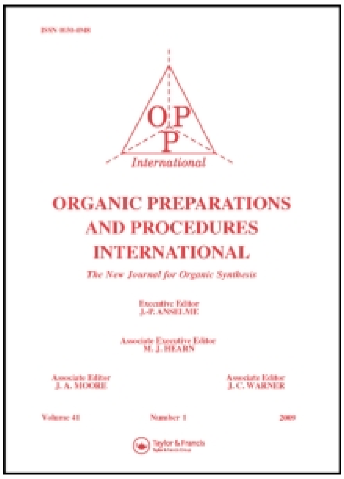


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

AN IMPROVED PREPARATION OF *m*- AND *p*-TETRAMETHYLXYLYLENEDIISOCYANATES

Wm. A. Henderson Jr.[a]; Vazken A. Alexanian[a]
[a] American Cyanamid Company Stamford Research Laboratories, Stamford, CT

To cite this Article Henderson Jr., Wm. A. and Alexanian, Vazken A.(1986) 'AN IMPROVED PREPARATION OF *m*- AND *p*-TETRAMETHYLXYLYLENEDIISOCYANATES', Organic Preparations and Procedures International, 18: 3, 149 — 155
To link to this Article: DOI: 10.1080/00304948609458137
URL: http://dx.doi.org/10.1080/00304948609458137

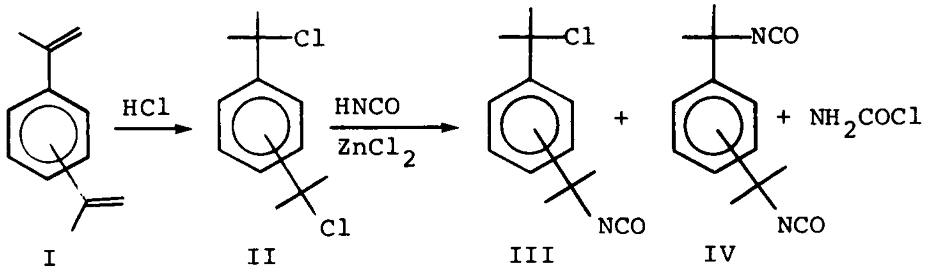
ORGANIC PREPARATIONS AND PROCEDURES INT. 18(3), 149-155 (1986)

AN IMPROVED PREPARATION OF
m- AND *p*-TETRAMETHYLXYLYLENEDIISOCYANATES

Wm. A. Henderson, Jr.* and Vazken A. Alexanian

American Cyanamid Company
Stamford Research Laboratories
1937 West Main Street, P.O. Box 60
Stamford, CT 06904-0060

Aliphatic diisocyanates react with polyols to give light stable polyurethanes with a variety of uses. Because of the enormous advantages offered by light stable polyurethanes, we became interested in developing a practical method for the synthesis of 1,3- and 1,4-bis(1-isocyanato-1-methylethyl)-benzene (IVa and IVb). Both isocyanates had been prepared previously by the reaction of the corresponding diolefins (Ia and Ib) with excess isocyanic acid in low yields because of self-polymerization of the diolefins and the isocyanic acid.[1]



(1)

$$2\ NH_2COCl + I \longrightarrow II + [2HNCO] \qquad (2)$$

They had also been obtained in two steps by the reaction of diolefins (I) with hydrogen chloride followed by reaction with sodium cyanate using $ZnCl_2 \cdot 2Py$ as a catalyst.[2] Since two equivalents of hydrogen chloride and base are consumed in this reaction, this approach is not attractive.

We now report a substantially improved, two-step preparation of IVa and IVb from the corresponding diolefins Ia and Ib and isocyanic acid via Eq. 1. The dichlorides II, prepared by the addition of hydrogen chloride to diolefin I, react with excess isocyanic acid in the presence of zinc chloride to give the desired isocyanates in high yield (Table I). Since carbamoyl chloride is formed as a by-product, its reaction with I (Eq. 2) would complete a process cycle wherein neither hydrogen chloride nor base is consumed. Hence, this approach is more economical than the methods previously described.

Although only four moles of isocyanic acid are required to form IV and carbamoyl chloride via Eq. 1, the reaction was at first run with a larger excess of isocyanic acid in order to favor the reaction of the intermediate carbonium ion with isocyanic acid and minimize the formation of oligomeric by-products (Run 2, Table I). When less isocyanic acid was used, a lower yield and conversion was obtained (Run 3). Highest yields were obtained when a stoichiometric amount of isocyanic acid was used, provided the addition of the catalyst was delayed with respect to II (Run 4). In the preferred method, the zinc chloride can be added either as a solution in ether, as the neat dietherate, or as the diketonate with 2-octanone or other ketones. While zinc bromide and bismuth bromide were effective catalysts in this reaction, 18 other Lewis acids screened gave little or no isocyanate products.

TABLE I

Preparation of m- and p-Tetramethylxylylene Diisocyanates (IVa and IVb) from Dihalides IIa and IIb in Toluene at 0°

Run	mmoles	II	Ratio II:HNCO:$ZnCl_2$	Time[a] (min.)	Yields Based on II (%) II	III	IV	Sum	Yield of IV[b] (%)
1	2	IIb	2:11:0.1[c]	60	3	12	51	66	46
2	2	IIa	2:11:0.1[d]	3	0	10	86	96	84
3	2	IIb	2:4:0.1[d]	4	27	20	21	68	41
4	2	IIb	2:4:0.05[e]	10	4	17	76	97	90

---

a. Measured from time when all reactants have been added.
b. Based on HNCO consumed and calculated from the following expression: $100(III+2xIV)/(HNCO_{init}-HNCO_{recov}-H_2NCOCl_{recov})$.
c. $ZnCl_2$ added last and all at once. d. $ZnCl_2$ and II added simultaneously over a period of 1.5 minute. e. $ZnCl_2$ and II added over 5 minute periods, with addition of $ZnCl_2$ delayed by 2 minutes with respect to II.

Interestingly, trace amounts of water in the solvent could be tolerated up to the amount required to convert the catalyst used to $ZnCl_2 \cdot 2H_2O$. Beyond that amount, the yields of III and IV dropped precipitously indicating complete catalyst deactivation. The reaction of II with isocyanic acid was also run in a continuous manner by metering solutions of the reactants and catalyst into a well stirred reactor cooled to -5°. With residence times of 1-4 minutes, yields were comparable to batch reactions. However, after periods in excess of 10 residence times, white solids accumulated on the walls of the reactor and, as a result, the yields decreased due to gradual deactivation of the zinc chloride catalyst.

Finally, the reaction was carried out successfully in a recycle mode which allowed recovery and reuse of the carbamoyl chloride by-product. Thus, diolefin I was added to a 10% excess of independently synthesized or recovered carbamoyl chloride in toluene at 0°. Within 5 minutes, the diolefin was completely converted to dichloride II, and isocyanic acid in 90% yield. After introducing additional isocyanic acid, zinc chloride etherate was added as usual to give the diisocyanate IV in 60-80% yield based on both I and isocyanic acid.

EXPERIMENTAL SECTION

Analyses.- Organic components of reaction mixtures were quantitated by programmed GC using a Hewlett Packard 5840A instrument, helium as carrier, and a 4 ft. column packed with 10% OV-17 and 10% SP2401 on 80/100 mesh Supelcoport. All analyses were run using octadecane as internal standard, added either to the reaction mixture or to each aliquot. Dihalides II dehydrohalogenated quantitatively in the GC inlet tube to I and were analyzed as such. Isocyanic acid was determined by extraction from the organic solution into aqueous caustic, acidification with hydrochloric acid, hydrolysis to ammonia, basification with sodium hydroxide, and quantification using an ammonia specific electrode. Carbamoyl chloride was determined by potentiometric titration for chloride using silver nitrate reagent.

Reactants.- 1,4-Bis(1-chloro-1-methylethyl)benzene (IIb) was prepared from *p*-diisopropenylbenzene by the method of Fritz and Rees.[3] The 1,3-isomer (IIa), a liquid, was prepared in the same way from *m*-diisopropenylbenzene and was used without further purification. Isocyanic acid was prepared by the air oxidation of hydrocyanic acid as described by Katz.[4] The isocyanic acid was scrubbed from the exit gas stream using a Dry Ice condenser, and collected at Dry Ice temperature in toluene. Solutions obtained by this method contained approximately 20% by weight isocyanic acid; after drying over 3A° molecular sieves, they were stored at -50°. Solutions showed little or no loss of isocyanic acid on storage for one month or more. Isocyanic acid solutions in solvents other than toluene were prepared by distillation under reduced pressure from a toluene solution into the desired solvent.

CAUTION. Extreme care must be taken to avoid higher concentrations, to keep the solution at approximately 0° while in use, and to avoid introduction of amines and other bases to the solution. At concentrations much above 20% in toluene, isocyanic acid precipitates to form a second phase which is subject to violent decomposition. Similarly, exposure of isocyanic acid either to heat (i.e. temperatures above 0°) or common bases causes violent decomposition. It is imperative, therefore, that safety shields and efficient hoods be used to prevent injury.

Preparation of 1,4-Bis(1-isocyanato-1-methylethyl)benzene (IVb).

A. From 1,4-Bis(1-chloro-1-methylethyl)benzene and Isocyanic Acid.- A solution of IIb (20 mmoles) in toluene (10 ml) and 1m zinc chloride in ether (1 mmole, 5 mole %) were simultaneously added to a toluene solution of isocyanic acid (110 mmoles) at -5° (250 ml flask cooled in a salt/ice bath) over a period of 1.5 minute with vigorous stirring. After 6 minutes, aliquots of the reaction mixture were removed and analyzed for organics and total isocyanic acid. Yields were 6% IIb, 15% IIIb and 66% IVb, total recovery 97% based on IIb, and 73% IIIb plus IVb based on isocyanic acid consumed. The reaction mixture was then filtered to remove the white solids. After evaporation of the filtrate under vacuum to remove the solvent, unreacted isocyanic acid and carbamoyl chloride, the residue was distilled at 110-130°C/1 mm to give 2.68g of IV, mp. 74-76°, lit.[1] 78°C.

B. From 1,4-Diisopropenyl Benzene (Ib) and Carbamoyl Chloride. Dry hydrogen chloride (0.73g, 20 mmoles) was introduced to a solution of isocyanic acid (0.86g, 20 mmoles) in toluene (3.44g) at 0° under a nitrogen atmosphere. Ib (1.58g, 10 mmoles) was introduced slowly to the resultant carbamoyl chloride solution over a period of ten minutes with stirring while maintaining the temperature at 0°C. After fifteen minutes tetramethyl-p-xylylene dichloride (IIb) was present in 80% yield. Isocyanic acid (23 ml) in toluene (100 mmole) was added at 0° with stirring followed by addition of 0.50 ml of 1M zinc chloride (0.50 mmole) in ether over a period of 2 minutes at 0°; after one hour, 1.54g of IVb had formed (63% yield based on Ib).

Preparation of 1,3-Bis(1-isocyanato-1-methylethyl)benzene (IVa).

A. From 1,3-Diisopropenyl Benzene and Carbamoyl Chloride.- 1,3-Diisopropenyl benzene (1.58g, 10 mmoles) was added to a suspension of carbamoyl chloride (1.47g, 22 mmoles) in toluene over a period of ten minutes at 0°C with stirring to give IIa. Treatment with isocyanic acid and zinc chloride (see above) gave 1.90g (78% yield based on the starting olefin) of IVa.

B. From 1,3-Diisopropenyl Benzene and Carbamoyl Bromide.- Carbamoyl bromide (2.48g, 20 mmoles) was prepared following the procedure above with the substitution of hydrogen bromide for hydrogen chloride. Then Ia was added (1.58 g, 10 mmoles) followed by isocyanic acid (100 mmoles) and zinc chloride (0.50 mmole) in ether (see above). After 30 minutes a mixture consisting of 13% tetramethyl-m-xylylene dibromide, 43% of the monoisocyanate-monobromide and 38% of IVa was obtained.

Continuous Preparation of 1,4-Bis(1-isocyanato-1-methylethyl)-benzene (IVb).- A continuous backstirred reactor with a volume of 4 ml was set up with provision for separate addition of three reactant streams - dichloride II in toluene, isocyanic acid in toluene, and zinc chloride in ether. The contents of the reactor were agitated with a magnetic stirrer and cooled in a salt/ice bath and reactants (IIb:HNCO:$ZnCl_2$) were introduced in a 2:11:0.1 ratio. After 5 residence times, the effluent was collected and analyzed by GC for organic components. The yields of IVb which were 90-94% initially, decreased after several half lives to 60% or less as white solids accumulated and deactivated the catalyst.

Acknowledgment.- The authors wish to acknowledge the contribution of Drs. L. W. Chang, P. S. Forgione, J. E. McClure, R. J. Proverb, J. A. Sedlak and B. Singh to the various phases of this work.

REFERENCES

1. F. W. Hoover and H. S. Rothrock, J. Org. Chem., 29, 143 (1964).
2. N. Nagato and T. Naito, U.S. Patent 4,130,577; C.A., 89, P179687s (1978).
3. A. Fritz and R. W. Rees, J. Poly. Sci., A-1, 10, 2365 (1972).
4. D. S. Katz, U.S. Patent 4,364,913; C.A., 98, P74842w (1983).

(Received September 16, 1985; in revised form January 22, 1986)