Sorbic acid prepared by the silver oxide oxidation of 2,4-hexadienal was dehydrated over alumina at 440–450° to give phenol which was identified as the tribromo derivative (m.p. 93–94°) prepared in the usual manner; with admixture an authentic sample gave no depression of m.p.

COLLEGE PARK, MD.

[CONTRIBUTION FROM RESEARCH DEPARTMENT, STANDARD OIL COMPANY (INDIANA)]

Effect of Acid Strength on Alkylation of Arenes with Olefins. I. *m*-Xylene with Ethylene

BY D. A. MCCAULAY AND A. P. LIEN

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m-Xylene, when alkylated with equimolar amounts of ethylene, gives product distributions that depend upon the acid strength of the catalyst. Hydrogen fluoride alone—a typical alkylation catalyst—forms predominantly polyethylxylenes. Hydrogen fluoride plus excess boron trifluoride—a much stronger acid—produces predominantly 1,3,5-ethylxylene along with relatively small amounts of polyethylxylenes. This difference is explained by the hypothesis that the stronger acid isomerizes the first-formed 1,3,4-ethylxylene into the 1,3,5-isomer. The latter, because it is much more basic than the other ethylxylenes, preferentially forms a positively charged σ-complex with the strong acid. This cation repels the incoming positively charged ethyl group, which must then react with uncomplexed *m*-xylene. Alkylation with strong acids can thus produce high yields of single isomers.

The rate of alkylation of arenes with olefins generally increases with the number of alkyl substituents in the ring.[1,2] In alkylation processes, therefore, high ratios of arene to olefin are used whenever high yields of a monoalkylated product are desired. Recent work on the disproportionation of alkylbenzenes[3] suggested that high yields of monoalkylate might be obtained by another method: the interaction of near-stoichiometric amounts of olefin and arene in the presence of an extremely strong acid catalyst.

Alkylation by this method requires an acid catalyst strong enough to form a σ-complex[4] with the alkylated arene. The σ-complex—a salt resulting from the addition of a proton to the arene, which acts as a base—bears a positive charge and so is not further alkylated by the electrophilic alkylating agent. Alkylated arenes are more basic than unalkylated arenes[5] and form more stable σ-complexes. Hence, the alkylated product is tied up preferentially, while the unalkylated aromatic is left free to react with incoming olefin.

This concept was tested by the conversion of *m*-xylene and ethylene to 1,3,5-ethylxylene in the presence of a strong acid: anhydrous hydrogen fluoride plus excess boron trifluoride. For comparison, the same reactants in the same mole ratios reacted in the presence of a weaker, but typical, alkylation catalyst: hydrogen fluoride alone.

Experimental

m-Xylene from Eastman Kodak Co. (White Label grade) was used without further purification. Ethylene, 98% pure, was obtained from Union Carbide and Carbon Corp. Commercial grades of hydrogen fluoride, 99.6% pure, and boron trifluoride, about 99% pure, were obtained from the Harshaw Chemical Co.

All experiments were carried out in a 1570-ml. carbon-steel autoclave fitted with a 1725-r.p.m. stirrer.[6] The *m*-xylene, hydrogen fluoride and boron trifluoride were charged to the autoclave. Ethylene was added at a uniform rate to the stirred mixture at a controlled temperature. Because no pressure built up during the addition step, the rate of alkylation must have been practically instantaneous. After reaction, the entire reactor contents were withdrawn into crushed ice. The hydrocarbon product was separated into successive carbon-number fractions by distillation through a column of thirty theoretical plates. The individual fractions were identified by their physical properties and by spectrometric analysis.

Results and Discussion

Detailed results are summarized in Table I. All four runs were made with about 2.5 moles each of *m*-xylene and ethylene and with 22 moles of hydrogen fluoride. In the first run, no boron trifluoride was used; in the other three about 3.5 moles was added.

TABLE I

ALKYLATION OF *m*-XYLENE WITH ETHYLENE

9 moles hydrogen fluoride per mole *m*-xylene

Experiment	1	2	3	4
BF_3, moles/mole xylene	0	1.6	1.2	1.3
Temperature, °C.	15	15	62	16
Olefin, addition time, min.	15	15	60	3960
Ethylene, moles/mole xylene	1.0	1.1	1.1	1.2
Product distribution, mole %				
Xylenes	62	27	5	1
1,3,5-Ethylxylene	1	32	83	81
1,3,4-Ethylxylene	15	12	0	0
1,2,3-Ethylxylene	4	2	0	0
Diethylxylenes	6	22	11	16
Triethylxylenes	2	5	1	2
Tetraethylxylenes	10	0	0	0
$(k_2/k_1)^a$	2.8	0.60	0.042	0.043

[a] k_1 = rate of ethylation of *m*-xylene. k_2 = rate of ethylation of ethylxylene.

In experiment 1, with hydrogen fluoride alone, only about 38% of the xylene reacted. The product distribution shows that 75% of the ethylene formed polyethylated xylenes. The 1,3,4- and the 1,2,3-isomers comprise most of the ethylxylene fraction. Evidently the positions in the ring that are *ortho* or *para* to the methyl groups react at a much faster rate than the unactivated meta position.

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[1] F. E. Condon, THIS JOURNAL, **70**, 2265 (1948).

[2] H. C. Brown and K. L. Nelson, paper presented before the Division of Organic Chemistry, 123rd Meeting of the American Chemical Society, Los Angeles, Calif., March 15–19, 1953.

[3] A. P. Lien and D. A. McCaulay, THIS JOURNAL, **75**, 2407 (1953).

[4] H. C. Brown and J. D. Brady, *ibid.*, **74**, 3570 (1952).

[5] D. A. McCaulay and A. P. Lien, *ibid.*, **73**, 2013 (1951).

[6] D. A. McCaulay, B. H. Shoemaker and A. P. Lien, *Ind. Eng. Chem.*, **42**, 2103 (1950).

Product distributions are sharply altered by going to a more acidic catalyst, as shown by experiment 2 with added BF_3. About 73% instead of 38% of the xylene reacted and about 55 instead of 75% of the ethylene formed polyethylxylene. The 1,3,5-isomer comprised about 70% of the ethylxylene, as opposed to about 5% in experiment 1. These differences are interpreted by postulating that, in the presence of the stronger catalyst, the 1,3,4-structure first formed partly isomerizes to the 1,3,5-structure. The 1,3,5-ethylxylene, which is more basic than its isomers by a factor of 150,[6] preferentially forms the positively charged σ-complex

$$[1,3,5\text{-}C_6H_3(CH_3)_2C_2H_5\cdot H]^+$$

This cation does not react with the incoming positively charged ethyl group. The ethyl group must then attack either the uncomplexed *m*-xylene or 1,3,4-ethylxylene.

According to this hypothesis, polyethylxylenes are formed by the addition of ethylene to 1,3,4-ethylxylene and not to 1,3,5-ethylxylene. If, therefore, the rate of isomerizing 1,3,4-ethylxylene were speeded up relative to the rate of ethylene introduction, the yield of polyethylated xylene should drop. The hypothesis was tested in two ways: by increasing the isomerization rate through the use of higher temperatures (experiment 3) and by slowing down the rate of ethylene addition (experiment 4). The resulting product distributions support the hypothesis in that *m*-xylene is alkylated preferentially to 1,3,5-ethylxylene. The *m*-xylene was more than 95% alkylated, as compared with only 38% with hydrogen fluoride alone.

The bottom line of the table gives the relative rates of ethylation of ethylxylene and *m*-xylene. These were calculated from the product distributions by means of the same equation employed by Condon[2]

$$\log\left(C_1 + C_2 - \left(\frac{k_2}{k_1}\right)C_2\right) = \frac{k_2}{k_1}\log C_1$$

where k_1 and k_2 are the rates of ethylation, and C_1 and C_2 are the final concentrations, of *m*-xylene and ethylxylene, respectively. Experiment 1 shows that ethylxylene alkylates 2.8 times faster than *m*-xylene. In experiments 3 and 4, where boron trifluoride was used, the order is reversed; *m*-xylene reacts about 25 times faster than ethylxylene. The relative rate constants are changed about 70-fold.

The explanation used here can also be applied to the results of Norris and Rubinstein.[7] They found that, when benzene is alkylated with ethyl chloride, the concentration of the aluminum chloride catalyst markedly affects the product distribution. A mole ratio of Al_2Cl_6 to aromatic greater than 1.0 gives mainly 1,3,5-triethylbenzene; less aluminum chloride produces a mixture of polyethylbenzenes. Evidently, HCl–$AlCl_3$ as well a HF–BF_3 selectively forms a σ-complex with the 1,3,5-trialkylbenzenes and thereby prevents further alkylation.

By using conditions that favor formation of σ-complexes, alkylation of the substituted benzene ring can thus be directed toward a single isomer. Alkylation with such super-acids as HF–BF_3 or HCl–$AlCl_3$ promises to become a general way to produce high yields of single isomers. Application to other arenes and other olefins will be the subject of future publications.

[7] J. F. Norris and D. Rubinstein, THIS JOURNAL, **61**, 1163 (1939).

WHITING, INDIANA

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Many-membered Carbon Rings. X. Reduction of Diametric Diketones to Monoketones[1]

BY A. T. BLOMQUIST, JULIANNE PRAGER[2] AND JOSEPH WOLINSKY

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Reduction of the readily available diametric diketones 1,9-cyclohexadecanedione and 1,10-cycloöctadecanedione to the muscone-like cyclohexadecanone and cycloöctadecanone has been achieved in good yield *via* catalytic hydrogenolysis of their mono-ethylenedithioketals.

Simple carbocyclic ketones having 14–18 ring members possess a characteristic musk-like odor very similar to that of the naturally occurring *dl*-muscone and civetone. Because of this they are of interest in perfumery as perfume bases and fixatives.

All practical syntheses of such ketones require as intermediates higher α,ω-dicarboxylic acids or their derivatives which are not readily available except through laborious syntheses from lower α,ω-bifunctional compounds.[3] The availability in fair yield of the diametric diketones 1,9-cyclohexadecanedione (I) and 1,10-cycloöctadecanedione (II) from azelaic and sebacic acids *via* cyclization of the bifunctional ketenes derived therefrom[4] prompted a study of the reduction of such diketones to monoketones.

Of the possible reduction methods which might be applicable here the elegant reductive desulfurization procedure of Wolfrom and Karabinos,[5]

[1] For the preceding paper in this series see A. T. Blomquist and A. Goldstein, THIS JOURNAL, **77**, 1001 (1955).

[2] Some of the work reported here was abstracted from part of the dissertation submitted by Julianne Prager in February, 1953, to the Graduate Faculty of Cornell University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] E. H. Rodd, "Chemistry of Carbon Compounds," Elsevier Publishing Co., 1953, Vol. III, Part A, pp. 270–273.

[4] A. T. Blomquist and R. D. Spencer, THIS JOURNAL, **69**, 472 (1947); **70**, 30 (1948).

[5] M. L. Wolfrom and J. V. Karabinos, *ibid.*, **66**, 909 (1944).