gas through in the presence of oxygen, at a total pressure of one atmosphere and at 15°. The reaction was followed by the pressure changes on a sulfuric acid manometer.

The light absorbed was measured with a thermopile–galvanometer system which was calibrated using a filament lamp from the Bureau of Standards and checked by experiments on Cl_2–O_3 mixtures. On insolation with light of 3650 Å. there was a sharp decrease in pressure which was eventually followed by an almost equally sharp increase in pressure. The decrease in pressure in the first part of the experiment appears to be due to the formation of Cl_2O_6 and its deposition on the walls. It is suggested that the increase in pressure which follows is due to the sensitized decomposition of Cl_2O_6 by Cl atoms.[5] Using higher concentrations of ClO_2, larger amounts of Cl_2O_6 accumulate and after-effects of insolation indicate that it may start to decompose at an appreciable rate before all the ClO_2 has decomposed, and furthermore it does not all decompose to $Cl_2 + O_2$. One would expect the state of the surface to be an important factor.

The final rise in pressure shows a close resemblance to that obtained with Cl_2–O_3.[6] A similar rise is recorded in one experiment[7] with Cl_2O and since the formation of ClO_2 has been shown to occur in this reaction it is possible that it can also be explained by the final decomposition of Cl_2O_6, which only occurs when Cl atoms are no longer used up by ClO_2, Cl_2O and O_3 in the different experiments. Quantitative experiments with 3650 Å. showed an over-all decrease in volume varying between 5 and 23 moles per einstein in the first part of different experiments on the photo decomposition of gaseous ClO_2, while the end gave increases in volume up to 10 moles per einstein absorbed, indicating that we are probably dealing with a chain reaction.

[5] Allmand and Spinks, *Chem. News*, **142,** 333 (1931).

[6] Allmand and Spinks, *J. Chem. Soc.*, 1652 (1931).

[7] Finkelnburg, Schumacher and Stieger, *Z. physik. Chem.*, **15B,** 153 (1931).

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RECEIVED FEBRUARY 9, 1932
PUBLISHED APRIL 6, 1932

ALKYLATIONS OF NITRILES IN LIQUID AMMONIA

Sir:

The reaction of phenylacetonitrile which has been communicated by J. A. Nieuwland and L. H. Baldinger [THIS JOURNAL, **54,** 828 (1932)] has also been observed by the writer and E. C. Knowles [Knowles, M. S. Dissertation, R. P. I., 1929]. Similar alkylations of nitriles in liquid ammonia have also been reported [Cloke, Anderson, Lachmann and Smith, THIS JOURNAL, **53,** 2791 (1931); Knowles and Cloke, "Substituted Phenylacetonitriles and Derivatives," in press]. These facts are mentioned since we are still at work on similar alkylations, which, however, are probably distinct from those under way at Notre Dame.

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ISOLATION OF SPARTEINE FROM LUPINUS BARBIGER (WATSON)

Sir:

Sparteine has been found in one species of lupine, *L. luteus*, where it is accompanied by a second alkaloid, lupinine. Although a number of other species of lupines has been examined these two alkaloids have not again been found. The isolation of sparteine from *L. barbiger*, recently effected in this Laboratory is, therefore, of interest.

Leaves and stems of this plant, collected at Hilltop, ten miles north of Fairview, Utah, were obtained through the courtesy of A. B. Clawson and were identified by W. W. Eggleston. The alkaloids were extracted[1] and submitted to the action of solvents to separate them. The fraction soluble in petroleum ether contained sparteine and a second base from which it could not be separated by fractional distillation in a vacuum. The mixture yielded a picrate, platinum chloride and methiodide which had the constants of sparteine. Separation was effected through the mercuric chloride double compound, from which pure sparteine could be recovered by treatment with ammonia, shaking out with chloroform, removing the solvent and distilling under reduced pressure. The greater part came over at 185° and 7 mm. and showed n_D^{27} 1.5256 and $[\alpha]_D^{30}$ $-6.07°$. Willstätter and Marx[2] gave $-5.96°$ at 20°. Moureu and Valeur[3] give n_D^{19} 1.5293. The indices of refraction for a specimen of authentic sparteine were determined in this Laboratory as 1.5263 (24°), 1.5253 (26°), 1.5248 (28°), 1.5242 (29°). The specimen from *L. barbiger* was positive to the Jorissen[4] H_2S–S and the modified Grant[5] tests for sparteine. The picrate melted at 205–206° and did not depress the m. p. of sparteine picrate. The platinum chloride melted with decomposition at 248° and did not depress the melting point of sparteine platinum chloride.

The hydrobromide melted at 197° and was levorotatory $[\alpha]_D^{29}$ $-18.33°$. Found: H_2O, 4.40, 4.54; Br, 38.51, 38.50. $C_{15}H_{26}N_2 \cdot 2HBr \cdot H_2O$ requires

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[1] The procedure was in general that already described, THIS JOURNAL, **47**, 2584 (1925).

[2] Willstätter and Marx, *Ber.*, **37**, 2351 (1904).

[3] *Bull. soc. chim. Paris*, [3] **29**, 1135 (1903).

[4] *Anal. Chim. Analyt.*, **16**, 412 (1911).

[5] *Am. J. Pharm.*, **97**, 38 (1925).