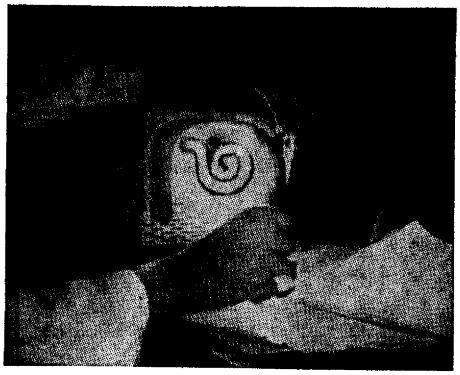

Fig. 1. The daylight-device in use.

29 cm, depth 13.5 cm). The case has four supporting legs which elevate the center of the lamp to 14 cm above the table. This is the distance found suitable for our purposes.

The light is shielded on two sides by a 6 cm wide cover.

The lamp is placed as illustrated by the photograph. The light falls obliquely from the left hand side down on the titration vessel. The colour of the liquid is thus observed against a background of non-reflecting white (a sheet of filter paper). If the light is mounted below the titration vessel, the end-point cannot be determined with the same accuracy as with the arrangement shown on the photograph. The light cover prevents direct light from reaching the eyes of the analyst. The case serves very conveniently as a support for the left hand which operates the cock of the micro burette.

Using this lighting device the colour at the end-point of the titration is clearly observed and at the same values as for titrations carried out in daylight, even when liquids of very low normalities are used (0.002 *N*).*

* The daylight-device can be obtained from PHILIPS Ltd. the Neon-factory, Copenhagen, Denmark. The complete apparatus is not yet put into serial production, but the tube and transformer, without mounting, will cost about 100 Danish crowns.

Received June 16, 1948.

The Synthesis of 1,2-Diiodoethene

ALEXIS C. PAPPAS

Universitetets Kjemiske Institutt, Blindern — Oslo, Norway

This paper deals with a method for the synthesis of 1,2-diiodoethene (acetylene-diiodide), which was invented in studying analytical methods for determining impurities in acetylene generated from calcium carbide and acetylene from storage cylinders and studying methods for purification of acetylene for laboratory use.

Among the analytical methods that may be used for the quantitative determination of gaseous phosphorus compounds in acetylene, the oxidation of these impurities by the action of iodine in an aqueous potassium iodide solution proposed by Maurichéau — Beaupré [1] is recommended. From the amount of iodine used for the oxidation the content of phosphine is calculated by using an empirical factor. This method was tried. It proved, however, impossible to obtain conformable results.

To purify acetylene from gaseous phosphorus, arsenic and sulphur compounds the method of Conn, Kistiakowskey and Smith [2] was used. The crude acetylene was passed through wash bottles containing iodine in aqueous potassium iodide solution. The acetylene leaving this solution had a characteristic odour. If the solution in the wash bottles was allowed to stand only for a few days with acetylene, the solution became pale and long needle-shaped crystals were formed. At the same time the purifying capacity of the solution diminished and became very low.

As will be shown in this paper, the cause of these two phenomena is the formation of 1,2-diiodoethene.

According to Beilstein's Handbuch der Organischen Chemie [3] diiodoethene may be prepared by the method of Berthelot, by the action of acetylene on iodine at an

elevated temperature, or by Ssabanejeff's method by passing acetylene through a solution of iodine in absolute alcohol. The best method, however, is that of Biltz: Imbibing iodine with absolute alcohol and passing acetylene in the mixture. After three or four days the mixture is poured into water and 1,2-diiodoethene separates. Beside the solid *trans*-isomer varying quantities of the liquid *cis*-isomer are formed.

Experimental. Acetylene was passed through a 0.2 *N* iodine in aqueous potassium iodide solution in Erlenmeyer flasks. These were then closed and the solutions were left under a slight pressure of acetylene. One sample was placed in complete darkness and another in the sunlight. After a short time, one day or more, long, white needle-shaped crystals were found to have been formed in both samples. The crystals were much entangled and looked like serpentine asbestos. The solutions had lost colour and a characteristic odour was noticed. A sumblimate of short, pink-coloured (due to some disengaged iodine) crystals was found to have deposited in the upper part of the flasks that had been exposed to sunlight, whereas there was no such deposit in the flasks placed in darkness.

The mass of crystals was filtered off, washed with potassium iodide solution, sodium hydroxyde solution and water, and dried between filter-papers. The mass was then recrystallized from alcohol. In the filtrate, *i. e.* in the iodine potassium iodide solution, the iodine content was determined by titration with sodium-thiosulphate.

In one experiment when the samples had been left for two days, 96 per cent of the iodine was found to have taken part in the reaction. As the addition of iodine to acetylene occurs slowly and the reaction stops when one molecule of iodine has been added [4], the probability is that only 1,2-diiodoethene is formed in the above mentioned reactions:

$$C_2H_2 + I_2 \rightarrow C_2H_2I_2$$

By comparing the weight of the mass of crystals with the calculated amounts of 1,2-diiodoethene corresponding to the iodine consumption, the yield was found to be 91 per cent.

The identity reactions that were made are given in the table and the data referring to the *trans*-isomer of 1,2-diiodoethene [5] are given for comparison.

	M.p. °C	B. p. °C	Mol. wt.	% I
$C_2H_2I_2$-*trans*-isomer	73	192	279.86	90.7
Product prepared by us	73.4	196—197	285.2	91.0

The molecular weight was determined by Pirsch' micromethod [6] by measuring the lowering of the freezing point in camphor. Tetrabromomethane could not be used because of its reaction with the compound *.

The data found for the unknown compound give evidence of the fact that the *trans*-isomer of 1,2-diiodoethene had been formed.

The *trans*-1,2-diiodoethene obtained has a characteristic not bad odour and crystallizes from alcohol in long monoclinic prisms, which could be pulverized only with great difficulties.

The crystals have a slight double refraction. They are insoluble in water, soluble in alcohol, ether and other organic solvents, volatile with alcohol and water vapour.

The compound is slightly volatile at room temperature, not sensitive to diffused light, but decomposes slightly under the direct influence of sunlight and by distillation.

* The author is indebted to Reidar Lie, stud.mag.scient., for his kind assistance in carrying out the determination of molecular weights.

There might also be a possibility that some of the *cis*-isomer of 1,2-diiodoethene were formed during the reaction. This is an oily liquid and has a melting point of 13.8° C below zero [5]. Attempts were made to isolate this compound by a fractional crystallization of the mother liquor when the *trans*-isomer had crystallized. It was, however, impossible to prove the presence of a *cis*-isomer, apparently it is not formed by this method. The reason may be that the *cis*-isomer decomposes slowly in the dark and faster in the light and that it is transferred to the *trans*-isomer in the presence of iodine.

After concluding this work the author came across a paper written by Keiser [7], in which he briefly mentions that acetylene-diiodide may be obtained by passing acetylene through a solution of iodine in potassium iodide. Keiser gives no reference and no details of the process and the method is not mentioned in Beilstein's Handbuch der Organischen Chemie.

The author is indebted to Professor Dr. H. Haraldsen for permission to work in his laboratory and to *Nansenfondet* for a grant.

1. Maurícheau-Beaupré, Z. *Calciumcarbid und Acetylen* (1907) 369; *cf.* Vogel, J. H. *Das Acetylen* Leipzig (1923) p. 96.
2. Conn, J. B., Kistiakowskey, G. B., and Smith, E. A. *J. Am. Chem. Soc.* **61** (1939) 1868.
3. Beilstein, F. K. *Handbuch der Organischen Chemie* 4th edition, Berlin, Vol. 1, syst. 11 (1918) p. 194.
4. Nieuwland, J. A., and Vogt, R. R. *The chemistry of acetylene* New York (1945) p. 106.
5. Lange, N. A. *Handbook of chemistry* Cleveland (1944) p. 322—23.
6. Pirsch, J. Z. *Z. Angew. Chem.* **51** (1938) 73.
7. Keiser, E. H. *Am. Chem. J.* **21** (1899) 261.

Received August 13, 1948.

Methylpyrazolonethiocarbamide and Aromatic Halogene Ketones

TORSTEN EKSTRAND

The Central Laboratories, Astra, Södertälje, Sweden

In attempts to prepare thiazolesubstituted pyrazolones we have used 3-methylpyrazolone(5)-1-thiocarbamide (I) [1]. It seemed probable that this compound in a normal way should react with halogene ketones to form thiazole derivatives. However, an unexpected reaction took place with some aromatic halogene ketones. *m*-Nitrophenacyl bromide reacted in the expected way with formation of II, R = $m\text{-}NO_2 \cdot C_6H_4$.

If the thiocarbamide was treated with phenacyl chloride no thiazole compound was obtained but phenacyl rhodanide (III, R = H; R′ = C_6H_5) in a yield of more than 70 %. Desyl chloride reacted in the same way, furnishing the corresponding rhodanide in a yield of nearly 90 % (III, R = R′ = C_6H_5).

In these cases the thiocarbamide obviously was splitt. Probably the pyrazolone nucleus was desintegrated too, because it was impossible to isolate the simple methylpyrazolone from the mother liquor.

Methylpyrazolonthioamide and m-nitrophenacyl bromide. Finely ground thioamide (5 g) and *m*-nitrophenacyl bromide (8 g) were suspended in ethanol (100 ml) and heated on a water bath for 30 minutes with reflux. After cooling to 0° over night the precipitate (8 g) was sucked off. Recrystallised from ethanol (500 ml), m. p. 235—236°. The analytical data agree with those of compound II, R = $m\text{-}NO_2 \cdot C_6H_4$

$C_{13}H_{10}O_3N_4S$ (302.3)

Calc.	N 18.5	S 10.6
Found	» 18.4	» 10.5