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]

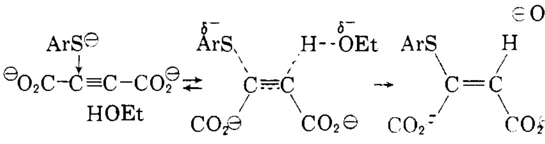
The Stereochemistry of the Base-catalyzed Addition of *p*-Toluenethiol to Disodium and Diethyl Acetylenedicarboxylate[1,2]

BY WILLIAM E. TRUCE AND ROBERT B. KRUSE

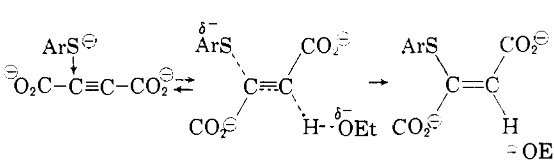
RECEIVED APRIL 4, 1959

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.



(1)



(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).

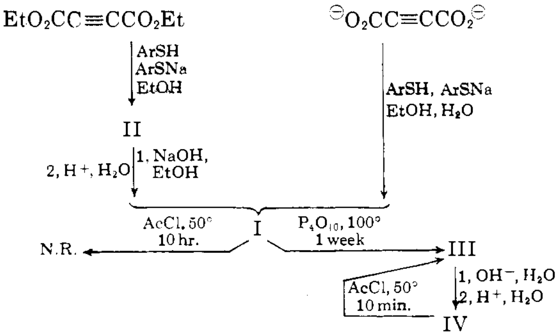
[2] Abstracted from the Ph.D. Thesis of Robert B. Kruse, Purdue University, 1959.

[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.



As would be expected by analogy with other negatively substituted acetylenic systems,[3b] the nucleophilic addition of p-toluenethiol to diethyl acetylenedicarboxylate proceeded in the normal *trans* fashion to yield compound II, b.p. 166–168° at 2.0 mm., characterized as diethyl p-tolylmercaptofumarate on the basis of its analysis and hydrolysis to the dibasic acid I.

Compound III, p-tolylmercaptomaleic anhydride, could be obtained from I only by prolonged heating at 100°, under vacuum and in the presence of phosphorus pentoxide. Under these conditions a sublimable anhydride (III), m.p. 75.5–76.5°, was obtained in low yields. This anhydride is presumably formed by initial thermal isomerization of p-tolylmercaptofumaric acid to p-tolylmercaptomaleic acid.[7]

The monomeric anhydride could be readily hydrolyzed by dissolving in aqueous base. Acidification of the resulting solution produced an acid, IV, m.p. 158.5–159.5°, which depressed the melting point of I and which gave a neutral equivalent and analysis in agreement with p-tolylmercaptomaleic acid. The configurational assignment was made on the basis of the fact that the acid was obtained by hydrolysis of the sublimable anhydride; strong additional evidence is afforded by the marked difference in behavior between this di-acid IV and compound I toward acetyl chloride. Compound IV could be converted to the anhydride III in essentially quantitative yield by refluxing with acetyl chloride for fifteen minutes.

The over-all *trans* addition of p-toluenethiol to acetylenes bearing electronegative (but not negatively charged) substituents, extended to diethyl acetylenedicarboxylate, has been explained as resulting from coulombic repulsion between the negative charge on the attacking thiolate group and the electron cloud being displaced from the "triple" bond.[3] However, it is likely that this effect is slight in comparison to the coulombic repulsion operating between two carboxylate groups, each bearing a full negative charge. The fact that the base-catalyzed addition of p-toluenethiol to disodium acetylenedicarboxylate proceeds in a *trans* manner is felt to be due to this repulsion forcing the carboxylate groups into a *trans* position relative to each other.

Experimental[8]

Preparation of Acetylenedicarboxylic Acid.—A sample preparation follows: A slurry of 200 g. (1.34 moles) of the monopotassium salt of acetylenedicarboxylic acid (Eastman Kodak Co., white label) in 300 ml. of distilled water was slowly acidified with concentrated H_2SO_4. During acidification crushed ice was simultaneously added so that the temperature was not allowed to rise above room temperature, thereby preventing decarboxylation of the desired product to propiolic acid.

The reaction mixture was extracted with five 200-ml. portions of ether and the combined ether layers were evaporated at room temperature under an air jet. The product, dried overnight in a vacuum dessicator containing H_2SO_4, was a white powder, m.p. 177–178° dec., yield 70–90%.

Preparation of Diethyl Acetylenedicarboxylate.—The acetylenedicarboxylic acid from the above reaction was converted to the diethyl ester as follows: Acetylenedicarboxylic acid (60 g., 0.58 mole) was dissolved in 150 ml. of absolute ethanol. To the solution was added 24 ml. of concentrated H_2SO_4. The flask was stoppered and the reaction mixture was allowed to stand with intermittent shaking for 72 hours at room temperature during which a layer of ester separated. At the end of this time, the mixture was poured over crushed ice and extracted with three 100-ml. portions of ether. The combined ether extract was dried over $CaCl_2$ and evaporated under reduced pressure. The crude ester thus obtained was purified by vacuum distillation (b.p. 60–62° at 0.3 mm.) to yield 68 g. (76%) of a clear, colorless liquid.

Reaction of Acetylenedicarboxylic Acid with p-Toluenethiolate Reagent.—To 200 ml. of absolute ethanol was added 9.2 g. (0.40 mole) of sodium. When the reaction was complete, 22.8 g. (0.200 mole) of acetylenedicarboxylic acid was added. While stirring, sufficient water was added to produce a clear solution (bringing the total volume to about 500 ml.) and high-purity nitrogen was introduced into the system. The passage of nitrogen was continued while a solution consisting of 24.8 g. (0.200 mole) of p-toluenethiol (Eastman Kodak Co., white label) in 100 ml. of absolute ethanol to which 0.2 g. (0.01 mole) of sodium had been added was dropped into the stirred solution of the acid salt at such a rate that the reaction mixture was not allowed to become cloudy until the last few milliliters of p-toluenethiolate reagent solution was added. After the addition was complete, the mixture was brought to reflux until a clear solution resulted (2 to 3 hours).

The reaction mixture was allowed to cool to room temperature and acidified with concentrated HCl. The crystals obtained upon filtration of the resulting mixture were dissolved in aqueous sodium bicarbonate and filtered to remove a small amount of unreacted p-toluenethiol (whose presence could be detected by its characteristic odor) along with any disulfide that may have been formed during the reaction. The sodium bicarbonate solution was again acidified with concentrated HCl and filtered. A crop of crystals of the crude product (38.6 g., 82%) was obtained. After three recrystallizations from aqueous ethanol followed by drying in a vacuum desiccator over H_2SO_4, a crop of light yellow needles was obtained, m.p. 167–168° dec.

Anal.[9] Calcd. for $C_{11}H_{10}O_4S$: C, 55.46; H, 4.20; neut. equiv., 119. Found: C, 55.01; H, 4.39; neut. equiv., 121.

Reaction of Diethyl Acetylenedicarboxylate with p-Toluenethiolate Reagent.—The addition of p-toluenethiol to diethyl acetylenedicarboxylate has been reported by Heine[10] to yield a crop of crystals the analysis of which was in agreement with that calculated for the diadduct, which separated spontaneously from the reaction mixture. He also obtained a small amount of an oil, b.p. 152–155° at 1.0 mm., which was presumably the monoadduct (the small amount obtained was insufficient for positive identification). Since the diadduct is not involved in the present investigation,

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[7] It should be noted that it is not necessary that the *cis* form be the more stable isomer for the anhydride to be formed in this way, nor is it necessary to attain an equilibrium between the two isomers, since any *cis* isomer formed would be immediately removed from the mixture by dehydration and subsequent sublimation.

[8] All microanalyses were carried out by Dr. C. S. Yeh and Mrs. B. Groten of the Purdue Chemistry Microanalytical Laboratory. All boiling and melting points are uncorrected.

[9] The discrepancies shown in the analyses of p-tolylmercaptofumaric and -maleic acids, slightly low in carbon and high in hydrogen, are probably due to the fact that removal of the last traces of water could not be carried out by heating under vacuum with a desiccant due to the formation of p-tolylmercaptomaleic anhydride.

[10] R. F. Heine, Ph.D. Thesis, Purdue University, 1957.

care was taken to employ reaction conditions which would tend to minimize its formation.

A solution of 34.0 g. (0.200 mole) of the diethyl ester of acetylenedicarboxylic acid in 100 ml. of absolute ethanol maintained under high purity nitrogen was treated with a catalytic amount (0.2 g., 0.01 mole) of sodium causing the solution to become a clear, deep red. A second solution of 24.8 g. (0.200 mole) of *p*-toluenethiol in 100 ml. of absolute ethanol was then added very slowly, over a period of three hours, with vigorous stirring. After addition was complete, the mixture was brought to reflux for 0.5 hour, and finally was allowed to cool. No crystals formed. The mixture was placed in 500 ml. of water and acidified with a small amount of concentrated HCl (2–3 ml.). A brown oil was formed which was isolated by extraction with three 100-ml. portions of ether and subsequent evaporation of the combined ether layers under reduced pressure. The oil was purified by distillation (b.p. 166–168° at 2.0 mm.); yield 53.2 g. (90.5%) of a clear yellow oil.

Anal. Calcd. for $C_{15}H_{18}O_4S$: C, 61.2; H, 6.12. Found: C, 61.08; H, 6.13.

Ester Saponification.—The product of addition of the *p*-toluenethiol reagent to diethyl acetylenedicarboxylate was saponified by dissolving in ethanolic KOH. The solution was acidified with concentrated HCl and the solid acid which precipitated was recrystallized from aqueous ethanol, m.p. 166–167°, mixture melting point with the product of addition of the *p*-toluenethiolate reagent to acetylenedicarboxylic acid, 166–166.5°.

Preparation of *p*-Tolylmercaptomaleic Anhydride.—When a sample of the dibasic acid obtained as described above was refluxed for 10 hours with acetyl chloride, the starting material could be recovered unchanged. Dehydration of this compound in moderate yield could be attained by mixing the di-acid (3.2 g., 0.013 mole) with 5.0 g. of phosphorus pentoxide and placing the mixture in a vaccum sublimator. The mixture was heated in boiling water for one week, keeping the pressure between 1 and 10 mm. The resulting yellow needles of anhydride were obtained in 30% yield (0.9 g.), m.p. 75.5–76.5°.

Anal. Calcd. for $C_{11}H_8O_3S$: C, 60.0; H, 3.64. Found: C, 59.70; H, 3.55.

Preparation of *p*-Tolylmercaptomaleic Acid.—A sample of the anhydride obtained in the above reaction was hydrolyzed by dissolving in aqueous NaOH, followed by acidification with concentrated HCl. The white crystals of di-acid thus obtained, m.p. 158.5–159.5°, depressed the melting point of the product of addition of *p*-toluenethiolate reagent to acetylenedicarboxylic acid to 145–148°.

Anal.[9] Calcd. for $C_{11}H_{10}O_4S$: C, 55.46; H, 4.20; neut. equiv., 119. Found: C, 55.11; H, 4.39; neut. equiv., 120.

A small sample of this acid (0.2 g., 0.001 mole) was placed in 15 ml. of acetyl chloride and the mixture was refluxed on a steam-cone for 15 min. At the end of this time the acetyl chloride was stripped off using a rotary film evaporator. Acetic acid formed in the reaction was evaporated under an air jet. Seeding the yellow oil remaining with a very small crystal of the anhydride produced by sublimation immediately produced an essentially quantitative yield of the anhydride, m.p. 75.5°, mixture melting point with the anhyride obtained by sublimation, 75.5°.

Acknowledgment.—The authors gratefully acknowledge the financial support of this work by the Diamond Alkali Co. and the National Science Foundation.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF PURDUE UNIVERSITY]

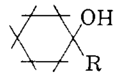
Factors Influencing the Direction of Elimination in Ester Pyrolyses

BY ROBERT A. BENKESER, JAMES J. HAZDRA AND MERWYN L. BURROUS

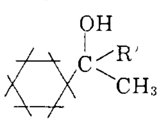
RECEIVED FEBRUARY 26, 1959

A series of structurally related alcohols of the general formula $RCH_2CHOHCH_2CH_3$ were pyrolyzed *via* their xanthate (Chugaev reaction) and acetate esters. The R group was made to vary systematically from methyl to ethyl, isopropyl and *t*-butyl. In every case only two isomeric olefins were formed. The relative amount of each was determined by vapor phase chromatography. It was found that as R varied from methyl to *t*-butyl, the relative proportion of that olefin isomer which contained the double bond closest to the R group increased from 1-to-1 (methyl) to 2.3-to-1 (*t*-butyl). Thus, when R was *t*-butyl, 70% 2,2-dimethyl-3-hexene and 30% 5,5-dimethyl-2-hexene were produced. It is proposed that the direction of elimination in ester pyrolyses is influenced by the interplay of three effects: (1) statistical factors, (2) relative thermodynamic stability of the olefin products and (3) steric effects which either hinder or assist the formation of the cis, coplanar transition state.

Recently[1] we demonstrated that in the case of five different alcohols (structures I and II below), Chugaev elimination proceeded so as to avoid



I



II

R = Me, Et, *i*-Pr
R′ = Me, H

forming a double bond *exo* to the six-membered ring.[2] In two of these compounds it achieved this by following the Hofmann rather than the Saytzeff rule, and in three cases it proceeded contrary to the accepted order for hydrogen removal (3° > 2° > 1°).[3] It was noted further that pyrolysis of the acetate of 1-methylcyclohexanol followed a strikingly similar pattern to the Chugaev reaction, in that the ratio of 1-methylcyclohexene/methylenecyclohexane produced was approximately 4/1 in both reactions. In this instance, at least, the acetate pyrolysis and Chugaev reaction gave very similar olefin distributions. In one sense this is a particularly satisfying observation since both reactions are thought to proceed by a similar mechanism involving a cyclic intramolecular six-membered ring transition state.[4] On the other hand it is a result that could not be predicted *per se* since there are important differences in the two reactions.[4a]

It has been suggested that steric considerations constitute the ultimate reason for the thermody-

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[1] R. A. Benkeser and J. J. Hazdra, THIS JOURNAL, **81**, 228 (1959).

[2] H. C. Brown, J. H. Brewster and H. Shechter, *ibid.*, **76**, 467 (1954).

[3] J. A. Mills, *J. Chem. Soc.*, 260 (1953); see also "Steric Effects in Organic Chemistry," edited by M. S. Newman, John Wiley and Sons. Inc., New York, N. Y., 1956, p. 313.

[4] P. G. Stevens and J. H. Richmond, THIS JOURNAL, **63**, 3132 (1942); (b) C. D. Hurd and F. H. Blunck, *ibid.*, **60**, 2419 (1938).

[4a] For example, the temperature of ester decomposition is different in the two cases; also sulfur atoms are involved in the one instance, rather than oxygen.