C-Alkylation of Active Methylene Compounds by Means of Alcohols. VI. A Facile Monoalkylation of Phenylacetonitrile[1]

SEIJI MIYANO* AND NOBUHIRO ABE

Department of Pharmaceutical Sciences, Fukuoka University, Fukuoka, Japan

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Alkylation of phenylacetonitrile by means of aliphatic primary alcohols (from ethyl to decyl and lauryl) and secondary alcohols (isopropyl, *sec*-butyl, and cyclohexyl) in the presence of sodium leads to the corresponding monoalkyl phenylacetonitriles in good to excellent yields. Addition of an equimolar amount of the ester of acetic acid and the alcohol to be used in alkylation is made as a means to decrease or avoid hydrolysis of phenylacetonitrile. A mechanism is proposed. Since the method involves simple manipulation and the use of alcohols as reagents, it can be recommended as a method superior to that previously used.

Preliminary reports[2] from this laboratory revealed that phenylacetonitrile is readily monoalkylated by means of higher boiling aliphatic alcohols (from *n*-heptyl to *n*-decyl and lauryl) and metallic sodium, whereas the conventional method[3] consists in heating under reflux the nitrile and alkyl halide in the presence of sodium amide in an inert solvent.

The research has now been extended to the study of lower molecular weight aliphatic alcohols.

The C-alkylation of active methylene groups by means of an aliphatic alcohol and sodium has been reported in only one case, namely the alkylation of fluorene.[4,5] The application of this procedure to a wide variety of active methylene compounds has failed. The water formed in the reaction causes hydrolysis of the cyano or ester group of the active methylene compounds with consequent loss of reactivity. In the previous communications, benzylation[1] and alkylation[2] of phenylacetonitrile were effected by addition to the reaction mixture of equimolar amounts of various esters, which reacted with the water formed.

With this device to protect the cyano group from hydrolysis, monoalkylation of phenylacetonitrile with a series of aliphatic alcohols has been achieved.

$$C_6H_5CH_2CN + ROH \xrightarrow[\substack{C_6H_5COOCH_3 \text{ (method A)}\\ CH_3COOR \text{ (method B)}}]{Na} C_6H_5\underset{\displaystyle R}{\underset{|}{C}}H{-}CN$$

The reactions were conducted at 210–220° (bath temperature) throughout. With the alcohols higher than *n*-heptyl (bp 176°) alkylation proceeded in good yield (61–74%). Higher temperatures did not result in an appreciable change in yield. On the other hand, the yield of *n*-hexylated phenylacetonitrile dropped to 27% (average of two runs), suggesting that the required reaction temperature is well above the boiling point (157°) of *n*-hexyl alcohol. Consequently, with the low-boiling aliphatic alcohols the use of an autoclave is essential.

The study of the addition of esters to the reaction mixtures in order to control hydrolysis was confined to two, methyl benzoate (method A) and an acetic acid ester involving the alcohol to be used for alkylation (method B). A comparison of the yields by the two methods in the alkylation of phenylacetonitrile by higher boiling alcohols is shown in Table I.

TABLE I[a]

α-ALKYLPHENYLACETONITRILES, $C_6H_5\underset{\displaystyle R}{\underset{|}{C}}HCN$

Compd	R	Bp, °C (mm)[b]	Yield, %[c] (method)	$n^{25}D$[d]
1	*n*-Heptyl[e]	128–130 (1.5)	73.4 (A) 78.3 (B)	1.4939
2	*n*-Octyl[f]	149–151 (2)	74.1 (A) 85.5 (B)	1.4907
3	2-Ethylhexyl[g]	138–140 (2)	61.0 (A) 76.7 (B)	1.4968
4	*n*-Nonyl[h]	157–159 (2)	86.1 (A) 76.6 (B)	1.4901
5	3,5,5-Trimethylhexyl[h]	139–141 (2)	73.2 (A) 80.0 (B)	1.4918
6	*n*-Decyl[h]	169–171 (2)	70.3 (A) 72.8 (B)	1.4882
7	Lauryl[h,i]	184–186 (2)	64.0 (A) 71.9 (B)	

[a] All compounds in Tables I–III gave satisfactory (±0.3) C, H, and N analyses. The data were made available to the Editor and the referees. [b] Boiling points of the redistilled products. [c] Based on phenylacetonitrile. [d] $n^{25}D$ of analytical samples. [e] Bp 139° (1.5 mm), $n^{20}D$ 1.4953: M. Makosza and B. Serafin, *Rocz. Chem.*, **39** (10), 140 (1965). [f] $n^{25}D$ 1.4932: D. Zavoianu and Fl. Cocu, *Rev. Chim. (Bucharest)*, **18** (1), 2 (1967). [g] Bp 175–178° (12 mm): Kali-Chemie A.-G., British Patent 748,064 (1956). [h] New compounds. [i] Mp 25–25.5°, colorless needles (from petroleum ether).

In the alkylation with the higher boiling alcohols that do not require an autoclave, the procedure consists in adding[6] the mixture of phenylacetonitrile and methyl benzoate to the preheated (200–210°) solution of sodium in 3–4 times the equivalent amount of alcohol and then raising the temperature of the mixture to 210–220°.

Method A offers the advantage of the ready availability of methyl benzoate. In three examples, however, *n*-heptylation, *n*-octylation, and 2-ethylhexylation, when equimolar amounts of methyl benzoate and nitrile were employed, some ester interchange occurred that led to the presence of traces of alkyl benzoate produced from the methyl benzoate and the alkylation alcohol. This interchange was detected in an ir analysis of the products[7] (ester carbonyl at 1718–1720 cm^{-1}). If 0.9

(1) Paper V: S. Miyano and N. Abe, *Chem. Pharm. Bull.*, **18**, 550 (1970).

(2) S. Miyano and N. Abe, *ibid.*, **15**, 1811 (1967).

(3) K. Ziegler, *Justus Liebigs Ann. Chem.*, **498**, 84 (1932); F. W. Bergstrom and W. C. Fernelius, *Chem. Rev.*, **12**, 135 (1933); **20**, 451 (1937); A. C. Cope, H. L. Holmes, and H. O. House, *Org. React.*, **9**, 107 (1957); H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965, p 184.

(4) K. L. Shoen and E. I. Becker, *J. Amer. Chem. Soc.*, **77**, 6030 (1955).

(5) D. N. Matthews and E. I. Becker, *J. Org. Chem.*, **21**, 1317 (1956).

(6) Addition should be made dropwise in order to keep a higher ratio of alcohol in the reaction medium and thus avoid a Thorpe type of self-condensation of the phenylacetonitrile.

(7) Usually two distillations resulted in products adequately pure to give correct analytical values.

TABLE II

PREPARATION OF α-ALKYLPHENYLACETONITRILES, $C_6H_5\underset{\displaystyle R}{\underset{|}{C}}HCN$, ACCORDING TO METHOD B

Compd	R	Bp, °C (mm)	Yield, %[a]	$n^{25}D$
8	Ethyl	120–126 (19)	62.5	1.5067[b]
9	*n*-Propyl	132–138 (19)	71.7	1.5029[c]
10	Isopropyl	127–134 (20)	56.6	1.5039[d]
11	*n*-Butyl	138–143 (16)	74.8	1.5003[e]
12	Isobutyl	134–139 (16)	68.0	1.4981[f]
13	*sec*-Butyl	103–105 (2)[g]	38.0	1.5038
14	*n*-Amyl	152–160 (13)[h]	66.5	1.4970[h]
15	Isoamyl	147–152 (18)[i]	72.2	1.4967
16	*n*-hexyl	161–166 (12)[j]	70.1	1.4949
17	Cyclohexyl	137–140 (3)[k]	56.5	

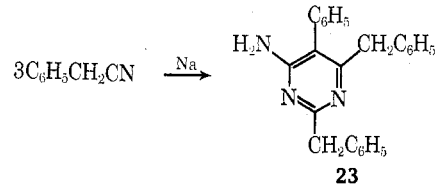
[a] Based on phenylacetonitrile. [b] $n^{25}D$ 1.5070: D. J. Cram and J. Allinger, *J. Amer. Chem. Soc.*, **76**, 4516 (1954). [c] $n^{25}D$ 1.5033: K. Mislow and C. M. Hamermesh, *ibid.*, **77**, 1590 (1955). [d] $n^{25}D$ 1.5032: D. J. Cram, F. A. A. Elhafez, and H. L. Niquist, *ibid.*, **76**, 22 (1954). [e] $n^{25}D$ 1.5003: K. Mislow and C. M. Hamermesh, *ibid.*, **77**, 1590 (1955). [f] $n^{25}D$ 1.4978–1.4985: A. W. Ruddy and T. J. Becker, British Patent 682,261 (1952); *Chem. Abstr.*, **48**, 740 (1954). [g] Bp 130–133° (12 mm): Kali-Chemie A.-G., British Patent 748,064 (1956); *Chem. Abstr.*, **52**, 12913 (1958). [h] Bp 150–152° (20 mm), $n^{25}D$ 1.5007: L. H. Boldinger and J. A. Nieuland, *J. Amer. Chem. Soc.*, **55**, 2851 (1933). [i] Bp 276°: A. Rossolymo, *Ber.*, **22**, 1237 (1889). [j] Bp 327°: A. Rossolymo, *ibid.*, **22**, 1237 (1889). [k] Mp 56–58° (from pentane): E. M. Hancock and A. C. Cope, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 219.

times the equivalent amount of methyl benzoate was employed, no ester carbonyl band appeared in the product. However, the very weak band of an amide carbonyl[8] at 1686 cm^{-1} was present instead. By one distillation this amide is readily removed.

When method B was used, the yields were improved in all examples (Table I) and one distillation of the products served to give pure material that showed in the infrared no ester or amide groups. The advantage of method B over method A is thus obvious in both purity and yield of product.

Method B was used exclusively in alkylation of phenylacetonitrile with low-boiling alcohols (ethyl to *n*-hexyl) in an autoclave. The results are shown in Table II. The only poor yield was in the alkylation with *sec*-butyl alcohol.

Alkylation with methanol, however, failed; 4-amino-2,6-dibenzyl-5-phenylpyrimidine (**23**),[9,10] a cyclic trimer



23

of phenylacetonitrile in 34.8% yield, was the resulting product.

The formation of compound **23** takes place exclusively. This may be due to the fact that methanol does not tend to dehydrogenate to formaldehyde in the presence of sodium under the conditions used. Moreover, methanol and sodium are incapable of reducing the expected unsaturated intermediates, as exemplified by the failure to reduce α-cyclohexylidenephenylacetonitrile with methanol and sodium.

It is noteworthy that secondary alcohols such as isopropyl, *sec*-butyl, and cyclohexyl alcohols are also reactive in this type of alkylation, but the yields are somewhat lower (Table II).

Other nitriles that were alkylated by this procedure are *o*- and *p*-chlorophenyl-, α- and β-naphthyl-, and α-pyridylacetonitriles (Table III). The reaction thus appears to be of quite general application.

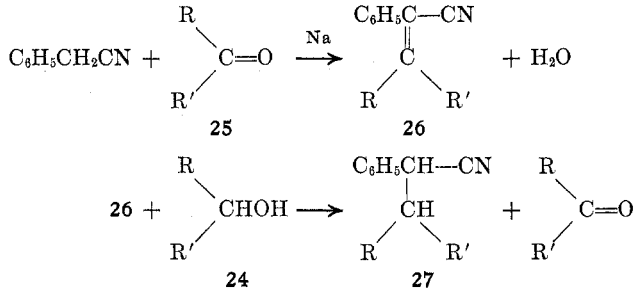
TABLE III

α-OCTYLNITRILE, $NC\underset{\displaystyle R}{\underset{|}{C}}H(CH_2)_7CH_3$

Compd	R	Bp, °C (mm)	Yield, %	$n^{25}D$
18	*o*-Chlorophenyl	157–162 (2)	65.4	1.5031
19	*p*-Chlorophenyl	165–170 (2)	79.7	1.5031
20	α-Naphthyl	200–203 (2)	67.4	1.5489
21	β-Naphthyl	200–205 (2)	85.3	1.5484
22	α-Pyridyl	147–153 (3)	83.5	1.4873

The mechanism of this general reaction is the same as that proposed for the C-benzylation of phenylacetonitrile and involves the two consecutive reactions shown in Scheme I.

SCHEME I



Weizmann and coworkers, in the study of the Guerbet condensation,[11] demonstrated that aliphatic alcohols in the presence of sodium at higher temperatures were dehydrated to aldehydes (**24** → **25**), which underwent the expected condensation with the active methylene compound. Moreover, the alcohols in the presence of sodium at temperatures over 200° are capable of reducing double bonds (**26** → **27**). Our experiments demonstrated that the product from the condensation of phenylacetonitrile and cyclohexanone was readily reduced with cyclohexanol and sodium to α-cyclohexylphenylacetonitrile (**27**). In a one-step reaction at a temperature of 135° only the unsaturated nitrile **26** could be isolated.

The alkylation procedure with higher boiling alcohols (heptyl and higher) consisted in the dropwise addition of a mixture of the phenylacetonitrile and alkyl acetate to a preheated (200–210°) solution of sodium in the appropriate alcohol.

On the other hand, the alkylation with lower boiling alcohols was carried out by heating gradually in an autoclave to 210–220° a mixture of phenylacetonitrile,

(8) The infrared value suggests that the phenylacetonitrile and/or the product was hydrolyzed to amide. However, the contaminant is so small in amount that there is no difficulty in its removal.

(9) E. F. Atkinson and J. F. Thorpe, *J. Chem. Soc.*, **89**, 1915 (1906).

(10) G. A. Reynolds, W. J. Humphlett, F. W. Swamer, and C. R. Hauser, *J. Org. Chem.*, **16**, 165 (1951).

(11) Ch. Weizmann, E. Bergmann, and L. Haskelberg, *Chem. Ind.* (*London*), **56**, 587 (1937).

alkyl acetate, the appropriate alcohol, and sodium. Under these conditions, the condensation of alkyl acetate and phenylacetonitrile probably takes place first to afford α-phenylacetoacetonitrile (**28**) as an intermediate, which then undergoes alcoholysis. This was established by keeping the reaction mixture using cyclohexyl acetate and cyclohexanol at 150–155° and isolating the intermediate compound **28** in 56.5% yield.[12]

$$C_6H_5CH_2CN + CH_3COOR \xrightarrow{Na} C_6H_5\underset{\displaystyle CO\\ \displaystyle CH_3}{\overset{|}{\underset{|}{CHCN}}} + ROH$$

28

The procedure just described has a great advantage over the one previously used in that it employs alcohols in place of halides and sodium in place of sodium amide and gives much more consistent results.

Experimental Section

Commercial aliphatic alcohols were purified by distillation before use. *o*-[13] and *p*-chlorophenyl-,[13] α-[14] and β-naphthyl-,[15] and α-pyridylacetonitriles[16] were prepared according to known methods.

Alkylation of Phenylacetonitrile with the Alcohols (*n*-Heptyl to *n*-Decyl and Lauryl) (Table I, 1–7). Method A.—In a typical example, 3.5 g (0.15 mol) of sodium was added portionwise to 65 g (0.5 mol) of *n*-octyl alcohol and the mixture was heated until all the sodium was in solution. To the preheated solution (200–210°) was added dropwise with stirring a mixture of 17.6 g (0.15 mol) of phenylacetonitrile and 18.4 g (0.135 mol) of methyl benzoate. In less than 5 min methanol started to distil briskly. The temperature was maintained at 210–220°. After the methanol was all distilled off the remaining mixture solidified to a pale-yellow cake. This was heated for an additional 10 min. The cooled mixture was dissolved in water, the oily layer was taken up in ether, and the ethereal extract was washed with water, dried (K_2CO_3), and distilled to give α-*n*-octylphenylacetonitrile: bp 145–150° (2 mm); yield 25.5 g (74.1% based on phenylacetonitrile); ir bands at 2242 (C≡N) and 1686 cm^{-1} ($CONH_2$, weak). The latter band disappeared completely after distillation.

Method B.—The procedure differs from method A merely in the use of the appropriate alkyl acetate in place of methyl benzoate. In a typical example, 17.6 g (0.15 mol) of phenylacetonitrile, 3.5 g (0.15 mol) of sodium, and 75 g (0.65 mol) of *n*-heptyl alcohol in the presence of 23.7 g (0.15 mol) of *n*-heptyl acetate gave 25.3 g (78.3%) of α-*n*-heptylphenylacetonitrile, ir band at 2242 cm^{-1} (C≡N).

α-Alkylphenylacetonitriles (Alkyl Is Ethyl to *n*-Hexyl) (Table II, 8–17).—α-Ethylphenylacetonitrile was prepared following method B. To a refluxing solution of 6.9 g (0.3 mol) of sodium in 80 g (100 ml, 1.74 mol) of absolute ethanol was added dropwise under stirring a mixture of 35.1 g (0.3 mol) of phenylacetonitrile and 26.4 g (0.3 mol) of ethyl acetate. The resulting suspension was placed in an autoclave and heated at 210–220° for 1.5 hr. The contents of the autoclave were filtered to remove crystals that had separated. The filtrate was freed from ethanol and the residue was dissolved in ether and dried (K_2CO_3). Evaporation of the ether followed by vacuum distillation of the residue gave 27.2 g (62.5%) of α-ethylphenylacetonitrile, bp 120–126° (19 mm).

The amounts of alcohols employed for 6.9 g (0.3 mol) of sodium are 100 ml for ethyl, *n*-propyl, and isopropyl alcohols; 120 ml for *n*-butyl, isobutyl, and *sec*-butyl alcohols; 130 ml for *n*-amyl and isoamyl alcohols; and 150 ml for cyclohexyl and *n*-hexyl alcohols. These amounts have been selected on the basis of the solubility of the sodium.

Experiments Supporting the Proposed Mechanism of Formation of Alkylphenylacetonitriles. α-Cyclohexylidenephenylacetonitrile.—To a solution of 2.8 g (0.12 mol) of sodium in 100 g (1 mol) of cyclohexanol was added dropwise a mixture of 14 g (0.12 mol) of phenylacetonitrile, 9.8 g (0.1 mol) of cyclohexanone, and 17 g (0.12 mol) of cyclohexyl acetate. The mixture was heated at 130–135° for 45 min. After cooling, water was added and the resulting oil extracted with ether. The ethereal extract was washed with water, dried (K_2CO_3), concentrated, and distilled to give 17.5 g (88.8%) of α-cyclohexylidenephenylacetonitrile, bp 140–143° (2 mm),[17] $n^{25}D$ 1.5635.

Anal. Calcd for $C_{14}H_{15}N$: C, 85.23; H, 7.66; N, 7.10. Found: C, 85.48; H, 7.59; N, 7.29.

Reduction of α-Cyclohexylidenephenylacetonitrile with Cyclohexanol to α-Cyclohexylphenylacetonitrile.—To a solution of 4.6 g (0.2 mol) of sodium in 100 g (1 mol) of cyclohexanol was added a mixture of 29.6 g (0.15 mol) of α-cyclohexylidenephenylacetonitrile and 28.4 g (0.32 mol) of cyclohexyl acetate. The mixture was heated with stirring in an autoclave at 210–220° for 1.5 hr and worked up as in the preparation of α-alkylphenylacetonitriles. A yield of 24.9 g of α-cyclohexylphenylacetonitrile, bp 135–140° (2 mm), was obtained. After one redistillation it boiled at 137–140° (2 mm) and solidified to colorless needles. The yield was 22.2 g (74%). One recrystallization from pentane gave crystals, mp 56–58°.

***n*-Octylation of *o*-Chlorophenylacetonitrile and Related Nitriles (Table III, 18–22).**—Preparation of α-*n*-octyl-*o*-chlorophenylacetonitrile **18** is illustrative. To a stirred solution of sodium octoxide prepared from 2.3 g (0.1 mol) of sodium and 80 ml of *n*-octyl alcohol was added dropwise a mixture of 15.2 g (0.1 mol) of *o*-chlorophenylacetonitrile and 17.2 g (0.1 mol) of *n*-octyl acetate at 215°. The mixture was stirred for 1.5 hr at the same temperature. After cooling, water was added and the oily layer was extracted with ether. The ethereal solution was dried (K_2CO_3), the ether removed, and the product distilled; 17.3 g (65.4%) of α-*n*-octyl-*o*-chlorophenylacetonitrile resulted.

Attempted Methylation of Phenylacetonitrile.—To a methanolic solution of sodium methoxide prepared from 6.9 g (0.3 mol) of sodium in 100 ml of methanol was added 35.1 g (0.3 mol) of phenylacetonitrile and 22.2 g (0.3 mol) of methyl acetate. The mixture was heated at 210–220° in an autoclave for 1.5 hr. After cooling, the crystalline substance was filtered off, washed with ether, and recrystallized from isopropyl ether to give 4 g of 4-amino-2,6-dibenzyl-5-phenylpyrimidine (**23**) as colorless needles, mp 106–107°.[18] The filtrate combined with washings was freed from solvent, mixed with water, and extracted with ether and the ethereal extract was dried (K_2CO_3). Distillation gave 12.2 g (34.8%) of unreacted phenylacetonitrile.

Attempted Methanol Reductions.—To a solution of 2.3 g (0.1 mol) of sodium in 50 ml of methanol was added a mixture of 19.7 g (0.1 mol) of α-cyclohexylidenephenylacetonitrile and 7.4 g (0.1 mol) of methyl acetate. The resulting mixture was heated with stirring at 210–220° in an autoclave for 1.5 hr. Methanol was distilled off and the residue was extracted with ether. The ethereal extract was dried (K_2CO_3), concentrated, and distilled. Only starting material was obtained.

Separation of Intermediary Phenylacetoacetonitrile 28.—To a solution of 2.8 g (0.12 mol) of sodium in 100 ml of cyclohexanol was added dropwise a mixture of 11.7 g (0.1 mol) of phenylacetonitrile and 17 g (0.12 mol) of cyclohexyl acetate at 150–155° and heated at the same temperature for 1 hr. After cooling, 100 ml of ether was added and the mixture was shaken with three 40-ml portions of water. The combined aqueous layer was cooled in a freezing mixture to −5° and neutralized with acetic acid to afford 9 g (56.5%) of phenylacetoacetonitrile **28**, which after crystallization from methanol gave needles, mp 88.5–89.5°.

Alcoholysis of α-Phenylacetoacetonitrile (28) by Cyclohexanol to α-Cyclohexylphenylacetonitrile (17).—A mixed slurry of 54.3 g (0.3 mol) of α-phenylacetoacetonitrile sodium salt and 150 g

(12) α-Phenylacetoacetonitrile (**28**) is usually prepared by condensation of phenylacetonitrile with ethyl acetate in the presence of sodium ethoxide: P. L. Jurian, J. J. Oliver, R. H. Kimball, A. B. Pike, and G. D. Jefferson, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1957, p 487.

(13) R. von Walther and L. H. Hirschberg, *J. Prakt. Chem.*, [2] **67**, 377 (1903).

(14) L. H. Briggs and J. M. Wilson, *J. Chem. Soc.*, 500 (1941).

(15) M. S. Newmann, *J. Org. Chem.*, **9**, 518 (1944).

(16) K. Winterfield and K. Flick, *Arch. Pharm. (Weinheim)*, **26**, 448 (1956).

(17) Bp 125–131° (0.7 mm): S. Archer and A. W. Rudd, British Patent 674,246 (1956); *Chem. Abstr.*, **47**, 7538 (1953).

(18) Mp 106–107°: ref 7.

(1.5 mol) of cyclohexanol was heated with stirring in an autoclave at 210–220° for 1.5 hr. After cooling, water was added and the oily layer that separated was extracted with ether. The ethereal extract was washed with water and dried (K_2CO_3), the ether was removed, and the residue was distilled; 35.5 g (59.5%) of α-cyclohexylphenylacetonitrile[19] resulted which soon solidified to light-yellow prisms. After two recrystallizations from methanol the product melted at 56–58°.

Registry No.—**1**, 5558-36-1; **2**, 15601-30-6; **3**, 17178-81-3; **4**, 17179-16-7; **5**, 30889-57-7; **6**, 17179-17-8; **7**, 17179-18-9; **8**, 769-68-6; **9**, 5558-78-1; **10**, 5558-29-2; **11**, 3508-98-3; **12**, 5558-31-6; **13**, 5558-32-7; **14**, 5558-33-8; **15**, 5558-34-9; **16**, 5558-35-0; **17**, 3893-23-0; **18**, 21764-73-8; **19**, 21764-74-9; **20**, 21764-71-6; **21**, 30878-93-4; **22**, 21764-72-7; **28**, 4468-48-8; α-cyclohexylidenephenylacetonitrile, 10461-98-0; phenylacetonitrile, 140-29-4.

(19) See footnote *k*, Table II.

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Behavior of Tungsten Hexachloride and Ethylaluminum Dichloride Cocatalyst System in Alkylation and Metathesis Reactions[1]

VIPIN M. KOTHARI* AND JAMES J. TAZUMA

Contribution No. 475 from the Research Division, The Goodyear Tire and Rubber Company, Akron, Ohio 44316

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We have discovered a novel behavior of the WCl_6–$C_2H_5AlCl_2$ when this cocatalyst was preformed in toluene. When this catalyst was treated with 2-pentene, instead of the expected metathesis of 2-pentene, a very rapid Friedel–Crafts alkylation of toluene was encountered. With benzene, the alkylation proceeded at a somewhat slower rate and was accompanied by an even slower 2-pentene metathesis reaction. Thus, in addition to phenylpentane, phenylbutane and phenylhexane were also formed. This is the first observance of metathesis during Friedel–Crafts alkylation. The behavior of the WCl_6–$C_2H_5AlCl_2$ catalyst system with pyridine or triphenylphosphine added as the ligand was also briefly studied. When either was added to the preformed WCl_6–$C_2H_5AlCl_2$, the alkylation was completely inhibited and a slow metathesis of olefin was observed. Alkylation of benzene with 1-dodecene gave the expected isomeric mixture of phenyldodecanes.

The use of WCl_6–$C_2H_5AlCl_2$ or RLi cocatalyst system *in situ* for olefin metathesis, sometimes also designated olefin dismutation or disproportionation, has been investigated by several workers.[2–4] The coordination mechanism for olefin metathesis has been proposed by Kothari[5] in which the reduced tungsten compound is coordinated to two olefin molecules *via* a four-centered "quasicyclobutane" type complex intermediate. This mechanism also applies to the reactions catalyzed by oxides of tungsten, molybdenum, or rhenium and soluble complexes of tungsten and molybdenum.[6,7]

The past investigations on the use of WCl_6–$C_2H_5AlCl_2$ cocatalyst were concerned with the fundamental aspects of the metathesis reaction as applied to linear vinylenic olefins[2,3,7] and the ring-opening polymerization of a variety of cyclo olefins.[8] However, these studies did not disclose the behavior of this catalyst when preformed in aromatic solvents. In toluene, this catalyst promoted a rapid Friedel–Crafts alkylation of toluene, whereas, in the case of benzene, both alkylation and metathesis reactions were observed. This behavior of the preformed catalyst system prompted us to carry out a more detailed investigation.

(1) (a) Presented in part at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970; (b) abstracted in *Chem. Eng. News*, **48**, 39 (1970).

(2) N. Calderon, H. Y. Chen, and K. W. Scott, *Tetrahedron Lett.*, 3327 (1967).

(3) N. Calderon, E. A. Ofstead, J. P. Ward, W. A. Judy, and K. W. Scott, *J. Amer. Chem. Soc.*, **90**, 4133 (1968).

(4) J. Wang and H. R. Menapace, *J. Org. Chem.*, **33**, 3794 (1968).

(5) Reference 4, footnote 6.

(6) C. P. C. Bradshaw, E. J. Howman, and L. Turner, *J. Catal.*, **7**, 269 (1967).

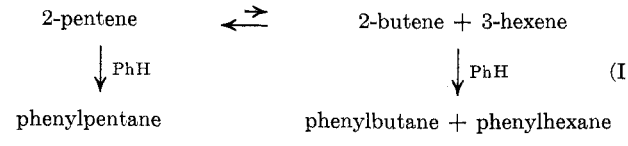
(7) G. C. Bailey, *Catal. Rev.*, **3** (1), 37 (1969), and references cited therein.

(8) N. Calderon, E. A. Ofstead, and W. A. Judy, *J. Polym. Sci., Part A-1*, **5**, 2209 (1967).

Results

Alkylation by 2-Pentene.—When WCl_6–$C_2H_5AlCl_2$ cocatalyst is preformed in toluene and treated with 2-pentene, an almost exclusive and very rapid alkylation of toluene is encountered in contrast to the metathesis of 2-pentene when this cocatalyst is prepared *in situ*. The term *in situ*, as employed in this discussion, pertains to the formation of a cocatalyst in the presence of the olefin. The isomer distribution for pentyltoluenes, based on infrared spectra, is para > ortho > meta. The isomer distribution was determined by comparing their band strengths in 700–800-cm^{-1} region. Due to many inherent differences in Friedel–Crafts catalyst systems, a quantitative comparison between catalysts is difficult. However, the high activity of the WCl_6–$C_2H_5AlCl_2$ case is indicated by the alkylation of nearly 1500 mol of toluene per mole of catalyst after 1 hr at 25°.

We have observed that, when WCl_6–$C_2H_5AlCl_2$ cocatalyst is preformed in benzene and added to a solution of 2-pentene in benzene, a reaction occurs which gives rise to phenylpentane, phenylbutane, and phenylhexane (I). The latter two products which account for about 10% of the products (Table I) are clearly the result of a 2-pentene metathesis reaction (eq I).



(I)

The small amount of these products formed indicates that under these conditions the rate of alkylation is