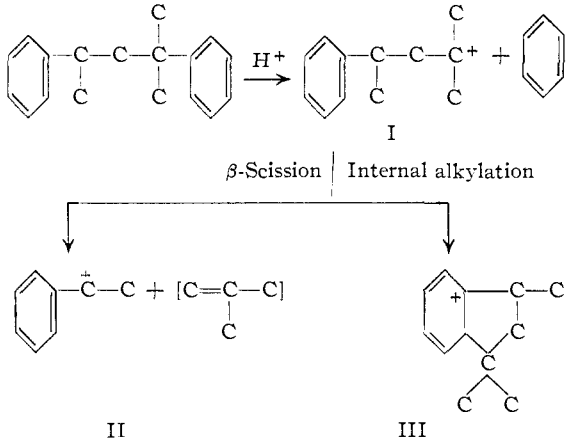
In the presence of the "modified" catalyst and hydrogen tertiary alkyl or cycloalkylarenes undergo hydrogenolysis (reductive dealkylation) most readily, secondary alkylarenes undergo only a partial hydrogenolysis while primary alkylarenes are stable under these conditions. The decreasing order of reactivity of alkylbenzenes, III > II > I, is characteristic of acid reactions.

The hydrogenolysis takes place under pressure of 10–75 atmospheres, at temperatures of 300–350° and in the presence of either nickel–kieselguhr, precipitated nickel or Raney nickel catalyst, "modified" by the addition of small amounts of thiophene to the reaction mixture. Thus, *tert*-butylbenzene yields at 350° 80% benzene 2-(*p*-tolyl)-2,4-dimethylpentane about 80% of toluene and 2,4-dimethylpentane and 1-methylcyclohexylbenzene yields 80% benzene and methylcyclohexane. Isopropylbenzene under similar conditions forms only 20% of benzene. This type of hydrogenolysis does not occur in the absence of sulfur-containing compounds.

This hydrogenolysis method can be used for a selective removal of one of the aromatic groups from a diarylcyclane in which one of the phenyl groups is attached to a tertiary and the other to a secondary carbon atom, *e.g.*, 1-methyl-1,3-diphenylcyclopentane formed benzene and 1-methyl-3-phenylcyclopentane. The hydrogenolysis can thus serve as a novel degradation method for determining structures of complex hydrocarbons.

The modified nickel catalyst can also act as a cycloalkylating catalyst. The hydrogenolysis of 10 g. of 2-methyl-2,4-diphenylpentane under 70 atmospheres of hydrogen and in the presence of 1.1 g. of nickel–kieselguhr catalyst and 0.2 g. of thiophene yielded a mixture of hydrocarbons which was composed of 41 mole % benzene, 24% ethylbenzene, 4% isopropylbenzene and 15% of about equal amount of 1,1,3-indan and hexylbenzene, the latter being composed mainly of 2-methyl-2-phenylpentane. The reactions leading to the various hydrocarbons may be explained by the usual acidic mechanism[1]



I, II and III may then form the corresponding hydrocarbons.

(1) The possible source of protons in reactions catalyzed by nickel was discussed in a previous paper: H. Pines, M. Shamaiengar and W. S. Postl, THIS JOURNAL, **77**, 5099 (1955).

The formation of isopropylbenzene can be explained by the initial removal of the phenyl which is attached to the secondary carbon atom of the diphenylhexane and this is then followed by a β-scission with the elimination of propylene and formation of a phenylisopropyl carbonium ion.

A transalkylation reaction was observed when *tert*-butylbenzene was hydrogenolyzed under 10 atmospheres of hydrogen. The products of the reaction contain *para*- and possibly also *meta*-di-*t*-butylbenzene.

Similarly toluene was alkylated with isobutylene in the presence of "modified" nickel catalyst at 350° and under an initial pressure of 5–8 atmospheres of hydrogen. About 35% of the isobutylene reacted to form a mixture of *m*- and *p*-*t*-butyltoluene. In the absence of thiophene the yield of *t*-butyltoluene was less than 4%.

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RECEIVED JANUARY 28, 1957

AN EXCEPTION TO THE RULE OF *trans*-NUCLEOPHILIC ADDITION[1]

Sir:

In the course of testing our "Rule of *trans*-Nucleophilic Addition"[1] over a wider range of systems, an exception to it was observed in the addition of sodium *p*-toluenethiolate to sodium propiolate.

When an alcoholic solution of sodium *p*-toluenethiolate is added to a cooled aqueous alcoholic solution of sodium propiolate, there is obtained a quantitative yield of product consisting of two *p*-tolylmercaptoacrylic acids, m.p. 144.5–145.5° (85–90% of total; *Anal.* Calcd. for $C_{10}H_{10}O_2S$: C, 61.83; N, 5.18. Found: C, 61.83; H, 5.25) and m.p. 136–137° (10–15% of total; Found: C, 62.07; H, 5.22). The compounds were assigned the structures, *trans*- and *cis*-β-*p*-tolylmercaptoacrylic acids, respectively, on the basis of the following evidence.

Infrared spectra of the two acids revealed a band at 7.80μ for the low-melting isomer, and a band at 8.42 μ for the high-melting isomer, indicative[1] of *cis* and *trans* configurations, respectively; bands associated with >C=CH_2 were absent. Furthermore, treatment of both isomers under Friedel–Crafts conditions[2] gave, from the low-melting isomer, an approximately 90% yield of 6-methylthiochromone, b.p. 138.0° (1.0 mm.), m.p. 69–70° (lit.[3] b.p. 194° (12 mm.), m.p. 69–70°). *Anal.* Calcd. for $C_{10}H_8OS$: C, 67.99; H, 5.12. Found: C, 68.09; H, 4.90. Essentially all of the high-melting isomer was recovered unchanged.

The fact that the above nucleophilic addition proceeds primarily *cis* may be due to the coulombic

(1) This constitutes Paper V in the series on Stereospecific Reactions of Nucleophilic Agents with Acetylenes and Vinyl-type Halides; refer to W. E. Truce, *et al.*, THIS JOURNAL, **78**, 695, 2743, 2748, 2752, 2756 (1956).

(2) S. Ruhemann and H. E. Stapleton, *J. Chem. Soc.*, **77**, 1197 (1900).

(3) F. Krollpfeiffer, *et al.*, *Ber.*, **58B**, 1654 (1925).

repulsion between the entering negatively-charged thiolate ion and the like-charged carboxylate group overshadowing the similar repulsion between the thiolate ion and the pair of electrons it is displacing from the acetylenic group. This latter repulsion seems to be a satisfactory explanation for the usual *trans* nucleophilic additions.

This argument leads to the prediction that similar nucleophilic additions to acetylenes bearing negatively charged substituents should also proceed *cis* rather than *trans*. It is gratifying to note that there is reasonable evidence for a *cis* addition of ammonium sulfite to salts of propiolic acid to form *trans*-2-sulfoacrylic acid.[4]

The above explanation for *cis*-nucleophilic addition of *p*-toluenethiol to sodium propiolate is supported by the observation that such additions to the two acetylenes, ethyl propiolate and benzylacetylene (bearing similarly electronegative but *uncharged* substituents), proceed in the normal *trans* fashion, the products being ethyl *cis*-2-*p*-tolyl-mercaptoacrylate and *cis*-1-benzoyl-2-*p*-tolyl-mercaptoethene, respectively. Saponification of the former product gave a compound identical with the minor product obtained by like treatment of sodium propiolate.

We hope soon to develop information regarding whether or not nucleophilic addition can be forced to proceed *cis* as a result of *steric* factors as well as electronic factors. Also, data relating to the detailed mechanism of a *trans* nucleophilic addition will be forthcoming.

(4) H. J. Backer and A. E. Beute, *Rec. trav. chim.*, **54**, 523 (1935).

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RECEIVED JANUARY 18, 1957

A NEW ADENYL-SUCCINIC ACID DERIVATIVE CONTAINING SULFATE AND A PEPTIDE[1]

Sir:

Recently, the occurrence of adenine-succinic acid and adenyl-succinic acid has been reported from several laboratories. Yeast,[2] *Escherichia coli*,[3] mammalian liver[4] and cod liver[5] have been demonstrated to contain one or both of these compounds. In the present communication the authors wish to report the isolation and identification of a derivative of adenylsuccinic acid (I) from salmon liver.

The livers were excised from live spring (king) salmon at sea and immediately frozen in dry ice. The acid soluble phosphorus compounds were extracted into cold perchloric acid and chromatographed on Dowex-1 anion exchange resin exactly as previously described except that a refrigerated column and fraction collector were used.[6] The fraction under consideration (E) appeared immediately after adenosine diphosphate from the ion exchange column in a formic acid system (Fig. 1). Fraction E was separable into three components

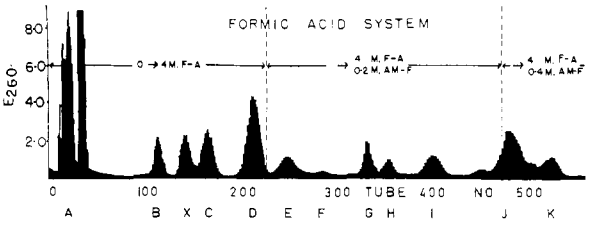
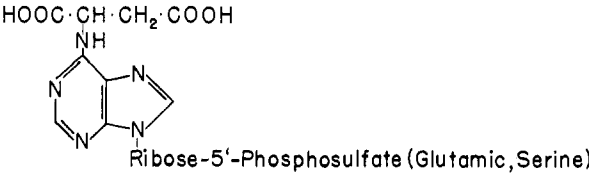


Fig. 1.—Gradient elution of nucleotides on a 1.0 × 20 cm. bed of Dowex-1 formate resin at 0°. The mixing volume was 500 ml. and 5-ml. fractions were collected.[6]

(E_1, E_2 and E_3) by paper chromatography (Table I). Compound I (E_2) moved centrally in relation to the other two and generally comprises approximately 80% of the fraction. It behaved as a single entity on several paper chromatograms (Pabst solvents 1, 2 and 3) and was electrophoretically homogeneous at several *p*H's. Compound I has an absorption maximum of 266 mμ in acid and gives positive tests for phosphate, sulfate and ribose, and a positive ninhydrin reaction. Analytical data on I shows an approximately equimolar ratio of adenine succinate, total P, ribose, sulfate, and *cis*



glycol (Table II). Acid hydrolysis (1.0 *N* HCl) of I for 10 minutes at 100° released a compound with an R_f identical to ribose-5′-phosphate (R-5′-P) and an ultraviolet absorbing compound (E_4). Substance E_4 showed no diazotizable amine,[7] was free from ribose phosphorus and sulfur and behaved similarly to adenine-succinic acid upon paper electrophoresis at *p*H 3.3 and 6.0.[4] Formic acid hydrolysis of E_4 followed by paper chromatography in several solvent systems yielded adenine, hypoxanthine (minor component), aspartic and fumaric acids, thus completing the identification of E_4 as adeninesuccinic acid.

Since periodate oxidation[8] of I showed a free *cis* glycol, and since R-5′-P was obtained by acid hydrolysis, the phosphate must be attached to the 5 position of ribose. Very mild acid hydrolysis (0.01 *N* HCl for 1 hr. at room temperature) of I produced a peptide and sulfate containing nucleotide which were separable chromatographically. Further treatment of the nucleotide in 0.01 *N* HCl for 10 minutes at 100° liberated inorganic sulfate and adenyl-succinic acid. The sulfate therefore must be attached to the phosphate. Compound I decomposes unless a refrigerated column is used. This suggests the possibility that adenyl succinate isolated from

(1) Presented in part at the 130th Meeting of the American Chemical Society, Atlantic City, September, 1956, but not abstracted.
(2) C. E. Carter and L. H. Cohen, THIS JOURNAL, **77**, 499 (1955).
(3) I. Lieberman, *ibid.*, **78**, 251 (1956).
(4) W. K. Joklik, *Biochem. Biophys. Acta*, **22**, 211 (1956).
(5) I. D. E. Storey and D. N. Love, *Biochem. J.*, **64**, 53P (1956).
(6) R. B. Hurlbert, H. Schmitz, A. F. Brumm and V. R. Potter, *J. Biol. Chem.*, **209**, 23 (1954).
(7) J. M. Ravel, R. E. Eakin and W. Shive, *J. Biol. Chem.*, **172**, 67 (1948).
(8) J. S. Dixon and D. Lipkin, *Anal. Chem.*, **26**, 1092 (1954).