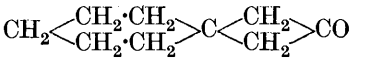
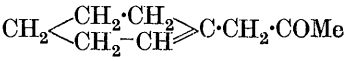
NOTES.

cyclo*Hexane*-spiro-cyclo*butanone*. By GEORGE ARMAND ROBERT KON.

IN a recent paper (this vol., p. 910) Vogel states that the author prepared *cyclo*hexane-*spiro-cyclo*butanone (I) by the dry distillation of calcium *cyclo*hexanediacetate, and that a similar ketone was not obtained from calcium *cyclo*heptanediacetate; this statement is then used to support the theory developed in the paper. It is not proposed to criticise this theory in detail, but it is necessary to point out that Vogel's quotation is incorrect and that (1) neither of the above calcium salts yields any trace of *spiro*-ketone, the ketonic product being in each case unsaturated, such as (II), a behaviour



(I.)



(II.)

which appears to be general in ββ-disubstituted glutaric acids (Kon, J., 1921, **119**, 810); (2) the ketone (I) was prepared by the action of potassium on ethyl *cyclo*hexanediacetate (Kon, J., 1922, **121**, 513); no experiments have been carried out on the *cyclo*heptane derivative and no comparison is therefore possible.—IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON, S.W. 7. [*Received, May 9th,* 1931.]

The Oxidation of N-*Methylhydroxylamine by Iodine*. By OSCAR L. BRADY and MARGARET D. PORTER.

KIRPAL (*Ber.*, 1892, **25**, 1715) suggested that *N*-methylhydroxylamine could be determined quantitatively by boiling it with Fehling's solution and weighing the cuprous oxide produced, the reaction

proceeding in accordance with the equation $3CH_3{\cdot}NH{\cdot}OH + 6CuO = 3Cu_2O + CH_3{\cdot}NH_2 + 2NH_3 + 2CO_2 + 2H_2O$. Brady and Goldstein (J., 1926, 2407) were unable to obtain concordant results by this method, but found that under regulated conditions *N*-methylhydroxylamine could be determined iodometrically. Two molecules of the base required one molecule of oxygen, and this suggested that the reaction proceeded thus: $2CH_3{\cdot}NH{\cdot}OH + O_2 = 2CH_2{:}NOH + 2H_2O$. Bamberger and Szolayski (*Ber.*, 1900, **33**, 3193) obtained benzaldoxime as one of the products of the oxidation of an aqueous solution of *N*-benzylhydroxylamine by air. No methylamine was formed, but, owing to the dilution at which the reaction had to be carried out to obtain concordant results and the difficulty of extracting formaldoxime, no evidence could then be obtained of the formation of the latter compound.

We have now been able to isolate formaldehyde from the oxidation product in the form of its dinitrophenylhydrazone.

N-Methylhydroxylamine hydrochloride (0·42 g.) was dissolved in water (100 c.c.). Solid sodium bicarbonate (0·315 g.) was added to 25 c.c. of this solution, which was then titrated with *N*/10-iodine solution as described by Brady and Goldstein (*loc. cit.*). The resultant solution was neutralised with hydrochloric acid, and a further quantity of concentrated hydrochloric acid (16 c.c.) was added to make it approximately 2*N* in hydrochloric acid, followed by 25 c.c. of a 1% solution of 2 : 4-dinitrophenylhydrazine in 2*N*-hydrochloric acid (Brady and Elsmie, *Analyst*, 1926, 77). After 18 hours, the feathery crystals which had separated were collected and identified as formaldehyde-2 : 4-dinitrophenylhydrazone by comparison with an authentic specimen. The reactions may be represented thus:

$$CH_3{\cdot}NH{\cdot}OH + I_2 = CH_2{:}NOH + 2HI.$$

$CH_2{:}NOH + C_6H_3(NO_2)_2{\cdot}NH{\cdot}NH_2 = CH_2{:}N{\cdot}NH{\cdot}C_6H_3(NO_2)_2 + NH_2{\cdot}OH$.—UNIVERSITY COLLEGE, LONDON. [*Received, April 30th*, 1931.]

A Sensitive Colour Reaction for Certain Quinones. By REGINALD CRAVEN.

p-BENZOQUINONE, *p*-benzoquinone dichloride, *o*-toluquinone, chloranil, α-naphthaquinone, and thymoquinone all yield an intense bluish-violet coloration, changing to blue, green, and finally reddish-brown, on the addition of 2—3 drops of ethyl cyanoacetate and excess (2 to 3 c.c.) of alcoholic ammonia (1 part of absolute alcohol and 1 part of aqueous ammonia, *d* 0·880). The reaction is intense

with 0·1 mg. per c.c. and is recognisable with 0·01 mg. per c.c., the duration of the blue colour being shortest with *p*-benzoquinone.

The reaction is not given with β-naphthaquinone, anthraquinone, 1 : 5-dichloro-2 : 6-diaminobenzoquinone (chloranilamide), or phenanthraquinone. It requires the presence of a labile hydrogen or halogen atom adjacent to the carbonyl group of the quinone.

The condensation products with *p*-benzoquinone, *o*-toluquinone, chloranil, and α-naphthaquinone have been isolated. Their preparation and constitution will form the subject of further communications.—ROBERT GORDON'S COLLEGES, ABERDEEN. [*Received, May 15th*, 1931.]