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.

Acknowledgment.—The authors gratefully acknowledge financial aid in the form of grants supplied by the U. S. Army Research Office, Durham, North Carolina, and by the National Institutes of Health, Bethesda, Maryland (CY-5841). The purchase of the nuclear resonance spectrometer was assisted by a grant from the National Science Foundation.

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

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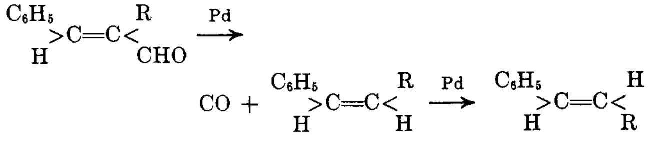
Received July 24, 1964

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.



$$\begin{matrix}C_6H_5 & & R\\ & >C=C< & \\ H & & CHO\end{matrix} \xrightarrow{Pd} CO + \begin{matrix}C_6H_5 & & R\\ & >C=C< & \\ H & & H\end{matrix} \xrightarrow{Pd} \begin{matrix}C_6H_5 & & H\\ & >C=C< & \\ H & & R\end{matrix}$$

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.

hyde. It can be seen that the rate constant ratio remains constant beyond 50% reaction. In some runs the ratios were measured well beyond 50% reaction, and they continued to remain constant. The number of determinations during a run as shown in Table I was typical of the rate data collected. In all cases, a first-order equation was followed.

TABLE I

COMPETITIVE DECARBONYLATION OF α-METHYL- AND α-ETHYLCINNAMALDEHYDE[a,b]

% Me, unreacted	% Et, unreacted	k_{Me}/k_{Et}
83	88	1.45
71	80	1.52
59	72	1.56
52	66	1.55
48	63	1.61
41	56	1.53
	Av.	1.54 ± 0.04[c]

[a] Catalyst: 400 mg. of A (palladium on charcoal, 10%). [b] Abbreviations used throughout: H for cinnamaldehyde; Me = α-methyl, Et = α-ethyl, *n*-Pr = α-*n*-propyl, *i*-Pr = α-isopropyl, and Ph = α-phenyl for substituted cinnamaldehydes. [c] Average deviation.

In order to be certain that a catalyst poison that might possibly be contaminating one or more of the aldehydes would not affect the relative rates, a study of the effect of thiourea on the rate constant ratio was made. Table II shows that the rate constant ratio is independent of the amount of poison added when the absolute rates are great enough to give a measureable amount of reaction within a few hours.

TABLE II

COMPETITIVE DECARBONYLATION RATES OF α-ETHYL- AND α-*n*-PROPYLCINNAMALDEHYDE IN THE PRESENCE OF THIOUREA[a]

Thiourea,[b] mg./g. of catalyst	$k_{Et}/k_{n\text{-}Pr}$
0	1.38 ± 0.05
20	1.45 ± 0.16
30	1.40 ± 0.05
50	*c*

[a] Catalyst: 300 mg. of B (palladium on charcoal, 10%). [b] In all runs where thiourea was added a drop in absolute rate was observed, and the drop became more marked with an increase in thiourea concentration. [c] Only 4% total aldehyde reacted in 6 hr.

The results shown in Table II were obtained in runs in which the amount of catalyst and solvent, and the initial amount and ratio of aldehydes were fixed. It seemed possible that the rate constant ratios might be a function of one or more of these parameters; *i.e.*, the true kinetics was more complicated than the limited data indicated. To give meaning to the relative rate constants to be determined, it was necessary to rule out this possibility. Table III gives the competitive rate constant for α-methyl- and α-ethylcinnamaldehyde as a function of the aforementioned parameters. It can be seen that, with the exception of the runs where the Me–Et ratio was 5.0 and 0.11, the initial aldehyde and catalyst concentration and the initial aldehyde ratio have no detectable effect on the competitive rate constant.

TABLE III

EFFECT OF CATALYST AND INITIAL TOTAL ALDEHYDE CONCENTRATION AND INITIAL ALDEHYDE RATIO ON COMPETITIVE DECARBONYLATION RATES

Catalyst		Me/Et,	Solvent, vol.,	
Type	Mg.	V./V.	ml.	k_{Me}/k_{Et}
A	600	1.0	100	1.55 ± 0.01
A	400	1.0	100	1.54 ± 0.04
A	200	1.0	100	1.51 ± 0.03
A	100	1.0	100	1.59 ± 0.04
B	300	1.0	100	1.54 ± 0.04
B	300	1.0	75	1.56 ± 0.04
B	300	1.0	50	1.54 ± 0.04
A	400	5.0	100	1.39 ± 0.07
A	400	0.30	100	1.55 ± 0.07
A	400	0.11	100	1.99 ± 0.42

In runs where the Me–Et ratio was 5.0, one aldehyde was reacting at an initial rate roughly seven times that of the other. In such cases one observes only one aldehyde concentration changing significantly. Thus, when the faster reacting aldehyde has gone one quarter to reaction completion, little of the slower reacting aldehyde has disappeared. If, on the other hand, the slower reacting aldehyde has changed in concentration to a considerable extent, the faster reacting aldehyde has all but disappeared and measurement of its concentration is difficult. These facts combined with the nature of eq. 1, which requires calculation of a ratio of logarithm differences, made measurements of competitive rates very susceptible to error when one aldehyde is reacting considerably faster than the other. In the run where the Me–Et ratio was 0.11, the value of the competitive rate constant, in light of the average deviation among determinations, is probably in agreement with the other values. Therefore, the results of these two runs do not invalidate the conclusion that the parameters studied have no effect on the competitive rate constant.

Table IV shows catalyst activity had no detectable effect on competitive decarbonylation rates. Although catalysts A and B had the same concentration of palladium on charcoal, they differed in activity. Catalyst C not only had a lower activity than A or B but, in addition, differed in its method of preparation and was pure palladium.

TABLE IV

EFFECT OF CATALYST ACTIVITY AND COMPOSITION ON COMPETITIVE RATES

Catalyst		
Type	mg.	k_{Me}/k_{Et}
A	400	1.54 ± 0.04
B	300	1.53 ± 0.03
C[a]	358	1.54 ± 0.01

[a] Unsupported palladium.

All these results indicated that a measurement of the competitive rate constants for a pair of aldehydes with the technique and conditions developed should give reliable relative rate constants. The experimental values of the competitive rate constants for the cinnamaldehydes studied are listed in Table V. The pairings of aldehydes and their ratios were chosen to provide comparable initial decarbonylation rates within the pair. The desirability of comparable rates has already been discussed.

In order to obtain valid relative rates from the competitive data shown in Table V, it was necessary to demonstrate that a calculated ratio for a pair of alde-

TABLE V

COMPETITIVE RATES OF DECARBONYLATION OF CINNAMALDEHYDE AND α-SUBSTITUTED CINNAMALDEHYDES

Aldehyde pair	Aldehyde ratio, v./v.	Catalyst Type	Catalyst Mg.	k_D/k_E
Me–Et	1.0	A	400	1.54 ± 0.04
Et–*n*-Pr	1.0	B	300	1.38 ± 0.05
Me–*n*-Pr	1.0	B	300	2.09 ± 0.09^a
Pr–*i*-Pr	1.0	B	350	1.51 ± 0.04
H–Me	0.5	B	600	4.94 ± 0.26
H–Ph	1.0^b	B	250	4.02 ± 0.50

^{a} Calcd. 2.13. ^{b} Weight ratio.

hydes and the experimental ratio were identical within experimental error. From the Me–Et and Et–*n*-Pr rate constant ratios the Me–*n*-Pr ratio was calculated. These aldehydes were chosen for two reasons. (1) The Me–Et ratio was the most reliable value among those determined because it had been reproduced in many runs. (2) The *n*-propyl derivative had a decarbonylation rate constant close to those of the methyl and ethyl derivatives. The calculated and observed ratios agreed within experimental error.

The data in Table V give the following relative rates of decarbonylation: isopropyl = 1.0, *n*-propyl = 1.5, ethyl = 2.1, methyl = 3.2, phenyl = 3.9, hydrogen (cinnamaldehyde) = 16. Thus substitution at the α-position has a small effect on the reactivity of cinnamaldehydes in decarbonylation. The direction of this effect of structure suggests that the effect may be one of steric hindrance. The position of phenyl indicates that electronic effects may also be operating.

In the Langmuir–Hinshelwood treatment of heterogeneous catalysis, two processes are considered to affect the observed reaction rate. First, an equilibrium adsorption of reactant or reactants occurs, and, second, reaction of the adsorbed species on the catalyst surface occurs. The observed competitive rate of decarbonylation, k_D/k_E, of aldehydes D and E is given by

$$k_D/k_E = \alpha k_D'/\beta k_E'$$

where α and β are the adsorption coefficients of aldehydes D and E, respectively, and k_D' and k_E' are the surface reaction rate constants. The adsorption coefficients measure the adsorbability of the aldehydes. According to this treatment then, the relative decarbonylation rates observed could be a reflection of either the relative aldehyde absorbabilities or the relative reactivities of the aldehydes in the surface reaction, or some combination of the two.

Experimental

Materials.—Eastman cinnamaldehyde, *p-t*-butyltoluene, and thiourea were used. α-Substituted cinnamaldehydes were prepared by the method of Kraft.[3] The aldehydes were based washed and redistilled prior to use.

Catalysts A and B were 10% palladium on charcoal (Norit S G Extra) prepared according to Mozingo's method.[4] A and B were prepared at different times. Catalyst C was made by suspending palladium chloride in boiling *p-t*-butyltoluene and passing hydrogen through the mixture until hydrogen chloride no longer evolved.

No kinetic runs were made in which equal quantities of catalysts A, B, and C were used in order to compare their activities. However, by calculating the absolute rate constants for the decomposition of α-methylcinnamaldehyde when the only parameter change was catalyst concentration (Table III), it was possible to show proportionality between the concentration of catalyst A and the rate constant for decomposition. On the assumption that this proportionality holds for catalyst B and C also, the kinetic data for the decomposition of α-methylcinnamaldehyde in the presence of each of these catalysts permit a calculation of the relative activities of the three catalysts. On this basis, catalyst B was 1.5 times more active than A and 7 times more active than C (on an equal palladium content basis).

Procedure.—A pair of aldehydes was injected with a syringe into a magnetically stirred mixture of catalyst and solvent refluxing under nitrogen at atmospheric pressure. The magnetic bar stirrer was Teflon coated. It had been previously established that Teflon had no effect on the observed relative reaction rates. Except where otherwise designated, 100 ml. of *p-t*-butyltoluene and a total of 4 ml. of aldehydes in a 1 to 1 volume ratio were used in a run. Because α-phenylcinnamaldehyde was a solid, 1.5 g. of of it and 1.5 g. of liquid aldehyde were first dissolved in 4 ml. of hot solvent. The resulting hot solution was then injected into 96 ml. of boiling solvent and catalyst.

A sample of the reaction mixture was removed within 1 min. after injection of reactants and was considered as having a composition at zero time. Periodically during a run, a sample was removed from the reaction mixture. At least four such samples, and in the majority of runs six, in addition to the zero time sample, were removed. The total volume removed during a run represented less than 2% of the reaction mixture. Samples were withdrawn until at least 50% of the more reactive aldehyde and in the majority of runs until more than 70% had disappeared. On the average, samples were removed over a period of 4.5 hr. The samples were prepared for analysis by cooling and filtering off the catalyst through Celite. For all runs the temperature was 191 ± 1°, and within a single run the temperature remained constant within 0.5.°.

Analysis and Kinetics.—By measuring the volume of carbon monoxide evolved from a known amount of aldehyde, it was established that over 95% of a given cinnamaldehyde decarbonylated when reaction was allowed to go to completion. It was also demonstrated that the aldehydes did not disappear when refluxed with solvent and charcoal alone for the average competitive reaction time. Thus the aldehyde disappeared only *via* decarbonylation. Advantage was taken of this fact in measuring the extent of decarbonylation by analyzing for unreacted aldehyde.

Samples were analyzed by gas chromatography with a 5 ft. × 0.25 in. 20% Silicone Dow 11 on 60–80 firebrick column. For accurate analysis of the aldehydes, it was necessary to inject large samples, 10 to 30 µl. Conditions were chosen so that peak heights were proportional to concentration (column temperature 185–275°). Except in the case of stilbene, products of decarbonylation were not observed in the chromatogram. They were assumed to be lost in the large solvent peak.

Because of the first-order kinetics of decarbonylation, peak heights could be used directly in the rate constant ratio equation. Therefore, actual concentrations were never calculated. The analytical data for a run with aldehydes D and E fit the following first-order equation for simultaneous reactions.

$$k_D/k_E = \frac{\log(\text{peak } D_0/\text{peak } D)}{\log(\text{peak } E_0/\text{peak } E)}$$

Acknowledgment.—This work was supported by a grant from the National Science Foundation.

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[3] W. M. Kraft, *J. Am. Chem. Soc.*, **70**, 3569 (1948).

[4] R. Mozingo, *Org. Syn.*, **26**, 77 (1946).