[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, STANDARD OIL CO. (INDIANA)]

Interaction of Xylenes with Ethylbenzene

BY M. C. HOFF

RECEIVED MAY 19, 1958

Ethylbenzene and each of the xylenes interact at 60° in the presence of excess hydrogen fluoride and boron trifluoride to yield benzene and 1,3-dimethyl-5-ethylbenzene (5-ethyl-*m*-xylene) as end products. Experiments carried out at short contact times show different reaction paths for each of the xylenes: *o*-Xylene is rapidly ethylated to an equilibrium mixture of 3- and 4-ethyl-*o*-xylene, which then isomerizes to 5-ethyl-*m*-xylene. *m*-Xylene is present mainly as a cation and is ethylated more slowly than *o*-xylene. The only product found is 5-ethyl-*m*-xylene; 4-ethyl-*m*-xylene isomerizes too rapidly to be detected. *p*-Xylene is not ethylated directly because no position is highly activated and all are blocked by adjacent methyl groups. Instead, it isomerizes to *m*-xylene and then reacts. The ethyl group donor in all the reactions appears to be diethylbenzene formed by rapid disproportionation of ethylbenzene.

A previous paper[1] reported the different interactions of the xylenes with ethylbenzene in the presence of hydrogen fluoride plus excess boron trifluoride. At 20–25°, mixtures of ethylbenzene and *m*-xylene or *p*-xylene formed benzene and diethylbenzene, but no ethylxylenes; ethylbenzene and *o*-xylene formed 1,2-dimethyl-4-ethylbenzene (4-ethyl-*o*-xylene) and little diethylbenzene. At 60°, however, all xylenes interacted with ethylbenzene to form benzene and 1,3-dimethyl-5-ethylbenzene. The inactivity of *p*-xylene at 20–25° was attributed to the steric blocking of all alkylation positions, that of *m*-xylene at 20–25° to its existence in the reaction medium principally as a cation.

The reaction paths by which each of the xylenes and ethylbenzene interacts to yield 1,3-dimethyl-5-ethylbenzene have now been studied. Mixtures of ethylbenzene and each of the xylenes were allowed to react, and the composition of the reaction mixture was determined at five different stages of completion. The data show how the basicity, structure and reactivity of the different xylenes affect the reaction paths by which each interacts with ethylbenzene to form 1,3-dimethyl-5-ethylbenzene.

(1) D. A. McCaulay, M. C. Hoff, Norman Stein, A. S. Couper and A. P. Lien, THIS JOURNAL, **79**, 5808 (1957).

Experimental

The alkylbenzenes used were at least 99.7% pure. Ethylbenzene, *o*-xylene and *p*-xylene were Phillips Research Grade; *m*-xylene was recrystallized from commercial material. Hydrogen fluoride from Matheson Co. and boron trifluoride from Baker and Adamson were used directly from commercial cylinders.

All runs were carried out in a 250-ml. Hastelloy B Magne-Dash reactor. The aromatic mixture (0.40 mole, about 50 ml.) was charged to the reactor, liquid hydrogen fluoride was metered in from a Jerguson gauge protected with a Kel-F liner, stirring was started, and water at 60° was circulated into the room-temperature bath containing the reactor. When the reactor temperature reached 45°, the boron trifluoride was charged rapidly from a calibrated pressure vessel. The heat of complex formation was just sufficient to raise the reactor temperature almost instantaneously to 60°. After the desired contact time, the product was discharged in 5 to 10 seconds from the bottom of the reactor vessel directly into a 1-liter polyethylene bottle containing crushed ice and water. With this technique reliable runs could be made at contact times as short as two minutes.

Mixtures of individual xylenes (75 mole %) with ethylbenzene (25 mole %) were allowed to react for 2, 5, 15, 30 and 120 minutes at 60° with 10 moles of hydrogen fluoride and 2.5 moles of boron trifluoride per mole of total arene. Pressure was 600 p.s.i. Products were analyzed by precise fractionation and infrared absorption of cuts and blends.

TABLE I

PRODUCT COMPOSITION, MOLE %

	o-Xylene					*m*-Xylene					*p*-Xylene				
Reaction time, minutes	2	5	15	30	120	2	5	15	30	120	2	5	15	30	120
Benzene	22.7	21.9	21.6	22.8	23.2	9.9	12.9	16.1	20.4	21.5	8.3	11.6	13.6	17.9	22.5
Toluene	0.4	0.6	1.1	1.3	2.8	0.2	0.2	0.6	1.2	2.4	0.7	0.8	0.8	0.9	2.5
Ethylbenzene	1.4	2.2	1.0	1.0	0.4	6.1	4.7	4.1	1.2	0.4	10.1	5.7	4.0	2.3	0.8
o-Xylene	9.2	4.7	1.4	0.8	0.5	0.6	0.7	1.3	0.8	0.9	0.5	0.8	0.9	0.8	0.7
m-Xylene	42.6	47.7	51.7	49.8	47.2	72.1	66.2	60.7	53.8	50.5	65.6	67.0	64.9	58.8	49.0
p-Xylene	0.3	0.4	0.8	0.6	0.5	1.1	1.3	1.1	1.0	0.9	6.4	1.9	1.0	0.7	0.8
1,3,5-Trimethylbenzene	.2	.1	.6	.4	2.5	..	1.1	0.1	0.8	1.7	0.1	0.2	0.8	.8	1.1
1,2,4-Trimethylbenzene	.6	.5	.7	.6	0.1	..	..	..	.3	0.1	..	0.4	0.4	..	0.2
1,3-Diethylbenzene	.7	.6	.9	.1	0.5	6.6	5.3	2.5	.1	..	7.3	7.8	4.4	2.1	..
1,3-Dimethyl-5-ethylbenzene (5-ethyl-*m*-xylene)	6.2	10.0	18.6	22.3	23.0	2.8	6.6	12.4	20.0	21.5	1.0	3.2	8.2	14.5	21.6
1,2-Dimethyl-4-ethylbenzene (4-ethyl-*o*-xylene)	13.8	10.1	1.5	0.3	0.1	0.6	1.0	1.0	0.4	0.1	..	0.6	1.0	0.8	0.7
1,2-Dimethyl-3-ethylbenzene (3-ethyl-*o*-xylene)	1.9	1.2	0.1	..	0.3	..	..	0.1	..	..	..	..	..	0.4	0.1

Discussion of Results

The data from fifteen runs are summarized in Table I. Although the compositions at short con-

tact times differ, compositions at 120 minutes are about the same for all xylenes.

Figure 1 summarizes the behavior of the xylenes. The differences in reactivity observed at 25°[1] are also found at 60°. *o*-Xylene reacts with all available ethyl groups almost instantaneously and the remaining *o*-xylene isomerizes to *m*-xylene. By contrast, *p*-xylene isomerizes rapidly to *m*-xylene, and ethylated products form only slowly. *m*-Xylene also exhibits a slow formation of ethylated products and a very slow isomerization to *o*- and *p*-xylene. Figure 2 shows how the product composition varies with reaction time for each of the three xylene systems.

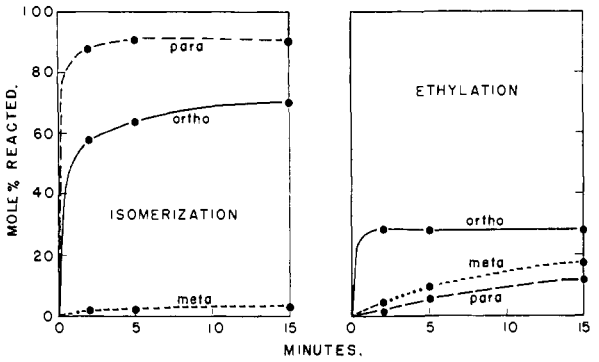


Fig. 1.—Behavior of xylenes.

In the *o*-xylene system, ethylbenzene disappears rapidly with the formation of 4-ethyl-*o*-xylene, 3-ethyl-*o*-xylene, 5-ethyl-*m*-xylene and benzene (not shown). Both ethyl-*o*-xylenes then disappear while 5-ethyl-*m*-xylene continues to form. Only traces of diethylbenzene are formed.

The *m*-xylene system shows a similar but less rapid decrease in ethylbenzene, accompanied by a rapid increase in diethylbenzene, 5-ethyl-*m*-xylene and benzene. Diethylbenzene then disappears as 5-ethyl-*m*-xylene increases. No 2- or 4-ethyl-*m*-xylene was detected.

The *p*-xylene system is much like the *m*-xylene system. Here, a maximum in the rate of formation of 5-ethyl-*m*-xylene seems to occur at the highest concentration of diethylbenzene. No 2-ethyl-*p*-xylene was detected.

Reaction Paths.—Several reaction paths for interaction of ethylbenzene with the xylenes are possible. All involve equilibrium reactions in which the most basic alkylbenzenes—those having a 1,3- or 1,3,5-configuration—are favored.[1]

Under the reaction conditions, ethylbenzene disproportionates rapidly,[2] and either ethylbenzene or diethylbenzene is a possible ethyl group donor. If ethyl group transfer to the xylene—transethylation—takes place before isomerization, each xylene produces a different ethylxylene, which can isomerize to the final product, 5-ethyl-*m*-xylene. However, if isomerization to *m*-xylene takes place before transethylation, all xylenes would have the same reaction path: that of *m*-xylene.

Some insight into the reasons for the differences in behavior of the xylenes can be obtained from the calculations summarized in Table II. These data

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

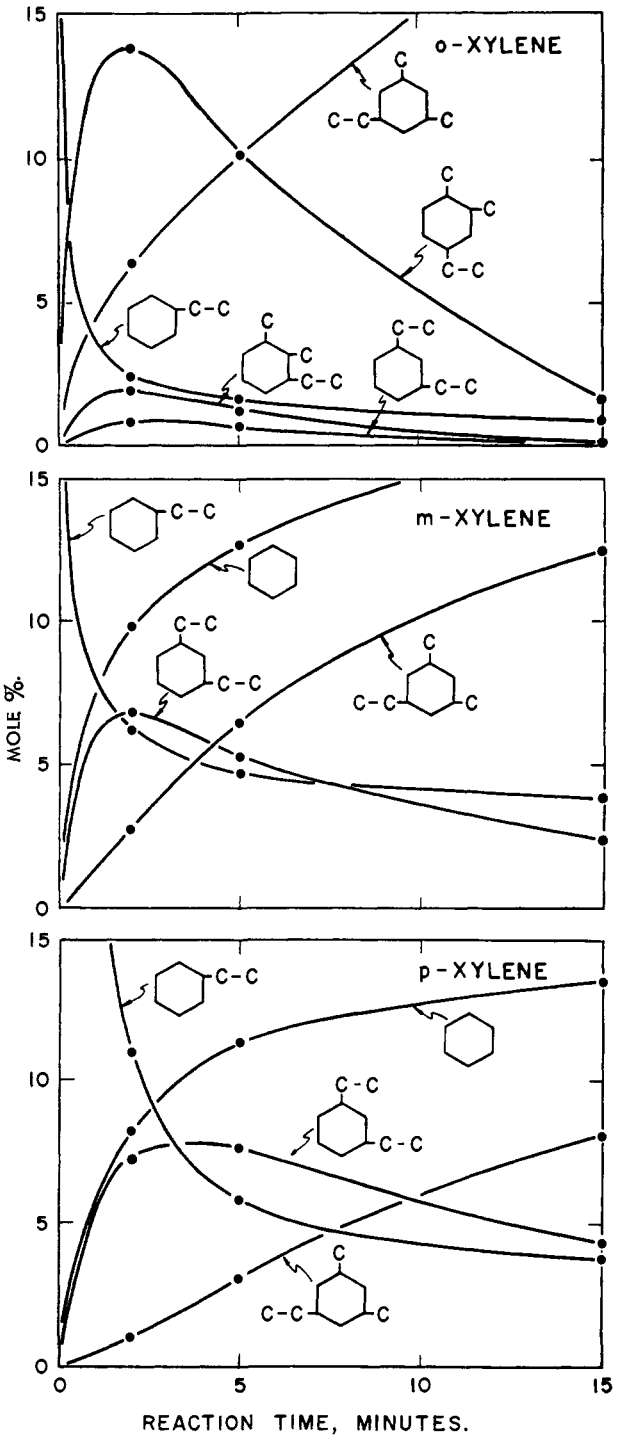


Fig. 2.—Product composition.

show that *p*-xylene isomerizes about five times as fast as *o*-xylene; it is transethylated about one-fourth as fast as *m*-xylene and one-sixteenth as fast as *o*-xylene. However, because transethylation involves transfer of an ethyl group from an ethyl- or diethylbenzene cation, only uncomplexed xylene can accept ethyl groups. An approximation of the initial transethylation rates for each xylene isomer in an HF–BF_3 system would then be the product of the relative transethylation rate and the relative con-

centration of uncomplexed xylene: *ortho* = 40, *meta* = 1 and *para* = 5. On this basis, *m*-xylene, normally the most reactive xylene isomer, is less reactive under these conditions than *p*-xylene, and both are much less reactive than *o*-xylene. Comparison of *m*- and *p*-xylene ethylation rates is made difficult by the rapid isomerization of *p*-xylene.

TABLE II

RELATIVE REACTIVITY OF XYLENES

	ortho	*meta*	*para*
Relative isomerization rate[a]	1	..	5
Relative concentration of uncomplexed xylene[b]	10	1	20
Relative transethylation rate[c]			
2-Position	...	0.01	0.24
3-Position	0.12	..	...
4-Position	3.98	0.37	...
5-Position	...	0.62	...
Total	4.10	1.0	0.24

[a] See D. A. McCaulay and A. P. Lien, THIS JOURNAL, **74**, 6246 (1952). [b] See D. A. McCaulay, B. H. Shoemaker and A. P. Lien, *Ind. Eng. Chem.*, **42**, 2103 (1950). [c] Based on a total rate of unity for *m*-xylene and the assumption that rates for transethylation are similar to those found for transmethylation in work as yet unpublished.

In the reaction of *o*-xylene with ethylbenzene, the rapid formation of 4-ethyl-*o*-xylene shows that *o*-xylene accepts ethyl groups faster than it isomerizes. At 2 and 5 minutes, when sufficient quantities are present for accurate measurement, the ratio of 3-ethyl-*o*-xylene to 4-ethyl-*o*-xylene is 1:7, substantially larger than calculated ratio of 1:33. The observed ratio probably is not formed directly but results from rapid isomerization of 4-ethyl-*o*-xylene. In Fig. 3, plots of the log of the

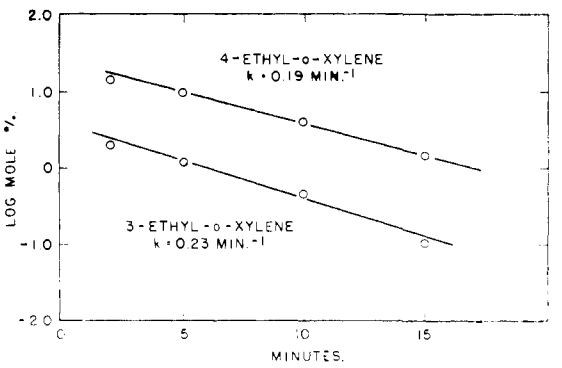
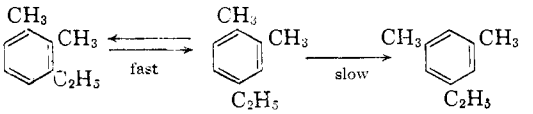


Fig. 3.—Disappearance of ethyl-*o*-xylenes; $-d(EX)/dt = k(EX)$.

concentration against time show a constant ratio of 3- to 4-ethyl-*o*-xylene as both disappear. The ratio is constant because ethyl group migration is much faster than the methyl-group migration necessary to form 5-ethyl-*m*-xylene



3-ethyl-*o*-xylene 4-ethyl-*o*-xylene 5-ethyl-*m*-xylene

Because transethylation is undoubtedly slower than ethyl group isomerization,[3] the equilibrium ratio of isomers, 1:7, appears as the product.

With *m*-xylene, isomerization to *o*-xylene and *p*-xylene is negligible. Relative transalkylation rates indicate that about equal amounts of the 4- and 5-ethyl-*m*-xylene should form, but no 4-ethyl-*m*-xylene is detected. The absence of this compound is attributed entirely to the extreme mobility of the ethyl group,[2] which results in rapid isomerization to the stabilized 5-ethyl-*m*-xylene.

With *p*-xylene, the only product resulting from direct transethylation, 2-ethyl-*p*-xylene, is not detected. Initial formation followed by rapid isomerization to 5-ethyl-*m*-xylene is not a tenable explanation because 2-ethyl-*p*-xylene should isomerize no faster than 4-ethyl-*o*-xylene,[4] which is found in substantial quantity in the reaction of ethylbenzene with *o*-xylene. Because of a slow transethylation rate and a rapid isomerization rate, all of the *p*-xylene reacts by first isomerizing to *m*-xylene.

In the *m*- and *p*-xylene systems, ethylbenzene disproportionates rapidly to yield *m*-diethylbenzene. The equilibrium constant for this disproportionation reaction is[2]

$$K = \frac{[\text{benzene}][\text{diethylbenzene}]}{[\text{ethylbenzene}]^2} = 89$$

Values for the equilibrium constant calculated from the runs made with *m*-xylene and *p*-xylene are

Minutes	2	5	10	15	20	25
m-Xylene	1.9	3.1	2.8	2.9	3.0	3.5
p-Xylene	0.6	2.8	3.4	4.1	4.4	6.2

These values are small compared with 89 and indicate that diethylbenzene is disappearing as fast as it is being formed. They suggest that transethylation takes place through diethylbenzene rather than directly from ethylbenzene. If the reaction took place through ethylbenzene, *K*-values of 89 or higher should be obtained after 2 to 3 minutes, when the diethylbenzene concentration reaches maximum.

Also, if the reaction took place mostly through ethylbenzene, then the rate of formation of 5-ethyl-*m*-xylene would be highest at time zero, when the concentration of ethylbenzene is highest. If diethylbenzene is the transalkylating agent, the rate of formation of 5-ethyl-*m*-xylene will be maximum at the peak diethylbenzene concentration. Under the conditions of the present study, reaction is too fast to establish this point firmly, although the maximum rate of formation of 5-ethyl-*m*-xylene from *p*-xylene appears to coincide with maximum diethylbenzene concentration.

That *m*-diethylbenzene is the ethyl group donor can be reasoned independently. The transfer of an ethyl group from ethylbenzene to *m*-xylene would require the close approach of an ethylbenzene cation to *m*-xylene. Inasmuch as *m*-xylene is 2000 times more basic than ethylbenzene, proton transfer appears much more probable than much slower

(3) D. A. McCaulay and A. P. Lien, THIS JOURNAL, **74**, 6246 (1952).

(4) Isomerization to 5-ethyl-*m*-xylene should proceed at the same rate, because both isomers require the shift of a methyl group that is *ortho-para* activated by a methyl group and an ethyl group.

alkyl group transfer. *m*-Diethylbenzene by contrast is of about the same basicity as *m*-xylene, can compete favorably with *m*-xylene for protons and should thus be able to transfer an ethyl group to the *m*-xylene ring.

WHITING, IND.

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF NEW MEXICO]

The Synthesis of 7-Methyl-, 10-Methyl-, 6,7-Dimethyl- and 7,10-Dimethyl-3,4-benzpyrenes[1,2]

BY JOSEPH L. COMP[3] AND GUIDO H. DAUB

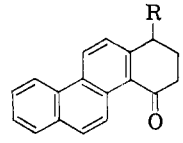
RECEIVED JUNE 25, 1958

The Reformatsky reaction of 4-keto-1,2,3,4-tetrahydrochrysene (III) with ethyl α-bromopropionate followed by dehydration, hydrolysis and reduction of the Reformatsky product afforded α-(1,2,3,4-tetrahydro-4-chrysenyl)-propionic acid (V) which was cyclized to 6-keto-7-methyl-6,7,7a,8,9,10-hexahydro-3,4-benzpyrene (VI). Reduction, dehydration and dehydrogenation of VI afforded 7-methyl-3,4-benzpyrene (10% over-all yield from phenanthrene). The reaction of methylmagnesium iodide with VI followed by dehydration and dehydrogenation gave 6,7-dimethyl-3,4-benzpyrene (VIII) (6% over-all yield from phenanthrene). 2-Acetylphenanthrene, prepared in two steps from 9,10-dihydrophenanthrene, underwent the Stobbe condensation with diethyl succinate in the presence of sodium hydride to give a mixture of half-esters. The half-ester mixture was decarbethoxylated and reduced to γ-(2-phenanthryl)-valeric acid (X), which was cyclized to 4-keto-1-methyl-1,2,3,4-tetrahydrochrysene (XI). The Reformatsky reaction of XI with ethyl bromoacetate, followed by dehydration, hydrolysis and reduction of the hydroxy-ester thus produced, gave 1-methyl-1,2,3,4-tetrahydro-4-chrysenylacetic acid (XIII). The acid XIII was cyclized with anhydrous hydrogen fluoride to 6-keto-10-methyl-6,7,7a,-8,9,10-hexahydro-3,4-benzpyrene (XIV) and this ketone upon reduction followed by dehydration and dehydrogenation afforded 10-methyl-3,4-benzpyrene (XV) (4% over-all yield from phenanthrene). The Reformatsky reaction of XI with ethyl α-bromopropionate, followed by dehydration, hydrolysis and reduction, gave α-(1-methyl-1,2,3,4-tetrahydro-4-chrysenyl)-propionic acid (XVII). Cyclization of XVII with anhydrous hydrogen fluoride gave 6-keto-7,10-dimethyl-6,7,7a,-8,9,10-hexahydro-3,4-benzpyrene (XVIII), which upon reduction and dehydrogenation was converted to 7,10-dimethyl-3,4-benzpyrene (XIX) (6% over-all yield from phenanthrene). These hydrocarbons are being evaluated for carcinogenic activity at Northwestern University Medical School, Evanston, Ill.

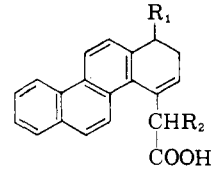
We wish to report new syntheses of the 7-[4] and 10-[5] monomethyl-3,4-benzpyrenes as well as the synthesis of two new dimethyl-3,4-benzpyrenes, namely, the 6,7- and 7,10-dimethyl derivatives.[6]

The Friedel–Crafts acylation of 9,10-dihydrophenanthrene[7] with succinic anhydride in nitrobenzene[8] gave a 98% yield of β-(9,10-dihydro-2-phenanthroyl)-propionic acid (I). Reduction of I by either the Clemmensen method[9] or Wolff–Kishner method[10] afforded γ-(9,10-dihydro-2-phenanthryl)-butyric acid (II) in 84 and 97% yields, respectively. The acid II was converted to 4-keto-1,2,3,4-tetrahydrochrysene (III) in four steps as described by Bachmann and Struve.[9]

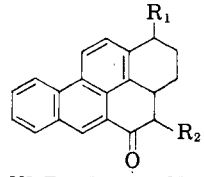
The Reformatsky reaction of the chrysenone III with ethyl α-bromopropionate produced an intermediate hydroxy-ester, which was dehydrated and hydrolyzed to give an 81.5% yield of a mixture of isomeric chrysenyl-propionic acids from which a 33% yield of one isomer, probably α-(1,2-dihydro-4-chrysenyl)-propionic acid (IV), was obtained by crystallization from methanol. Hydrogenation of IV over Adams catalyst gave a 75.5% yield of α-(1,2,3,4-tetrahydro-4-chrysenyl)-propionic acid (V), which was cyclized with anhydrous hydrogen fluoride to give a quantitative yield of 6-keto-7-methyl-6,7,7a,8,9,10-hexahydro-3,4-benzpyrene (VI) as an oily mixture of isomers



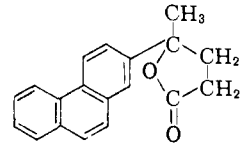
III, R = H
XI, R = CH_3



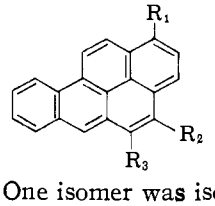
IV, R_1 = H, R_2 = CH_3
XII, R_1 = CH_3, R_2 = H
XVI, R_1 = R_2 = CH_3



VI, R_1 = H, R_2 = CH_3
XIV, R_1 = CH_3, R_2 = H
XVIII, R_1 = R_2 = CH_3



IX



VII, R_1 = R_3 = H, R_2 = CH_3
VIII, R_1 = H, R_2 = R_3 = CH_3
XV, R_1 = CH_3, R_2 = R_3 = H
XIX, R_1 = R_2 = CH_3, R_3 = H

One isomer was isolated from this mixture in 52% yield. The Meerwein–Ponndorf–Verley reduction of VI, with subsequent dehydration and dehydro-

(1) From the dissertation presented by Joseph L. Comp to the graduate faculty of the University of New Mexico in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) This investigation was supported in part by a research grant (C-1595) from the National Cancer Institute of the National Institutes of Health, U. S. Public Health Service.

(3) Graduate Research Assistant, February, 1952, to February, 1956.

(4) D. D. Phillips and D. N. Chatterjee, THIS JOURNAL, **80**, 4360 (1958).

(5) J. L. Adelfang and G. H. Daub, *ibid.*, **77**, 3297 (1955).

(6) For reference to previous papers in this series see W. C. Doyle and G. H. Daub, *ibid.*, **80**, 5252 (1958).

(7) D. D. Phillips, *Org. Syntheses*, **34**, 31 (1954).

(8) A. Burger and E. Mosettig, THIS JOURNAL, **59**, 1302 (1937).

(9) W. E. Bachmann and W. S. Struve, *J. Org. Chem.*, **4**, 456 (1939).

(10) D. D. Phillips, THIS JOURNAL, **75**, 3223 (1953).