ing 0.14 g. titanium tetrachloride for 14.5 hr. with isopropylmagnesium bromide made conventionally from 131 g. isopropyl bromide, 26 g. magnesium turnings, and 375 ml. anhydrous ether gave 11,056 ml. STP, 49% yield of propylene, b.p. −48.5° (740 mm.), identified by its infrared spectrum. Other volatile products were distilled by heating the reaction mixture with a boiling water bath for 3 hr. at atmospheric pressure and 2 hr. more as the pressure was reduced gradually to 1 mm. Fractional distillation gave ether and 55.7 g. (48%) of triethylsilane, b.p. 109.5–110.5°, n_D^{20} 1.4117–1.4122, identified by its infrared spectrum. Hydrolysis and fractional distillation of 65.3 g. boiling below 170° gave (1) 11.4 g. (7%) of propyltriethylsilane, b.p. 56.5–65° (19 mm.), n_D^{20} 1.4310–1.4312, containing 84% of the *n*-propyl isomer and (2) 22 g. (18% recovery of triethylsilyl groups as hexaethyldisiloxane) b.p. 104.5–117.5° (19 mm.), n_D^{20} 1.4339–1.4341.

Carrying out the reaction without the added titanium tetrachloride gave no propylene, no triethylsilane, and no *n*-propyltriethylsilane. There was obtained a complex mixture of products shown by infrared analysis to consist of a 7% yield of isopropyltriethylsilane and about 80% recovery of triethylchlorosilane and triethylbromosilane from halogen interchange.

Refluxing 140 g. diethyldichlorosilane containing 0.1 wt. % titanium tetrachloride for 18 hr. with isopropylmagnesium bromide (made conventionally from 250 g. isopropyl bromide, 49 g. magnesium turnings, and 750 ml. anhydrous ether), distilling the ether by heating the reaction mixture on boiling water bath for 5 hr., heating the residue on a boiling water bath for 20 hr., distilling all volatile products by gradually reducing the pressure to 1 mm. in about 1 hr., and finally fractionally distilling all the volatile products from the reaction gave: (1) 0.79 mole propylene, b.p. −48° (740 mm.), identified by its infrared spectrum and (2) 69.7 g., b.p. 132.5°, n_D^{20} 1.4189–1.4190, 0.54 mole, 60% yield of a mixture of propyldiethylsilanes containing 54% of the *n*-propyl isomer and 50% of the isopropyl isomer, the total being more than 100% owing to experimental error.

Adding 151 g. of hexene-1 to 2 moles of isopropylmagnesium bromide just prior to adding 140 g. diethyldichlorosilane containing 0.1 wt. % titanium tetrachloride and then carrying out the reaction as before gave: (1) 97.6 g., 64% recovery, of hexene-1, b.p. 62.5–63.5°, n_D^{20} 1.3878 identified by its infrared spectrum; (2) 0.71 mole propylene, b.p. −48° (740 mm.), identified by its infrared spectrum; (3) 53 g., b.p. 128–132°, n_D^{20} 1.4183–1.4198, 46% yield of a mixture containing 42% *n*-propyldiethylsilane and 57% isopropyldiethylsilane; and (4) 14.9 g., b.p. 58–70° (7.5 mm.), n_D^{20} 1.4323–1.4329, 9.8% yield of *n*-hexyldiethylsilane (Calcd. for $C_{10}H_{24}Si$: C, 69.6; H, 14.0; Si−H, 1.00. Found: C, 70.0; H, 14.4; Si−H, 0.98.) identical with an authentic specimen by infrared comparison.

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Novel Ring Expansion and Nitrogen Insertion Reactions of Isatogens[1]

Sir:

We wish to report two types of novel ring expansion and nitrogen insertion reactions of isatogens. Action of tetracyanoethylene[2] on 2-phenylisatogen[3] (Ia) in equimolar proportions in refluxing xylene for 1.5–10 hours produced a black solution from which the known 3,4-dihydro-2-phenyl-4-quinazolinone[4] (IIa) was isolated in 30–39% yield; long white needles (from acetone), m.p. 242.5–243.5°; reported m.p. 235–236°[4]; the mixed melting point with a sample (m.p. 241–243°) prepared by heating anthranilic acid with thiobenzamide[4] was undepressed, 241–243°, and the infrared spectra in Nujol were identical; ν_{NH} 3170m, 3120m, 3060m (CH?, strongest), $\nu_{C=O}$ 1666s, $\nu_{C=N,\ C=C}$ 1605ms cm.$^{-1}$ in Nujol; λ_{max} (95% C_2H_5OH) mμ (log ε): 218 (4.38), 237 (4.45), 290 (4.18); 317 infl. (3.98). Our sample of IIa from Ia was also converted[4] by action of phosphorus pentachloride in refluxing phosphorus oxychloride to the known[4] derivative, 4-chloro-2-phenylquinazoline (III); white crystals (after sublimation at 100°/0.5 mm.), m.p. 127.5–128.5°; reported m.p. 124–124.5°[4]; λ_{max} (tetrahydrofuran) mμ (log ε): 260 infl. (4.60), 266 (4.64), 286 infl. (4.26), 324 infl. (3.63), 338 infl. (3.46). Hydrogenation at 2 atm. of IIa in methanol over Raney nickel catalyst gave a decahydro derivative in 64% yield; colorless platelets (from methanol–water), m.p. 202–202.5° (sublimes above 150°); ν_{NH} 3310w, 3140w, $\nu_{C=O}$ 1649s, $\nu_{C=C}$ 1607m cm.$^{-1}$ in Nujol; λ_{max} (95% C_2H_5OH) mμ (log ε): 230 (3.86), 235 infl. (3.83), 270 (3.82), 315 infl. (2.19).

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(2) R. A. Carboni, *Org. Syntheses*, **39**, 64 (1959).

(3) (a) F. Kröhnke and M. Meyer-Delius, *Chem. Ber.*, **84**, 932 (1951); (b) F. Kröhnke and I. Vogt, *Chem. Ber.*, **85**, 376 (1952).

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Anal. Calcd. for $C_{14}H_{20}N_2O$ (232.32): C, 72.38; H, 8.68; N, 12.06; Found: C, 72.62; H, 8.59; N, 11.79.

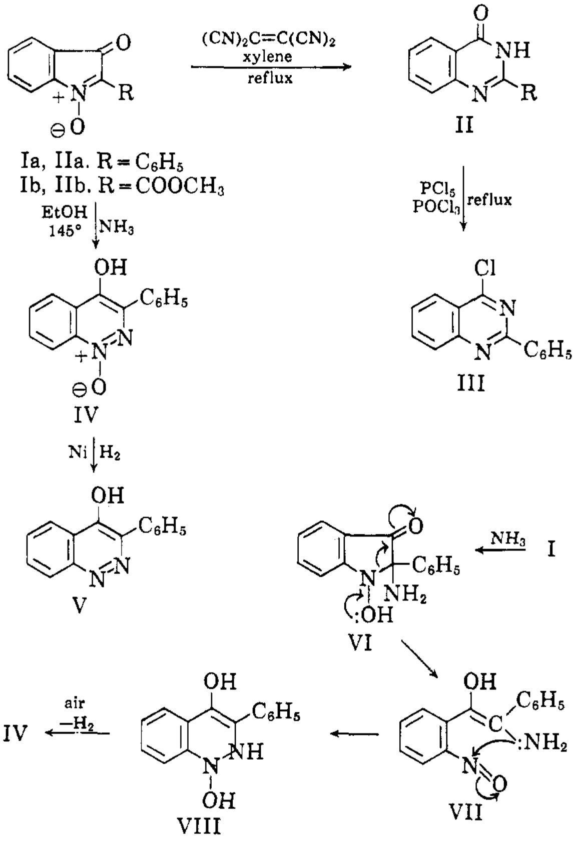
The ring expansion and nitrogen insertion reaction caused by tetracyanoethylene may be quite general among isatogens; the corresponding reaction with methyl isatogen-2-carboxylate[5] (Ib) in refluxing xylene for 4 hours again produced a black solution from which the previously unknown methyl 3,4-dihydro-4-quinazolinone-2-carboxylate (IIb) was isolated in 43% yield; long colorless needles (from acetone), m.p. 203–204° (after being dried for 6 hours at 100°/1 mm.); ν_{NH} 3130m, 3110m, 3050m (CH?, strongest), $\nu_{C=O}$ 1727 ms, 1650s, $\nu_{C=N,\ C=C}$ 1603ms cm.$^{-1}$ in Nujol; λ_{max} (95% C_2H_5OH) mμ (log ϵ): 229 (4.29), 255 infl. (3.74), 297 (3.99), 318 infl. (3.75).

Anal. Calcd. for $C_{10}H_8N_2O_3$ (204.18): C, 58.82; H, 3.95; N, 13.72; Found: C, 59.12; H, 4.06; N, 13.90.

The oxidation state of the 3,4-dihydro-4-quinazolinone products (II) indicates that the nitrogen atom inserted from the tetracyanoethylene must have an oxidation state equivalent to that of nitrogen in ammonia. Nevertheless, reaction of 2-phenylisatogen with ammonia in ethanol at 140–145° in an autoclave for 6 hours takes a different course, leading to ring expansion and nitrogen insertion at a different point, giving the previously unknown 3-phenyl-4-cinnolinol 1-oxide (IV) in 26% yield; long yellow-green needles (from methanol–water), m.p. 220–227° (sublimes to a white solid above 198°); ν_{OH} 3060w (CH?), 2690m, $\nu_{\overset{+}{N}-\overset{\ominus}{O}}$ 1277 cm.$^{-1}$ in Nujol; λ_{max} (95% C_2H_5OH) mμ (log ϵ): 225 (4.39), 246 infl. (4.09), 269 (4.09), 330 (3.95).

Anal. Calcd. for $C_{14}H_{10}N_2O_2$ (238.23): C, 70.58; H, 4.23; N, 11.76; Found: C, 70.52; H, 4.23; N, 11.61.

The reaction is assumed to proceed through the intermediates VI → VII → VIII → IV. 1,3-Addition of ammonia to IV to give VI has analogy in the corresponding additions to isatogens of cold methanol and ethanol (catalyzed by acid),[6] and of acetic anhydride[7] and acetyl chloride.[7] Dehydrogenation of VIII, possibly from air oxidation during the workup, would yield the oxidized final product (IV). Hydrogenation at 2 atm. of IV in ethanol over Raney nickel catalyst gave the known reduction product, 3-phenyl-4-cinnolinol[8] (V) in 45% yield: colorless needles (from methanol–water), m.p. 268–270°; reported m.p. 261–262°[8]; the mixed melting point with a sample (m.p. 267–269°) prepared by diazotization of 2-aminotolane[8] was undepressed, 269–271°, and the infrared spectra in Nujol were identical; ν_{OH} 3160w cm.$^{-1}$ in Nujol; λ_{max} (95% C_2H_5OH) mμ (log ϵ): 263 (4.21), 312 (4.08), 352 (4.07).



Formation of IIa by action of tetracyanoethylene on 2-phenylisatogen is not the result of cyanide ion; fusion of 2-phenylisatogen in potassium cyanide at 190–200° for 30 minutes gave a dark mass from which *N*-benzoylanthranilic acid was isolated in 6% yield, m.p. 170–180°; reported m.p. 182–183°[9]; the mixed melting point with an authentic sample[10] was undepressed, m.p. 180–182°, and the infrared spectra in Nujol were identical. 2-Phenylisatogen was recovered unchanged in 67% yield after being heated with acetonitrile, the simplest alkyl cyanide, at 175° in ethanol in an autoclave for 7 hours. Reaction of 2-phenylisatogen with acrylonitrile, the simplest α,β-unsaturated nitrile, in refluxing xylene for 4 hours also did not produce nitrogen insertion, but gave instead in 30% yield a 1:1 adduct, which will be described elsewhere.

The mechanism of the interesting transformation of I to II with tetracyanoethylene will be investigated further.

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[9] D. Zentmeyer and E. C. Wagner, *J. Org. Chem.*, **14**, 967(1949).

[10] We are indebted to Prof. E. Leete for an authentic sample of *N*-benzoylanthranilic acid.

[11] Melting points were determined on a calibrated Fisher-Johns hot stage.