10% amorphous sulfur and 90% crystalline sulfur, suggesting that the change from green to yellow simply consists of closing the ring.

If green sulfur consists of diradical chains, it would be expected to be paramagnetic in virtue of the unpaired electrons. A qualitative test using a powerful electromagnet showed that green sulfur is very slightly paramagnetic and becomes diamagnetic when it changes to yellow sulfur.

Rate measurements of the transition from green to yellow sulfur were conducted using the method previously described for purple sulfur. We repeated the rate measurements for purple sulfur and confirmed the previous result that there is an initial rapid reaction followed by a slower change at almost constant speed. In the present work we estimated the speed of the initial change for purple sulfur at the four temperatures: −107, −102, −98 and −88° and by plotting the logarithm of the rate against the reciprocal of the time obtained an activation energy of 2.0 kcal. as compared with the previously reported value of 3.1 kcal. for purple sulfur. Using the same method for green sulfur we obtained the value 3.9 kcal. for the activation energy of the change green → yellow sulfur.

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The Isolation of Diosgenin from Solanum Xanthocarpum[1]

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During the course of isolation of solasodine from the dried fruits of *Solanum xanthocarpum* we have encountered a persistent impurity which has now been identified as diosgenin.

Although Gupta and Dutt[2] have reported the isolation of a sterol, carpesterol, $C_{36}H_{54}O_4$, m.p. 248°, and a $\Delta^{\alpha,\beta}$-unsaturated lactone (solanocarpone) $C_{28}H_{42}O_7$, m.p. 78°, the presence of the sapogenin, diosgenin, had been undetected hitherto.

The occurrence of small amounts of diosgenin along with solasodine provokes an interesting speculation as to the possible mode of biogenesis of solasodine. This finding is also of interest in view of the recent report of Briggs and O'Shea[3] who obtained small amounts of diosgenin by treating N-nitrososolasodine with boiling aqueous acetic acid. The main product of this reaction was an isomer of diosgenin.

Experimental[4]

The finely ground dry fruits (2.62 kg.) of *Solanum xanthocarpum* were extracted in a Soxhlet extractor with petroleum ether (4 l., 65–75°) for 44 hours, then with methanol (3.5 l.) for 140 hours. The methanol extract was evaporated to dryness on the water-bath and the semi-solid mass taken up in 10% acetic acid, treated with charcoal at boiling temperature and filtered through Filter-cel. The filtrate was made basic with ammonia and the glycoside collected. After several triturations with petroleum ether the crude, partially solid material was dissolved in hot methanol and hydrochloric acid (2 *N* with respect to methanol), refluxed for 2.5 hours, an additional half-hour with charcoal, and finally filtered through Filter-cel. The precipitated, crude solasodine hydrochloride was collected. Further dilution of the mother liquor with ether yielded more of the same substance. The hydrochloride was dissolved in hot methanol, water added to incipient turbidity, and made alkaline with ammonia gas. The solasodine (24.23 g.) was collected after standing overnight. Eight grams of the above crude, dry solasodine was dissolved in 1200 cc. of dry ether and 140 cc. of 1% ethereal hydrogen chloride was added with agitation. After cooling in ice-water for one-half hour the solasodine hydrochloride was collected and washed with cold dry ether. The ethereal filtrate was washed with Na_2CO_3 solution, water and dried over Na_2SO_4. Evaporation of the solvent yielded 50 mg. of crude diosgenin which after chromatography and recrystallization from acetone afforded 8 mg. of needles, m.p. 194–198°. Its infrared spectrum was identical with that of an authentic specimen of diosgenin.

Anal. Calcd. for $C_{27}H_{42}O_3$: C, 78.21; H, 10.21. Found: C, 77.71; H, 10.00.

In another experiment the crude diosgenin was directly acetylated in the usual manner with acetic anhydride–pyridine and chromatographed over alumina. Crystallization from acetone and recrystallization from methanol yielded flat rods, m.p. 194.5–196°. Its infrared absorption spectrum likewise was identical with that of an authentic specimen of diosgenin acetate.

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[1] The *Solanum xanthocarpum* was obtained from the Institute of Agriculture, Anand, through the generous coöperation of the American Consul General, Bombay, India.

[2] M. P. Gupta and S. Dutt, *J. Ind. Chem. Soc.*, **15**, 95 (1938).

[3] L. H. Briggs and T. O'Shea, *J. Chem. Soc.*, 1654 (1952).

[4] The melting points are uncorrected and taken on the Kofler block.

Some Alkyl Thiocarbamates Prepared from Alkyl Thiocyanates by Riemschneider's Reaction

BY K. SCHMIDT AND P. KOLLEK-BÖS

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As was shown by Riemschneider and coworkers,[1a] the melting points of the primary aliphatic thiocarbamates differ only slightly from one another. On the basis of this observation the melting points of the hitherto unknown thiocarbamates, *n*-$C_{13}H_{27}$–, *n*-$C_{15}H_{31}$–, *n*-$C_{17}H_{35}$– and *n*-$C_{19}H_{39}$–$SCONH_2$, were predicted.

Since we had in connection with other investigations the thiocyanates *n*-$C_{13}H_{27}$–, *n*-$C_{15}H_{31}$–, *n*-$C_{17}H_{35}$– and *n*-$C_{19}H_{39}$–SCN at our disposal, we converted them by Riemschneider's reaction[1b,c] into the corresponding thiocarbamates and determined the melting points of the latter. The procedure followed was analogous to that given for the preparation of myristyl thiocarbamate.[1c] As is evident from the following table, there is good agreement between the predicted and the observed melting points of the four thiocarbamates.

	M.p., °C. Predicted	Obsd.
n-$C_{13}H_{27}SCONH_2$	110	109.5–110
n-$C_{15}H_{31}SCONH_2$	111–111.5	111.5
n-$C_{17}H_{35}SCONH_2$	111.5–112	111–112
n-$C_{19}H_{39}SCONH_2$	113	113.5

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[1] R. Riemschneider and co-workers, (a) *Angew. Chem.*, **64**, 420 (1952); (b) THIS JOURNAL, **73**, 5905 (1951); *Pharmazie*, **4**, 460 (1949): *Chimica e industria* (*Milan*), **34**, 353 (1952); *Z. Naturforsch.*, **7b**, 277 (1952); (c) *Monatsh.*, **84**, 316 (1953).