prethermostated thiol was injected into the reaction flask through the self-sealing Neoprene diaphragm by a syringe. The reaction was then initiated by stirring (usually 1000 rpm) the heterogeneous mixture. Completeness of reaction or extent of reaction was determined by gc analysis using an internal hydrocarbon standard and predetermined molar response factors.[23] Upon termination of the reaction, the reaction flask was transferred to the nitrogen drybox, the mixture was filtered to remove the hydrocarbon layer, the inorganic phase was washed with xylene (three volume excess) to remove any adsorbed or occluded product, and the filtrates were combined. Subsequent dilution with ethanol and storage in a coldbox (0°) precipitated the disulfides which were collected by filtration and dried to a constant weight. The structure of each disulfide was confirmed by its melting point and mixture melting point with the authentic disulfides prepared above. One exception to this procedure was 1,2-dithiacyclohexane. This disulfide was isolated by fractional distillation on a 16-in. silvered column equipped with a tantalum-wire spiral. Its boiling point (86–88° at 35 mm) and melting point (30–32°) agreed with reported values[22] and a mixture melting point with an authentic sample was not depressed. It should be noted that all disulfide yields were based on the amount of isolated product. Hence, the yields shown in Tables I and II represent minimum values.

Thiol Addition Reactions to 1-Dodecene.—Reaction mixtures in the 1-dodecanethiol addition reactions to 1-dodecene were prepared in the manner described above. In these studies, a 10/1 mole ratio of olefin/thiol was employed and the mole ratio of thiol/metal oxide was varied as shown in Tables III and IV. Cetane (0.01 mole) was added at the beginning of each reaction as an internal standard for gc analysis. Using predetermined molar response factors, it was then possible to compute the amount of thiol converted and the amount of sulfide and disulfide formed from each peak on the gas chromatograph at the end of the reaction. The glpc unit employed in these analyses was an F and M Model No. 609 flame-ionization gas chromatograph equipped with a Minneapolis Honeywell recorder and a disk integrator (Model No. 201). The injection port of the unit was maintained at 305° and the inlet pressure of helium was 36 psig. The block of the detector was maintained at a constant temperature of 245°. The helium flow through the column was 100 cc/min when measured at room temperature with a flowmeter. All quantitative data was obtained on a 3 ft, 20 wt % Carbowax (20 MM) on Chromosorb W column (0.25-in. stainless steel tubing). This column gave excellent separation of all mixtures used in the present study.[24]

Related Gas Chromatography Data.—In the above studies and in the rate studies listed in Tables V and VI, a series of molar response factors between the compound(s) of interest and its corresponding internal standard were computed. These values are summarized in Table VII. The competition studies on coupling and olefin addition reactions were carried out with 1-dodecanethiol because of the thermal stability of the resulting disulfide. Aromatic disulfides dissociate at fairly low temperatures and benzyl disulfide undergoes thermal decomposition (above 200°) to stilbene and presumably hydrogen sulfide and sulfur.[25] Occasionally, higher boiling compounds were detected in the gas chromatographs from the olefin addition reactions. Presumably, these were telomers which are frequently observed in free-radical olefin addition reactions.

TABLE VII

SUMMARY OF GAS CHROMATOGRAPHIC CONDITIONS

Reactant measured	Internal standard	Response factor	Preferred column temp, °C
1-Dodecanethiol	Cetane	1.41	185
Dodecyl sulfide	Cetane	1.20	225
Dodecyl disulfide	Cetane	1.82	290
Toluenethiol	Diphenylmethane	1.87	200
Benzenethiol	Toluene	1.15	200

Acknowledgment.—The author is indebted to Mr. John J. Mahon who performed all of the experimental work and to the Esso Research and Engineering Company especially the Process Research Division for the privilege of publishing this research.

---

[23] For a discussion on the significance of molar response factors, see A. E. Messner, D. M. Rosie, and P. A. Argabright, *Anal. Chem.*, **31**, 230 (1959).

[24] For other applications, see T. J. Wallace and J. J. Mahon, *Nature*, **201**, 816 (1964).

[25] E. Fromm, *Ber.*, **36**, 538 (1903).

The Metalation of 1-Methoxynaphthalene with *n*-Butyllithium

BRUCE M. GRAYBILL[1] AND D. A. SHIRLEY[2]

The University of Tennessee, Knoxville, Tennessee

Received November 5, 1965

The metalation of 1-methoxynaphthalene by *n*-butyllithium has been reinvestigated. Evidence from the metalation of 1-methoxynaphthalene-8-*d* indicates that metalation occurs concurrently at the 2 and 8 positions, and no rearrangement of the lithium from carbon 8 to carbon 2 is involved as proposed earlier. Attack at position 2 is favored, but the relative amounts of isomers formed seem to be influenced by the source of the *n*-butyllithium and how it is produced. Evidence from nmr proton spectra is presented for a coordination complex between the methoxy group and *n*-butyllithium.

The metalation of 1-methoxynaphthalene by *n*-butyllithium was first studied by Sunthanker and Gilman,[3] who reported that metalation followed by carbonation gave 1-methoxy-2-naphthoic acid in 25% yield.

More recently, Barnes and Nehmsmann[4] repeated this experiment and found a mixture of 1-methoxy-2-naphthoic acid and 8-methoxy-1-naphthoic acid. The latter results were interpreted in terms of the reaction sequence shown in Scheme I.

Acid III appeared to be formed in larger yield early in the reaction, but the amount decreased and the amount of acid IV increased as the reaction proceeded. This apparent change in acid content with reaction time was explained by postulating the equilibrium between the 8-lithio (I) and 2-lithio (II) compounds. Barnes[4] also calculated the electron densities of the ring carbon atoms in 1-methoxynaphthalene and came to the conclusion that position 8 contains the most acidic proton. Because of the experimental results and the electron-density calculations, Barnes concluded that metalation by *n*-butyllithium must take place first at the more acidic 8 proton followed by equilibrium with the thermodynamically more stable 2 isomer.

---

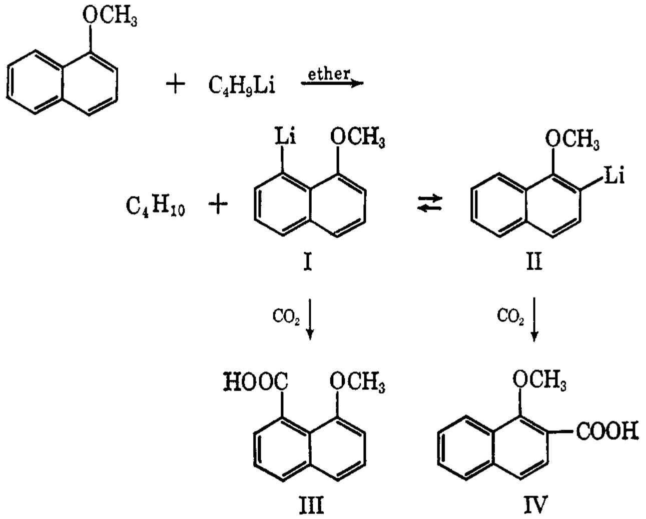
[1] National Science Foundation summer participant, 1965, from Graceland College, Lamoni, Iowa.

[2] To whom inquiries concerning this publication should be sent.

[3] S. V. Sunthanker and H. Gilman, *J. Org. Chem.*, **16**, 8 (1951).

[4] R. Barnes and L. Nehmsmann, *ibid.*, **27**, 1939 (1962).

SCHEME I

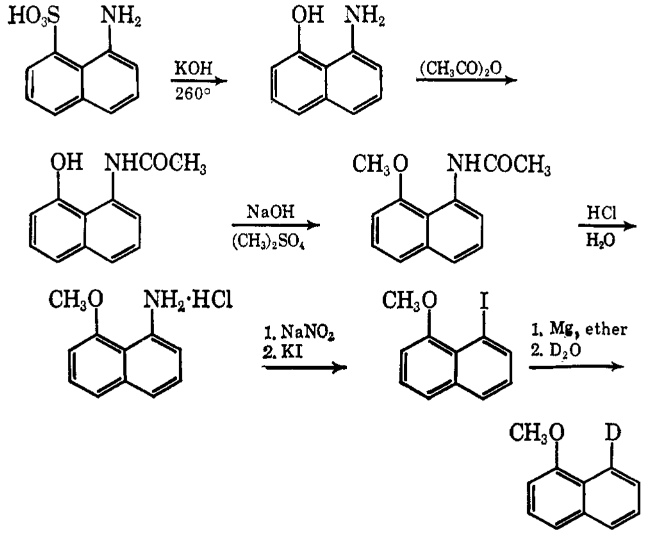


Since previous metalation reactions on aromatic ethers seem to go predominantly *ortho* to the ether group and since there seems to be no other case recorded in which lithium, introduced into aromatic and heterocyclic rings by a metalation reaction, moves to another ring position, we decided to reinvestigate this reaction. The principal method of approach was the metalation of 1-methoxynaphthalene-8-*d*, isolation of the evolved butane gas, and determination of the deuterium content of the butane. If indeed metalation occurs first in the 8 position, according to the Barnes mechanism, then only butane-1-*d* should be obtained.

Results and Discussion

The synthesis of 1-methoxynaphthalene-8-*d* is shown in Scheme II. The deuterated product was found by an nmr proton spectrum to be appreciably less than 100% deuterated in the 8 position. This was determined by comparison with a spectrum of unlabeled 1-methoxynaphthalene which showed the 8 proton to be at an appreciably lower field position (8.2 ppm relative to TMS = 0) than the other ring protons. A deuterium analysis performed by Dr. Josef Nemeth of Urbana, Ill., showed the sample to contain 67% of 1-methoxynaphthalene-8-*d* and 33% of unlabeled 1-methoxynaphthalene. It should be pointed out that rather low labeling levels from treatment of ether solutions of Grignard reagents with D_2O have been observed by other workers.[5]

SCHEME II



It should be pointed out that the nmr low field position for the 8 proton in 1-methoxynaphthalene accords with the suggestion by Barnes[4] that this proton is the most acidic of the ring protons in this compound. An alternative possibility is that the electrons of the methoxy group better shield the 8 proton than others.

The metalation of 1-methoxynaphthalene-8-*d* was run in ether with *n*-butyllithium. The evolved butane gas was collected in a cold trap. By measuring the intensity of the C–D stretching band at 2170 cm^{-1} a quantitative interpretation of the infrared spectrum of the collected butane was made. The results indicated that 96% of the sample was ordinary butane and only 4% was butane-1-*d*. In a similar metalation experiment with unlabeled 1-methoxynaphthalene, the reaction mixture was carbonated and the mixed monocarboxylic acids were converted to methyl esters and analyzed by vapor phase chromatography. This experiment indicated that the monocarboxylic acid mixture formed was 35% 8 isomer and 65% 2 isomer.

These results rule out the Barnes mechanism and strongly suggest that initial metalation by *n*-butyllithium occurs mainly in the 2 position with some concurrent attack at the 8 position. Although interpretation of the experimental results would have been more direct if deuteration had been near 100%, it seems clear that the data support the preceding statement. The hydrogen–deuterium isotope effect for metalation of thiophene[6] and anisole[7] with *n*-butyllithium at about room temperature have been determined carefully and give values for k_H/k_D of just above 6 for both systems. If *all* metalation of the mixture of 67% 1-methoxynaphthalene-8-*d* and 33% 1-methoxynaphthalene went through the 8 position with *no* isotope effect, the butane would consist of 67% butane-1-*d* and 33% ordinary butane. If the factor of 6 is introduced, the composition of the initial butane would be about 25% butane-1-*d* and 75% ordinary butane. Actually the 4% butane-1-*d* found in the butane corresponds rather closely to the expected value obtained from metalation of the mixture of labeled and unlabeled methoxynaphthalene in the 35:65 ratio of 8 metalation to 2 metalation with a k_H/k_D value of 6 for 8-position attack.

Another line of evidence against the Barnes interpretation was the result of deuterium analysis on a sample of 1-methoxy-2-naphthoic acid from carbonation of the metalation mixture. This material contained essentially the *same* amount of deuterium (68%) as the starting 1-methoxynaphthalene. This could only happen if the 2-acid had formed by direct metalation in the 2 position. A prior attack at the 8 position would have removed the deuterium from the 2-acid formed subsequently.

Several metalation experiments were made on unlabeled 1-methoxynaphthalene to determine the relative amounts of the 2 and 8 isomers produced. It was observed that the isomer ratio changed, depending on

---

[5] J. A. Zoltewicz and J. F. Bunnett, *J. Am. Chem. Soc.*, **87**, 2641 (1965).

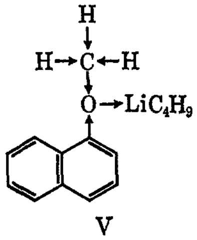
[6] D. A. Shirley and K. R. Barton, *Tetrahedron*, in press.

[7] J. P. Hendrix, Ph.D. Dissertation, University of Tennessee, 1965.

the origin and nature of the *n*-butyllithium reagent. Commercial *n*-butyllithium ("salt free" in hexane) used in ether–hexane mixtures produced 83% of the 2 isomer (IV) and 17% of the 8 (III). Change of the mole ratio of *n*-butyllithium:1-methoxynaphthalene (from 1:1 to 2:1) did not seem to affect this isomer distribution. However, *n*-butyllithium, produced from 1-bromobutane and lithium metal in ether, which contained dissolved lithium bromide and likely some alkoxide, gave an isomer ratio of 65% of the 2 isomer to 35% of the 8. Some reference has been made previously in the literature to the change in activity of the organometallic compound, which change seems to be dependent on dissolved salts[8] or alkoxide ions.[9]

This change in the relative rate of attack at the two positions does not seem to be due to dissolved lithium bromide or lithium alkoxide. When anhydrous lithium bromide and ether were added to commercial, "salt-free" *n*-butyllithium in a metalation experiment, very little change in the isomer ratio resulted (86% 2 isomer and 14% 8 isomer). In another metalation with commercial *n*-butyllithium containing added ether and 10 mole % lithium ethoxide, the ratio of 2 isomer to 8 isomer was 87:13%. This unusual sensitivity of isomer distribution to the nature of the *n*-butyllithium may help explain Barnes'[4] difficulty in obtaining reproducible results.

It has long been recognized that apparently the most important factor in determining the position of metalation is the relative ring-proton acidity caused by the inductive effect of any groups attached to the aromatic ring. In the case of aromatic ethers, this inductive influence should be enhanced by coordination of the butyllithium with the unshared pair of electrons on oxygen. Evidence was obtained for the presence of a coordination complex between butyllithium and 1-methoxynaphthalene (approximately a 1:1 mole ratio) from the nmr proton spectrum of the mixture in hexane. The methoxyl hydrogens were shifted downfield 14 cps in the presence of the organometallic. A similar downfield shift of protons α to ether linkages has been reported for a mixture of ethyl ether and *n*-butyllithium.[10] The ring proton at the 8 position was moved slightly upfield about 5 cps, whereas the other ring protons moved slightly downfield, with changes in band shapes. These shifts in the nmr proton positions can be qualitatively explained by a coordination complex (V). The stronger inductive effect of the coordination complex would increase the acidities of the methyl and ring protons. The contrary movement of the 8 proton upfield may be due to a more important decreased electron shielding by oxygen after coordination with butyllithium.


V

In summary, we feel that the Barnes'[4] mechanism involving equilibrium between the 8-lithio and 2-lithio compounds (I to II) does not operate and that the orientation of the entering metal atom is under kinetic control.

Experimental Section

All nmr spectra were obtained using a Varian A-60 instrument and measured relative to tetramethylsilane as an internal standard.

8-Amino-1-naphthol.—The procedure was similar to that described by Fichter and Gogeur.[11] 8-Amino-1-naphthalenesulfonic acid (67 g, 0.3 mole) was made into a paste with water and introduced into a mixture of 120 g of sodium hydroxide and 120 g of potassium hydroxide, heated to 200° in a copper pan. The temperature was then slowly increased as the molten mixture was stirred. Considerable spattering occurred at this point. When the temperature reached 260°, the thick brown melt turned dark, became homogeneous, and gave off white fumes. The mixture was then cooled rapidly to avoid further harmful oxidation. The solidified cake was dissolved in 1500 ml of water and filtered. The filtrate was then acidified with hydrochloric acid and filtered again. Neutralization of the acid filtrate with sodium bicarbonate yielded the cream aminonaphthol. Some black tarry residue precipitated initially and was skimmed off and discarded. After filtering, washing, and drying, the product weighed 30 g (63%), mp 84–87° (lit.[11] mp 95°). The crude 8-amino-1-naphthol was used without further purification.

8-Acetylamino-1-naphthol.—In a solution of 37 ml of acetic anhydride and 70 ml of glacial acetic acid was placed 54 g (0.34 mole) of 8-amino-1-naphthol. The solution was refluxed for 10 min and then poured into 1 l. of water. The precipitated N-acetyl derivative was filtered off and washed thoroughly with water. The total yield of product was 53 g (78%) after recrystallization from ethanol–water (1:2): mp 169–170° (lit.[11] mp 168°).

8-Acetylamino-1-methoxynaphthalene.—8-Acetylamino-1-naphthol (52 g, 0.26 mole) was dissolved in 650 ml of a 2% solution of sodium hydroxide. This mixture was stirred at room temperature while 50 ml (66 g) of dimethyl sulfate was added dropwise in 90 min. The solution was kept alkaline and stirred for 45 min longer. The insoluble solid which precipitated from solution was filtered off, washed with water, dried, and weighed. The yield was 50.2 g (90%), mp 128–129° (lit.[11] mp 128°).

8-Methoxy-1-naphthylamine Hydrochloride.—8-Acetylamino-1-methoxynaphthalene (60 g, 0.28 mole) was dissolved in a solution of 500 ml of ethanol and 100 ml of concentrated hydrochloric acid. After the solution had been refluxed for 3 hr most of the ethanol was distilled. About 500 ml of water was added and the solution was treated with charcoal. Small platelike crystals were obtained after cooling the decolorized filtrate. The yield of dry product was 54 g (93%), mp 215–220°.

8-Iodo-1-methoxynaphthalene.—In a solution of 250 ml of water containing 30 ml of sulfuric acid was dissolved 24 g (0.14 mole) of 8-methoxy-1-naphthylamine hydrochloride. The solution was stirred and cooled to 5° while 10.2 g (0.15 mole) of sodium nitrite in 30 ml of water was added dropwise.

The cold diazonium salt solution was then added with stirring to a hot (70°) mixture of 75 g of potassium iodide in 250 ml of water containing 3 ml of sulfuric acid. The dropwise addition of the yellow diazonium salt solution to the hot potassium iodide was complete in 1 hr. The reaction was stirred and heated 10 min longer, and then ice was added. The dark red oil on the bottom of the flask was removed by extraction with five 50-ml portions of benzene. Some black benzene-insoluble residue remained. The combined benzene extracts were dried over magnesium sulfate, filtered, and evaporated to about 80 ml. This solution was then chromatographed on an alumina (Woelm, neutral, activity grade I) column by eluting with benzene. The dark azo compounds and other impurities remained on the column. Evaporation of the benzene solution from the column gave a light yellow solid product. The yield was 21.2 g (54%). Recrystallization of the compound from ethanol–water afforded crystals which melted sharply at 65°.

---

(8) T. V. Tolalaeva, A. N. Rodionov, and K. A. Kocheshkov, *Dokl. Akad. Nauk SSSR*, **154** (No. 1), 174 (1964).

(9) A. A. Morton and J. L. Eisenmann, *J. Org. Chem.*, **23**, 1469 (1958).

(10) Z. K. Cheema, G. W. Gibson, and J. F. Eastham, *J. Am. Chem. Soc.*, **85**, 3517 (1963).

(11) F. Fichter and R. Gogeur, *Ber.*, **39**, 3331 (1906).

Anal. Calcd for $C_{11}H_9O$: C, 46.50; H, 3.19. Found: C, 46.15, 46.30; H, 3.35, 3.38.

1-Methoxynaphthalene-8-*d*.—In a 500-ml three-necked flask equipped with condenser, stirrer, and dropping funnel was placed 3.3 g (0.13 g-atom) of magnesium turnings. The flask was dried with a flame and flushed thoroughly with dry nitrogen. About 20 ml of a solution of 33.4 g (0.118 mole) of 8-iodo-1-methoxynaphthalene in 120 ml of anhydrous ether was introduced through the dropping funnel. The reaction was initiated with a few drops of ethyl iodide, and then the remaining ether solution of 8-iodo-1-methoxynaphthalene was added dropwise with stirring over a period of 35 min. After the addition, the reaction mixture was heated under reflux for 2 hr.

To the Grignard reagent was added 15 g of deuterium oxide (99.9%) dropwise with stirring. The resulting slurry was stirred and refluxed for 1.5 hr. The ether layer was decanted and dried over magnesium sulfate. After filtration, the ether was stripped from the filtrate *in vacuo* to yield 18 g of crude product. This liquid product was distilled (bp 107–110° at 1 mm) to give 13 g (70%) of 1-methoxynaphthalene-8-*d*.

Vapor phase chromatographic analysis of the product was made on a Wilkins–Anderson Model A-700 Autoprep with a silicone column (20 ft × 3/8 in., Wilkens–Anderson Co. SE-30) at 230°. The retention time of 6.2 min was identical with that for the unlabeled 1-methoxynaphthalene. The infrared spectrum of the deuterated compound had a C–D stretching band at 2310 cm^{-1} which was of low intensity.

A proton nmr spectrum in CCl_4 was obtained on a Varian A-60 spectrometer and compared with the unlabeled compound. The *peri* proton (8 position) was located downfield (8.2 ppm relative to TMS) from the other aromatic protons since this band was of sharply reduced intensity in the deuterated sample.

Metalation of 1-Methoxynaphthalene-8-*d* and Analysis of Evolved Butane.—*n*-Butyllithium was prepared from 11 g (0.08 mole) of 1-bromobutane (Eastman), 1.2 g (0.17 g-atom) of lithium ribbon, and 100 ml of anhydrous ether according to the procedure of Gilman and co-workers.[12] A collection system for the butane gas was attached to the reaction vessel containing the *n*-butyllithium and the system was swept with nitrogen. The exit gas from the condenser was passed through a sulfuric acid scrubber, a drying tube filled with soda lime and calcium chloride, and finally through a cold trap, equipped with inlet and outlet stopcocks and immersed in a solid carbon dioxide–acetone bath. To the stirred *n*-butyllithium solution was added 10 g (0.063 mole) of 1-methoxynaphthalene-8-*d* in 10 ml of ether at room temperature. The reaction was held under gentle reflux with stirring and the butane was collected. The reaction solution turned a red-orange color. Approximately 1.5 ml of colorless liquid butane was collected after 2 hr.

The butane was transferred to a 10-cm infrared gas cell *via* a vacuum manifold with an attached manometer. A gas pressure of 400 mm was used in order to observe the C–D stretching band at 2170 cm^{-1}.[13] The infrared spectra were obtained on both a Perkin-Elmer Infracord and Model 237 spectrophotometers.

In order to determine the relative amounts of butane and butane-1-*d*, a sample of pure butane 1-*d* was prepared[13] from butyllithium and deuterium oxide. A graph of the optical density for the 2170-cm^{-1} band *vs.* pressure of butane-1-*d* gave a straight line. By using this graph as a standard, the amount of butane-1-*d* was determined in the collected samples. The analytical results were 96% butane and 4% butane-1-*d*.

Carbonation of Lithio-1-methoxynaphthalene-8-*d*.—The metalation reaction in the above experiment was heated under reflux for 20 hr and then poured over crushed solid carbon dioxide. After acidification with dilute acid, about 25 ml of additional ether was added and the ether layer was extracted with three 100-ml portions of 5% sodium bicarbonate. Acidification of the bicarbonate extracts yielded a light yellow product. The yield of the somewhat sticky crude acid was 4.1 g, mp 100–125°. The acid mixture was easily recrystallized from ethanol–water but still melted over a range, 110–117°. The acid was then dissolved in alcoholic potassium hydroxide, and the precipitated potassium salt was filtered off and dissolved in water. Acidification of the aqueous solution of the potassium salt gave pure white acid, mp 124°. Recrystallization from benzene gave needles which melted sharply at 126–127°, which is the melting point for the 1-methoxy-2-naphthoic acid.[3]

Metalation of 1-Methoxynaphthalene. Experiment 1. With Commercial *n*-Butyllithium.—In a 1-l. three-necked flask equipped with magnetic stirrer, dropping funnel, and condenser was placed 230 ml of 1.6 *M* (0.368 mole) *n*-butyllithium in hexane (Foote Mineral Co. product). Anhydrous ether (200 ml) was added to the solution under nitrogen. To this solution was added 44 g (0.28 mole) of 1-methoxynaphthalene in 50 ml of ether. The reaction was stirred and refluxed for 20 hr. An insoluble solid was present in the red-orange solution. The reaction mixture was poured over powdered solid carbon dioxide and acidified with dilute hydrochloric acid, and the hydrocarbon layer was separated and extracted several times with 10% aqueous sodium bicarbonate solution. The combined bicarbonate extracts were acidified with hydrochloric acid and the crude solid acid was filtered off. The yield was 16.7 g (29%), mp 95–115°. Analysis of the methyl esters of the crude acid mixture is presented under the vpc analysis section.

Experiment 2. With Commercial *n*-Butyllithium.—Another metalation was run under similar conditions using a 2:1 molar ratio of *n*-butyllithium to 1-methoxynaphthalene. From 10 g (0.63 mole) of 1-methoxynaphthalene, 83 ml (0.13 mole) of 1.6 *M* *n*-butyllithium in hexane, and 100 ml of ether, refluxed for 22 hr and carbonated, was obtained a total of 4 g (31%) of crude acid. Valeric acid was present in the crude product. Analysis of the acid was by vpc of the corresponding methyl esters.

Experiment 3. Commercial Butyllithium Containing Added Lithium Bromide.—1-Methoxynaphthalene (5 g, 0.032 mole) in 10 ml of ether was added under nitrogen to a solution of 3.8 g (0.044 mole) of anhydrous lithium bromide, 25 ml of 1.6 *M* (0.04 mole) *n*-butyllithium in hexane, and 75 ml of ether. The metalation reaction was run at reflux temperature for 22 hr and then carbonated. The yield of crude acid was 1.4 g (22%). Analysis was made by vpc and is presented in Table I.

TABLE I

Isomer	Yield, % Expt 1	Expt 2	Expt 3	Expt 4	Expt 5
Methyl 1-methoxy-2-naphthoate	83	83	86	78	65
Methyl 8-methoxy-1-naphthoate	17	17	14	11	35
Unidentified isomers	Trace	Trace	Trace	11	

Experiment 4. Commercial Butyllithium Containing Added Lithium Ethoxide.—*n*-Butyllithium (41 ml of 1.6 *M*; 0.065 mole) in hexane was added under nitrogen to 80 ml of anhydrous ether containing 0.3 g (0.006 mole) of absolute ethanol. To the resulting clear solution was added 10 g (0.063 mole) of 1-methoxynaphthalene and the reaction was stirred and refluxed for 22 hr. Carbonation and work-up of the product gave 3.2 g (25%) of crude acid. The vpc analysis is presented in Table I.

Experiment 5. With Butyllithium Prepared in Ether.—*n*-Butyllithium was prepared by the method of Gilman[12] from 11 g (0.08 mole) of 1-bromobutane, 1.3 g (0.19 g-atom) of lithium metal, and 100 ml of ether. To the butyllithium solution was added 10 g (0.63 mole) of 1-methoxynaphthalene. The mixture was refluxed for 19 hr and carbonated, and 2.4 g (19%) of crude acid was isolated. Analysis was again made by vpc.

Vapor Phase Chromatographic Analysis of Acids from Metalation Reactions.—The crude mixture of acids obtained from the carbonation of lithio-1-methoxynaphthalene was analyzed by vpc of the corresponding methyl esters. A silicone (SE-30) column attached to a Wilkins–Anderson Model A-700 Autoprep was used.

In each case studied, the crude acids were allowed to react with excess diazomethane prepared from N-methyl-N-nitroso-*p*-toluenesulfonamide in ether.[14] Excess ether and diazomethane were evaporated *in vacuo*, and the crude concentrated solution of methyl esters was then analyzed.

Two major peaks in the vpc were present in each case. These components were subsequently identified as methyl 1-methoxy-2-naphthoate (retention times of 15.3 min at 200° and 21.4 min at 180°) and methyl 8-methoxy-1-naphthoate (retention times of 16.7 min at 200° and 23.8 min at 180°). Identification of

---

[12] H. Gilman, J. Beel, C. Brannen, M. Bullock, G. Dunn, and L. Miller, *J. Am. Chem. Soc.*, **71**, 1499 (1949).

[13] K. R. Barton, Ph.D. Dissertation, The University of Tennessee, 1963.

[14] T. H. DeBoer, *Rec. Trav. Chim.*, **73**, 229 (1954).

these two isomers was made by trapping out the separate compounds at the exit port of the instrument. The methyl ester of smaller retention time was a liquid which, after saponification in alcoholic potassium hydroxide and acidification of the potassium salt, yielded pure white 1-methoxy-2-naphthoic acid, mp 126–127° (lit.[3] mp 126–127°).

The methyl ester with a longer retention time was collected as a solid, mp 46–48° (lit.[15] for methyl 8-methoxynaphthoate, mp 51–52°). Saponification of this ester with alcoholic potassium hydroxide and isolation of the free acid gave 8-methoxy-1-naphthoic acid which melted at 159–160° after recrystallization from benzene (lit.[15] mp 162–163°).

There were some additional minor peaks which followed these two major products on the chromatograph and probably represented trace quantities of other isomers. The results are shown in Table I. The relative amounts of the isomers are given as "percentage yield" of each isomer, with the total amount of monocarboxylic acids from a metalation run representing 100%. The data were derived from relative peak areas from the chromatograms and assume equal instrumental response from equal numbers of molecules of each isomer. It should be noted that an appreciable quantity of other isomers was formed in the run containing added lithium ethoxide, and this may be another case of apparent alteration of metalation rates at different ring positions due to the presence of alkoxides.[9,16] If the other isomers are neglected in expt 4, the ratio of metalation in the 2 position to the 8 position is 87:13, not significantly different from the other runs.

Acknowledgments.—The authors are grateful to the National Science Foundation for financial support of this work and to Spencer Watson and John Jacobus for the determination of the nmr spectra.

---

[15] E. Bretscher, H. Rule, and J. Spence, *J. Chem. Soc.*, **115**, 1500 (1928).

[16] A. A. Morton, C. E. Claff, and F. W. Collins, *J. Org. Chem.*, **20**, 428 (1955).

Tracer Studies of Acid-Catalyzed Reactions. III. Preparation of Perdeuterio Olefins and Cyclopropane by Reaction with Deuterium over Alumina

J. G. Larson, Joe W. Hightower, and W. Keith Hall

Mellon Institute, Pittsburgh, Pennsylvania

Received November 12, 1965

Very pure alumina, prepared from either redistilled aluminum isopropoxide or from a commercially available β-alumina trihydrate, is an excellent catalyst for exchanging the hydrogen atoms in olefins or cyclopropane without causing extensive saturation or skeletal isomerization. This method has been used successfully to prepare ethylene-d_4, propylene-d_6, the three *n*-butenes-d_8, the three *n*-pentenes-d_{10}, and cyclopropane-d_6.

Alumina has long been known to be a catalyst for H_2–D_2 exchange,[1-3] for double-bond, *cis–trans*,[4-7] and skeletal isomerizations[8] in olefins, for saturating olefins,[9] for isomerizing cyclic paraffins,[10-12] for cracking hydrocarbons,[13] and for dehydrating alcohols.[14] This communication reports other useful reactions for which alumina is a catalyst, *i.e.*, for replacing hydrogen atoms in olefins and cyclopropane with deuterium without saturating the olefins or opening the cyclopropane ring. By repeated equilibration of the hydrocarbon with fresh deuterium, it is possible to prepare the perdeuterio compounds with isotopic purities greater than 98%. A detailed study of this reaction may lead to a better understanding of hydrocarbon interactions with these and other heterogeneous oxide catalysts.

Results and Discussion

The nine unsaturated perdeuterio compounds which we have prepared are listed in Table I. Column 3 shows the initial pressure of the hydrocarbon admitted to the circulation system, but up to 50% was lost through a constant capillary bleed into the mass spectrometer during the deuterium treatments; this could have been avoided. Column 4 shows the average pressure of deuterium used in each of the doses numbered in column 5. The per cent isotopic purity is simply the ratio 100D/(D + H) in the final hydrocarbon.

No detectable polymerization or skeletal isomerization occurred, and the only other products formed from the olefins were small amounts (last column) of normal paraffins. For cyclopropane the number in column 9 includes 0.2% propane and 22.9% propylene. In all cases the "yield" of perdeuterio material was greater than 75%, and this could probably be improved by lowering the temperature. This improvement would depend on the assumption that the energy of activation for exchange is lower than that for saturation. For this assumption, we have some evidence.

Both the butenes and pentenes underwent rapid *cis–trans* and double-bond isomerization, for after the first D_2 treatment the three *n*-olefins were in thermodynamic equilibrium. It is not known whether the exchange reaction is associated with the isomerization of the butenes and pentenes.

Alumina, prepared from the commercial β-alumina trihydrate, was also shown to catalyze the exchange of propylene and *n*-butenes without causing saturation of the olefins. Other less pure aluminas were tried and found unsuitable. Small amounts of transition

---

[1] V. C. F. Holm and R. W. Blue, *Ind. Eng. Chem.*, **43**, 501 (1951); **44**, 107 (1952).

[2] S. W. Weller and S. G. Hindin, *J. Phys. Chem.*, **60**, 1506 (1956).

[3] S. G. Hindin and S. W. Weller, *Advan. Catalysis*, **9**, 70 (1957).

[4] R. G. Hay, J. Coull, and P. H. Emmett, *Ind. Eng. Chem.*, **41**, 2809 (1949).

[5] J. Turkevich and R. K. Smith, *J. Chem. Phys.*, **16**, 466 (1948).

[6] N. F. Foster and R. J. Cvetanovic, *J. Am. Chem. Soc.*, **82**, 4274 (1960).

[7] H. R. Gerberich, J. G. Larson, and W. K. Hall, *J. Catalysis*, **4**, 523 (1965).

[8] W. O. Haag and H. Pines, *J. Am. Chem. Soc.*, **82**, 2488 (1960).

[9] S. G. Hindin and S. W. Weller, *J. Phys. Chem.*, **60**, 1501 (1956).

[10] R. M. Roberts, *ibid.*, **63**, 1400 (1959).

[11] W. K. Hall, F. E. Lutinski, and H. R. Gerberich, *J. Catalysis*, **3**, 512 (1964).

[12] J. G. Larson, H. R. Geberich, and W. K. Hall, *J. Am. Chem. Soc.*, **87**, 1880 (1965).

[13] S. E. Tung and E. McIninch, *J. Catalysis*, **3**, 229 (1964).

[14] H. Pines and W. O. Haag, *J. Am. Chem. Soc.*, **83**, 2847 (1961).