excess of lithium, norbornene was the principal product and was itself reduced to norbornane only to a small extent. Thus norbornadiene apparently reacts more rapidly than does norbornene which apparently reacts more rapidly than other olefins such as cyclohexene.[7] A similar order of reactivity for these olefins toward *p*-thiocresoxy radical[3] and toward aqueous silver ion[5] has been reported. The relative degrees of strain in the olefinic compounds probably account in large measure for this order.[3,5] However, the fact that isolable quantities of norborane were formed even though unchanged norbornadiene was recovered in the product mixture indicates that the differences in reactivities of norbornadiene and norbornene toward lithium in ethylamine are not great.

If the reduction involves the addition of lithium atoms (or of solvated electrons), then perhaps it should not be surprising that the course of the reaction with the diene should be more similar to free radical additions[3] than to cationic ones[4] insofar as the manifestation of conjugative properties are concerned.

EXPERIMENTAL

Norbornadiene and *norbornene* were supplied without charge by Shell Chemical Corp. and by Du Pont Polychemicals Dept., respectively; they were freshly distilled from sodium before use. *Norbornane* was prepared by the low pressure hydrogenation of norbornene with Raney nickel catalyst. Gas chromatography[12] and infrared spectroscopy[13] revealed no contaminants in the norbornene and norbornane samples and only traces of contaminants in the norbornadiene sample. A sample containing 81% *nortricyclene* and 19% norbornene graciously was supplied by Dr. Paul R. Schleyer, Princeton University, and was used without further purification as the source of authentic nortricyclene for spectral comparisons.

Reduction of norbornadiene. Lithium shot (8 mesh, 6.25 g., 0.90 g.-atom) was added to 250 ml. of anhydrous ethylamine in a flask equipped with stirrer, dropping funnel, Dry Ice condenser, and nitrogen atmosphere. The characteristic deep blue color developed quickly and after 30 min. stirring, norbornadiene (36.8 g., 0.40 mole) was added rapidly dropwise. After about half of the diene had been added, the blue color suddenly disappeared. The mixture appeared white with a lump of lithium floating in it. After 15 min., a muddy tan color developed and after 30 min. the lithium was no longer visible. The mixture was stirred for a total of 7 hr. Solid ammonium chloride (49 g., 0.90 mole) was added (attended by considerable heat evolution and probably some loss of volatile product material by entrainment) and the thick mixture was left standing overnight. Water was added and the mixture was extracted twice with ether. The ether solution was washed twice with water, twice with dilute hydrochloric acid, and again with water. After being dried with magnesium sulfate, it was distilled to give 22.2 g. of material, b.p. 95–103°, nearly all of which solidified in the receiver. Gas chromotography[12] resolved the distillate into three fractions (besides carbon tetrachloride solvent) which were shown by comparison of retention times and infrared spectra[13] with those of authentic samples to be norbornadiene (25%), norbornene (48%), and a mixture of norbornane and nortricyclene (27%). Although the last peak was symmetrical, the infrared spectrum of this fraction showed absorption for both norbornane and nortricyclene. Comparison with spectra of standard mixtures (absorbancies at 12.27 μ and 12.51 μ for norbornane and nortricyclene, respectively) indicated that this fraction of the product mixture consisted of 63% norbornane and 37% nortricyclene.

The products from the Benkeser reduction of norbornadiene then were 64% norbornene, 23% norbornane, and 13% nortricyclene.

In another experiment, with a 50% excess of lithium, no diene was recovered. The product, obtained in 74% yield, was found to be 24% norbornene, 55% norbornane, and 21% nortricyclene. Because of inadvertent loss of material by evaporation prior to analysis, these figures are less reliable than those above.

In both experiments small amounts of high boiling residue remained in the pot undistilled.

Reduction of norbornene. The same procedure was used twice with lithium, ethylamine, and norbornene. The deep blue color faded during addition of olefin and was essentially gone when addition was complete. The blue color continually redeveloped around the floating lump of lithium and the stirred mixture was aqua to lavender in color during the entire reaction period (7 hr.). Except for a very small amount of recovered norbornene in one experiment, norbornane was obtained in about 33% yield as the only product (gas chromatographic and infrared spectral analyses). A little high boiling residue remained in the pot undistilled.

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[12] Beckman GC-2 instrument; 6-ft. silicone column, 70–100°, 40–60 ml./min. flow rate of He, CCl_4 solutions.

[13] Beckman IR-5 instrument; CS_2 solutions.

Preparation of 3-Fluorophthalic Anhydride

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For the synthesis of some polycyclic fluorine compounds, substantial quantities of 3-fluorophthalic anhydride were required. The ease with which the readily accessible 3-nitrophthalic anhydride can be converted by gaseous chlorine into the 3-chloro-compound,[1-3] led us to suspect that the chlorine atom in the latter might be reactive enough for a nucleophilic substitution reaction with potassium fluoride. Indeed, at 280–290° this reaction gave a 50% yield of the hitherto unknown 3-fluorophthalic anhydride.[4]

Similar exchange reactions with potassium fluoride have been observed for chlorine activated by nitro groups[5-7] or by a combination of a nitro-

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(1) A. A. Ponomarenko, *Zhur. Obshcheĭ Khim.*, **20**, 469 (1951); *Chem. Abstr.*, **44**, 7810 (1950).

(2) M. S. Newman and P. G. Scheurer, *J. Am. Chem. Soc.*, **78**, 5004 (1950).

(3) C. Shaw and Y. Thomas (to Imperial Chem. Ind.), British Patent **357,165**; *Chem. Abstr.*, **26**, 5768 (1932).

(4) The isomeric 4-fluorophthalic anhydride has been prepared before [F. F. Blicke and F. D. Smith, *J. Am. Chem. Soc.*, **51**, 1865 (1929)].

(5) H. B. Gottlieb, *J. Am. Chem. Soc.*, **58**, 532 (1936).

(6) H. G. Cook and B. C. Saunders, *Biochem. J.*, **41**, 558 (1947).

group and a N=C double bond.[8] To the best of our knowledge, an analogous activation by a carbonyl group has not been observed before;[9] indeed, on the whole, experience has shown that in such cases fluorine is *the most easily replaceable substituent*.

3-Chlorophthalic anhydride did not react with potassium cyanide under the same operating conditions.

EXPERIMENTAL

3-Chlorophthalic anhydride was prepared according to Newman and Scheurer[2] from 3-nitrophthalic anhydride[10] and gaseous chlorine. The temperature of the bath was kept exactly at 250°, the liquid product poured into a mortar and, after it solidified, ground to a fine powder. It was not necessary to distill it; already in its crude stage it melted at 118–124° and after trituration with anhydrous ether at 125–127°. The yield was 76%.

3-Fluorophthalic anhydride. In a Claisen flask (for distillation of solid compounds) of 100-ml. capacity, 20 g. of anhydrous potassium fluoride[11] was covered with a layer of 20 g. of 3-chlorophthalic anhydride and the mixture heated at 280–290° for 45 min. Distillation at 220–225°, 80 mm. gave a clean fraction (11 g.), which solidified spontaneously and was recrystallized from 75 ml. of toluene, m.p. 160°; yield, 9 g. (50%).

Anal. Calcd. for $C_8H_3FO_3$: C, 57.8; H, 1.8; F, 11.4. Found: C, 58.1; H, 2.1; F, 11.0.

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[7] G. C. Finger and C. W. Kruse, *J. Am. Chem. Soc.*, **78**, 6034 (1956). See also J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 273 (1951).

[8] G. C. Finger and L. D. Starr, *J. Am. Chem. Soc.*, **81**, 2674 (1959).

[9] One may recall the easy replacement of sulfonic acid groups by molecular chlorine in the α-positions of the anthraquinone system. See, *e.g.*, V. V. Kozlov, *J. Gen. Chem.* (*U.S.S.R.*), **17**, 289 (1947); *Chem. Abstr.*, **42**, 550 (1948).

[10] *Org. Syntheses*, **Coll. Vol. I**, 408 (1941).

[11] Analytical grade (Messrs. Baker and Adamson, anhydrous, granulated) was used. It is necessary that the *p*H of an aqueous solution be about 8.0.

Unsymmetrical Quaternary Carbon Compounds. III. The Preparation and Resolution of Aliphatic Trialkylacetic Acids[1,2]

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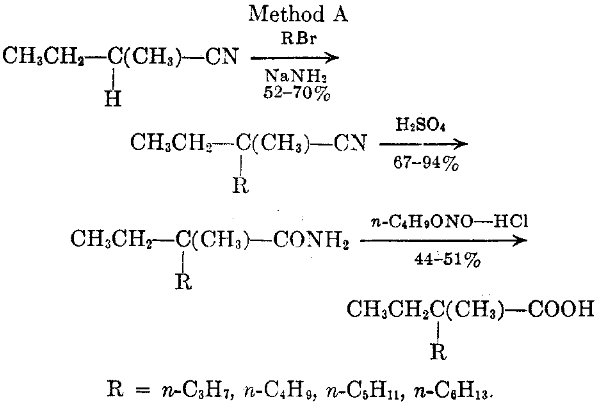
Trialkylacetic acids have been prepared by at least six different methods.[3–9] However, only the two procedures indicated by methods A and B seemed to afford convenient, general routes for the preparation of unsymmetrical, racemic trialkylacetic acids. Method A was derived from work of Sperber, Papa, and Schwenk[4,10] and method B was modified from the report of Hudson and Hauser.[5]

For method A, 2-methylbutanenitrile was prepared by the monoalkylation of propanenitrile with ethyl bromide in the presence of sodium amide,[3,4,10] a process which furnished only 30–36% of monoalkylation product and 12% of the dialkylation product, 2-ethyl-2-methylbutanenitrile. Better yields would have resulted from dehydration of the 2-methylbutanamide.[11]



$$\text{Method A}$$

$$\underset{\displaystyle H}{CH_3CH_2—C(CH_3)—CN} \xrightarrow[NaNH_2,\ 52–70\%]{RBr} \underset{\displaystyle R}{CH_3CH_2—C(CH_3)—CN} \xrightarrow[67–94\%]{H_2SO_4} \underset{\displaystyle R}{CH_3CH_2—C(CH_3)—CONH_2} \xrightarrow[44–51\%]{n\text{-}C_4H_9ONO—HCl} \underset{\displaystyle R}{CH_3CH_2C(CH_3)—COOH}$$

$R = n\text{-}C_3H_7,\ n\text{-}C_4H_9,\ n\text{-}C_5H_{11},\ n\text{-}C_6H_{13}.$

The second alkylation with *n*-propyl, *n*-butyl, *n*-amyl, and *n*-hexyl bromides was more efficiently performed (52–70% yields). Hydrolysis of these nitriles in sulfuric acid[4] gave 67–94% yields of the amides. However, conversion of the amides to the corresponding acids with butyl nitrite and hydrochloric acid furnished poor yields (44–51%) of acids; for these acids contained the butyl ester, presumably because of water contamination in the reactants.

Method B essentially followed the procedure of Hudson and Hauser[5] substituting sodium hydride

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[1] Paper II of this series was F. S. Prout, E. P.-Y. Huang, R. J. Hartman, and C. J. Korpics, *J. Am. Chem. Soc.*, **76**, 1911 (1954).

[2] Abstracted from the Masters Theses of Bohdan Burachinsky (1959) and Herbert L. Young (1953) and the Senior Thesis of William T. Brannen, Jr. (1958).

[3] K. Ziegler and H. Ohlinger, *Ann.*, **495**, 84 (1932).

[4] N. Sperber, D. Papa, and E. Schwenk, *J. Am. Chem. Soc.*, **70**, 3091 (1948).

[5] B. E. Hudson, Jr. and C. R. Hauser, *J. Am. Chem. Soc.*, **62**, 2457 (1940).

[6] C. L. Carter and S. N. Slater, *J. Chem. Soc.*, 130 (1946).

[7] W. v. E. Doering and K. B. Wiberg, *J. Am. Chem. Soc.*, **72**, 2608 (1950).

[8] S. Ställberg-Stenhagen, *Arkiv. Kemi*, **3**, 273 (1951).

[9] A. Haller and E. Bauer, *Compt. rend.*, **148**, 127 (1909); J. G. Aston, J. T. Clarke, K. A. Burgess, and R. B. Greenburg, *J. Am. Chem. Soc.*, **64**, 300 (1942); A. A. Sacks and J. G. Aston, *J. Am. Chem. Soc.*, **73**, 3902 (1951); C. T. Lester and J. R. Proffitt, Jr., *J. Am. Chem. Soc.*, **71**, 1877 (1949); C. Schuerch, Jr., and E. H. Huntress, *J. Am. Chem. Soc.*, **70**, 2824 (1948); J. Cason, *J. Org. Chem.*, **13**, 227 (1948); A review is given by A. C. Cope, H. L. Holmes, and H. O. House, *Organic Reactions*, IX, 107–331 (1957).

[10] *Cf.* also G. L. Goerner and A. A. Holzschuh, *J. Org. Chem.*, **23**, 1346 (1958).

[11] C. L. Stevens and T. H. Coffield, *J. Am. Chem. Soc.*, **73**, 103 (1951).