peaks at mass-to-charge ratios of 112 (C_3F_4), 93 (C_3F_3), 74 (C_3F_2), 69 (CF_3), 52 (C_2F_2) and 31 (CF).[7] Compounds such as perfluoroethylene and perfluorocyclobutane show CF_3 peaks,[8] but tetrafluoroallene gave an unusually high value at 69.

Addition of chlorine to tetrafluoroallene gave 1,2,2,3-tetrachloro-1,1,3,3-tetrafluoropropane, a liquid with the same b.p., refractive index and infrared spectrum as an authentic sample.

Tetrafluoroallene polymerized even at low temperatures; at room temperature under pressure polymerization occurred in a few hours to yield first a liquid and then a white solid. The polymerization is being studied.

(7) A modified Westinghouse Model LV mass spectrometer was used. We wish to thank Mr. Robert D. Vanselow for this spectrogram.

(8) "Catalog of Mass Spectral Data," National Bureau of Standards, American Petroleum Institute Research Project 44, spectra 361 and 362.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA THOMAS L. JACOBS
LOS ANGELES 24, CALIFORNIA RONALD S. BAUER

RECEIVED JULY 23, 1956

A CONVENIENT SYNTHESIS OF γ-TROPOLONE

Sir:

The theoretical significance of tropone and the three isomeric tropolones (monohydroxytropones) has directed much effort toward the synthesis of these compounds. Tropone, tropolone and β-tropolone have been known for some time.[1] Recently, Nozoe and co-workers succeeded in preparing γ-tropolone (I) for the first time by acid hydrolysis of 4-bromotropone, a by-product obtained in 5–10% yield from the bromination of cycloheptanone.[2] In the same year, Johnson and co-workers reported an alternate synthesis starting from 3,6-dimethoxycycloheptatrienecarboxylic acid, obtained in quite low yield from hydroquinone dimethyl ether and diazoacetic ester.[3] As a part of a general study of the elimination reactions of bicyclic quaternary salts, we have investigated the base degradation of teloidinone methobromide (II), in the hope of developing a convenient route to γ-tropolone (I)

Teloidinone, prepared by a Robinson "biosynthesis,"[4] gave II, m.p. 218–219° (dec.), in almost quantitative yield when treated with excess methyl bromide in ethanol at room temperature. The degradation was carried out by dissolving II and two equivalents of base in distilled water and heating the solution on the steam-bath. The formation of I was followed by periodically removing aliquots from the reaction mixture and measuring the intensity of the 360 mμ absorption band exhibited by γ-tropolone in 0.1 *N* sodium hydroxide.[2,3] A variety of bases were found to produce I in yields of 45%. Sodium bicarbonate and barium hydroxide were equally effective in bringing about the desired elimination; refluxing II in anhydrous pyridine was somewhat less

II I

satisfactory. The concentration of the solution in which the degradation was carried out decidedly affected the yield of desired product. Thus, when a solution of II (66.5 mg.) and sodium bicarbonate (42.0 mg.) in 50 ml. of water was heated on a steam-bath for two hours, a 45% yield of I was obtained. However, when II (3.33 g.) and barium hydroxide (2.20 g.) were dissolved in 50 ml. of water and heated for two hours, only 24% of γ-tropolone formed. Precipitation of the barium ion by addition of Dry Ice followed by concentration of the solution to a volume of 3 to 5 ml., gave rise to I in 20% yield. After recrystallization, the product, m.p. 211–212°, showed infrared maxima (Nujol) at 6.10, 6.26, 6.60, 7.78 and 8.25 μ; its ultraviolet spectrum showed $\lambda_{max}^{0.1\ N\ NaOH}$ 360 mμ (4.33), 227 mμ (4.31) and $\lambda_{max}^{CH_3OH}$ 336 mμ (4.22), 228 mμ (4.20). These properties are in good agreement with those reported earlier for I.[2,3]

Acknowledgment.—The authors are deeply indebted to the Research Corporation for the support of this research through a Frank Gardner Cottrell grant.

(5) American Viscose Corporation Fellow, summer 1956.

DEPARTMENT OF CHEMISTRY
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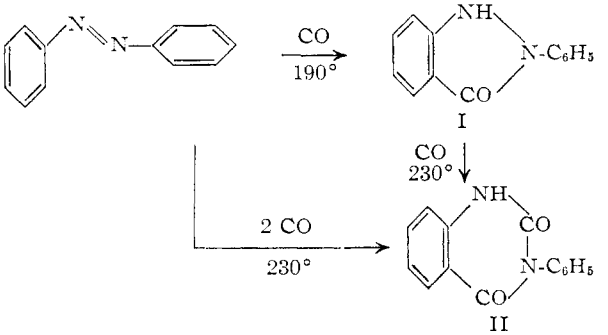
RECEIVED AUGUST 15, 1956

THE REACTION OF AZOBENZENE AND CARBON MONOXIDE

Sir:

Previously we have shown that Schiff bases react with carbon monoxide in the presence of cobalt octacarbonyl to yield phthalimidines.[1] We have now found that azobenzene reacts similarly with one molecule of carbon monoxide (150 atmospheres pressure in all cases) to form indazolone, I, at 190° and with two molecules of carbon monoxide at 230° to yield 3-phenyl-2,4-dioxo-



(1) For an excellent review see P. L. Pauson, *Chem. Revs.*, **55**, 9 (1955).

(2) T. Nozoe, T. Mukai, Y. Ikegama and T. Toda, *Chem. and Ind.*, 66 (1955).

(3) R. S. Coffey, R. B. Johns and A. W. Johnson, *ibid.*, 658 (1955).

(4) J. C. Sheehan and B. M. Bloom, THIS JOURNAL, **74**, 3825 (1952).

(1) S. Murahashi and S. Horiie, THIS JOURNAL, **77**, 6403 (1955).

1,2,3,4-tetrahydroquinazoline, II. That the formation of II probably proceeds through I was shown by the fact that I reacts with carbon monoxide to give II in quantitative yield at 230°. Similar conversions to analogs of I and II were carried out with 4-chloroazobenzene and 4-dimethylaminoazobenzene.

These reactions constitute the first examples of the formation of the indazolone ring system and its conversion to the tetrahydroquinazoline ring system by the use of carbon monoxide. In the case of the substituted azobenzenes ring closure occurred on the ring containing the substituent, as shown by alkaline hydrolysis to form the 5-substituted-2-aminobenzoic acids. Further studies on the reaction of carbon monoxide with other ring systems are under way.

Experimental.—A solution of 5 g. of azobenzene and 1 g. of dicobalt octacarbonyl in 50 ml. of benzene was heated at 230° under 150 atmospheres pressure of carbon monoxide for two hours to give 3 - phenyl - 2,4 - dioxo - 1,2,3,4 - tetrahydroquinazoline, II, m.p. 277°, in 80% yield. The structure was established by comparison (mixed m.p. and infrared spectra) with an authentic sample prepared from anthranilic acid and phenylurea.[2] The same product was obtained in smaller yield when iron pentacarbonyl was used, but was not obtained with nickel carbonyl.

In a similar experiment with dicobalt octacarbonyl (190°, 150 atmosphere of carbon monoxide) a 55% yield of 2-phenylindazoline, I, m.p. 204°, was obtained together with a smaller amount of II and diphenylurea. The identity of I was established by comparison (mixed m.p. and infrared spectra) with an authentic sample prepared from the amide of anthranilic acid.[3]

With dicobalt octacarbonyl and carbon monoxide at 230° 4-chloroazobenzene gave 23.8% of 2-phenyl-5-chloroindazolone, m.p. 233° (*Anal.* Calcd. for $C_{13}H_9ClN_2O$: C, 63.9; H, 3.7; N, 11.5. Found: C, 63.6; H, 3.8; N, 10.6) and 45% of 3-phenyl-6-chloro-2,4-dioxo-1,2,3,4-tetrahydroquinazoline, m.p. 264° (*Anal.* Calcd. for $C_{14}H_9ClN_2O_2$: C, 61.8; H, 3.3; N, 10.3. Found: C, 61.1; H, 3.4; N, 9.6). Similarly with 4-dimethylaminoazobenzene there were obtained 80% of 2-phenyl-5-dimethylaminoindazolone, m.p. 217° (*Anal.* Calcd. for $C_{15}H_5N_3O$: C, 71.1; H, 5.9; N, 16.6. Found: C, 71.5; H, 5.7; N, 16.9) and 18% of 3-phenyl-6-dimethylamino-2,4-dioxo-1,2,3,4-tetrahydroquinazoline, m.p. 281° (*Anal.* Calcd. for $C_{16}H_{15}N_3O_2$: C, 68.3; H, 5.3; N, 14.9. Found: C, 67.7; H, 5.1; N, 14.7).

(2) F. Kunckell, *Ber.*, **43**, 1234 (1910).

(3) K. von Auwers and K. Hüttenes, *ibid.*, **55**, 1112 (1922).

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RECEIVED JUNE 27, 1956

STRUCTURE OF THE AMINOSUGAR DERIVED FROM STREPTOTHRICIN AND STREPTOLIN B

Sir:

On acid hydrolysis, the *streptomyces* antibiotics streptothricin[1] and streptolin B[2] yield, *inter alia*, carbon dioxide, ammonia, L-β-lysine,[3,4] streptolidine,[5] and a strongly reducing substance, the structure of which has now been elucidated.

Through chromatography of the hydrolysates, Compound 2 was obtained as a crystalline hydrochloride, m.p. 152–162° dec., $[\alpha]^{21}D$ +5.6° (5 min.) → −18.7° (4 hr. and final) (*c* 2.9, water) (Calcd. for $C_6H_{13}NO_5 \cdot HCl$: C, 33.42; H, 6.54; N, 6.49; Cl, 16.45. Found: C, 33.54; H, 6.64; N, 6.50; Cl, 16.71). Compound 2 gave positive ninhydrin, Tollens, and Elson–Morgan reactions; it reduced five moles of sodium periodate, yielding ammonia, one mole of formaldehyde, and five moles of formic acid. Degradation by means of ninhydrin yielded xylose, which was identified by paper chromatography. Compound 2 phenylosazone displayed an X-ray diffraction pattern indistinguishable from that of L-gulose phenylosazone, and was identified on the basis of its rotation as D-gulose phenylosazone. These data limit the possible structures to two: 2-amino-2-deoxy-α-D-gulose and 2-amino-2-deoxy-α,D-idose.

Accompanying the hexosamine in the hydrolysates was a related substance, Compound 1, which was isolated as a crystalline hydrochloride, m.p. 235–240° dec. (monohydrate), $[\alpha]^{25}D$ +44.8° (anhydrous) (*c* 3.5, water) (calcd. for $C_6H_{11}NO_4 \cdot HCl$: C, 36.46; H, 6.12; N, 7.09; Cl, 17.94. Found: C, 36.36; H, 5.75; N, 7.67; Cl, 17.89) A mixture of Compounds 1 and 2 was produced, as evidenced by paper chromatography, when either pure component was treated with hot, dilute hydrochloric acid. Compound 1 gave a positive ninhydrin reaction, but negative Tollens and Elson–Morgan reactions. Two moles of sodium periodate was reduced, affording ammonia, one mole of formic acid, but no formaldehyde. The major periodate oxidation product yielded a crystalline dimedone derivative, m.p. 135.6–136.2° $[\alpha]^{25}D$ −13.3° (*c* 0.8, ethanol), which, by virtue of rotational, infrared spectral, and mixed melting point comparison, was identified as the dimedone derivative of *cis*-1,3-dioxolane-2,4-carboxaldehyde, secured by periodate oxidation of 1,6-anhydro-β-D-gulopyranose.[6] Compound 1 is therefore the 1,6-anhydrosugar derived from Compound 2.

Comparison of the molecular rotations of various α- and β-sugars with the rotations of the corresponding aminosugar anomers reveals that replacement of a hydroxyl by an amino group does not result in any significant numerical change.[7] Since

(1) H. E. Carter, R. K. Clark, Jr., P. Kohn, J. W. Rothrock, W. R. Taylor, C. A. West, G. B. Whitfield and W. G. Jackson, THIS JOURNAL, **76**, 566 (1954).

(2) E. E. Smissman, R. W. Sharpe, B. F. Aycock, E. E. van Tamelen, and W. H. Peterson, *ibid.*, **75**, 2029 (1953).

(3) H. E. Carter, W. R. Hearn, E. M. Lansford, Jr., A. C. Page, Jr., N. P. Salzman, D. Shapiro and W. R. Taylor, *ibid.*, **74**, 3704 (1952).

(4) E. E. van Tamelen and E. E. Smissman, *ibid.*, **74**, 3713 (1952).

(5) Streptolidine is the trivial name we have assigned to the aminoimidazoline amino acid[1] present in the acid hydrolysis of both antibiotics. Details relating to the structure of streptolidine will be submitted in a separate contribution.

(6) Kindly supplied by Dr. N. K. Richtmyer, National Institute of Arthritis and Metabolic Diseases, Bethesda, Maryland.

(7) This relationship also holds for the pair 1,6-anhydro-β-D-altropyranose, [M] +345, and 3-amino-3-deoxy-1,6-anhydro-β-D-altropyranose, [M] +340.