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.

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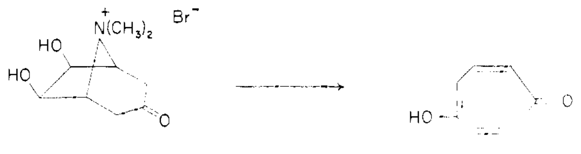
RECEIVED JULY 23, 1956

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 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]



II I

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

[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).

[5] American Viscose Corporation Fellow, summer 1956.

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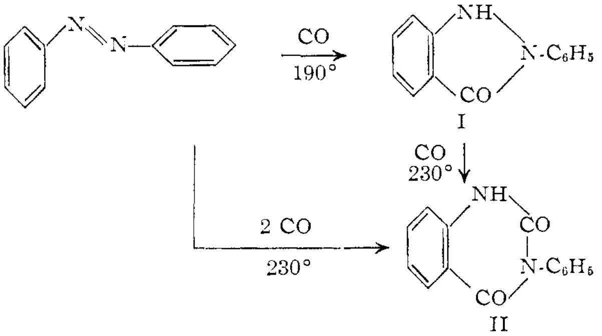
RECEIVED AUGUST 15, 1956

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-



II

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