Alkylation of Benzene with 8-Methyl-1-nonene. V. Effect of the Catalyst on the Isomerization of Secondary Carbonium Ions

HUSNI R. ALUL* AND GILBERT J. MCEWAN

Research and Development Department, Monsanto Industrial Chemicals Company, St. Louis, Missouri 63166

Received February 25, 1972

8-Methyl-1-nonene alkylates benzene in the presence of Friedel–Crafts catalysts to afford various amounts of secondary and tertiary alkylbenzenes. With $AlCl_2 \cdot HSO_4$ the positive charge barely reaches the tertiary position which is eight carbon atoms away from the double bond. However, with HF and *n*-hexane the tertiary isomer accounts for more than 70% of the product alkylbenzene. Other alkylation catalysts afford results that lie between these two extremes. Very strong catalysts such as $AlCl_3 \cdot HCl$ interfere in the results by isomerizing the secondary alkylbenzenes and dealkylating the tertiary isomer. The presence of a methyl group on the alkyl chain changes the general pattern of the chromatogram of the product alkylbenzenes.

Alkylation of benzene with a long-chain olefin such as 1-dodecene in the presence of Friedel–Crafts catalysts affords all the possible phenylalkanes except the 1-phenyl isomer.[1,2] The mechanism of the reaction and the relative rates of isomerization and alkylation of the intermediate carbonium ions have been discussed in a number of publications and need not be repeated here.[1–5] The extent of the isomerization reaction depends on the experimental conditions such as choice of the catalyst, solvent, and temperature of the reaction.[4,5] This raises the interesting question as to how far down the chain does the positive charge reach before the attack on benzene takes place. Such a question cannot be answered from the alkylation of benzene with an α olefin such as 1-dodecene since an isomer such as 2-phenyldodecane can be produced from either the second or eleventh carbon atom. On the other hand, an olefin such as 8-methyl-1-nonene (**1**) permits the determination of the precursor of each phenylalkane.

Results and Discussion

The synthesis of **1** was carried out by standard reactions and the details are given in Experimental Section. Benzene was alkylated with **1** in the presence of various catalysts under conditions which do not permit product isomerization and the products were analyzed by gas–liquid chromatography (Figures 1a and 1b). Selected peaks of the chromatogram were identified by the use of authentic samples of methyl-substituted phenylnonanes. The 2-methyl-2-phenylnonane was obtained by alkylation of benzene with 2-methyl-1-nonene,[6] and the 2-methyl-3-phenyl, 2-methyl-4-phenyl, and 2-methyl-5-phenyl isomers were obtained by the Grignard reactions of the corresponding alkyl bromides and ketones. The resulting alcohols were dehydrated with $KHSO_4$ and the alkenes were hydrogenated in the presence of 10% palladium on charcoal. All the samples were distilled in a ten-plate column, and all showed a purity of 95% or better by glc. The other peaks were readily identified from their position in the chromatogram in a manner similar to that of straight-chain alkylbenzenes.[1,2,4]

Table I lists the amounts of the various isomers obtained. As in the reaction of benzene with 1-dodecene, HF–*n*-hexane permitted extensive isomerization of the secondary cations to the tertiary prior to alkylation. On the other hand, $AlCl_2 \cdot HSO_4$ led to relatively slower isomerization, much less 2-phenyl derivative (9.7%) and a significant rise in the amount of the 8 isomer (61.3%). This result parallels our experience with 1-dodecene and *trans*-6-dodecene, where in the presence of HF–*n*-hexane the alkylation step is sufficiently slow to permit the intermediate carbonium ions to attain the equilibrium conditions thus rendering the position of the double bond in the olefin immaterial.[4]

In the absence of *n*-hexane, *i.e.*, in the presence of HF alone, the rate of the alkylation reaction is increased relative to the isomerization reaction and the amount of the tertiary isomer decreases from 71.0 to 56.5%. The smallest amount of 2-methyl-2-phenylnonane produced in the absence of product isomerization is obtained with $AlCl_2 \cdot HSO_4$ where, in contrast to the HF–*n*-hexane system, only 9.7% is obtained (Figure 1b). This small amount of the tertiary alkylbenzene is accompanied by a significant rise in the amount of the 8 isomer (61.3%). Apparently the presence of a large anion in the ion pair slows down the isomerization reaction and permits the alkylation reaction to compete more effectively.[5,7]

Alkylation in the presence of $AlCl_3 \cdot HCl$ at 35° results in the smallest amount of the tertiary isomer. However, this is not because the charge fails to reach the end of the chain, but rather because of the vulnerability of the tertiary alkylbenzene to attack by the strong catalyst $AlCl_3 \cdot HCl$ which results in dealkylation of the product. Under these conditions the yield of alkylbenzene drops to 30%, and the reaction is accompanied by the formation of substantial amounts of isoparaffins. Under the same conditions an authentic sample of 2-methyl-2-phenylnonane suffered extensive dealkylation and even isomerization to the secondary alkylbenzenes. When the alkylation reaction is carried out at 0° and in the presence of recycled aluminum chloride, which is known to be weakened by the presence of strong organic bases,[8,9] dealkylation is suppressed, the amount of the tertiary isomer increases to 22.9%, and the yield of alkylbenzene rises to 80%. Attenuation of $AlCl_3$ with nitromethane

---

[1] A. C. Olson, *Ind. Eng. Chem.*, **52**, 833 (1960).

[2] R. D. Swisher, F. E. Kaelble, and S. K. Liu, *J. Org. Chem.*, **26**, 4066 (1961).

[3] S. N. Patinkin and B. S. Friedman in "Friedel–Crafts and Related Reactions," Vol. II, G. Olah, Ed., Interscience, New York, N. Y., 1964, Chapter 14, p 3.

[4] H. R. Alul and G. J. McEwan, *J. Org. Chem.*, **32**, 3365 (1967).

[5] H. R. Alul, *ibid.*, **33**, 1522 (1968).

[6] J. R. Nooi, J. J. Muller, M. C. Testa, and S. Willemse, *Recl. Trav. Chim. Pays-Bas*, **88**, 398 (1969).

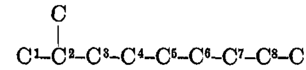
[7] H. R. Alul and G. J. McEwan, unpublished work.

[8] G. A. Olah and M. W. Meyer, ref 3, Vol. I, p 736.

[9] N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 141 (1964).

TABLE I

GLC ANALYSIS OF 2-METHYL-*n*-PHENYLNONANE



$$C^1-\overset{\displaystyle C\,|}{C^2}-C^3-C^4-C^5-C^6-C^7-C^8-C^9$$

Reaction	Catalyst	Temp, °C	Yield, %	2-Phenyl[c]	3-Phenyl[c]	4-Phenyl[c]	5-Phenyl[c]	6-Phenyl[c]	7-Phenyl[c]	8-Phenyl[c]
1	HF	0–5	88	56.5	0.8	2.9	8.9	6.5	8.9	15.5
2	HF + *n*-hexane	0–5	86	71.0	0.5	2.1	6.9	4.6	5.8	9.1
3	HF[a]	55	86	30.7	0.6	1.9	8.1	8.0	15.7	35.0
4	$AlCl_2 \cdot HSO_4$	35–40	75	9.7	0.1	0.8	4.3	5.1	18.7	61.3
5	$AlCl_3 \cdot CH_3NO_2$	35–40	75	24.8	0.5	1.8	8.6	8.3	16.7	39.3
6	$AlCl_3 \cdot HCl$	35–40	30	3.2	1.2	8.6	11.7	12.7	21.2	41.4
7	$AlCl_3 \cdot HCl$[b]	0–5	80	22.9	0.5	1.6	8.0	8.1	17.1	41.8

[a] Reaction was carried out in the absence of a liquid catalyst phase to minimize isomerization under these conditions.[5] [b] Recycled aluminum chloride was used in this experiment to prevent product isomerization or dealkylation.[4] [c] Registry no.: 2-phenyl, 36614-69-4; 3-phenyl, 36614-70-7; 4-phenyl, 36614-71-8; 5-phenyl, 36614-72-9; 6-phenyl, 36614-73-0; 7-phenyl, 36614-74-1; 8-phenyl, 36614-75-2.

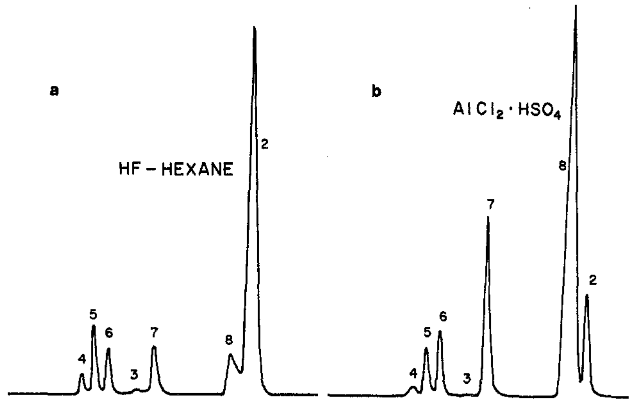


Figure 1.—Gas–liquid chromatograms for methylphenyldodecanes obtained from alkylation of benzene with 8-methyl-1-nonene in the presence of (a) HF–hexane and (b) $AlCl_2 \cdot HSO_4$.

also suppresses the dealkylation reaction and leaves the tertiary alkylbenzene intact. It is interesting to note that the amount of the 8-phenyl isomer is greater than that of the 7 isomer in spite of the fact that the positive charge is allowed to reach the other end of the chain. This indicates that the 8-carbonium ion, located near the end of the chain, reacts more rapidly with benzene than the other secondary carbonium ions and is in accord with the behavior of the dodecenes where the amount of 2-phenyldodecane is greater than that of the 3 isomer even from *trans*-6-dodecene where the positive charge is introduced near the center of the chain.[5] This is also in agreement with Nenitzescu's observation that some of the carbonium ions may react with benzene without undergoing rearrangement.[10]

An interesting feature of the isomer distributions reported in Table I is the sharp drop in the amount of the 4 and 3 isomers compared to the 5 isomer and other secondary alkylbenzenes and the subsequent rise in the amount of the tertiary alkylbenzene. Except for the case with $AlCl_3 \cdot HCl$, which involves product isomerization, the amount of the 3 isomer is below 1% of the total alkylbenzene obtained. This can also be seen from Figures 1a and 1b. Apparently the rate of the alkylation reaction from the corresponding carbonium ion is slow due to the presence of an isopropyl group next to the carbon atom carrying the positive charge. This steric factor is probably responsible for the absence of secondary alkylbenzene from the alkylation of benzene with 3-methyl-1-butene.[11] The failure of the secondary isomer to form is not only due to the great speed with which the secondary carbonium ion isomerizes to the tertiary but also to the fact that the alkylation reaction is greatly slowed down by the adjacent isopropyl group. It is quite probable that addition of only one or two more carbon atoms to the chain would result in some secondary alkylbenzene from the carbon atoms other than the one next to the isopropyl group. This conclusion is in agreement with the results of Geiseler, *et al.*, on the alkylation of benzene with 1-heptene in which they find the isomerization of the double bond to be only about six times faster than the alkylation reaction.[12]

As noted above alkylation with $AlCl_2 \cdot HSO_4$ produces the smallest amount of 2-methyl-2-phenylnonane. In fact, by the time the positive charge migrates from the C-8 to the C-5 atoms nearly 90% of the carbonium ions react with benzene. Had the methyl group on the chain not interfered with the alkylation rates of the carbonium ions from the C-3 and C-4 atoms, it is probable that these two positions would be the extent to which the positive charge reaches in alkylations with $AlCl_2 \cdot HSO_4$. In other words the charge migrates about five carbon atoms with this catalyst. On the other hand, alkylation with the HF–hexane system, which affords 71.0% of the tertiary alkylbenzene, obviously permits the charge to migrate much farther down the chain in the absence of a methyl group.

Experimental Section

Synthesis of 8-Methyl-1-nonene.—The reaction between a Grignard solution prepared from 2 mol of isoamyl bromide and 2.1 mol of ethylene oxide was carried out as described by Dreger.[13] The product, isoheptyl alcohol, distilled at 99–103° (45 mm) (lit.[14] 98–101° (45 mm), yield 58% of theoretical.

The product was converted into the bromide by reaction with hydrobromic and sulfuric acids as described by Kamm and Mar-

---

[10] C. D. Nenitzescu, *Rev. Roum. Chim.*, **9**, 5 (1964).

[11] V. N. Ipatieff, H. Pines, and L. Schmerling, *J. Amer. Chem. Soc.*, **60**, 353 (1938).

[12] G. Geiseler, P. Hermann, and G. Kürzel, *Chem. Ber.*, **98**, 1695 (1965).

[13] E. E. Dreger, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1941, p 306.

[14] J. Cason, *J. Amer. Chem. Soc.*, **64**, 1109 (1942).

vel.[15] The isoheptyl bromide[16] was obtained in 90% yield and distilled at 84–85° (45 mm) [lit.[14] 83° (45 mm)].

The Grignard reagent from 1 mol of isoheptyl bromide was prepared and treated with allyl bromide according to the directions of Vogel.[17] The product, 8-methyl-1-nonene, was distilled in a ten-plate column at 170–171°. No impurities could be detected in the product by glpc analysis. *Anal.* Calcd for $C_{10}H_{20}$: C, 85.63; H, 14.37. Found: C, 85.36; H, 14.41.

Alkylation of Benzene with 8-Methyl-1-nonene.—All the alkylation reactions have been described previously.[4,5] The crude akylbenzenes were analyzed by glpc before distillation to avoid any discrepancy due to the fact that the internal alkylbenzenes tend to have slightly lower boiling points than the ones near the end of the chain. The chromatograph used was an F & M Model 810 equipped with a recorder and an Infotronics digital readout system. The stainless steel column was 200 ft × 0.01 in. and was coated with OV7.[18] The crude products were then distilled in a ten-plate column, and the fraction boiling at 100–108° (2 mm) ($n^{25}D$ 1.4810) was collected. The yields and isomer distributions appear in the table.

Registry No.—**1,** 26741-24-2; benzene, 71-43-2.

---

[15] O. Kamm and C. S. Marvel, ref 13, p 30.

[16] A recent investigation of the reaction of alcohols with hydrobromic acid showed that primary alcohols do not undergo isomerization during the reaction: W. Gerrard and H. R. Hudson, *J. Chem. Soc.*, 2310 (1964).

[17] I. Vogel, "Practical Organic Chemistry," Wiley, New York, N. Y., 1961, p 240.

[18] This is 20% phenyl-substituted methyl silicone available from Supelco, Inc., Bellefonte, Pa. 16823.

The Base-Catalyzed Condensation of Acetophenone and Isobutyraldehyde. A Reexamination of the Monomeric and Dimeric Adducts

WENDELL L. DILLING,* NANCY B. TEFERTILLER, AND JERRY P. HEESCHEN

E. C. Britton Research and Chemical Physics Research, Dow Interdiscipline Group, The Dow Chemical Company, Midland, Michigan 48640

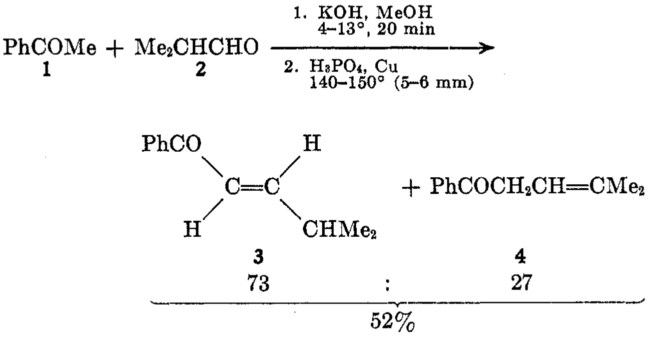
Received May 17, 1972

The base-catalyzed condensation of acetophenone (1) and isobutyraldehyde (2) at 4–13° followed by dehydration at 140–150° with phosphoric acid and copper gave a 73:27 mixture of 1-phenyl-4-methyl-*trans*-2-penten-1-one (3) and 1-phenyl-4-methyl-3-penten-1-one (4). Condensation of 1 and 2 at 55° gave both diastereomers of 3-isopropyl-2-(2-methylpropenyl)-1,5-diphenyl-1,5-pentanedione (5 and 6) and a ~70:30 mixture of 4 and 3. Heating the high-melting diastereomeric dimer 5 with sodium acetate at 170–200° gave a 72:28 mixture of 4 and 3. Attempted equilibration of 3 and 4 with potassium hydroxide in methanol gave rapid conversion of the conjugated isomer 3 to 1-phenyl-3-methoxy-4-methyl-1-pentanone (10) followed by a slower reaction of 3, 4, and probably 10 to give the dimers 5 and 6. This paper clarifies some earlier reports on the products of the base-catalyzed condensation of 1 and 2.

The base-catalyzed condensation of acetophenone (1) and isobutyraldehyde (2) (and dehydration) under a variety of conditions has been reported to give either the α,β-unsaturated ketone **3** (stereochemistry unspecified)[1–5] and/or the dimer **5** (stereochemistry unspecified).[3,6] The dimer **5** on heating with sodium acetate reportedly gave the ketone **3**.[3] During the course of some other work we had need of the ketone **3**, which we set out to prepare by the methods described above. It became apparent very soon after our work was initiated that most of the literature reports of the synthesis of **3** were partially in error. This paper describes our work on the unraveling of the major processes which occur during the reaction of acetophenone (1) and isobutyraldehyde (2) in the presence of base, and on some of the subsequent transformations of the products of these reactions.

Results

The low-temperature base-catalyzed condensation of acetophenone (1) and isobutyraldehyde (2) and subsequent dehydration were carried out according to the procedure of Stanishevskii and Tishchenko.[5] The exact details of part of the process were not reported by these authors. In addition to the reported product **3** (determined to be mainly trans), an appreciable amount of the unconjugated isomer **4** also was obtained (73:27 ratio, 52% yield). A small amount (≤5% of **3**) of the cis isomer **7** of **3** may have been formed (see Experimental Section). The structure proof of both isomers **3** and **4** will be presented below.



The high-temperature condensation of the ketone **1** with the aldehyde **2** was carried out as described by Kulka and coworkers.[3] In addition to the high-melting dimer **5**, another lower melting dimer **6** also was isolated. On the basis of nmr data which are described below, these dimers tentatively have been assigned the diastereomeric structures reported by Anet.[6] After the addition of sodium acetate a small amount of the monomers **3** and **4** could be distilled from the reaction mixture, but the major isomer was the unconjugated one, **4**. Kulka and coworkers[3] reported the isolation of the high-melting dimer in 60% yield and the conjugated monomer **3** in 22% yield.

---

[1] H. Thoms and H. Kahre, *Arch. Pharm.* (*Weinheim*), **263**, 241 (1925).

[2] W. D. Emmons, *J. Amer. Chem. Soc.*, **79**, 5739 (1957).

[3] K. Kulka, R. J. Eiserle, J. A. Rogers, Jr., and F. W. Richter, *J. Org. Chem.*, **25**, 270 (1960).

[4] R. A. Rao and R. R. Rao, *Indian J. Chem.*, **4**, 280 (1966); *Chem. Abstr.*, **65**, 13623 (1966).

[5] L. S. Stanishevskii and I. G. Tishchenko, *Vestsi Akad. Navuk Belarus. SSR, Ser. Khim. Navuk*, 123 (1967); *Chem. Abstr.*, **67**, 32422 (1967).

[6] R. Anet, *J. Org. Chem.*, **26**, 246 (1961).