TABLE II

DECOMPOSITION OF NO, NH_3 MIXTURES AT VARYING NO CONCENTRATIONS[a]

T, °C.	Reactants, mm. NH_3	Reactants, mm. NO	$(N_2)_\infty$, mm.	½ Reaction time, min. obsd.	½ Reaction time, min. calcd.	$k_a = 10_8$
702	17.5	882	182	9.0	9.5	19
		682	172	17.0	17.0	
		482[b]	140	24.0	36.0	
		482	174			
725	3.5	896	82	5.5	5.5	36
		696	67	9.0	9.0	
740	7.0	893	84	2.5	2.6	74
		693	76	4.6	4.5	
755	17.5	882	158	1.8	1.9	104
		682	132	3.2	3.2	
		682[b]	152	3.4	3.2	

[a] All pressures measured at reaction temperatures. Half-reaction time calculated from

$$t_{\frac{1}{2}}(\text{calcd.}) = \frac{2}{k_a[(NO) - 2(N_2)_\infty]}\left[\frac{1}{[2(N_2)_\infty - (NO)_0]}\ln\left\{\frac{(NO)}{2[(NO)_0 - (N_2)_\infty]}\right\} - \frac{(N_2)}{(NO)_0[(NO)_0 - (N_2)_\infty]}\right]$$

[b] The reactants for the last runs at 702 and 755° contained added N_2 to give an initial pressure of 900 mm.

from 482 mm. nitric oxide at 702° can be raised almost to the yield from 882 mm. nitric oxide by the addition of inert gas to give the same initial pressure. The effect is observed at 755° also.

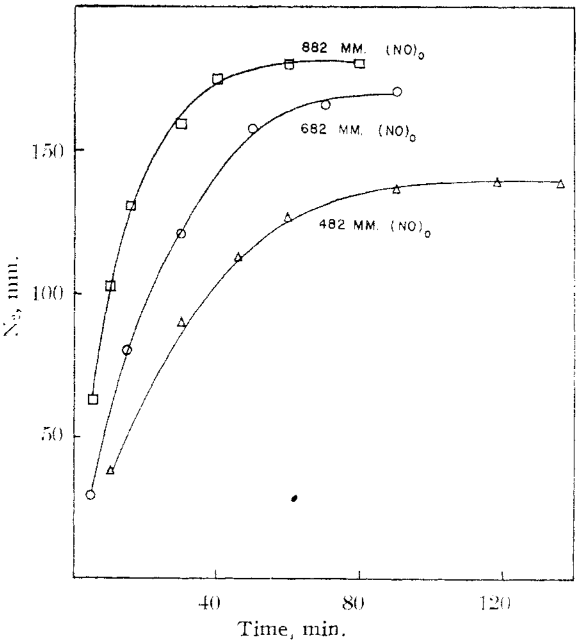


Fig. 2.—Evolution of N_2 from NO, NH_3 mixtures at 702° containing 17.5 mm. NH_3 initially. Initial NO pressure is marked on each curve.

The rate equations

$$-\frac{d(NH_3)}{dt} = k_a(NH_3)(NO)^2$$

$$\text{and } \frac{d(N_2)}{dt} = k_b(NH_3)^{\frac{1}{2}}(NO)^2$$

are consistent with our observations. Because then $(N_2)_\infty = (2k_b/k_a)(NH_3)_0^{\frac{1}{2}}$, characteristics (1) and (4), and $t_{\frac{1}{2}}$ = approximately $2\ln 2/k_a \cdot (NO)_0^2$, characteristics (2) and (3) (more exactly, $t_{\frac{1}{2}}$ is given in the footnote to Table II). But other choices of exponents in the rate equations will not give these relations.

An obvious interpretation of the one-half order ammonia dependence of the rate of formation of nitrogen is that ammonia itself is not the catalytic agent, but that two catalytic particles arise from each ammonia molecule consumed in a rate determining reaction. An inert gas effect in increasing the yield of nitrogen is then explicable because of the possibility of diffusion of the catalytic particles to the vessel wall and their destruction there.

The catalytic particles might be NH_2 radicals, and since the thermal decomposition of hydrazine to NH_2 is first order and homogeneous, in part, above 650–700°,[3] we looked into the possibility of inducing the decomposition of nitric oxide by hydrazine at 800°. The higher temperature was chosen to increase the fraction of hydrazine decomposing unimolecularly in the gas phase. This reaction is not clean: nitrogen (but less than the moles of hydrazine taken) is formed at room temperature when hydrazine is mixed with nitric oxide, and the slow decomposition of nitric oxide is appreciable in our apparatus at 800°. It is scarcely worthwhile to tabulate the yields. Nitric oxide is decomposed by 0.2–1.0% hydrazine at 800° and gives nitrogen in yields comparable to those obtained with the same amount of ammonia at 700–750° although the reaction with hydrazine is less reproducible. We conclude from the runs with hydrazine, rather as we began, that the catalytic framents might be, but need not necessarily be, NH_2 radicals.

The foregoing data are insufficient to illuminate the mechanism. If one identifies X with NH_2 in the four equations set down in the introduction to this paper, assumes that NH_2 radicals are generated two for every ammonia molecule consumed in a reaction 1st order in ammonia and 2nd order in nitric oxide, and supposes that the radicals are destroyed two at a time in the gas phase, then one can arrive at rate equations agreeing with those deduced above. But the values of k_a in Table II give a temperature dependence of the consumption of ammonia corresponding to an activation energy of 70 ± 5 kcal./mole. This large activation energy suggests that the formation of NH_2 radicals cannot be both termolecular and relatively fast and so the question of mechanism must be left open.

[3] M. Szwarc, *Proc. Roy. Soc.* (*London*), **198A**, 267 (1949).

BALLISTIC RESEARCH LABORATORIES
ABERDEEN PROVING GROUND, MD. RECEIVED JULY 13, 1951

The Reaction of Some Aryllithium Compounds with Epichlorohydrin

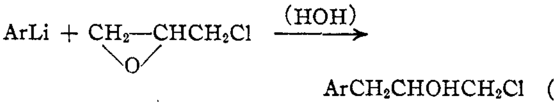
BY HENRY GILMAN, BURT HOFFERTH AND JULIAN B. HONEYCUTT

In connection with the synthesis of some alkamine ethers,[1] it was of interest to prepare a series of aromatic secondary alcohols by the action of

---

[1] B. Hofferth, Doctoral Dissertation, Iowa State College, 1950.

aryllithium reagents upon epichlorohydrin.[2] Accordingly, phenyl-, *p*-tolyl-, 1-naphthyl- and *p*-dimethylaminophenyllithium were treated with epichlorohydrin to give satisfactory yields of the corresponding arylpropylene chlorohydrins.

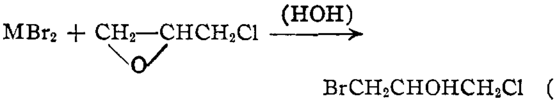


$$\mathrm{ArLi} + \underset{\diagdown O \diagup}{\mathrm{CH_2{-}CHCH_2Cl}} \xrightarrow{\text{(HOH)}} \mathrm{ArCH_2CHOHCH_2Cl} \quad (1)$$

The reaction of 9-fluorenyllithium under like conditions did not produce an isolable product.

Similar reactions employing Grignard reagents have been carried out with epichlorohydrin to give generally unsatisfactory conversions to the desired products. The best yield of 1-chloro-3-phenyl-2-propanol prepared from phenylmagnesium bromide was 18.2%.[3] Yield data were not given in reports of authors employing *p*-tolylmagnesium bromide[4] and 1-naphthylmagnesium bromide.[3c] The product, 1-chloro-3-(*p*-dimethylaminophenyl)-2-propanol, which was prepared from *p*-dimethylaminophenyllithium has not been reported.

It has been shown previously[5] that the low yields of substituted chlorohydrins prepared from the less reactive organometallic compounds resulted from competition between reaction (1) and reaction (2) where M is a metallic cation capable of coordination with ether oxygen.



$$\mathrm{MBr_2} + \underset{\diagdown O \diagup}{\mathrm{CH_2{-}CHCH_2Cl}} \xrightarrow{\text{(HOH)}} \mathrm{BrCH_2CHOHCH_2Cl} \quad (2)$$

With phenylcadmium chloride,[6] for example, the only material isolated after 13 hours of reaction at room temperature was a dense liquid believed to be a mixture of glycerol bromochlorohydrin and glycerol dichlorohydrin.

The opening of the oxide ring by lithium bromide present in phenyllithium solutions may be responsible for the low yields obtained under ordinary conditions, since equivalent quantities of phenyllithium and epichlorohydrin at ether-reflux temperature gave only 9.8% of 1-chloro-3-phenyl-2-propanol. When initially lower temperatures and longer reaction periods were employed the yield was raised to 67%.

Experimental

All boiling points are uncorrected. The following example is typical of the procedures used to prepare three other chlorohydrins, the properties of which are reported in Table I.

1-Chloro-3-phenyl-2-propanol.—Epichlorohydrin (0.44 mole) in 60 ml. of anhydrous ether was placed in a 500-ml. three-necked flask fitted with a nitrogen inlet tube, mechanical stirrer and dropping funnel. The flask and contents were cooled to −78° in a Dry Ice–trichloroethylene-bath and 290 ml. (0.44 mole) of phenyllithium were added during a period of one-half hour. The mixture was stirred at −78° for 1.5 hours and then the bath was allowed to warm slowly to 0°.

TABLE I

SOME 3-ARYL-1-CHLORO-2-PROPANOLS

Ar–	Yield, %	B.p., uncor. °C.	B.p., uncor. Mm.	$n^{20}\mathrm{D}$	$d^{20}{}_{20}$	Chlorine, % Calcd.	Chlorine, % Found
p-$\mathrm{CH_3C_6H_4}$–	42	140–143	12	1.5366	1.126	19.22	19.30
1-$\mathrm{C_{10}H_7}$–	43	180–182	0.2	1.6189	1.236	16.09	15.86
p-$\mathrm{(CH_3)_2NC_6H_4}$–	38	36–38	0.13	1.5208	1.023	17.78	17.99

The hydrolysis[7] was carried out in dilute sulfuric acid containing crushed ice. The ether layer was separated and washed successively with water, sodium carbonate solution and water. Subsequent to the drying of the extract over anhydrous sodium sulfate, the ether was removed by distillation. The product was distilled at 132–142° (13–17 mm.) to yield 50.5 g. (67.4%) of distillate having $n^{20}\mathrm{D}$ 1.5426. The 3,5-dinitrobenzoate melted at 119.5–120.5°. The reported $n^{25}\mathrm{D}$ and m.p. are 1.5470 and 120–121°, respectively.[3a]

In another preparation 0.18 mole of phenyllithium was treated with 0.18 mole of epichlorohydrin under similar conditions. The yield was 36.6 g. (66.2%) of product having b.p. 125–127° (11–12 mm.), $n^{20}\mathrm{D}$ 1.5420 and $d^{20}{}_4$ 1.155.

Anal. Calcd. for $\mathrm{C_9H_{11}ClO}$: Cl, 20.80. Found: Cl, 20.70.

---

[2] For a discussion of the mechanism of the opening of oxide rings, see S. Winstein and R. B. Henderson in R. C. Elderfield, "Heterocyclic Compounds," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 27–42.

[3] (a) C. F. Koelsch and S. M. McElvain, THIS JOURNAL, **52**, 1164 (1930); see also (b) E. Fourneau and M. Tiffeneau, *Bull. soc. chim. France*, [4] **1**, 1227 (1907), and (c) E. Fourneau, J. Tréfouel and J. Tréfouel, *ibid.*, [4] **43**, 454 (1928).

[4] R. R. Read, H. Lathrop and H. L. Chandler, THIS JOURNAL, **49**, 3118 (1927).

[5] (a) I. Ribas and E. Tapia, *Anales soc. españ. fis. quim.*, **28**, 636, 691 (1930) [*C. A.*, **24**, 4265 (1930)] and (b) J. K. Magrane and D. L. Cottle, THIS JOURNAL, **64**, 484 (1942).

[6] Prepared by the addition of a small excess of fused and pulverized cadmium chloride to a solution of phenylmagnesium bromide.

[7] Color Test I should be negative before hydrolysis. See H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).

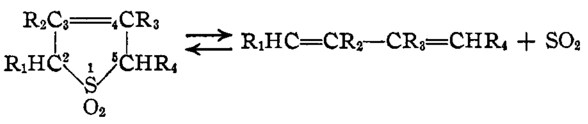
THE CHEMICAL LABORATORY
IOWA STATE COLLEGE
AMES, IOWA

RECEIVED NOVEMBER 3, 1951

Thermal Dissociation of 3-Phenyldihydrothiophene-1-dioxide

BY OLIVER GRUMMITT AND HELEN LEAVER

A comparison of the rates of thermal dissociation of the cyclic sulfones of butadiene, piperylene, isoprene, 1,3-dimethylbutadiene and 2,3-dimethylbutadiene to the diolefin and sulfur dioxide has



shown that this reaction is facilitated by 2-methyl substitution and is hindered to a smaller degree by 3-methyl substitution.[1] In extending this study to sulfones of arylbutadienes it was found that *cis*- and *trans*-1-phenyl-1,3-butadiene did not add sulfur dioxide to give either a cyclic sulfone or a polysulfone.[2] The sulfone of 2-phenyl-1,3-butadiene[3] was selected next.

While undertaking to prepare 2-phenyl-1,3-butadiene from methylethylphenylcarbinol by dehydration, bromination and debromination according to Backer and Strating,[3] the more convenient synthesis of Price, *et al.*, based on the condensation of α-methylstyrene, formaldehyde and acetic acid to 2-phenyl-4-acetoxy-1-butene and thermal de-

---

[1] O. Grummitt, A. E. Ardis and J. Fick, THIS JOURNAL, **72**, 5167 (1950).

[2] (a) O. Grummitt and F. J. Christoph, *ibid.*, **73**, 3479 (1951); (b) O. Grummitt and J. Splitter, Organic Division, A.C.S. Meeting, Chicago, Illinois, September 5, 1950.

[3] H. J. Backer and J. Strating, *Rec. trav. chim.*, **53**, 525 (1934).