

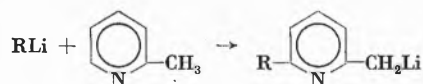
## Kurze Mitteilungen

Bis am 15. des Monats bei der Redaktion eingehende Kurze Mitteilungen werden in der Regel am 15. des folgenden Monats veröffentlicht. Es werden auch Manuskripte aus dem Ausland angenommen

### Selective Side Chain Lithiation of Toluene and Methylpyridines\*

Benzylolithium and its nitrogen heterocyclic analogs, the picolylolithiums, are of great synthetic value for the introduction of the benzyl and the pyridylmethyl groups into various organic structures. Thus, the availability of these compounds as shelf reagents similar to *n*-butyllithium would be most desirable. The discovery<sup>1</sup> that tertiary amines catalyze the metalation of toluene by lithium alkyls seemed for a while to provide an easy access to benzylolithium. However, the use of *N,N,N',N'*-tetramethylethylenediamine (TMEDA), one of the most effective amines, does not lead solely to benzylolithium, but rather to a mixture of side chain and ring-metalated products. Thus, according to a report<sup>1</sup> on the telomerization of ethylene with toluene as telogen, a 9 : 1 ratio of side chain-to-ring metalation products was obtained.

The mole ratio of toluene to *n*-butyllithium employed in these studies was approximately 300 to 1. Polyolithiation was reported<sup>2</sup> to occur even when toluene and *n*-butyllithium were used in equimolar quantities. CHALK and HOOGEBOOM<sup>3</sup> also observed that the ratio of side-chain to ring-metalated products in this reaction was 9 : 1. This ratio was constant independent of the time of reaction. In the case of the metalation of methylpyridines by organolithium reagent such as phenyllithium or *n*-butyllithium, it was found<sup>4,5</sup> the desired picolylithium product was always contaminated with a significant quantity of the product derived from the addition of the organolithium reagent to the azomethine linkage of the methylpyridine:



This report furnishes evidence that these metalations are general Lewis base-catalyzed reactions allowing the use of milder, more stereoselective reagents to obtain exclusively side-chain metalated derivatives. Thus, with the appropriate choice of metalating agent and Lewis base, specificity has been achieved in the side-chain lithiation of toluene and of 2- and 4-methylpyridines.

Benzylolithium was prepared free of ring-metalated by-products by a combination of *n*- or *sec*-butyllithium and tetrahydrofuran (THF). 2- and 4-Pyridylmethylolithiums ( $\alpha$ - and  $\gamma$ -picolylolithium) were prepared in excellent yield with THF and 2-thienyllithium.

It has been recognized<sup>6</sup> that the reactivity order amongst a series of organometallics depends not only upon the reference substrate but also upon the structure of the Lewis base that is kinetically involved. Two important roles have been attributed to Lewis bases in the reactivity of organometallics. The first, a thermodynamic role, is namely, the formation of coordination complexes with the lithium reagent, and the second role, a kinetic role, is the kinetic dependency of the reaction rate on the concentration of available base. From a detailed kinetic analysis<sup>7</sup> of the effect of various ethers and amines on the hydrogenolysis of *n*-butyllithium, an estimate of the relative effectiveness of the ether in the activation of *n*-butyllithium towards molecular hydrogen parallels that expected from its complex-forming ability. Proceeding from diethyl ether to 7-oxabicyclo [2-2.1] heptane, the molecular rigidity increases and one may assume that the oxygen atom becomes less sterically hindered by its neighboring groups. An extrapolation of the isokinetic effect for these ethers and TMEDA, with some degree of uncertainty, indicates that TMEDA is  $10^3$  to  $10^4$  times effective. This tremendous increase in efficacy may be the reason why TMEDA can activate *n*-butyllithium to such an extent that it can not discriminate side chain from ring sites in the metalation of toluene.

Table I. Effect of Ether Structure on the Reactivity of *n*-Butyllithium Toward Molecular Hydrogen

Ether	Relative Reactivity
Diethyl Ether	1.0
Tetrahydropyran	1.7
Tetrahydrofuran	2.8
7-Oxabicyclo [2-2.1] Heptane	3.1
TMEDA	$10^3$ to $10^4$

Information concerning the order of reactivity amongst a series of lithium alkyls shows that there is a marked dependence of the order on the reference substrate<sup>8</sup>. It is well known that lithium alkyls react with ethers and amines, resulting in the loss of carbon-lithium activity.

<sup>6</sup> C. G. SCRETTAS and J. F. EASTHAM, *J. Amer. Chem. Soc.* 88 (1966) 5668.

<sup>7</sup> C. G. SCRETTAS, PhD Thesis, University of Tennessee, 1966.

<sup>8</sup> R. WAACK and P. WEST, *J. Amer. Chem. Soc.* 86 (1964) 4494.

\* Received January 14, 1970.

<sup>1</sup> (a) G. G. EBERHARDT and W. A. BUTTE, *J. Org. Chem.* 29 (1964) 2928.

(b) C. G. SCRETTAS and J. F. EASTHAM, *J. Amer. Chem. Soc.* 87 (1965) 3278.

(c) A. W. LANGER JR., *Trans. N. Y. Acad. Sci.* 27 (1965) 741.

<sup>2</sup> R. WEST and P. C. JONES, *J. Amer. Chem. Soc.* 90 (1968) 2656.

<sup>3</sup> A. J. CHALK and T. J. HOOGEBOOM, *J. Organometal Chem.* 11 (1968) 615-8.

<sup>4</sup> C. C. KLOPPENBURG and J. P. WIBAUT, *Rec. Trav. Chim. Pays-Bas* 65 (1946) 393-407.

<sup>5</sup> J. W. HEY and J. P. WIBAUT, *Rec. Trav. Chim. Pays-Bas* 72 (1953) 513.

Table II. Metalation of Toluene

RLi	Base	(RLi)/(Base)	(Toluene)/(Base)	Reaction Temp. (°C)	Time (hrs)	Yield
<i>n</i> -BuLi	Et <sub>2</sub> O	1 : 2	30 : 1	25	48	43 <sup>a</sup>
<i>n</i> -BuLi	THF	1 : 2	30 : 1	27	48	73 <sup>a</sup>
<i>n</i> -BuLi	THF	1 : 30	15 : 1.1	10	72	95 <sup>b</sup>
<i>sec</i> -BuLi	Me <sub>3</sub> N	1 : 2	5 : 1	28	12	75 <sup>a</sup>
<i>sec</i> -BuLi	THF	1 : 2	1.9 : 1	0	38	89 <sup>b</sup>
<i>sec</i> -BuLi	THF	1 : 38	1.9 : 1	10	3.5	100 <sup>b</sup>
<i>sec</i> -BuLi	Et <sub>2</sub> O	1 : 1	2 : 1	-10	17	52 <sup>b</sup>
<i>sec</i> -BuLi	Me <sub>2</sub> O	1 : 5	5 : 1	-50 to r. t.	21	70 <sup>a</sup>
<i>sec</i> -BuLi	THF	1 : 6	6 : 1.25	-30 to +15	0.5	93 <sup>b</sup>
<i>sec</i> -BuLi	THF	1 : 2.8	2.5 : 1	-15 to r. t.	3	95 <sup>b</sup>
<i>t</i> -BuLi	Me <sub>2</sub> O	1 : 7	3 : 1	-10 <sup>c</sup>	12	79 <sup>a</sup>
<i>t</i> -BuLi	THF	1 : 1.25	1.75 : 1	-15	2	60 <sup>a</sup>

<sup>a</sup> As phenylacetic acid after carbonation.

<sup>b</sup> By oxidimetric titration<sup>9</sup> and *n*-butane analysis.

<sup>c</sup> The temperature rose gradually to room temperature and stirring was continued for the indicated period.

Table III. Derivatization of Preformed Pyridylmethylolithiums

Isomer	Pyridyl-methylolithium (moles)	Benzonitrile (moles)	Benzophenone (moles)	Reaction Temp. °C	Reaction Time (hrs)	Phenacyl-pyridine (grams)	Diphenyl Carbinol (grams)	Melting Point of Purified Product	Yield %
2	0.2	0.2	—	80	1	35	—	52-54	89
2	0.05	—	0.05	r. t.	16	—	14	151-152	98
3	0.2	0.2	—	80	0.5	26	—	51-53	66
3	0.05	—	0.05	r. t.	16	—	12	122-125	87
4	0.1	0.1	—	r. t.	48	22	—	112-113	100
4	0.14	—	0.15	r. t.	16	—	36	151-152	94

This suggests that while a large excess of base would accelerate metalation of an aromatic substrate, it might accelerate to an even greater extent the cleavage of base, which is in direct competition with the desired metalation. The desired metalation could also be favored by an increased concentration of the aromatic substrate. It has been found that good yields can be obtained in the metalation of toluene with butyllithium by controlling the relative ratio—(Base) : (BuLi) : (Substrate). Concentration conditions were chosen such that the desired reaction proceeds at a convenient rate at the smallest possible (Base) : (BuLi) ratio. Temperature also has a considerable effect upon the relative rates of base-cleavage and substrate metalation. Lower temperatures suppress the cleavage reaction. As can be seen from Table II, simple ethers and amines can catalyze the metalation of toluene with varying degrees of success. THF appears to be the most satisfactory. In some experiments, yields of metalation are taken as being synonymous with yields of carboxylic acids obtained by carbonation of the metalation products. In the experiments where the yields were determined by titrating<sup>9</sup> the active lithium, subsequent GLC analysis of butane evolved on hydrolysis confirmed the degree of completion of the reaction. Only one trimethylsilyl derivative was found in the case of the metalation of toluene with *sec*-

butyllithium and THF. The preparation of benzylolithium from toluene by metalation with *sec*-butyllithium and THF is a facile and always high yield reaction. A solid, yellow 1 : 1 benzylolithium-THF complex was obtained at low RLi/base ratios.

With the above considerations in mind, an organolithium reagent was sought having a lower order of reactivity than *n*-butyllithium or phenyllithium toward methyl-pyridines and thus being capable of selectively metalating the methyl group without also adding to the azomethine linkage. Thus, picolylolithium reagents were prepared from the corresponding methylpyridines by metalation with 2-thienyllithium. This organolithium reagent in conjunction with THF as the Lewis base shows a considerably lower reactivity towards methylpyridines than does phenyllithium, and was found to be highly selective for metalating side chains in methylpyridines. The high yields and purity of picolylolithiums thus prepared indicates that 2-thienyllithium in the presence of THF has virtually no reactivity toward the azomethine group of the heterocyclic ring.

A solid green 1 : 1- $\gamma$ -picolylolithium-THF complex was isolated and characterized. This ratio is consistent with previous results<sup>8</sup> obtained with organolithium-tertiary amine complexes, in which allyl and benzylolithium reagents formed complexes with an RLi/base ratio equal to unity.

Solutions of 2- and 4-picolylolithiums in benzene-THF (70-30) were found to be very stable at refrigeration

<sup>9</sup> P. F. COLLINS *et al.*, *Anal. Chem.* 33 (1961) 468.

temperature. Thus, no appreciable loss of carbon-lithium activity (in 1 to 1.5 N solutions) occurred during a nine-month storage period.

Derivatization of the picolylolithiums in THF medium by reaction with benzophenone or benzonitrile produced the corresponding carbinols or phenacylpyridines in very good yields (Table III).

### Experimental

All liquid reagents and solvents were distilled before use and stored over Linde No. 4A molecular sieves. The *sec*-butyllithium was used either in a hexane solution or as a solution in the hydrocarbon to be metalated. Equipment employed in the metalations simply consisted of a three-necked round bottom flask of one or two liter capacity (Ts 24/40 joints), fitted with a mechanical stirrer, a  $-100$  to  $+50^{\circ}\text{C}$  thermometer, a graduated dropping funnel, and a gas (Nitrogen) inlet for the maintenance of an inert atmosphere within the reaction system.

#### Benzylolithium

To a solution of 18 ml of *sec*-butyllithium (14.1 grams, 0.22 moles) dissolved in 180 ml of toluene was added, slowly, 40 ml of tetrahydrofuran (THF) at  $-15 \pm 1^{\circ}\text{C}$ . When about three-fourths of the THF had been added, the temperature rose rapidly to  $0^{\circ}\text{C}$ , and the entire mixture froze into a yellow crystalline mass. The remainder of the THF was added at once, and the solution was allowed to attain room temperature at which point most of the solid dissolved. Addition of an additional 10 ml of THF dissolved the remaining solid to give a clear orange-red solution. The total reaction period was about 3 hours. Oxidimetric analysis using  $\text{V}_2\text{O}_5$  indicated that little or no active base had been lost during the reaction. The solution was 0.93 N in active base, 0.98 N in total base. These values were substantiated by the modified Gilman double titration procedure using ethylene dibromide<sup>10</sup>. Gas chromatographic analysis of hydrolyzed and active samples of the solution for *n*-butane using a 20% DMS column ( $30^{\circ}$ ) indicated that 98 per cent of the *sec*-butyllithium had reacted. An aliquot of the solution was trimethylsilylated with trimethylchlorosilane and analyzed by PTGC on a 5% SE-30 column. Only one trimethylsilyl derivative was obtained, corresponding to benzyltrimethylsilane.

#### 2-Lithiothiophene

To a solution of 178 grams (168 ml, 2.1 moles) of thiophene and 130 grams (146 ml, 1.8 moles) of tetrahydrofuran in 330 ml of benzene was added slowly 168 ml of 90 weight per cent *n*-butyllithium (1.8 moles) over a period of one hour, while maintaining the temperature between  $30$  and  $35^{\circ}\text{C}$ . The resulting dark solution was stirred for 16 hours at room temperature. A 50 ml aliquot of the solution was reacted with an equivalent of benzophenone. On workup the resulting 2-thienyldiphenyl carbinol (m.p.  $125$ – $127^{\circ}\text{C}$ , lit.<sup>11</sup> m.p.  $129$ – $130^{\circ}$ ) was obtained in 84 per cent yield.

#### $\alpha$ -Picolylolithium

To 30 ml of a 1.7 N solution of 2-thienyllithium in benzene-tetrahydrofuran solution was added 9.15 grams (10 ml, 0.1 moles) of 2-methylpyridine ( $\alpha$ -picoline). The resulting dark green mixture was stirred at room temperature for 16 hours, and then 9.0 grams (0.05 moles) of benzophenone dissolved in

50 ml of ether was added. Stirring was continued for three hours. Workup of the mixture gave a solid product, which, after steam distillation, weighed 13.5 grams and melted at  $135$ – $145^{\circ}\text{C}$ . The crude yield of 1,1-diphenyl-2-(2-pyridyl)-ethanol was quantitative based on benzophenone. After one recrystallization from boiling hexane it melted at  $151$ – $152^{\circ}\text{C}$  (lit.<sup>12</sup> m.p. =  $150$ – $151^{\circ}\text{C}$ ).

In another preparation of  $\alpha$ -picolylolithium, 35 ml of 2-methylpyridine was added to 225 ml of a 0.99 N solution of 2-thienyllithium and the resulting mixture heated to  $50$ – $53^{\circ}\text{C}$  for 2 hours. Titration of an aliquot of the deep green solution with *sec*-butyl alcohol<sup>13</sup> to a disappearance of color indicated the presence of at least 90 per cent of the original active base. To the solution of  $\alpha$ -picolylolithium was added, at once, 20.6 grams (0.20 moles) of benzonitrile and the mixture was refluxed for one hour. After workup, 35 grams of a crude solid product was obtained (89% yield). On recrystallization, the product melted at  $52$ – $54^{\circ}\text{C}$  (lit.<sup>14</sup> m.p. =  $54^{\circ}\text{C}$ ).

#### $\beta$ -Picolylolithium

Following the procedure given above for  $\alpha$ -picolylolithium, a 0.82 N solution of  $\beta$ -picolylolithium in benzene-tetrahydrofuran medium was prepared. Reaction with benzophenone gave a 87 per cent yield of crude  $\beta$ -picolyl 1,1-diphenylcarbinol m.p.  $122$ – $125^{\circ}\text{C}$  (lit.<sup>12</sup> m.p. =  $121$ – $122^{\circ}\text{C}$ ), while reaction with benzonitrile gave a 66 per cent yield of crude  $\beta$ -phenacylpyridine, a recrystallized sample of which melted at  $51$ – $53^{\circ}\text{C}$  (lit.<sup>14</sup> m.p. =  $48.5$  to  $49.5^{\circ}\text{C}$ ).

#### $\gamma$ -Picolylolithium

Following the procedure for the preparation of  $\alpha$ -picolylolithium, a 0.85 N solution of  $\gamma$ -picolylolithium in benzene-tetrahydrofuran medium was prepared from 2-thienyllithium and  $\gamma$ -picoline. A green, crystalline 1:1  $\gamma$ -picolylolithium-tetrahydrofuranate complex could be prepared by evaporating about 15 per cent of the solvents under vacuum. The stoichiometry of the complex was established by a combination of pH titration and vapor phase chromatography. One sample of the solid was hydrolyzed and titrated with standard acid using a pH meter. Two sharp breaks in the pH versus ml acid curve were obtained corresponding to lithium hydroxide (pH 10.9) and  $\gamma$ -picoline (pH 4.3). The lithium to  $\gamma$ -picoline correspondence was 1:1. A second sample was quenched with *sec*-butyl alcohol and analyzed for THF and  $\gamma$ -picoline by VPC. The normalized peak areas had a 1:1 correspondence.

The crude  $\gamma$ -picolylidiphenylcarbinol and  $\gamma$ -phenacylpyridine derivatives were obtained in 94 per cent and 100 per cent yields respectively. Their melting points after recrystallization were  $151$ – $152^{\circ}\text{C}$  (lit.<sup>12</sup> m.p.  $159$ – $160^{\circ}$ ) and  $112$ – $113^{\circ}\text{C}$  (lit.<sup>15</sup> m.p. =  $112$ – $113^{\circ}\text{C}$ ) respectively.\*

C. G. SCRETTAS<sup>a</sup>, J. F. ESTHAM<sup>b</sup> and C. W. KAMIENSKI<sup>c</sup>  
Lithium Corporation of America, Bessemer City  
(North Carolina, U.S.A.)

<sup>a</sup> Address: Royal Hellenic Institute, Athens (Greece).

<sup>b</sup> Address: Department Chemistry, University of Tennessee, Knoxville (Tennessee).

<sup>c</sup> Author to whom replies should be sent: Lithium Corporation of America, Bessemer City (North Carolina).

<sup>12</sup> W. S. MERRELL Co., Brit. Patent 765,854, January 16, 1957.

<sup>13</sup> S. C. WATSON and J. F. EASTHAM, *J. Organometal. Chem.* 9 (1967) 165–8.

<sup>14</sup> A. MILLER, C. OSUCH, N. GOLDBERG and R. LEVINE, *J. Amer. Chem. Soc.* 78 (1956) 674.

<sup>15</sup> W. VON E. DOERING and W. McEWEN, *J. Amer. Chem. Soc.* 73 (1951) 696–7.

\* Belgian Patent No. 716,716, Aug. 30, 1968, C. G. SCRETTAS to Lithium Corporation of America covers the selective side chain lithiation of alkyipyridines and alkyquinolines described in this paper.

<sup>10</sup> H. GILMAN and F. CARTLEDGE, *J. Organometal. Chem.* 2 (1964) 447.

<sup>11</sup> T. POSNER and I. SICHERT, *Ber. dtsh. chem. Ges.* 63 B (1930) 3078–88.

## Quantitative gas-chromatographische Analyse der Wasserstoffisotopen $H_2$ , HD, $D_2$ auf geätztem Glas\*

### Summary

A fast quantitative routine determination of the isotope molecules  $H_2$ , HD,  $D_2$  with a conventional gas chromatographic apparatus is described. The column, 2 m in length and 4 mm i.D., was filled with alkaline-etched and  $Fe_2O_3$ -impregnated glass-powder or beads of 0,09 to 0,12 mm diameter. After activation at 300°C, a complete separation of HD/ $D_2$  in 2 minutes at 77°K was obtained using  $H_2$  as carrier gas with a flow rate of 75 ml/min. With a catharometer as detector and 0,5 ml samples of  $H_2$ , HD,  $D_2$ -mixtures, analysis in the concentration range between 0,05 to 100% of D are possible.

Seit der ersten gas-chromatographischen HD/ $D_2$ -Trennung unter Verwendung von  $H_2$  als Trägergas<sup>1</sup> sind zahlreiche Veröffentlichungen über dieses Thema erschienen<sup>2</sup>. Es konnten die Gemische *p*- $H_2$ , *o*- $H_2$ , HD, *o*- $D_2$ , *p*- $D_2$  und  $H_2$ , HD, HT,  $D_2$ , DT,  $T_2$  auf Kapillar-<sup>3</sup> bzw. gepackten<sup>4</sup> Säulen vollständig getrennt werden. Außerdem wurde die Nachweisempfindlichkeit der Detektion genügend stark erhöht, um auch die stabilen Moleküle in allen praktisch interessanten Konzentrationsbereichen bestimmen zu können<sup>5</sup>. Als besonders geeignete stationäre Phase hat sich alkalisch geätztes Glas erwiesen, womit eine vollständige  $H_2$ , HD,  $D_2$ -Trennung in einer Säule von 35 cm Länge erreicht wurde<sup>6</sup>.

Für die routinemäßige Anwendung der gas-chromatographischen Wasserstoffisotopenanalyse, z. B. der quantitativen HD/ $D_2$ -Bestimmung in der Katalysatorforschung, sind Einfachheit, Reproduzierbarkeit und Schnelligkeit der Analyse entscheidende Faktoren, verglichen mit hoher Trennleistung und Nachweisempfindlichkeit. Die im folgenden beschriebene Anordnung und Arbeitsweise entspricht diesen Forderungen.

Weiches, Na-reiches Glas beliebiger Herkunft und Qualität wird zerstoßen und gesiebt. Das Glas kann in Form von Pulver oder Kugeln mit einem Durchmesser von etwa 0,09 bis 0,12 mm verwendet werden. Die Ätzung der Glasoberfläche wird durch Behandeln mit 10prozentiger NaOH-Lösung bei 100°C durchgeführt<sup>7</sup>. Rühren und mehrmaliges Auswechseln der NaOH-Lösung (Intervallen von 2 Stunden) ist für eine gleichförmige Ätzung aller Glasteilchen notwendig. Der Verlauf der Reaktion kann durch Probeentnahme und Betrachtung des Glases unter dem Mikroskop kontrolliert werden. Je nach der Natur des verwendeten Glases ist die Behandlung nach 5 bis 10 Stunden

beendet, wenn sich eine gleichförmige, milchig-weiße Schicht auf den Glasparkeln gebildet hat. Die NaOH-Lösung wird abgossen und das Glas 2- bis 3mal mit Wasser gewaschen, bis es klar, aber nicht alkalifrei bleibt. Um die *ortho-para*-Wasserstoff-Umwandlung zu katalysieren<sup>8</sup>, wird das getrocknete Glas in eine wässrige  $FeCl_3$  (1-m)-Lösung gebracht und nach einigen Minuten durch Absaugen auf einer Fritte von der überschüssigen Lösung getrennt, aber nicht gewaschen.

Mit einer wässrigen Ammoniaklösung 1 : 1 wird schließlich  $Fe_2O_3$  ausgefällt, nach etwa 3 Minuten abgossen, 3- bis 4mal mit Wasser gewaschen, bei 120°C getrocknet, nochmals gesiebt und in ein Kupferrohr von 4 mm i.D. und 2 Meter aktiver Länge eingefüllt. Anschließend wird das Rohr gewunden und die leeren, zum Probengeber bzw. Detektor führenden Enden mit Glaswollepfropfen und Glasstäben oder Glasperlen gefüllt, um das Totvolumen klein zu halten. In einem Stickstoff- oder trockenen Luftstrom wird die Säule 5 Stunden bei 300°C aktiviert.

Als Trägergas dient  $H_2$ , der bei einem Reinheitsgrad von etwa 99,99% nicht noch über Molekularsieb bei 77°K gereinigt werden muß. Die Adsorption dieses Trägergases bei der Arbeitstemperatur von 77°K bewirkt eine teilweise Desaktivierung der stationären Phase, wodurch symmetrische Peaks erhalten werden. Bei einem Trägergasstrom von etwa 75 ml/min beträgt der Druckabfall in der Säule etwa 0,2 Atm. Als Detektor dient ein gewöhnliches Katarometer mit Filamenten, dessen Empfindlichkeit bei einer Probenmenge von 0,5 ml im allgemeinen ausreicht, um HD- und  $D_2$ -Bestimmungen im Konzentrationsbereich von etwa 0,05% HD bzw. 0,03%  $D_2$  bis 100% durchzuführen. Die Dauer einer Analyse beträgt 2 Minuten. Eine Eichung mit bekannten  $H_2$ ,  $D_2$ -Gemischen ist wegen der Nichtlinearität des Signals bei höheren  $D_2$ -gehalten erforderlich. Die Eichung für HD erfolgt nachträglich durch eine katalysierte Gleichgewichtseinstellung zwischen  $H_2$ , HD,  $D_2$ , wobei der bekannte Verlust an  $D_2$  in Form von HD im Chromatogramm auftritt.

Die Säule ist praktisch unbegrenzt verwendbar. Wenn nach längerem Betrieb oder Dosierung von Proben mit vielen Verunreinigungen die Auflösung schlechter wird, genügt ein zeitweiliges Entfernen der flüssigen Luft, wobei die gasförmigen Verunreinigungen vom  $H_2$ -Strom wieder ausgespült werden. Gegebenenfalls kann die Säule in beschriebener Weise bei 300°C reaktiviert werden. Die Verwendung von  $H_2$  als Trägergas bietet keine nennenswerten Nachteile für die quantitative  $H_2$ , HD,  $D_2$ -Bestimmung, da auch bei Proben mit verschiedenen chemischen Stoffen eine globale Messung des molekularen Wasserstoffgehaltes gas-chromatographisch mit einer kurzen Säule aus Aktivkohle oder Molekularsieb 5 A bei Zimmertemperatur und  $N_2$ -Trägergas möglich ist. Wenn dennoch He oder Ne an Stelle von  $H_2$  als Trägergas bevorzugt werden sollte, muß die Säule bei Zimmertemperatur mit Wasserdampf gesättigt und dann ungefähr eine Stunde bei etwa 80°C ausgeheizt werden.

\* Eingegangen am 13. Februar 1970.

<sup>1</sup> S. OHKOSHI, Y. FUJITA und T. KWAN, *Bull. chem. Soc. Japan*, 31 (1958) 770.

<sup>2</sup> S. AKHTAR und A. H. SMITH, *Chem. Rev.* 64 (1964) 261.

<sup>3</sup> M. MOHNKE und W. SAFFERT, *Gas Chromatography 1962*, Hamburg, (M. VAN SWAAY, ed.), Butterworth, London 1962, S. 216.

<sup>4</sup> C. GENTY und R. SCHOTT, *Anal. Chem.* 42 (1970) 7.

<sup>5</sup> M. MOHNKE, O. PIRINGER und E. TATARU, *J. Gas. Chromatogr.* 6 (1968) 117.

<sup>6</sup> O. PIRINGER, 5. Intern. Tagung über Trennmethode: *Säulenchromatographie, Lausanne 1969*, erscheint in Sonderband der *Chimia*.

<sup>7</sup> A. LIBERTI, *Gas Chromatography 1966*, Ed. A. B. Littlewood, Institute of Petroleum, London 1967, S. 95.

<sup>8</sup> W. R. MOORE und H. R. WARD, *J. Physic. Chem.* 64 (1960) 832.

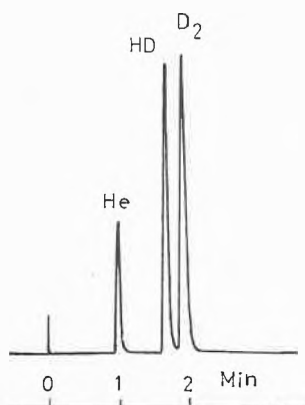


Abb.1. HD/D<sub>2</sub>-Trennung auf NaOH-geätztem Glas unter Verwendung von H<sub>2</sub> als Trägergas und eines Wärmeleitfähigkeitdetektors

Das Wasser bewirkt in diesem Fall die teilweise Desaktivierung zur Erhaltung symmetrischer Peaks. Die optimale Aktivierungstemperatur hängt von der Quali-

tät der stationären Phase ab und kann leicht durch das analytische Ergebnis ermittelt werden. Die angegebene Säulenlänge ist bei Probemengen von 0,5 bis 1 ml, wie sie bei Verwendung von Katarometern notwendig sind, erforderlich. Bei Probemengen von der Größenordnung eines Mikroliter und empfindlicheren Detektoren können infolge viel geringerer Belastung wesentlich kürzere Säulen verwendet werden<sup>6</sup>.

Abb.1 veranschaulicht eine Trennung nach obiger Vorschrift auf Glaskugeln der Firma Minnesota Mining and Manufacturing Company.

Wir danken dem Schweizerischen Nationalfonds zur Förderung der Wissenschaftlichen Forschung für die Unterstützung dieser Arbeit.

T. GÄUMANN, \* O. PIRINGER und A. WEBER

Institut de Chimie Physique EPF-L, avenue des Bains 31,  
1007 Lausanne

\* Permanente Adresse: Institut für Atomphysik, Cluj  
C.P. 75 (Rumänien)