5,7-dinitroindoline, followed by nitration of the resulting indole at the now available 3-position,[2] and subsequent deacetylation. The compound was resistant to chromic acid oxidation.

Experimental

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

1-Acetyl-5-nitroindoline (II).—A solution of 5-nitroindoline[16] (8.63 g., 0.0525 mole) in acetic anhydride (100 cc.) was refluxed for 1 hr., then cooled, and the resulting mixture poured into an excess of water. The mixture was stirred until all of the acetic anhydride dissolved. The precipitate was recrystallized from acetone–methanol, yielding pale yellow needles (9.74 g., 90%), m.p. 177–179°; lit.[22] m.p. 173.5–175.5°; $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ mμ (log ϵ): 231 (4.01), 340 (4.12); $\nu_{\mathrm{NH}}^{\mathrm{Nujol}}$ none, $\nu_{\mathrm{C=O}}^{\mathrm{Nujol}}$ 1667 (s), $\nu_{\mathrm{NO_2}}^{\mathrm{Nujol}}$ 1513 (s), 1319 (s) cm.$^{-1}$.

1-Acetyl-5,7-dinitroindoline.—Fuming nitric acid (*d* 1.5, 6 cc.) was added dropwise, with stirring, at a temperature maintained below 16°, to a mixture of 1-acetyl-5-nitroindoline (3.00 g., 0.0145 mole) and acetic anhydride (70 cc.) cooled initially to 10° in an ice bath. The resulting solution was then removed from the ice bath and stirred until the temperature reached 40°, at which point it was poured into ice–water and the mixture stirred until all of the acetic anhydride dissolved. The resulting precipitate was recrystallized from acetone–methanol, giving yellow needles (1.87 g., 51%), m.p. 207–212°. Sublimation at 200° (1 mm.) and recrystallization of the sublimate from acetone–methanol yielded the analytical sample, m.p. 210–212°; $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ mμ (log ϵ): 226 (4.23), 265 infl. (3.75), 345 (4.02); $\nu_{\mathrm{C=O}}^{\mathrm{Nujol}}$ 1695 (s), $\nu_{\mathrm{NO}}^{\mathrm{Nujol}}$ 1546 (s), 1520 (s), 1344 (s), 1299 (vs) cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_9N_3O_5$ (251.20): C, 47.81; H, 3.61; N, 16.73. Found: C, 48.05; H, 3.73; N, 16.45.

5,7-Dinitroindoline (I). **A. From 1-Acetylindoline**.—The compound was prepared,[16] along with 5-nitroindoline, by nitration of 1-acetylindoline, except that the procedure for purification of the dinitro product was changed. The crude dinitro product was not recrystallized from xylene but was dissolved in benzene–ethyl acetate (4:1 by volume) and placed on a column of neutral alumina (25 g.) which had been packed wet with petroleum ether (b.p. 60–68°). Elution with 4:1 benzene–ethyl acetate gave in 2% yield orange needles, m.p. 244–245°; lit.[16] 5%, yellow crystals, m.p. 243–244°; $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ mμ (log ϵ): 218 (4.03), 263 (4.00), 364 (4.15), 404 infl. (3.90); $\nu_{\mathrm{NH}}^{\mathrm{Nujol}}$ 3290 (m), $\nu_{\mathrm{NO_2}}^{\mathrm{Nujol}}$ 1534 (ms), 1497 (ms), 1335 (ms), 1312 (s) cm.$^{-1}$.

Anal. Calcd. for $C_8H_7N_3O_4$ (209.16): C, 45.94; H, 3.37; N, 20.09. Found: C, 46.06; H, 3.42; N, 19.86.

B. From 1-Acetyl-5-nitroindoline.—Fuming nitric acid (*d* 1.5, 4 cc.) was added dropwise, with stirring, to a solution of 1-acetyl-5-nitroindoline (2.00 g., 0.00970 mole) in acetic anhydride (50 cc.) kept at 15°. The yellow solution was then stirred at room temperature for 0.75 hr., during which time it warmed up to a maximum temperature of 35°. The solution was poured into water and stirred until all of the acetic anhydride had dissolved. The resulting yellow precipitate was refluxed in concentrated hydrochloric acid (50 cc.) for 1 hr. and the mixture cooled. The precipitate was recrystallized from acetone–ethanol, with charcoal, yielding light orange needles (0.85 g., 42%), m.p. 244–245°. There was no depression in m.m.p. 244–245° with the sample prepared from 1-acetylindoline, and the infrared spectra in Nujol were identical.

Oxidative Degradation of 5,7-Dinitroindoline.—A solution of chromium(VI) oxide (1.50 g., 0.0150 mole) in water (5 cc.) was added to a suspension of 5,7-dinitroindoline (0.66 g., 0.00316 mole) in acetic acid (100 cc.). The resulting black solution was stirred at room temperature for 40 hr., and then poured into an excess of water. The green aqueous solution was extracted with ethyl acetate. The ethyl acetate solution was extracted with aqueous saturated sodium bicarbonate until carbon dioxide was no longer evolved. The ethyl acetate solution was then concentrated to a small volume, and petroleum ether (b.p. 60–68°) was added. The resulting orange precipitate was recrystallized from ethyl acetate–benzene, with charcoal, yielding **5,7-dinitroisatin** (III) as orange-yellow crystals (0.26 g., 35%), m.p. 209–210°; lit.[23,24] m.p. 209–210°; $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ mμ (log ϵ): 239 (4.07), 257 infl. (4.02), 323 (4.06), 393 (3.42); $\nu_{\mathrm{NH}}^{\mathrm{Nujol}}$ 3290 (m), $\nu_{\mathrm{C=O}}^{\mathrm{Nujol}}$ 1773 (s), 1754 (ms), 1631 (s), $\nu_{\mathrm{NO_2}}^{\mathrm{Nujol}}$ 1558 (s), 1541 (ms), 1337 (vs), 1289 (s) cm.$^{-1}$. There was no depression in m.m.p. 209–210° with a sample of m.p. 209–210° prepared[23] by nitration of isatin, and the infrared spectra in Nujol were identical.

The sodium bicarbonate extracts were acidified to pH 2 with aqueous hydrochloric acid, and the resulting solution was extracted with ethyl acetate. The ethyl acetate extracts were dried over magnesium sulfate and concentrated until only acetic acid remained as a solvent, and then water was added. The brown precipitate was recrystallized from methanol–water, yielding **3,5-dinitroanthranilic acid** (IV) as golden yellow needles (0.08 g., 11%), m.p. 256°; lit.[25,26] m.p. 256°, lit.[27] 265°, lit.[28] 268°; $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ mμ (log ϵ): 237 (4.09), 336 (4.11), 392 (3.87); $\nu_{\mathrm{NH}}^{\mathrm{Nujol}}$ 3370 (m), 3250 (m), $\nu_{\mathrm{C=O}}^{\mathrm{Nujol}}$ 1672 (s), $\nu_{\mathrm{NO_2}}^{\mathrm{Nujol}}$ 1515 (ms), 1328 (vs) cm.$^{-1}$.

3,5,7-Trinitroindole (V).—1-Acetyl-5-nitroindoline (6.09 g., 0.0295 mole) was added slowly to fuming nitric acid (*d* 1.5, 24 cc.) at 5° and then the solution was poured into an excess of water. The resulting precipitate was recrystallized twice from acetone–methanol, once with charcoal, yielding white needles (1.67 g., 22%), m.p. 232–233°; $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ mμ (log ϵ): 216 (4.30), 286 (4.11); does not obey Beer's law in the long wave-length region, $\lambda_{\max}$ 413 very broad: $c = 1.444 \times 10^{-4}$ mole/l. (3.03), $c = 6.19 \times 10^{-5}$ mole/l. (3.26), $c = 4.12 \times 10^{-5}$ mole/l. (3.37); $\nu_{\mathrm{NH}}^{\mathrm{Nujol}}$ 3360 (m), $\nu_{\mathrm{NO_2}}^{\mathrm{Nujol}}$ 1531 (s), 1379 (s), 1344 (s) or 1307 (s), cm.$^{-1}$. The compound is soluble in aqueous 1% sodium hydroxide but not in saturated sodium bicarbonate solution.

Anal. Calcd. for $C_8H_4N_4O_6$ (252.14): C, 38.11; H, 1.60; N, 22.22. Found: C, 38.25; H, 1.70; N, 21.76.

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The Free-Radical-Induced Reaction of Ethylene with 1,1,2,2-Tetrabromoethane

M. ROGOZINSKI AND L. M. SHORR

Israel Mining Industries Laboratories,
P.O. Box 313, Haifa, Israel

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Attempts to telomerize ethylene with 1,1,2,2-tetrabromoethane (TBE) to obtain compounds of the type $CHBr_2CHBr(C_2H_4)_nBr$ did not give rise to these materials but produced α,ω-dibromo *n*-alkanes. These appear to be products of the indirect telomerization of ethylene with bromine. Thus, when ethylene and TBE reacted under pressure in the presence of benzoyl peroxide at 100° the reaction product contained 1,2-dibromoethylene, 1,2-dibromoethane, 1,4-dibromobutane, 1,6-dibromohexane (putative), and bromobenzene. The latter undoubtedly originated from the initiator. Because of its low concentration, that component of the product assumed to be 1,6-dibromohexane could not be positively identified.

The relatively high concentration of 1,2-dibromoethylene and the fact that no other high-boiling materials were shown by gas chromatography clearly indictates that the expected telomerization between TBE and ethylene did not occur. Similar results were obtained in reactions between TBE and ethylene with thermal initiation at 200°.

The presence of both 1,2-dibromoethylene and 1,2-dibromoethane can be explained by the decomposition

TABLE I

PRODUCT COMPOSITION

Experiment no.	Reaction product, composition in moles/100 g.				
	Bromobenzene	1,2-Dibromoethylene	$Br(C_2H_4)_nBr$		
			$n = 1$	$n = 2$	$n = 3$
1	0.0038	0.043	0.037	0.0037	
2	0.025	0.14	0.070	0.062	0.005
3	0.040	0.16	0.074	0.041	0.0004

TABLE II

INITIAL REACTION MIXTURE COMPOSITION[a]

Experiment no.	Ethylene pressure, p.s.i.	Moles of C_2H_4			Moles of benzoyl peroxide per mole of TBE
		Dissolved in TBE[b]	In gas phase[c]	Total	
1	600	0.29	0.94	1.23	0.01
2	1400	0.46	4.72	5.18	0.1
3	1300	0.50	4.52	5.02	0.1

[a] At ambient temperature, 26°. [b] Approximate values obtained from an experimentally established solubility curve of ethylene in TBE as a function of pressure. [c] Calculated from literature data (J. B. Maxwell, "Data Book on Hydrocarbons," D. Van Nostrand Co., Inc., New York, N. Y., 1955).

of TBE into 1,2-dibromoethylene and bromine with the subsequent reaction between the latter and ethylene to give 1,2-dibromoethane. However, these are not the usual TBE decomposition products.[1] Neither does it explain the presence of 1,4-dibromobutane nor the possible presence of 1,6-dibromohexane.

A mechanism involving the following steps is proposed for the formation of these compounds.

$$\mathrm{CHBr_2{-}CHBr_2 + R\cdot \longrightarrow CHBr_2{-}CHBr\cdot + RBr} \tag{1}$$

$$\mathrm{CHBr_2{-}CHBr\cdot \longrightarrow CHBr{=}CHBr + Br\cdot} \tag{2}$$

$$\mathrm{Br\cdot + C_2H_4 \longrightarrow BrC_2H_4\cdot} \tag{3}$$

$$\mathrm{BrC_2H_4\cdot} + n\mathrm{C_2H_4 \longrightarrow Br(C_2H_4)_{n+1}\cdot} \tag{4}$$

$$\mathrm{Br(C_2H_4)_{n+1}\cdot + CHBr_2{-}CHBr_2 \longrightarrow Br(C_2H_4)_{n+1}Br + CHBr_2{-}CHBr\cdot} \tag{5}$$

1,2-Dibromoethane and 1,4-dibromobutane could also be formed by the following.

$$\mathrm{BrC_2H_4\cdot + Br\cdot \longrightarrow BrC_2H_4Br} \tag{6}$$

$$\mathrm{2BrC_2H_4\cdot \longrightarrow Br(C_2H_4)_2Br} \tag{7}$$

1,6-Dibromohexane cannot be produced by a chain termination step, but only by a mechanism similar to eq. 4 and 5. The positive identification of this material would thus be proof of a telomerization mechanism.

However, a material balance clearly indicates that the chain terminating steps of eq. 6 and 7 cannot be major contributors to the formation of the respective products, and agrees well with eq. 1–5. If reaction 7 is the major contributor to the formation of 1,4-dibromobutane, then, for 2 moles of bromobenzene produced in the initiation step, 1 mole of 1,4-dibromobutane should form. This is not borne out by the results as can be seen from Table I. Therefore, reaction 7 can be only a minor side reaction. Furthermore, if 1,2-dibromoethane is formed principally by reaction 6, then again 2 moles of bromobenzene would have been formed for each mole of 1,2-dibromoethane produced. Neither is this supported by the experimental results. Alternatively, if both reactions, as indicated in eq. 6 and 7, are occurring simultaneously then the sum of the moles of 1,2-dibromoethane and 1,4-dibromobutane should equal half the moles of bromobenzene, which was not found to be the case.

It, therefore, appears that the reaction between 1,1,2,2-tetrabromoethane and ethylene under free-radical conditions is a telomerization of ethylene by bromine, the tetrabromoethane acting as a bromine carrier. The low yields probably result from the low solubility of ethylene in TBE, which reached a value of only 40 mole % at 3000 p.s.i. at ambient temperature.

It is of interest to note that a similar reaction did not occur with 1,1,2,2-tetrachloroethane and ethylene. The product of this reaction consisted of a complex mixture of high-boiling materials containing only traces of 1,2-dichloroethane and 1,2-dichloroethylene.

Experimental

Reactions were performed in a 500-ml. rocking autoclave. Conditions common to all experiments were the amount of TBE, 100 ml. (0.855 mole); initiator, benzoyl peroxide; reaction temperature, 100°; reaction period, 3 hr. Reaction conditions which varied are given in Table II.

As part of the initiator was converted to benzoic acid the products were filtered prior to gas chromatographic analysis on silicone grease. The product of experiment 2, for example, was found to have the following composition: bromobenzene, 4%; 1,2-dibromoethylene, 26%; 1,2-dibromoethane, 13%; 1,4-dibromobutane, 13%; 1,6-dibromohexane (putative), 1%; 1,1,2,2-tetrabromoethane, 36%. The residual 7% consisted mainly of tribromoethylene and pentabromoethane, both of which are free-radical-induced decomposition products of TBE.[1] Identifications, except for 1,4-dibromobutane and 1,6-dibromohexane, were by retention time comparison. Bromobenzene and 1,4-dibromobutane were separated by fractional distillation and characterized by their specific gravity, refractive index, and infrared spectra. The material believed to be 1,6-dibromohexane had a gas chromatographically estimated boiling point of 251°, which is in fair agreement with the literature value of 243°.[2]

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