or nitromethane and $H_2{}^{18}O$ after treatment (heterogeneous system) at 150° for 16 hr in 0.5 N hydrochloric acid or sodium hydroxide.

Since electron-withdrawing or -donating substituents often cause considerable variations in exchange rate,[3,4] it was decided to investigate the exchange behavior of *p*-methoxy-, *p*-methyl-, *p*-chloro-, and *p*-dinitrobenzene.

The conditions used were (1) dilute acid, 0.1 M RNO_2, 0.12 M $HClO_4$, 80% dioxane–20% $H_2{}^{18}O$ (1.66 atom %), 100°, 24 hr; (2) strong acid, 0.1 M RNO_2, 7.75 M $HClO_4$, 0.83 atom % $H_2{}^{18}O$ (homogeneous solution without added dioxane), 100°, 48 hr; (3) dilute base (using *p*-methoxy- and *p*-chloronitrobenzene only), 0.1 M RNO_2, 0.62 M NaOH, 50% dioxane–50% $H_2{}^{18}O$ (1.66 atom %), 100°, 16 hr. (Under more drastic basic conditions, the nitro compounds could not be recovered from the solutions.) At the end of the reaction period, the nitro compounds were recovered, recrystallized, and analyzed for oxygen-18. No excess oxygen-18 was found in any of the nitro compounds under any of the reaction conditions.

This lack of exchange makes it very clear that the nitro group is far less susceptible than the carboxyl group to acid- or base-catalyzed nucleophilic attack.

Experimental Section

Acidic Exchange Experiments.—Approximately 0.24-g samples (0.1 M solutions) of *p*-methoxy-, *p*-methyl-, *p*-chloro-, and *p*-dinitrobenzene were refluxed for 24 hr in 15 ml of 80% dioxane–20% $H_2{}^{18}O$ (1.66 atom % oxygen-18) 0.12 M in perchloric acid. The solutions were poured onto ice, and the precipitated nitro compounds were filtered, dried, recrystallized from heptane, and analyzed for oxygen-18. No excess was found. The chance that exchange might be very rapid and hence that the nitro compounds might be undergoing complete back exchange during the work-up procedure was considered. That this was not the case was shown by the fact that *p*-dinitrobenzene showed no exchange when recovery was effected by rapid cooling (Dry Ice bath) without the addition of ice or water.

In the strong acid experiments approximately 0.24-g samples of the nitro compounds were dissolved in 15 ml of 7.75 M perchloric acid in which the water was enriched in oxygen-18 to the extent of 0.83 atom %. The samples were heated in sealed tubes in a steam bath for 48 hr, and then cooled in a Dry Ice bath. The precipitated nitro compounds were filtered, recrystallized from heptane, and analyzed for oxygen-18. No excess was found.

Basic Exchange Experiments.—Approximately 0.24-g samples of *p*-methoxy- and *p*-chloronitrobenzene were refluxed for 16 hr in 20 ml of 50% dioxane–50% $H_2{}^{18}O$ (1.66 atom % oxygen-18) 0.62 M in sodium hydroxide. The solutions were poured onto ice, and the precipitated nitro compounds were worked up and analyzed as before. No excess oxygen-18 was found. Several sets of more drastic basic conditions were tried, but none gave positive results. Without an added organic solvent, two-phase systems were obtained at all temperatures. When sufficient dioxane was added to dissolve the nitro compounds, the sodium hydroxide was relatively insoluble. Using alkaline aqueous alcohol solutions, the nitro compounds could not be recovered; after a relatively short time only a thick, brown paste was obtained.

Isotopic Analyses.—The oxygen-18 in the nitro compounds was converted to carbon dioxide by pyrolysis at 500° for 5 hr with 1:1 mixture of mercuric chloride and mercuric cyanide.[7] (The fact that carbon dioxide was obtained in all cases shows that the lack of exchange is not due to failure of the nitro oxygens to be converted to an analyzable form.) The m/e 46/44 ion current ratio was determined in an isotope ratio mass spectrometer, and these results were converted to atom per cent oxygen-18. In all cases, within the experimental measurement errors, the samples contained the natural abundance of oxygen-18.

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[7] D. Rittenberg and L. Ponticorvo, *Intern. J. Appl. Radiation Isotopes*, **1**, 208 (1956); M. Anbar and S. Guttmann, *ibid.*, **5**, 233 (1959).

Ionization Constants of 3- and 4-Substituted *cis*- and *trans*-Cinnamic Acids in 50% Ethanol

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The ionization constants of a series of *meta*-substituted *trans*-cinnamic acids and a series of *meta*- and *para*-substituted *cis*-cinnamic acids have been measured in 50% ethanol at 25°. For the *trans* series ρ is +0.68, and $-\log K_0 = 5.68$. In the *cis* series the *meta* and *para* compounds describe two separate lines, corresponding with ρ values of +0.63 ($-\log K_0 = 5.22$) and +0.77 ($-\log K_0 = 5.17$), respectively.

The question of the relative abilities of *cis*- and *trans*-ethylenic groups to transmit electronic effects has been of interest for some time. Data related to this question are the rates of alkaline hydrolysis of a series of *cis*- and *trans*-ethyl cinnamates.[2] The somewhat larger Hammett ρ value of 1.31 for the *trans* series (compared with 1.12 for the *cis*) appeared consistent with the longer wavelength of *trans* absorption[2,3] in suggesting a superior π-bond interaction across the ethylenic system in *trans* isomers. However, the limited data on the ionization of the *cis*-cinnamic acids in water[4] suggested a larger substituent effect on acidity than in the *trans* acids.[5] We have, therefore, reexamined these series, in 50% ethanol as the solvent, using a larger number (eight) of *cis* acids. The ionization constants of *trans*-cinnamic acids in this solvent have not previously been reported, and are of interest for comparison with the phenylpropiolic acids and other series. Only *trans*-cinnamic acids with *meta* substituents having relatively invariant σ values have been examined. (A number of *para*-substituted acids are of insufficient solubility for convenient potentiometric measurement). Both *meta*- and *para*-substituted *cis*-cinnamic acids have been included in this study. The results are shown in Table I.

TABLE I

APPARENT pK_a VALUES FOR *meta*- AND *para*-SUBSTITUTED *cis*- AND *trans*-CINNAMIC ACIDS IN 50% ETHANOL AT 25.0°

Substituent	*cis*		
	meta	*para*	*trans, meta*
OCH_3		5.38	5.62
CH_3		5.30	5.72
H	5.22		5.68
F		5.11_5	5.44
Cl	4.99	5.02	5.42_5
Br			5.42
NO_2	4.77	4.58	5.19_5

ρ for the *trans* series is +0.68 (average deviation ±0.008 σ unit). The data for the *cis* compounds are scattered, and fit a single line with an average devia-

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[1] Support of the work at the University of Houston by the Robert A Welch Foundation through Grant E-136 is gratefully acknowledged.

[2] J. J. Bloomfield and R. Fuchs, *J. Org. Chem.*, **26**, 2991 (1961).

[3] S. Lindenfors, *Arkiv Kemi*, **14**, 227 (1959).

[4] W. A. Roth and R. Stoermer, *Ber.*, **46**, 260 (1913).

[5] ρ values of 0.643 and 0.466 have been reported[2] for the *cis*- and *trans*-cinnamic acids, respectively.

tion of at least ±0.05. Because these rather large deviations in the *cis* series might largely result from a change from water (the reference solvent for σ value measurements) to 50% ethanol, the pK_a data have also been plotted against the average σ values derived from four series of benzoate ester hydrolyses in mixed aqueous solvents.[6] Although the fit of the *cis* series is slightly improved (average deviation ±0.035) by the use of the "mixed-solvent σ values," the fit of the *trans* acids actually becomes poorer (average deviation ±0.017). Thus, it does appear that the solvent effect on σ is of major importance in these series.

The *meta*- and *para*-substituted *cis*-cinnamic acids appear to fall with high precision on two separate lines: $\rho_p = +0.77$ ($-\log K_0 = 5.22$); $\rho_m = +0.63$ ($-\log K_0 = 5.17$).

Discussion

Substituent Effects.—A complete discussion of this behavior seems premature. The acidities of a series of thiophenoxyacetic acids in 50% dioxane[7] are also best correlated by separate lines for *meta* and *para* substituents ($\rho_m = ca.\ 0.5$; $\rho_p = ca.\ 0.7$) whether σ or $\sigma_p{}^0$ values are used. One is tempted to believe that the *cis*-like eclipsed conformation might be a necessary structural feature of series having unequal ρ_p and ρ_m values. However, similar behavior is shown by the 3- and 4-substituted 1-naphthoic acids.[8] ($\rho_{4\text{-Y}} = ca.\ 1.75$; $\rho_{3\text{-Y}} = ca.\ 1.3$) which have a quite different spatial geometry.[9]

Comparison of Cinnamic Acids with Other Systems.—A larger ρ for the *trans* than the *cis* series would be expected from the analogy with ester hydrolysis, although the possibility of a larger, direct electrostatic effect exists in the *cis* acids. The value of ρ for the ionization of phenylpropiolic acids in 50% ethanol is +0.625,[10] compared with +0.63 for the *cis*- and +0.68 for the *trans*-cinnamic acids in the same solvent. This is consistent with the ester saponification data, where ρ values are +1.1,[12] +1.1,[2,11] and +1.25,[2,11] respectively. The acetylenic unit may approach the *cis* ethylenic group in electronic transmitting ability, but the *trans* ethylenic linkage appears consistently superior to the other two. (See Table II for physical properties.)

TABLE II

PHYSICAL PROPERTIES OF *cis*- AND *trans*-CINNAMIC ACIDS

Substituent	Mp, °C	Lit. mp, °C	Source[a]	Solvent[b]
		trans		
m-OCH_3	118.3–118.9	118–118.5[c]	C	Heptane–DME
m-CH_3	117.6–118.2	115[d]	B	Heptane
H	133.0–134.0	134[c]	C	EtOH–H_2O
m-F	166.2–166.8	166–167[c]	B	EtOH–H_2O
m-Cl	162.6–163.2	163.5–164.5[c]	C	EtOH–H_2O
m-Br	180.1–180.5	178–179[e]	B	MeCN
m-NO_2	204.5–205.0	204[c]	B	EtOAc
		cis		
p-OCH_3	69.3–71.0	69.2–69.4[f]	H	Hexane–Bz
p-CH_3	77.2–77.9	75–76[g]	H	H_2O
H	67.4–68.8	68[h]	H	Hexane
p-F	78.2–79.0	*i*	H	Heptane
p-Cl	111.6–112.7	112.0–112.3[f]	H	H_2O
m-Cl	69.9–70.6	65.0–65.5[j]	H	H_2O
m-NO_2	156.4–157.3	155–156[k]	P	EtOH–H_2O
p-NO_2	144.6–145.2	143[k]	P	EtOH–H_2O

[a] C = commercial. B = prepared from the substituted benzaldehyde and malonic acid in 1,2-dimethoxyethane. The procedure is otherwise that of ref 2. H = prepared by hydrogenation of the corresponding ethyl phenylpropiolate,[2] followed by saponification with KOH in aqueous ethanol, and acidification. P = photoisomerization of *trans* acid. The *m*-nitro compound was irradiated in ammonium hydroxide solution[k] for 2 hr using an internal 550-w Hanovia high-pressure mercury arc. The *para* isomer was irradiated in dioxane solution (yield *ca.* 1% of purified *cis* acid). [b] Each compound was recrystallized two to five times. Solvent designations are DME, 1,2-dimethoxyethane; EtOH, ethanol; MeCN, acetonitrile; EtOAc, ethyl acetate; Bz, benzene. [c] J. D. S. Ritter and S. I. Miller, *J. Am. Chem. Soc.*, **86**, 1507 (1964). [d] W. v. Miller and G. Rhode, *Ber.*, **23**, 1899 (1890). [e] S. Gabriel, *ibid.*, **15**, 2291 (1882). [f] D. S. Noyce and H. S. Avarbock, *J. Am. Chem. Soc.*, **84**, 1644 (1962). [g] R. Stoermer, F. Grimm, and E. Lange, *Ber.*, **50**, 959 (1917). [h] C. Liebermann, *ibid.*, **23**, 2510 (1890). [i] *Anal.* Calcd for $C_9H_7O_2H$: C, 65.06; H, 4.25. Found: C, 65.49; H, 4.38. [j] S. Lindenfors, *Arkiv Kemi*, **12**, 267 (1958). [k] F. Wollring, *Ber.*, **47**, 111 (1914).

Experimental Section

Cinnamic Acids.—The *trans* acids were either purchased (Eastman, Aldrich) or synthesized by the piperidine-catalyzed reaction of malonic acid and the corresponding benzaldehyde in 1,2-dimethoxyethane solution. The *cis* acids were prepared by the photoisomerization of the *trans* acids, or by the saponification of the *cis* ethyl cinnamates prepared[2] by the hydrogenation of the appropriate ethyl phenylpropiolate.

Acidity Measurements.—The 50% (by volume) aqueous ethanol was prepared from commercial absolute alcohol, and the composition was established by density measurement. Samples of 2.5×10^{-4} mole of the acids were dissolved in 50 ml of the solvent in a water-jacketed beaker (solution concentration, 0.005 *M*; temperature, 25.0°) and maintained under an atmosphere of prepurified nitrogen saturated with 50% ethanol. Potentiometric titration was carried out (Sargent Model D recording titrator) using 0.5 *N* NaOH and calomel and glass electrodes. The pH at one-half neutralization was taken as the apparent pK_a. Variations of as much as ±0.05 pH can be obtained depending on standardization and electrode equilibrium procedures.

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(6) C. K. Hancock and C. P. Falls, *J. Am. Chem. Soc.*, **83**, 4214 (1961); K. Kindler, *Ber.*, **69**, 2792 (1936); E. Tommila, *Ann. Acad. Sci. Fennicae, Ser. A59*, **No. 9** (1942); and B. Jones and J. Robinson, *J. Chem. Soc.*, 3845 (1955). These "mixed solvent σ values" follow: *p*-NO_2, + 0.79; *m*-NO_2, +0.70; *m*-Br, +0.34; *m*-Cl, +0.33; *m*-F, +0.31; *p*-Cl, +0.25; *p*-F, +0.12; *m*-OCH_3, +0.06; *m*-CH_3, −0.08; *p*-CH_3, −0.14; *p*-OCH_3, −0.26.

(7) D. J. Pasto, D. McMillan, and T. Morphy, *J. Org. Chem.*, **30**, 2688 (1965).

(8) M. J. S. Dewar and P. J. Grisdale, *J. Am. Chem. Soc.*, **84**, 3546 (1962).

(9) A somewhat different point of view has been expressed by a referee, as follows. The data for the *cis*-cinnamic acids excepting the *p*-nitro compound can be represented by a single line ($\rho = +0.63$, $-\log K_0 = 5.20$, average deviation, ±0.036). The *p*-nitro group is the only substituent in the study capable of a strong +R interaction with the ethylenic linkage, and a σ^- value might be appropriate. The precise value of σ^- to be used might be difficult to predict because of the large solvent dependence [R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *ibid.*, **85**, 3146 (1963)]. The statement might equally well apply to the thiophenoxyacetic acids[7] where the sulfur could act as a −R group interacting through the ring with the +R *p*-nitro group. It appears unlikely, however, that the interaction of a *p*-nitro group with the $CH{=}CHC({=}O)O^-$ group would be sufficiently greater than that with the $CH{=}CHC({=}O)OH$ group to make σ^- values appropriate. No such duality of ρ exists in the analogous saponification of ethyl cinnamates [K. Kindler, *Ber.*, **69**, 2792 (1936)], nor has the *p*-nitro substituent an unusual σ value. Certainly the argument is not appropriate to the observed dual ρ values for the 1-naphthoic acids.[8] Abnormally positive values of $\sigma_{p\text{-}NO_2}$ are not peculiar to systems with −R side chains nor to mixed-solvent media. See, for example, the ionization of β-phenylpropronic acids [J. F. J. Dippy and R. H. Lewis, *J. Chem. Soc.*, 1008 (1937); J. F. J. Dippy and J. E. Page, *ibid.*, 357 (1938)], and phenylacetic acids [J. F. J. Dippy, S. R. C. Hughes, and B. C. Kitchener, *ibid.*, 1275 (1964)] in water. It has been demonstrated [J. Hine, *J. Am. Chem. Soc.*, **81**, 1126 (1959)] that the assumption in the Hammett equation that $\rho_m = \rho_p$ cannot be completely general.

(10) A value of 0.69 is obtained from the data of I. Benghiat and E. I. Becker, *J. Org. Chem.*, **23**, 885 (1958). Making use of only reliable *meta* substituents a value of +0.625 has been obtained.[11]

(11) K. Bowden, *Can. J. Chem.*, **41**, 2781 (1963).

(12) R. Fuchs, *J. Org. Chem.*, **28**, 3209 (1963).

However, a uniform procedure was used throughout the measurements reported, and repeated measurements were made with the unsubstituted compounds during the study to ensure internal consistency. The pK_a differences within each series are probably correct to within 0.01–0.02 unit.

A Direct Synthesis of 1,3,5-Tri-*t*-butylbenzene

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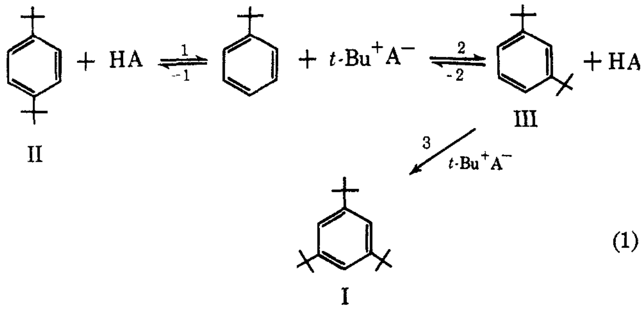
Consideration of the mechanism of isomerization of *t*-butylbenzenes has led to the development of a direct, high-yield synthesis of 1,3,5-tri-*t*-butylbenzene (I). The normal method of synthesis of I involves *t*-butylation of 1,4-di-*t*-butylbenzene (II) in the presence of aluminum chloride.[1] Barclay has shown that alteration of the solvent composition and reaction temperature greatly enhances the preparative value of this reaction.[2] However, the use of II in the synthesis of I appears puzzling. Available data strongly indicate that *t*-butylbenzenes isomerize by dealkylation–alkylation processes.[3] If this is correct, *t*-butylbenzene must be an intermediate in the synthesis of I (eq 1) and would appear to be an equally suitable and a much more convenient starting material.



(1)

It is possible that the conversion of II to I occurs *via* an intramolecular shift of a *t*-butyl group slightly prior to, or synchronous with, the attack of a third *t*-butyl cation. Such a situation might explain the need for II as a direct precursor to I.[4] The investigation described here was designed to test the intramolecular character of the rearrangement of II and explore the utility of *t*-butylbenzene as a reactant in the synthesis of I.

Our studies confirm that the low-temperature alkylation of II with excess *t*-butyl chloride is an exceedingly rapid and efficient method of synthesis of I.[2] With careful temperature control, I can be isolated in 70–85% yield. Cyclialkylated products which have been isolated by the use of Bartlett's procedure are very minor components of the product mixture.[5] Withdrawal and chromatographic analysis of aliquots of the reaction mixture reveal no detectable 1,3-di-*t*-butylbenzene at any stage of the reaction; II and I are the only major aromatic constituents.[6]

A study of the rearrangement and alkylation of 1,4-di-*t*-butylbenzene-*β*-*t* showed that the resulting 1,3,5-tri-*t*-butylbenzene contained less than 20% of the initial tritium activity. The constancy of the tritium activity of I as a function of reaction time (Table I) precludes significant loss of activity *via* dealkylation–alkylation of the product.

TABLE I
TRITIUM ACTIVITY OF 1,3,5-TRI-*t*-BUTYLBENZENE

Reaction time, min	1,3,5-Tri-*t*-butylbenzene,[a] %	Activity × 10^{-6} cpm mmole^{-1} [b]
1	86	0.178
2	91	0.183
5	96	0.183
12	99	0.183
20	99	0.179

[a] Denotes per cent of product in unpurified sample. Dimers of isobutylene were not included in product distribution computation (ref 5a). [b] Activity of the reactant was 0.915 × 10^6 cpm mmole^{-1}.

Alkylation of *t*-butylbenzene using conditions analogous to those employed in the alkylation of II proved to be somewhat hazardous. That is, addition of aluminum chloride to a cold (−7°) mixture of *t*-butylbenzene and *t*-butyl chloride normally resulted in an initial exothermic reaction evolving considerable quantities of isobutylene and hydrogen chloride.[7] However, strong cooling of the reaction mixture to about −40° permitted smooth addition of aluminum chloride without loss of control. Following addition, slow warming of the reaction mixture to −10° and continued reaction at that temperature afforded I, isolable without distillation in 75–85% yield. The alkylation of *t*-butylbenzene-*β*-*t* was found to yield I with loss of about 75% of tritium activity.

These results are in harmony with the reaction scheme shown in eq 1. The loss of all but 20% of tritium activity upon rearrangement and alkylation of 1,4-di-*t*-butylbenzene-*β*-*t* clearly implies that predominant, if not complete, intermolecular transfer of *t*-butyl groups occurs during isomerization. The absence of significant quantities of 1,3-di-*t*-butylbenzene at any stage of the reaction may be indicative that the rate of step 2 is much slower than step 3 (eq 1).[8] If this condition prevails, then suitably designed experiments measuring the loss of tritium activity upon rearrangement and alkylation of II can yield data concerning the relative rate of aluminum chloride catalyzed *t*-butylation of *t*-butylbenzene. Further investigation of this aspect is in progress. Of present importance, these results demonstrate that the once elusive hydrocarbon, 1,3,5-tri-*t*-butylbenzene, can be

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(1) P. D. Bartlett, M. Roha, and R. M. Stiles, *J. Am. Chem. Soc.*, **76**, 2349 (1954).

(2) L. R. C. Barclay and E. E. Betts, *Can. J. Chem.*, **33**, 672 (1955).

(3) (a) R. H. Allen, *J. Am. Chem. Soc.*, **82**, 4856 (1960); (b) M. J. Schlatter, *ibid.*, **76**, 4952 (1954); (c) M. J. Schlatter and R. D. Clark, *ibid.*, **75**, 361 (1953).

(4) The existence of intramolecular isomerizations of *t*-butyl groups remains the subject of speculation; see G. A. Olah, C. G. Carlson, and J. C. Lapierre, *J. Org. Chem.*, **29**, 2687 (1964); G. A. Olah, S. H. Flood, and M. E. Moffat, *J. Am. Chem. Soc.*, **86**, 1060 (1964).

(5) (a) P. C. Myhre and W. M. Schubert, *J. Org. Chem.*, **25**, 708 (1960); (b) L. R. C. Barclay and E. E. Betts, *J. Am. Chem. Soc.*, **77**, 5735 (1955).

(6) Prolonged reaction times, exceeding the time required to convert II to I, do lead to detectable amounts of various cyclialkylated products.[5]

(7) This gas evolution quickly subsides and that material remaining in the flask is converted to I in good yield.

(8) The results of S. Watari [*Bull. Chem. Soc. Japan*, **36**, 747 (1963)] are in accord with this conclusion.