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A NOVEL ROUTE TO STILBENE. CATALYTIC OXIDATIVE DEHYDRODIMERIZATION OF TOLUENE.

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Much attention has hitherto given to the generation of stilbene because of its synthetic value in the manufacture of dyestuffs, pharmaceuticals, and organic intermediates. Sometime ago, Y. Fujiwara, I. Moritani, M. Matsuda, and S. Teranishi[1], and R. S. Shue[2] reported the synthesis of stilbene from the olefin arylation of benzene with styrene in the presene of palladium(II) compounds; and P. B. Venuto and P. S. Landis[3], from the reaction of benzyl-type mercaptans over zeolites. In this communication, however, a simple synthetic method of stilbene from the catalytic oxidation of toluene is provided.

The reaction was carried out in a conventional flow system under atmospheric pressure. Catalyst used was Bi_2O_3-SnO_2 (Bi/Sn=1 atom/atom) activated in the stream of air at 700°C for 6 hours. Toluene was passed over the catalyst-bed with O_2 using N_2 as a diluent. The products were analyzed by gas chromatography. IR and mass spectrometry were also used for identification in some cases. The main products found were stilbene, bibenzyl, benzene, and CO_2. Very small amounts of phenanthrene, benzoic acid, benzaldehyde, and biphenyl were also observed.

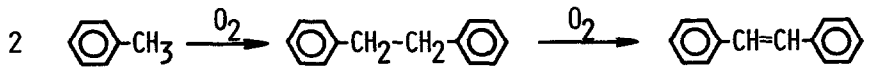
Data given in Table 1 were typical results obtained in which the catalyst used was 3 grams and the contact time was 15 g-cat. hr/mole. As shown in Table 1, the complete combustion of toluene to CO_2 was controlled by varying the

TABLE 1. TYPICAL RESULTS

Reaction Temperature, °C	385	445	505	555	555	450
Feed Composition, molar ratio N_2 : O_2 : Toluene	3:3:4	3:3:4	3:3:4	3:3:4	3:2:4	3:3:2.5
Toluene Conversion, mole %	4	15	16	18	14.5	18
Product Distribution, mole %						
Stilbene[4]	42	24	25	23	27	19
Bibenzyl	10	9	11	14	13	8
Benzene	32	20	20	19	25	15
Carbon dioxide	9	43	41	40	31	53
Others[5]	7	4	3	4	4	5

reaction conditions, *e. g.*, lowering the reaction temperature to about 400°C, or reducing the oxygen content in feed, and by doing so, stilbene was produced in a higher selectivity.

Based on the limited data available from the present study, the oxidative dehydrodimerization pathway seems reasonable for the formation of stilbene with bibenzyl.



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4. The cis-isomer was included.
5. Phenanthrene, benzoic acid, benzaldehyde, and biphenyl were included.