$$\text{AIBN} \xrightarrow{k_{11}} (2\text{R}\cdot) + \text{N}_2 \qquad (11)$$

$$(2\text{R}\cdot) \xrightarrow{k_{12}} \text{R–R} \qquad (12)$$

$$(2\text{R}\cdot) \xrightarrow{k_{13}} 2\text{R}\cdot \qquad (13)$$

$$\text{R}\cdot + \text{I}_2 \longrightarrow \text{RI} + \text{I}\cdot \qquad (14)$$

Here the photometric experiment measures k_{11}, hence $\Delta V_{11}^{\pm} = 3.8$ cc./mole. k_{obs} for the iodine experiment is actually $k_{11}k_{13}/(k_{12} + k_{13})$, or, under pressure where $k_{13} \ll k_{12}$, it approaches $k_{11}k_{13}/k_{12}$ and we obtain

$$\frac{\text{d} \ln k_{\text{obs}}}{\text{d}P} = \frac{\Delta V_{12}^{\pm} - \Delta V_{11}^{\pm} - \Delta V_{13}^{\pm}}{RT} \qquad (15)$$

Accordingly $\Delta V_{12}^{\pm} - \Delta V_{13}^{\pm} = 5.56$ cc./mole. Since $\Delta V_{12}^{\pm}$ is presumably negative, $\Delta V_{13}^{\pm} < 5.56$ cc./mole which may be compared with our value of <8 cc./mole for the *t*-butoxy radical. Stated qualitatively, pressure favors retention of the radicals in the solvent cage where they can combine, rather than diffusing out into the solution.

Qualitatively, benzoyl peroxide follows the same pattern, showing larger values of $\Delta V^{\pm}$ in CCl_4, a solvent necessarily unreactive toward benzoyloxy radicals, than in acetophenone. These results suggest the generalization that, except in the case of initiators yielding fragments sufficiently reactive to attack substrates while in the solvent cage, high pressures will decrease the chain starting-efficiency of initiators which dissociate homolytically to initiate free radical chains.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Reaction Rates by Distillation. VIII. The Alkylation of Aromatic Compounds by Benzyl Alcohols and Benzhydrols[1]

BY ERNEST F. PRATT AND HAROLD J. E. SEGRAVE[2]

RECEIVED APRIL 11, 1959

It has been found, contrary to expectation, that in the alkylation of aromatic compounds by phenylcarbinols the yields tend to decrease as the electron-releasing ability of a *para* substituent in the carbinol increases, while, as expected, the yields tend to increase as the electron-releasing ability of the substituent on the compound being alkylated increases (Table I). As the reactivity of the phenylcarbinol increases its selectivity in alkylating either of two aromatic compounds was found to increase, as would be expected if the derived carbonium ion is the attacking particle. It has been shown that the compound being alkylated is involved in the rate-controlling step of the reaction and that selected aromatic compounds are smoothly benzylated upon warming them with benzyl alcohol and anhydrous *p*-toluenesulfonic acid on the steam-bath for 15 minutes. The formation of benzhydryl butyl ether, which proceeds readily in toluene solution at low concentrations of *p*-toluenesulfonic acid, is almost completely suppressed in favor of alkylation of the toluene at high concentrations of the acid (Table II).

In Table I are shown the results of alkylations of anisole, toluene and benzene by a variety of benzyl alcohols and benzhydrols with *p*-toluenesulfonic acid as the catalyst. The procedure was that previously described in which the by-product water is collected as rapidly as formed by distillation into a Dean–Stark trap.[3] The tendency for the yield to increase with an increase in electron-releasing ability of the substituent on the compound being alkylated was expected, but the tendency for the yield to decrease with an increase in electron-releasing ability of the substituent on the alcohol, that is with an increase in reactivity of the alcohol, was somewhat unexpected.

The increasing catalyst concentrations required in the experiments of Table I (see Experimental), as the electron-releasing ability of the substituent on the alcohol was decreased, show, in agreement with previous observations,[3] that the alcohol is involved in the rate-controlling step. Since, however, these experiments were carried out at the widely differing boiling points of the compounds being alkylated, it is not directly evident whether they are also involved in the rate-controlling process. Benzene, toluene and mesitylene were, therefore, benzylated at the reflux temperature of a 3:1 by volume mixture of cyclohexane and nitrobenzene. With a 1:4 molar ratio of benzyl alcohol to compound being benzylated the yields of monobenzylated products were 21, 39 and 62%, respectively, and a 75% yield of water was obtained in 339, 130 and 65 minutes. A 100 ± 2% total yield of water was obtained in all cases, indicating self-benzylation of the alcohol was also occurring. This was confirmed experimentally when it was found that a molecule of water per molecule of benzyl alcohol was readily evolved in the absence of any other alkylatable compound and a resinous product was formed. The tendency for the yield of monobenzylated product to increase among benzene, toluene and mesitylene in that order, which is also the order of increasing reactivity, is well understood on this basis and it is clear that both the compound being alkylated and the alcohol are involved in the rate-controlling process. The closely related trends in yields shown in the horizontal rows of Table I can reasonably be explained on the same basis.

It is apparent (Table I) that the yields for the more reactive benzhydrols are in general lower than those for the corresponding benzyl alcohols. This results chiefly from the tendency of the intermediate symmetrical dibenzhydryl ethers[3] to disproportionate more readily than do the analogous dibenzyl ethers.[4] Thus from the experiments

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[1] For the preceding paper in this series see E. F. Pratt and J. Lasky, THIS JOURNAL, **78**, 4310 (1956).

[2] From the Ph.D. thesis of Harold J. E. Segrave, May, 1952.

[3] E. F. Pratt, R. K. Preston and J. D. Draper, THIS JOURNAL, **72**, 1367 (1950).

[4] J. F. Norris and R. C. Young, *ibid.*, **52**, 753 (1930).

TABLE I

THE EFFECT ON YIELDS OF ALKYLATED PRODUCT OF VARYING SUBSTITUENTS IN BOTH REACTANTS

R	Yields,[a] % Anisole	Toluene	Benzene
	p-$RC_6H_4CH_2OH$		
CH_3O	85[b]	21	0
CH_3	83	87	62
H	89[b]	90[b]	78[b]
Cl	92[b]	..	87
	$(p$-$RC_6H_4)_2CHOH$		
$(CH_3)_2N$	0	..	..
CH_3O	39	..	..
CH_3	43	33	0
H	93[b]	91[b]	84
Cl	..	..	87

[a] Total yield of water was 95 to 104% for the benzyl alcohols and 87 to 100% for the benzhydrols except that with *p,p'*-dimethylbenzhydrol and benzene the yield was only 76%. [b] These expts. were previously reported in ref. 3.

with *p,p'*-dimethylbenzhydrol and anisole, toluene and benzene (Table I), 0, 12 and 31% yields of *p,p'*-dimethylbenzophenone and 0, 11 and 36% yields of *p,p'*-diphenylmethane were isolated.

As expected from extrapolation of the trends shown in Table I Michler's hydrol smoothly alkylated dimethylaniline in 81% yield.[5] It is of particular interest that benzene served as an inert solvent for this reaction although in certain previous attempts to employ this solvent for the alkylation of phenol or mesitylene by benzyl alcohol[3] the chief product was diphenylmethane arising from attack on the solvent. The ability of highly reactive analogs of benzyl alcohol to select the more reactive analogs of benzene in place of benzene itself for alkylation now appears to be general. Thus, the alkylation of anisole in benzene solution by benzhydrol, by *p*-methylbenzhydrol[6] and by anisyl alcohol as well as the alkylation of phenol in benzene solution by triphenylcarbinol[3] proceeded smoothly in 60 to 80% yields.[7]

Although as the reactivity of a compound increases its selectivity ordinarily decreases, in the foregoing cases the more reactive alcohols proved to be more selective. If, however, the attacking particles are not the alcohols, but the carbonium ions derived from them, the apparent anomaly is resolved since the order of reactivity of the carbonium ions is the reverse of that for their alcohol precursors. On this basis the increasing yields from right to left in Table I are a reasonable result of the ability of the anisyl carbonium ion, for example, to survive more collisions with benzene than with anisole and the increasing yields from top to bottom are a reasonable result of the ability of anisole, for example, to survive more collisions with the *p,p'*-bis-(dimethylamino)-benzhydryl carbonium ion than with the benzhydryl carbonium ion.

Since only half as much water is evolved when an alcohol O-alkylates itself to give the symmetrical ether as when it C-alkylates an aromatic ring, the shape of the curves obtained upon plotting the volume of water collected *versus* time show a marked flattening midway in the process if intermediate ether formation is extensive.[3] Examination of such curves for the experiments of Table I shows that the more reactive the alcohol the more selective it tends to be in O-alkylating itself in preference to C-alkylating the benzene, toluene or anisole. Thus with anisole the flattening was much more extensive for *p,p'*-dimethoxybenzhydrol than for benzhydrol itself and with toluene the flattening was much more extensive for anisyl than for benzyl alcohol. The ease of self-etherifying benzhydrol and the difficulty of self-etherifying benzyl alcohol in benzene without extensive alkylation of the solvent have been reported previously.[8] In fact with several *p*-substituted benzyl alcohols in anisole O-alkylation was so slight that good rate constants calculated for C-alkylation were obtained over the 20 to 80% portion of the reaction,[3] while with benzhydrol in benzene C-alkylation was so slight that good rate constants for O-alkylation were similarly obtained.[9] All of the results on selective reactivity are consistent with the interpretation that the less stable carbonium ions tend to react with the first molecule they strike while the more stable ions tend to survive numerous collisions and select the reaction with the lowest energy requirements. The same general explanation of closely related processes which apparently proceed predominantly *via* carbonium ions have been published recently[10,11]; the interpretation presented above was, however, developed independently.[2,12]

In the first half of Table II it is shown that at low concentrations of *p*-toluenesulfonic acid, butyl alcohol in toluene underwent O-alkylation by benzhydrol to give a good yield of the ether while at high concentrations of the acid the toluene solvent underwent C-alkylation to give good yields of the triphenylmethane. When the excess acid is present it appears that conversion of the butyl alcohol to $\mathrm{Bu}{:}\overset{\overset{\mathrm{H}}{\cdot\cdot}}{\underset{\cdot\cdot}{\mathrm{O}}}{:}\mathrm{HO_3SC_6H_4CH_3}$-*p* blocks its reaction with benzhydrol. Corroborating, but less clean-cut results were obtained with benzyl alcohol in benzene as shown in the last half of Table II. Related results were previously obtained upon varying the proportion of benzyl alcohol at constant acid concentration.[9]

This method of blocking the reaction of an alcohol was also applied in a study of O-alkylation *versus* S-alkylation. In conformity with the fact that mercaptans are less basic than alcohols it was found that the yields of benzhydryl butyl ether and

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(5) It is pertinent to note that the alkylation of amines by Friedel-Crafts procedures is generally unsuccessful. For example, see C. C. Price, "Organic Reactions," Vol. 3, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 6.

(6) E. F. Pratt and L. Q. Green, THIS JOURNAL, **75**, 275 (1953).

(7) The fact that benzene served as an inert solvent for Baeyer condensations which involved alkylation of dimethylaniline by a variety of highly reactive intermediate benzhydrols (ref. 6) is consistent with this interpretation.

(8) E. F. Pratt and J. D. Draper, THIS JOURNAL, **71**, 2846 (1949).

(9) E. F. Pratt and P. W. Erickson, *ibid.*, **78**, 76 (1956).

(10) C. G. Swain, C. B. Scott and K. H. Lohmann, *ibid.*, **75**, 137 (1953).

(11) H. C. Brown and K. LeRoi Nelson, *ibid.*, **75**, 6292 (1953), and later papers from their laboratory.

(12) Valuable discussions of pertinent alkylations have also been given recently by H. Hart, W. L. Spliethoff and H. S. Eleuterio, *ibid.*, **76**, 4547 (1954), and R. A. Benkeser and R. B. Gosnell, *ibid.*, **78**, 4914 (1956).

TABLE II

ALKYLATION *versus* ETHERIFICATION[a]

BuOH:Phenyl carbinol, ratio	PTS,[b] mole	$t_{50\%}$, min.[c]	Etherif., %	Alkyl., %
Benzhydrol and butyl alcohol in toluene				
1:1	0.256	5	0	77
1:1	.001	46	79	0
3:1	.512	5	11	60
3:1	.004	20	91	0
Benzyl and butyl alcohols in benzene				
1:1	0.256	22	0	74[d]
1:1	.064	1520	34	44
3:1	.512	34	19	64
3:1	.128	1210	59	9[e]

[a] One-eighth mole of benzhydrol or benzyl alcohol was used in all cases; the average yield of water was 0.121 mole or 97%. [b] *p*-Toluenesulfonic acid. [c] The time required for a 50% yield of water to collect. [d] This expt. was previously reported in ref. 9. [e] Expt. carried out by Dr. P. W. Erickson.

benzhydryl octyl thioether formed changed from 41 and 18% at low acid concentration to 0 and 60% at high acid concentration.

It was found that when a 2:1 molar ratio of anhydrous *p*-toluenesulfonic acid and benzyl alcohol in a large excess of benzene was warmed on the steam-bath for 15 minutes benzylation proceeded smoothly. In this way benzene, toluene and mesitylene were alkylated by benzyl alcohol in 80 to 90% yields; benzene was alkylated under the same conditions by *p*-chlorobenzyl and *p*-methylbenzyl alcohols as well as by dibenzyl ether in 70 to 80% yields. Ordinarily reaction is indicated by precipitation of the hydrate of the acid within about 3 minutes.

Experimental[13]

Starting Materials and Products.—All constituents of all reaction mixtures were carefully purified by standard methods until the refractive indices or melting points agreed closely with the values in the literature. Products were isolated by straightforward distillation and crystallization procedures after freeing the reaction mixtures of the acid catalyst by extraction with sodium bicarbonate solutions and with water. Unless otherwise noted the refractive indices or melting point of known products agreed satisfactorily with the values in the literature. It has previously been shown that toluene and anisole alkylate almost exclusively at the *p*-position under these general conditions,[3] but the possibility of the presence of minor amounts of the *o*-isomer in the liquid products must be recognized.

Experiments of Table I.—The apparatus employed for these experiments has been described previously.[3] A solution of the specified amount of *p*-toluenesulfonic acid monohydrate in 450 ml. of the compound being alkylated was heated under reflux until no more water collected in the trap. Fifty ml. of a solution of 0.125 mole of the desired phenylcarbinol in the compound being alkylated was then added and refluxing was continued while taking frequent readings of time, water volume and temperature until evolution of the by-product water was complete. The average temperatures were 157, 113 and 81.5° for the experiments in anisole, toluene and benzene, respectively; within a given experiment the temperature variation was almost invariably less than ±0.5°.

For anisyl alcohol with anisole (A) the catalyst concentration employed in the experiment of Table I was 0.00025 molar and the time required for the evolution of a 50% yield of water was 27 minutes.[3] With toluene (T) the corresponding data were 0.008 molar and 11 minutes; since the reaction rate decreased greatly the catalyst concentration was doubled at 57% completion. With benzene (B) the data were 0.004 molar and 44 minutes; here it was necessary to double the catalyst concentration at 55% completion and to double it again, to 0.016 molar, at 60% completion. After the final addition of catalyst the odor of formaldehyde was noted and 1.46 g. of *p,p'*-dimethoxydiphenylmethane was isolated from the reaction mixture. It melted at 48–49° both alone and when mixed with authentic material. A small amount of the same product was also isolated from the preceding experiment. Apparently some of the anisyl alcohol undergoes a reverse Baeyer condensation to give formaldehyde and anisole which is then alkylated by more of the anisyl alcohol. Related decompositions have been previously described.[14]

For *p*-methylbenzyl alcohol (Table I) the corresponding data were: (A) 0.16 molar and 47 min., (T) 0.032 molar and 134 min., (B) 0.128 molar and 7 min. For benzyl alcohol[3]: (A) 0.032 molar and 164 min., (T) 0.064 molar and 85 min., (B) 0.128 molar and 82 min. For *p*-chlorobenzyl alcohol: (A) 0.032 molar and 296 min.,[3] (B) 0.256 molar and 21 min. For *p,p'*-dimethylaminobenzhydrol[15] it was necessary to increase the catalyst concentration portionwise to 0.01 molar so the time required for the evolution of a 50% yield of water was not significant. For *p,p'*-dimethoxybenzhydrol: (A) 0.000125 molar and 92 min.; the catalyst concentration was doubled at 50% completion and doubled again, to 0.0005 molar, at 56% completion. *p,p'*-Dimethoxydiphenylmethane (1.6 g.) and *p,p*-dimethoxybenzophenone (2.8 g.) as well as the expected product were isolated from the reaction mixture.[4] For *p,p'*-dimethylbenzhydrol the data were: (A) 0.001 molar and 4 min. The 4,4'-dimethyl-4''-methoxytriphenylmethane distilled at 202° (0.07 mm.), n^{25}_{D} 1.5980 (*Anal.* Calcd. for $C_{22}H_{22}O$: C, 87.38; H, 7.34. Found: C, 87.52; H, 7.44). (T) 0.064 molar and about 3 min. The tris-*p*-tolylmethane could not be crystallized although a m.p. of 63° is recorded. It was, therefore, analyzed. *Anal.* Calcd. for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 92.24; H, 7.72. (B) 0.256 molar and 20 min.; the catalyst concentration was doubled at 66% completion. For benzhydrol the data were: (A) 0.001 molar and 130 min.[3] (T) 0.064 molar and 12 min.[3] (B) 0.512 molar and 22 min. For *p,p'*-dichlorobenzhydrol: (B) 0.512 molar and 23 min. The product distilled as an oil in 87% yield and analyzed as *p,p'*-dichlorotriphenylmethane. *Anal.* Calcd. for $C_{19}H_{14}Cl_2$: C, 72.86; H, 4.51. Found: C, 72.54; H, 4.52. Crystallization from methanol, with 66% recovery, gave white needles which melted at 53–53.5°.[16] *Anal.* Found: C, 72.94; H, 4.31.

Benzylation of Benzene, Toluene and Mesitylene in an Inert Solvent.—A 3:1 by volume mixture of cyclohexane and nitrobenzene was used as the solvent; the nitrobenzene was added in order to increase the solubility of the *p*-toluenesulfonic acid. One-eighth mole of benzyl alcohol and 0.064 mole of the acid were used in 500 ml. of reaction mixture according to the general procedure described above. The reaction temperatures were 84.7 ± 0.1°, 87.4 ± 0.1° and 89.3 ± 0.1° for the benzylation of benzene, toluene and mesitylene, respectively, and 1:4 molar ratios of benzyl alcohol to compound being alkylated were employed with the results given in the discussion. When a 1:8 molar ratio of benzyl alcohol to toluene was employed, the yield rose to 61%, the time for a 50% yield of water fell to 57 min. and the temperature rose to 89.9 ± 0.3°.

When the foregoing procedure was followed except that no compound to be alkylated was added, evolution of water proceeded to give 50, 75 and 102% yields in 98, 406 and 3400 min. Attempted isolation of reaction products gave only resinous material.

Benzene as an Inert Solvent for Selected Alkylations.—For the alkylation by Michler's hydrol 0.0625 mole of this alcohol, 0.250 mole of dimethylaniline and 0.000125 mole of *p*-toluenesulfonic acid in sufficient benzene to give a total volume of 250 ml. were employed in the above described procedure. A 98% yield of water collected after 450 min. of refluxing at about 85°. An 81% yield of leuco crystal violet which melted at 171–175° was obtained.[17]

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(13) We are indebted to Dr. Mary Aldridge for the microanalyses.

(14) T. R. Govindachari, K. Nagarajan and P. C. Parthasarathy, *J. Chem. Soc.*, 912 (1958).

(15) We wish to thank the du Pont Co. for a generous supply of this compound.

(16) All melting points are corrected.

(17) This experiment is referred to in footnote 6 of ref. 6.

For the alkylation by benzhydrol 0.0625 mole of this alcohol, 0.25 mole of anisole and 0.008 mole of *p*-toluenesulfonic acid were used in 250 ml. of benzene solution. The final yield of water was 93%. The crude *p*-benzhydrylanisole was obtained in 89% yield by distillation; crystallization from 95% ethanol gave a 66% yield of crystals which melted at 60–61°.

When the preceding experiment was repeated using anisyl alcohol in place of the benzhydrol with 0.001 mole of catalyst the total yield of water was 103%. Distillation at 158–159° (1.5 mm.) gave a colorless sirup in 62% yield calculated as *p,p'*-dimethoxydiphenylmethane. Recrystallization twice from aqueous ethanol gave a 34% yield of crystals which melted at 49.5–51°.

Reactions of Table II.—The same general procedure was used here as for the experiments of Table I; the total volume of the reaction mixture was 500 ml. for the experiments with benzhydrol in toluene and 1000 ml. for the experiments with benzyl alcohol in benzene. Distillation of the products from the last three experiments of Table II gave good, but not quantitative, separation of the benzyl butyl ether and diphenylmethane. In these cases the approximately 15% of mixed products obtained in the intermediate fractions was apportioned according to the results of calculation based on the weights and refractive indices of the fractions.

O-Ether *versus* S-Ether Formation.—Five hundred ml. of a solution of 0.375 mole of octyl mercaptan, 0.375 mole of butyl alcohol, 0.125 mole of benzhydrol and 0.004 mole of *p*-toluenesulfonic acid in 3:1 by volume cyclohexane and nitrobenzene were heated under reflux in the standard apparatus. A 98% yield (0.122 mole) of water was evolved in 440 min. at about 89.5°. The products were obtained by distillation in the usual fashion.

In the experiment at high acid concentration it was necessary to use 1:1.1 by volume cyclohexane and nitrobenzene and a total volume of 1000 ml. in order to get the 0.512 mole of *p*-toluenesulfonic acid into solution. The amounts of mercaptan, butyl alcohol and benzhydrol were the same as in the preceding paragraph. At the reflux temperature of about 93° reaction proceeded rapidly; a 50% yield of water was obtained in 13 min.

In order to obtain benzhydryl octyl thioether for comparison purposes and to demonstrate the applicability of the distillation method to thioether formation, the experiment at low acid concentration was repeated except that no butyl alcohol was added. A 98% yield of water was evolved in 89 minutes. The desired benzhydryl octyl thioether distilled in 93% yield as a viscous yellow liquid at 157–163° (0.3 mm.). Redistillation gave a 69% yield at 171° (0.5 mm.), n^{25}_D 1.5522. *Anal.* Calcd. for $C_{21}H_{28}S$: C, 80.71; H, 9.03. Found: C, 80.97; H, 9.03.

Alkylation without Distillation of the By-product Water.—One-fourth mole of *p*-toluenesulfonic acid monohydrate was dehydrated in the usual way in 500 ml. of the aromatic compound to be alkylated. One-eighth mole of the desired phenylcarbinol was then added to the hot solution and the mixture heated 15 minutes on the steam-bath. The benzene solutions were ordinarily heated under reflux since they boil on the steam-bath. Except for the experiment in which anisole was benzylated a precipitate of *p*-toluenesulfonic acid monohydrate appeared within about 3 minutes.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

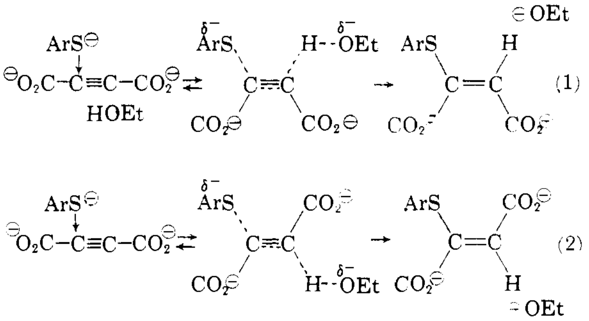
The Stereochemistry of the Base-catalyzed Addition of *p*-Toluenethiol to Disodium and Diethyl Acetylenedicarboxylate[1,2]

BY WILLIAM E. TRUCE AND ROBERT B. KRUSE

RECEIVED APRIL 4, 1959

The base-catalyzed additions of *p*-toluenethiolate reagent to disodium acetylenedicarboxylate and diethyl acetylenedicarboxylate proceed in accord with the Rule of *trans*-Nucleophilic Addition.

After the demonstration that *p*-toluenethiolate reagent adds to sodium propiolate[3] in violation of the Rule of *trans*-Nucleophilic Addition,[4] presumably due to a coulombic effect between the negatively charged carboxylate substituent and the attacking thiolate group, it was of interest to study the base-catalyzed addition of *p*-toluenethiol to the disodium salt of acetylenedicarboxylic acid. The stereochemistry of this addition might be governed either by the coulombic repulsion between one of negatively charged carboxylate substituents and the attacking thiolate group, or by the coulombic repulsion between the two negatively charged carboxylate substituents. These alternatives are represented in a simple classical manner by paths 1 and 2, respectively in the formula chart. The dotted lines in these representations show bonds in the process of being formed or broken in the transition state.[5] This view offers one explanation for the observed stereoselectivity of addition, *i.e.*, intuitively it would be expected that the coulombic repulsions would be greater and the transition state less stable in path 1 than in path 2.



The experimental evidence that the nucleophilic addition of the elements of *p*-toluenethiol to acetylenedicarboxylic acid did indeed proceed by path 2 is presented in outline form. Compound I, m.p. 168°, was characterized as *p*-tolylmercaptofumaric acid on the basis of its neutral equivalent, analysis and behavior toward refluxing acetyl chloride when an attempt was made to dehydrate the di-acid.[6]

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(1) This constitutes Paper XI in the series, "Stereospecific Reactions of Nucleophilic Agents with Acetylenes and Vinyl-type Halides"; for preceding paper see THIS JOURNAL, **81**, 4931 (1959).

(2) Abstracted from the Ph.D. Thesis of Robert B. Kruse, Purdue University, 1959.

(3) (a) W. E. Truce, D. L. Goldhamer and R. B. Kruse, THIS JOURNAL, **81**, 4931 (1959); (b) W. E. Truce and R. F. Heine, *ibid.*, **79**, 5311 (1957).

(4) W. E. Truce, *et al.*, *ibid.*, **78**, 695, 2743, 2748, 2752, 2756 (1956).

(5) W. E. Truce and R. F. Heine, *ibid.*, **81**, 592 (1959).

(6) R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," Chapter 18, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 559.