sulfate was also added until the iodine color had been discharged. The resulting solution was extracted with three 100-ml. portions of ether, and dried over magnesium sulfate. Distillation of the solvents afforded 42.7 g. of the crude iodo compound, VII. Attempted distillation of the crude iodo compound resulted in much decomposition; however, a fairly good boiling sample could be obtained b.p. 106-110° (0.3 mm.).

Hydrogenation of VII to Give (+)-*cis*-3-Methylcyclohexanol.—Crude VII, 39.8 g. (0.165 mole) was dissolved in anhydrous methanol; 48.4 g. (0.35 mole) of potassium carbonate was added to the methanolic solution, and the volume was adjusted to 250 ml. by the addition of methanol. Platinum oxide, 2 g., was added to the mixture, and it was hydrogenated on a Parr low pressure hydrogenation apparatus. The compound absorbed 14.1 pounds of hydrogen (calculated, 14.2 pounds) in 75 minutes. The mixture from the hydrogenation was filtered, and the methanol was distilled through a short column. The cooled residue from the distillation contained a large quantity of potassium iodide. The liquid residue was taken up in ether, and the potassium iodide was washed with three 50-ml. portions of ether. The combined ether washes were dried over magnesium sulfate, and distilled through a short column. The product was distilled through a short column to give two fractions No. 1, b.p. 168-174°, $n^{25}\text{D}$ 1.4580, 7.65 g.; No. 2, b.p. 174-178°, $n^{25}\text{D}$ 1.4587, 1.33 g. Redistillation of these two fractions afforded 7.1 g. of crude (+)-*cis*-3-methylcyclohexanol, b.p. 170-173°, $[\alpha]_{\text{obsd.}}$ +20.91 (homog. in a 1-dm. tube).

The alcohol obtained above was used to prepare derivatives without further purification. The **α-naphthylurethan** after three crystallizations from petroleum ether had m.p. 146.7-147.5° (lit.[12b] 147-148°).

The **3,5-dinitrobenzoate** was prepared, and after 4 crystallizations from 95% ethanol it had m.p. 96.4-97.4° (lit.[12b] 97-98°).

The **phenylurethan** after two crystallizations from petroleum ether had m.p. 116.4-117.2° (lit.[12b] 117-118°).

Further purification of the crude alcohol was carried out by conversion of 6.8 g. to the acid phthalate in the usual manner. After removal of neutral impurities, regeneration of the alcohol by hydrolysis afforded 3.16 g. of (+)-*cis*-3-methylcyclohexanol, b.p. 173-175°, $n^{18}\text{D}$ 1.4620, $\alpha^{18}\text{D}$ +1.76° (homog. in a 1-dm. tube).

Isolation and Properties of 1,3-Endomethyleneoxycyclohexane.—During the distillation of the (+)-*cis*-3-methylcyclohexanol, a fairly large quantity of solid material came over as a forerun. This material was sublimed twice; after this treatment it had m.p. 94-97.5° (sealed tube), $\alpha^{19.4}\text{D}$ +81.7° (*c* 1.8, in 95% ethanol). A satisfactory analysis of the compound could not be obtained because of its extremely high volatility. The melting point of the oxide and its general properties agreed quite well with those reported for the optically inactive oxide.[10]

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DEPAUL UNIVERSITY]

Unsymmetrical Quaternary Carbon Compounds. I. The Alkylation of Ethyl 2-Cyano-3-methyl-2-pentenoate with Aliphatic Grignard Reagents

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The reaction of several aliphatic Grignard reagents with ethyl 2-cyano-3-methyl-2-pentenoate has been studied. The normal Grignard reagents *added* to this conjugated system to give *t*-alkylcyanoacetic esters in 34-51% yields and *reduced* this conjugated system to furnish ethyl 2-cyano-3-methylpentanoate in 20-30% yields. The other propyl and butyl Grignard reagents have also been evaluated. The alkylated cyanoacetic esters have been hydrolyzed and decarboxylated to form the 3-ethyl-3-methyl substituted nitriles and acids, further confirming the character of the addition.

This work extends the findings of Alexander, McCollum and Paul[1] and Kohler and Reimer[2] showing that Grignard reagents add to ethyl alkylidenecyanoacetates, $R_2C{=}C(CN)COOC_2H_5$, to furnish ethyl *t*-alkylcyanoacetates, $R_3C{-}CH(CN){-}COOC_2H_5$, with little or no interference by reaction of the Grignard reagents with the ester or cyano groups. Several other examples of analogous alkylations of similar conjugated systems occur in the literature.[3]

In our extension of this work with the cyanoacetates, the alkylidene group was *s*-butylidene and the Grignard reagents were propyl, butyl, pentyl, hexyl, isobutyl, isopropyl, *s*-butyl, *t*-butyl and neopentyl. Yields were 34-51% with the *n*-alkylmagnesium bromides. Alexander, McCollum and Paul[1] have reported a yield of 42% on the comparable reaction of *n*-butylmagnesium bromide on ethyl 2-cyano-3-methyl-2-butenoate (*s*-propylidene homolog). A variety of changes in alkylation procedure led to no better method than the one given by these authors.[1] Isobutylmagnesium bromide, however, gave only an 8% yield and neopentylmagnesium bromide gave 0% yield. The *s*-butyl and *t*-butyl analogs gave 8 and 3% yields, respectively. Oddly enough, isopropylmagnesium bromide furnished a 38% yield of the desired product, an observation which conflicts with the findings of Alexander and his colleagues.[1]

Ethyl 2-cyano-3-methylpentanoate, $C_2H_5{-}CH(CH_3){-}CH(CN){-}COOC_2H_5$, and olefins (propylene from *n*-propylmagnesium bromide) were obtained in a reaction concurrent with the addition. This reduction product was much more important in the reactions with isobutyl- and *s*-butylmagnesium bromides and *t*-butylmagnesium chloride than with the normal isomers.

The highly hindered character of these *t*-alkylcyanoacetic esters has led to a convenient alkaline hydrolysis furnishing the *t*-alkylacetonitriles, $R_3C{-}$

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[1] E. R. Alexander, J. D. McCollum and D. E. Paul, THIS JOURNAL, **72**, 4791 (1950).

[2] E. P. Kohler and M. Reimer, *Am. Chem. J.*, **33**, 333 (1905).

[3] (a) E. P. Kohler, *ibid.*, **34**, 132 (1905); (b) S. Wideqvist, *Arkiv. Kemi, Mineral. Geol.*, **B23**, No. 4 (1946); (c) B. Riegel, S. Siegel and W. M. Lilienfeld, THIS JOURNAL, **68**, 984 (1946); (d) B. Riegel, S. Siegel and D. Kritchevsky, *ibid.*, **70**, 2950 (1948); (e) J. H. Wotiz and J. S. Matthews, *ibid.*, **74**, 2559 (1952). *Cf.* also H. Gilman, "Organic Chemistry, An Advanced Treatise," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 611, 673, 674.

TABLE I

THE ALKYLATION OF ETHYL 2-CYANO-3-METHYL-2-PENTENOATE WITH VARIOUS ALKYLMAGNESIUM BROMIDES, R-Mg-Br

Bromide, R-	B.p., °C.	B.p., Mm.	Yield, %	$n^{25}D$	d^{25}	Sapn. equiv., Calcd.	Sapn. equiv., Found[a]	Nitrogen, %, Calcd.	Nitrogen, %, Found	Reduction, %
n-C_3H_7-	150-153	22	33.7	1.4429	0.9501	211.3	209	6.63	6.72	37
s-C_3H_7-	147-152	21-20	38.6	1.4497	.9680	211.3	214	6.63	6.71	19.5
n-C_4H_9-	160-162	21	51.3	1.4435	.9406	225.3	226	6.22	5.94	29.5
s-C_4H_9-	154-155	15	7.8	1.4522	.962	225.3	220	6.22	6.35	40
i-C_4H_9-	148-150	15	8.5	1.4449	.9452	225.3	221	6.22	6.37	79
t-C_4H_9-[b]	140-147	10	3.0	1.4515	.949	225.3	240	6.22	6.35	63
n-C_5H_{11}-	168-170	20	48.7	1.4449	.9342	239.3	238	5.85	6.00	22
n-C_6H_{13}-	182-183	22	45.2	1.4462	.9283	253.4	252	5.53	5.75	24

[a] The saponification equivalents were performed by heating the sample of ester-nitrile in 1 N alcoholic potassium hydroxide for an hour. Little or no involvements of the nitrile result. Neither does decarboxylation occur under these conditions except with the t-butyl derivative. [b] t-Butylmagnesium chloride (S. V. Puntambeker and E. A. Zoellner, "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 524) was prepared in a 1.2-mole quantity and treated with 0.6 mole of ethyl 2-cyano-3-methyl-2-pentenoate. The product could not be purified as carefully as the others due to the small amount available. The high saponification equivalent is probably due to failure of the saponification to be completed because of hindrance. Spontaneous decarboxylation of the acid-nitrile during hydrolysis obscured the end-point to some extent.

CH_2CN. More vigorous hydrolysis of these nitriles with alkali has furnished the t-alkylacetic acids, R_3C-CH_2COOH.

Experimental[4]

Ethyl 2-Cyano-3-ethyl-3-methylhexanoate.—The method followed Alexander, McCollum and Paul.[1] n-Propylmagnesium bromide was prepared under nitrogen with 111 g. of n-propyl bromide and 21.9 g. of magnesium in 450 cc. of ether. To this Grignard reagent there was added 125.3 g. of ethyl 2-cyano-3-methyl-2-pentenoate[5] in 250 cc. of benzene in one hour. Reflux was spontaneous with evolution of some gas. After the addition was completed the brownish, opalescent reaction mixture was heated under reflux for an hour. Then the mixture was poured onto ice and acidified with dilute sulfuric acid. The aqueous phase was separated and extracted with two portions of benzene. The three extracts were washed with water and saturated sodium chloride solution and dried with sodium sulfate. The solvent was removed and the product was fractionated furnishing three fractions: A, b.p. 122-128.5° (24-23 mm.), 46.7 g. (36.8%, calcd. as reduction product), $n^{25}D$ 1.4289; B, b.p. 128.5-147° (23 mm.), 21.5 g., $n^{25}D$ 1.4350; C, b.p. 147-152° (23 mm.), 53.2 g. (33.7%), $n^{25}D$ 1.4427. There was a 13.5-g. residue.

Refractionation of fraction C (from several runs) gave the purified product, b.p. 150-153° (22 mm.). A center cut, b.p. 152.5° (22 mm.), $n^{25}D$ 1.4429, was reserved for analyses (Table I).

No improvement in yield could be effected by various modifications in several 0.25-mole runs (normal yields 25-31%). Alkylation with di-n-propylcadmium furnished only 12% of the desired ester but gave a 59% yield of reduction product.[3c] When piperidine acetate was added to di-n-hexylcadmium, the alkylidene ester was apparently polymerized and none of the expected product was obtained.[3c] A twofold excess of Grignard reagent had no effect on the yield (29%). The addition of the Grignard reagent to a mixture of ethyl 2-cyano-3-methyl-2-pentenoate and magnesium bromide effected no change in the yield (26%).[6]

In one 0.25-mole run the effluent gases (presumably propylene and some ether) were passed through a solution of bromine in carbon tetrachloride. This resulting solution was washed with cold 5% sodium hydroxide solution until the brown color of bromine was eliminated. Then the mixture was washed, dried and distilled to furnish 11.2 g. (22%, based on 0.25 mole of alkylidene ester) of **propylene bromide**, b.p. 140-144° (747 mm.), $n^{25}D$ 1.5186. The index of refraction for a known sample of propylene bromide was $n^{25}D$ 1.5183.

Fraction A was probably the reduction product, **ethyl 2-cyano-3-methylpentanoate**, and on refractionation it had a boiling range of 123.5-127° (23-22 mm.). A center cut was reserved for analysis: b.p. 126° (22 mm.), $n^{25}D$ 1.4277, d^{25} 0.9614, sapn. equiv., 168 (calcd., 169.2). Alexander and Cope[7] have reported b.p. 99-100° (7 mm.), $n^{25}D$ 1.4267, d^{25}_4 0.9615.

The above procedure was followed for other alkyl Grignard reagents listed in Table I. In addition, neopentylmagnesium bromide was tested and gave no addition product. The analytical data in Table I were determined on intermediate cuts collected during the fractional distillations.

3-Methylpentanoic Acid.—Ethyl 2-cyano-3-methylpentanoate (33.8 g.) was heated under reflux for five hours with a solution of 45 g. of potassium hydroxide in 150 cc. of ethylene glycol. This mixture was diluted and extracted with ether. (Only about 0.5 g. of neutral material was ultimately obtained.) The aqueous phases were acidified with hydrochloric acid and extracted with ether. The ethereal extracts were washed, dried and distilled to furnish after decarboxylation 15.6 g. (67.2%) of 3-methylpentanoic acid; b.p. 195-198° (743 mm.), $n^{25}D$ 1.4138, neut. equiv., 117.2 (calcd., 116.16) (lit. b.p. 197.2-197.8°, $n^{20}D$ 1.4159).[8]

3-Ethyl-3-methylhexanenitrile.—As an example of the method used to prepare nitriles from ester-nitriles 107 g. of ethyl 2-cyano-3-ethyl-3-methylhexanoate was added to a solution of 57 g. of potassium hydroxide in 200 cc. of ethylene glycol and heated under reflux for five hours. During the reflux the nitrile separated. This mixture was cooled, diluted with 200 cc. of water and extracted with three portions of ether. After washing with water and saturated sodium chloride solution and drying with sodium sulfate the ether was removed. The nitrile was fractionally distilled furnishing 48.4 g. (68.6%) of product as the only fraction; b.p. 103-104° (30-28 mm.), $n^{25}D$ 1.4291.

The aqueous phases from the above extraction of nitrile were acidified with hydrochloric acid and extracted with ether. The ether was removed, the acids were decarboxylated and distilled to furnish 13.3 g. of impure material, b.p. 99-185° (23-40 mm.). This material was separated into acidic and neutral materials. The neutral fraction was distilled to give 9.1 g. (12.8%, total yield, 81.4%) of nitrile, b.p. 85-92° (9 mm.), $n^{23}D$ 1.4290.

The analyses and properties of intermediate fractions of this and other homologous nitriles prepared by this method are listed in Table II. The other nitriles in the series were prepared by the same procedure except that only three hours of boiling was required to effect the nearly complete decarboxylation and separation of the nitrile phase. The yields in Table II are yields obtained from the neutral fraction: no effort was made to recover nitrile from the acidic fraction except in the case cited above.

3-Ethyl-3-methylhexanoic Acid.—Fifty-six grams of 3-ethyl-3-methylhexanenitrile was added to a solution of 90 g. of potassium hydroxide in 300 cc. of ethylene glycol. This mixture was heated under reflux and stirred with a Hersh-

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(4) All boiling points are uncorrected. Fractionations were effected through a 60-cm., heated Vigreux column with no head. Elemental analyses were all by Micro-Tech Laboratories, Skokie, Illinois. Densities are given in absolute units (g./cc.).

(5) A. C. Cope, C. M. Hofmann, C. W. Wyckoff and E. Hardenbergh, THIS JOURNAL, **63**, 3452 (1941).

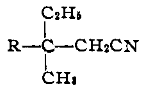
(6) *Cf.* C. G. Swain and H. B. Boyles, *ibid.*, **73**, 870 (1951).

(7) E. R. Alexander and A. C. Cope, *ibid.*, **66**, 887 (1944).

(8) M. Hommelen, *Bull. soc. chim. Belg.*, **42**, 243 (1933).

TABLE II

3-ETHYL-3-METHYLALKANENITRILES

 $R-C(C_2H_5)(CH_3)-CH_2CN$	Boiling point, °C.	Mm.	Yield, %	n^{25}D	d^{25}	Nitrogen, % Calcd.	Found
n-C_3H_7-	103–104	31	68.6[a]	1.4291	0.8286	10.06	9.84
s-C_3H_7-	103–103	25–24	86.7	1.4363	.8461	10.06	10.06
n-C_4H_9-	112–113	22	76.6	1.4328	.8300	9.14	8.94
n-C_5H_{11}-	127–130	23–25	83.0	1.4358	.8302	8.37	8.33
n-C_6H_{13}-	139–140	20–19	86.0	1.4379	.8314	7.73	7.80

[a] The yield was 81.4% of nitrile when the acid nitrile was worked up (see nitrile preparation).

TABLE III

3-ETHYL-3-METHYLALKANOIC ACIDS, $R-(C_2H_5)(CH_3)C-CH_2COOH$

R-	Boiling point, °C. (15 mm.)	Yield, %	n^{25}D	d^{25}	Equiv. wt. Calcd.	Equiv. wt. Found	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
n-C_3H_7-	136–137	95.1	1.4377	0.9205	158.24	159.1	68.31	68.28	11.46	11.73
s-C_3H_7-	138–140	89.6	1.4460	.9409	158.24	159.6	68.31	68.43	11.46	11.65
n-C_4H_9-	147.5–149	96.4	1.4406	.9135	172.26	173.1	69.72	69.60	11.70	11.73
n-C_5H_{11}-	157–160	91.4	1.4426	.9071	186.29	188.3	70.92	70.77	11.91	11.90
n-C_6H_{13}-	169–171	90.5	1.4449	.9030	200.31	202.3	71.95	71.92	12.08	12.02

berg stirrer for 13 hours.[9] (After 2.5 hours the mixture appeared to be homogeneous.) The cooled reaction mixture was diluted with 300 cc. of water and extracted with three portions of ether to remove neutral materials. The aqueous residues were acidified with concentrated hydrochloric acid and extracted three times with ether. The extracts were washed with water and saturated sodium chloride solution and dried with sodium sulfate. After removal of the ether the acid was distilled from a Claisen flask; b.p. 139–140.5° (24–22 mm.), 60.2 g. (95.1%), n^{25}D 1.4375.

The other acids in the series are listed in Table III. The preparation was the same except that the period of heating varied between 12–15 hours. The analytical data refer to values taken on intermediate fractions obtained upon refractionation of these acids.

Direct Hydrolysis of a *t*-Alkylcyanoacetic Ester to Obtain an Acid.—A mixture of 45.1 g. of ethyl 2-cyano-3-ethyl-3-methyloctanoate, 45 g. of potassium hydroxide and 150 cc. of ethylene glycol was heated under reflux for 10 hours. (There were still two phases.) This mixture was separated into acidic and neutral fractions as described above in the preparation of 3-ethyl-3-methylhexane nitrile. The neutral extract was distilled to furnish two fractions: 14 g. (44%, calcd. as nitrile), b.p. 123–130° (20 mm.), n^{25}D 1.4350, and 7.3 g. (21%, calcd. as amide), b.p. 130–190° (20 mm.), n^{25}D 1.4560. The acid fraction was distilled to give 6.4 g. (18%), b.p. 165–167° (23 mm.), n^{25}D 1.4489.

Longer heating would certainly have given a better yield of acid; but this result seemed to indicate that an advantage would be gained by using the two-step method described above.

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[9] Because of the corrosive action of the alkali it is best to use a cheaper, single-necked, round-bottomed flask and to operate the stirrer through a 50–60 mm. condenser in this reaction. Although a mole of water is required for this reaction, no water was added since it was assumed that the reagents were sufficiently wet to supply this need.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS]

Concentration Effects in the Lithium Aluminum Hydride Reduction of 3,4-Epoxy-1-butene

BY RICHARD FUCHS AND CALVIN A. VANDERWERF

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In the S_N2 ring opening of 3,4-epoxy-1-butene by lithium aluminum hydride, the percentage of the alcohol resulting from attack at the secondary carbon of the epoxide varied from 30% at high lithium aluminum hydride concentrations to 17% at an epoxide–hydride mole ratio of 1:4, with a corresponding increase in the alcohol resulting from primary attack. The percentage of secondary attack was likewise decreased by partial alcoholysis of the hydride prior to reduction of the epoxide, leaving $[AlH_3OR]^-$ as the predominant ionic species. These results are consistent with two postulations: (1) that the lithium aluminum hydride reduction of epoxides is initiated by attack at the epoxide by the series of ions $[AlH_4]^-$, $[AlH_3OR]^-$, $[AlH_2(OR)_2]^-$ and $[AlH(OR)_3]^-$, which, although electronically similar, increase in steric requirements in the order written; and (2) that steric factors are important in determining the position of attack and hence the direction of ring opening.

The importance of steric *vs.* electronic factors in the direction of S_N2 ring opening in epoxides is still a controversial question which deserves further study. The role played by steric factors can best be demonstrated with an epoxide in which steric and electronic factors act in opposition and with a series of electronically similar bases with different steric requirements.

3,4-Epoxy-1-butene was chosen for study because resonance stabilization in the transition state[1] favors secondary attack, whereas the steric factor favors primary attack. Thus the ratio of the two isomeric alcohols formed by ring opening in any given reaction gives an indication of the relative importance of the two factors. It is known that base-catalyzed ring opening of 3,4-epoxy-1-butene may show a range from essentially 100% secondary

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[1] P. D. Bartlett and S. D. Ross, THIS JOURNAL, **70**, 926 (1948).