 10^{-4}$)
Benzylidene	262 (0.98),[b] 269 (1.15),[b] 277 (1.30),[b] 307 (1.77),[b] 330 (1.98)	275 (1.93)
p-Chlorobenzylidene	262 (0.7),[b] 268 (0.82),[b] 276 (0.96),[b] 315 (1.70),[b] 338 (1.96)	279 (1.95)
p-Nitrobenzylidene	257 (1.51),[b] 261 (1.54), 265 (1.50),[b] 273 (1.30),[b] 292 (0.80),[b] 419 (2.37)	332 (1.25)
Furfurylidene	258 (0.30),[b] 262 (0.36),[b] 265 (0.43), 274 (0.46), 328 (0.59)	287 (1.17)
Diphenylmethylene	262 (0.62),[b] 269 (0.64),[b] 275 (0.68), 321 (0.87)	275 (0.96)
Fluorenylidene	288 (0.75),[b] 297 (0.89), 309 (0.90), 372 (2.25),[b] 386 (2.35)	297 (1.67), 306 (1.57),[b] 332 (1.86)
Camphorylidene	256 (0.48),[b] 260 (0.50), 266 (0.50), 273 (0.43), 290 (0.29)[b]	276 (0.20)
Fenchonylidene	258 (0.62),[b] 264 (0.57),[b] 272 (0.48),[b] 298 (0.40)	276 (0.35)

[a] Spectra were determined in chloroform using a Cary recording spectrophotometer (Model 11). [b] Inflection points.

ether (300 ml.) was added to precipitate the phosphonium bromides. After a short while the solid was collected by suction filtration and washed with ice-cold water to remove triethylammonium bromide. The remaining solid was crystallized from chloroform–ethyl acetate mixture. Analytical samples were prepared from the same solvent.

Triphenylphosphazine (Table II).—They were prepared from the corresponding phosphonium bromides (see Table I) by treating them with sodamide in liquid ammonia. The residue left behind after the evaporation of ammonia was extracted with boiling ethylcyclohexane. Upon cooling the extract, the colored phosphazines precipitated. Analytical samples were also prepared by recrystallization from ethylcyclohexane.

α-N-Alkyl-β-N-alkylidene- and -arylidenehydrazinotriphenylphosphonium Iodides (Table III).—A mixture of appropriate triphenylphosphazine (0.01 mole) and 15 ml. of methyl or ethyl iodide was refluxed for different periods of time (see Table III). The reaction mixture was then cooled to room temperature and an excess of ethyl acetate was added. The precipitate that separated was collected by suction filtration. Analytical samples were obtained by recrystallization from a mixture of chloroform and ethyl acetate.

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Relative Rates of Decarbonylation of Cinnamaldehyde and *trans*-α-Substituted Cinnamaldehydes

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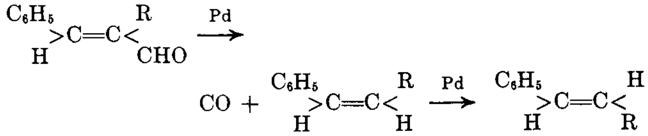
The relative rates of palladium-catalyzed decarbonylation of cinnamaldehyde and *trans*-α-substituted cinnamaldehydes were determined at 191 ± 1°. The observed order of reactivity was cinnamaldehyde > α-phenyl- > α-methyl- > α-ethyl- > α-*n*-propyl- > α-isopropylcinnamaldehyde.

Recently a stereochemical study of palladium-catalyzed decarbonylation of *trans*-α-substituted cinnamaldehydes was reported.[1] The major path taken by the aldehydes, and possibly the only one, led to retention of configuration. The product was capable under reaction conditions of isomerizing to configurational and double-bond positional isomers.



To extend the mechanistic data concerning decarbonylation a study of the kinetics of decarbonylation was undertaken. Cinnamaldehyde and *trans*-α-substituted cinnamaldehydes were chosen for the study because of their availability to us, because some knowledge of their reaction path had been gained through the stereochemical study, and because the variation in structure of these aldehydes seemed suitable for the determination of the magnitude of a steric effect in the reaction.

The decarbonylation of cinnamaldehyde was found to be kinetically first order.[2] However, the rate constant was difficult to reproduce accurately from run to run. Because it appeared that the decarbonylation rates of the cinnamaldehydes did not differ greatly,[1] it was felt that observed differences in rates between aldehydes might be significantly affected by experimental error if absolute rates were measured. Instead, relative rates were measured. Pairs of aldehydes were decarbonylated in boiling *p*-*t*-butyltoluene. Thus, any indeterminate error would affect both aldehyde rates. *p*-*t*-Butyltoluene was chosen because it appeared to offer little chance of solvent or solvent–aldehyde reaction and at the same time furnished a high reaction temperature. It is the purpose of this paper to describe the results of this relative rate study.

The decarbonylation of a pair of cinnamaldehydes, D and E, followed the first-order equation for simultaneous reactions.

$$k_D/k_E = \frac{\log([D]_0/[D])}{\log([E]_0/[E])} \qquad (1)$$

Table I illustrates results of a typical competitive decarbonylation of α-methyl- and α-ethylcinnamalde-

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[1] N. E. Hoffman, A. T. Kanakkanatt, and R. F. Schneider, *J. Org. Chem.*, **27**, 2687 (1962).

[2] A. T. Kanakkanatt, M.S. Thesis, Marquette University, 1960.