1-butenyl ethyl ether (11.1 g., 0.11 mole of fraction II) in benzene (25 ml.). The reaction was slightly exothermic, and the temperature of the mixture was maintained below 30° by intermittent cooling. After standing for 16 hr., the mixture had completely lost its yellow color. Analysis by g.l.p.c. of the reaction mixture showed only one major product peak, no evidence of any isomeric cyclobutanone, and the presence of a small amount of tetramethyl-1,3-cyclobutanedione. Distillation of the mixture gave, after removal of the solvent, 13 g. (69%) of pure **2a**: b.p. 66–67° (6 mm.); $n^{20}\mathrm{D}$ 1.4304; n.m.r. spectrum (neat), singlets at 1.07 and 1.19 (methyl groups), triplet at 0.97 and quintet at 1.66 (ethyl group), triplet at 1.19 and quartet at 3.58 (ethoxy group), quartet at 3.28 (proton on the carbon adjacent to the carbonyl group), and doublet (J = 8.0 c.p.s.) at 3.88 (proton on the carbon bearing the ethoxy group) p.p.m.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.6; H, 10.7. Found: C, 70.3; H, 10.6.

Reaction of Dimethylketene with 1b.—Dimethylketene (7.2 g., 0.103 mole) was added by means of a syringe to a solution of **1b** (10.3 g., 0.103 mole, fractions XXV–XXVIII) in benzene (25 ml.). The reaction was slightly exothermic and the temperature of the mixture was maintained below 30° by intermittent cooling. After standing for 19 hr., the mixture still possessed the characteristic yellow color of dimethylketene; however, after 40 hr., the yellow color had disappeared. Analysis by g.l.p.c. showed that the reaction solution consisted of 57% tetramethyl-1,3-cyclobutanedione, 38% **2b**, 5% **2a**, benzene, and unchanged **1b**. The mixture was distilled to give 23 g. of forerun followed by 0.3 g. of material with b.p. *ca.* 65° (6 mm.). The forerun consisted of 31% **1b** and 69% benzene. The n.m.r. spectrum of this mixture verified the absence of **1a**. The 0.3 g. of higher boiling material was a mixture of 30% **2a** and 70% **2b**.

Ketenes. VII. Some Reactions of 3-Ethoxy-2,2-dimethylcyclobutanone with Aromatic Amines[1]

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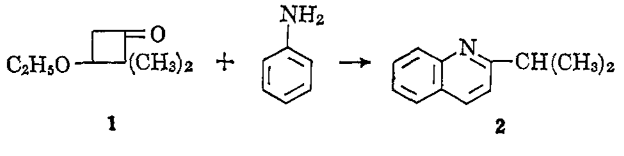
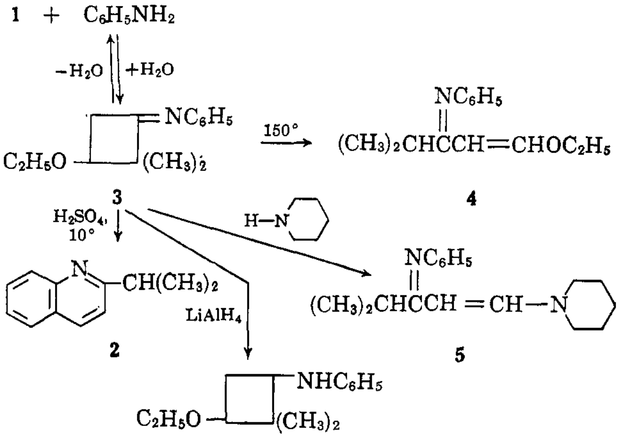
In an earlier paper in this series[2] we described the preparation of 3-ethoxy-2,2-dimethylcyclobutanone (1) from dimethylketene and ethyl vinyl ether. This paper is a report of some investigations of the reactions of 1 with aromatic amines. Aniline and 1, when refluxed in toluene with *p*-toluenesulfonic acid as a catalyst and with the water which was formed allowed to remain in the system, gave a 52% yield of 2-isopropylquinoline (2). A substantial amount (27%) of formanilide was obtained as a by-product in the reaction. This quinoline synthesis was extended to a few substituted anilines to give the new quinolines listed in Table I. The yields varied markedly with the nature and position of the substituent, but not enough examples were run to allow generalized predictions regarding substituents. It appears that *meta*-substituted anilines, particularly those with electron-donating groups, give the best yields. *m*-Toluidine and *m*-phenetidine gave a 70% yield of 2-isopropyl-7-methylquinoline[3] and a 55% yield of 7-ethoxy-2-isopropylquinoline, respectively. *o*- or *p*-Anisidine gave very low yields of the corresponding quinolines. *m*-Chloroaniline gave a 55% yield of a mixture of 5-(and 7-) chloro-2-isopropylquinoline.



The exact mechanism for the formation of 2 is not clear. However, it was observed that modifications of the reaction conditions led to the formation of entirely different products. For instance, the anil of **1**, N-(3-ethoxy-2,2-dimethylcyclobutylidene)aniline (**3**), was prepared in 61% yield by heating **1** and aniline in the presence of aniline hydrochloride in toluene at 48° *in vacuo* and by removing water as it was formed. This low temperature was essential to the success of the reaction, as was demonstrated when this reaction was tried in refluxing toluene. At the higher temperature the water removed was 76% of the theoretical amount, but no **3** was obtained. Small amounts of ethyl alcohol, 3-methyl-2-butanone, N,N′-diphenylformamidine, unchanged **1**, and aniline, together with a large amount of black syrup, were produced.

The formation of **3** was found to be readily reversible. Exposure of **3** to atmospheric moisture for several hours gave **1** and aniline. When **3** was heated at 150° for 30 min., a ring-opening reaction to give N-(3-ethoxy-1-isopropylallylidene)aniline (**4**) in 82% yield took place. The reaction has a formal resemblance to the ring-opening reactions of 3-dialkylaminocyclobutanones having one or more α-hydrogen atoms.[4] N-(1-Isopropyl-3-piperidinoallylidene)aniline (**5**) was produced in 44% yield by the action of piperidine on **3** in refluxing toluene (Scheme I). We found that this ring-opening reaction was not confined to the anil; 3-ethoxy-2,2-dimethylcyclobutanone (**1**) and piperidine on refluxing in toluene underwent a similar reaction to give 4-methyl-1-piperidino-1-penten-3-one (**6**).[5] Treatment of **3** with cold, concentrated sulfuric acid gave 2-isopropylquinoline (**2**) in 76% yield.

SCHEME I



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(1) Paper VI: J. C. Martin, V. W. Goodlett, and R. D. Burpitt, *J. Org. Chem.*, **30**, 4309 (1965).

(2) R. H. Hasek, P. G. Gott, and J. C. Martin, *ibid.*, **29**, 1239 (1964).

(3) By analogy to other quinoline syntheses, the 7-methyl isomer rather than the 5-methyl isomer was the expected product. This was verified by the n.m.r. spectrum of our compound.

(4) R. H. Hasek and J. C. Martin, *J. Org. Chem.*, **28**, 1468 (1963).

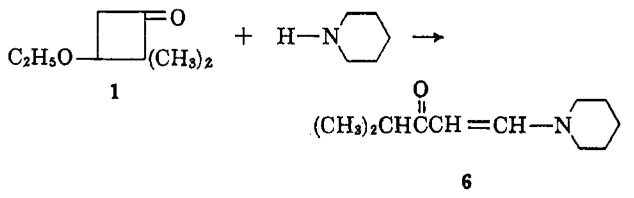
(5) One rationale for this reaction presupposes that the ethoxy group of **1** is replaced by the piperidino group to give 2,2-dimethyl-3-piperidinocyclobutanone as an intermediate. According to reference **4**, this would be expected to open to **6**.

TABLE I

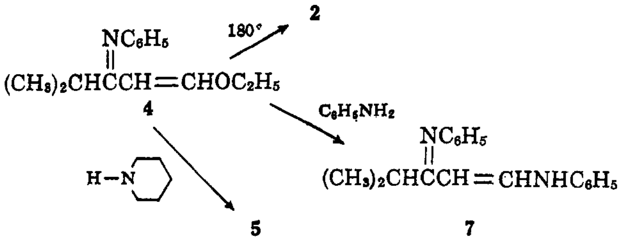
SUBSTITUTED QUINOLINES FROM 3-ETHOXY-2,2-DIMETHYLCYCLOBUTANONE

Aniline	2-Isopropyl-quinoline	Yield, %	B.p., °C. (mm.)	n^{20}D	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
2-Methoxy	8-Methoxy	2	107–108 (0.7)	1.5933	$C_{13}H_{15}NO$	77.6	76.8	7.5	7.5	7.0	6.4
4-Methoxy	6-Methoxy	3.5	115–117 (0.1)	1.5887	$C_{13}H_{15}NO$	77.6	76.4	7.5	7.6	7.0	6.6
3-Methyl	7-Methyl	70	139–142 (7)	1.5788	$C_{13}H_{15}N$	84.3	83.9	8.2	8.2	7.6	7.8
3-Ethoxy	7-Ethoxy	55	99–100 (0.05)	1.5769	$C_{14}H_{17}NO$	78.1	77.8	8.0	8.0	6.5	6.5
3-Chloro	5- (and 7-) Chloro[a]	55	81–82 (0.05)	1.5922	$C_{12}H_{12}ClN$	70.1	69.7	5.9	5.9	6.8	6.7
4-Nitro	6-Nitro	5	58–60.5[b]	...	$C_{12}H_{12}N_2O_2$	66.7	66.8	5.6	5.7	13.0	13.3

[a] The presence of two isomers was detected by g.l.p.c. [b] Melting point, recrystallized from hexane.

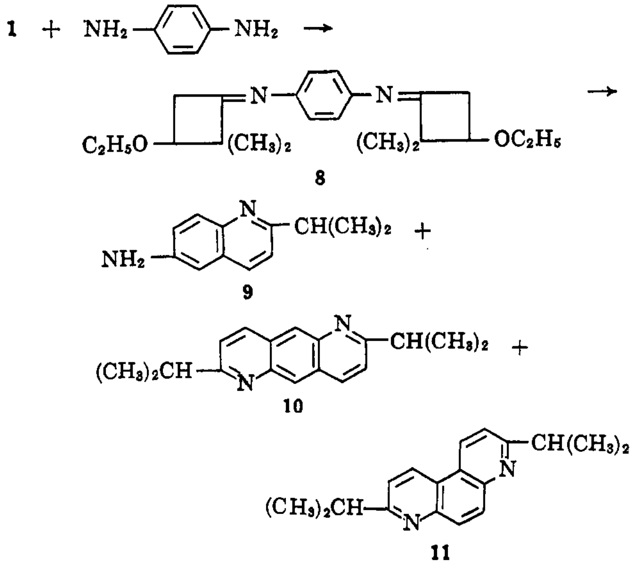


The unsaturated imine **4** was converted to **2** in 70% yield by refluxing in *o*-dichlorobenzene in the presence of *p*-toluenesulfonic acid for 21 hr. The alkoxy group of **4** was readily exchanged with amines; *e.g.*, aniline gave a 70% yield of N,N′-(3-isopropyl-1-propen-1-yl-3-ylidene)dianiline (**7**) and piperidine gave an 81% yield of **5**.



In a further extension of the quinoline synthesis, **1** and *p*-phenylenediamine in toluene solution were refluxed at 50° *in vacuo* in the presence of *p*-phenylenediamine hydrochloride as a catalyst to give the dianil **8**. This crude product was treated with cold, concentrated sulfuric acid to give a 19% yield of 6-amino-2 isopropylquinoline (**9**), a 2% yield of 2,7-diisopropylpyrido[2,3-*g*]quinoline (**10**), and a 42% yield of 3,8-diisopropyl-4,7-phenanthroline (**11**). The assignment of structures for **9**, **10**, and **11** was based on their n.m.r. spectra. (See Scheme II.)

SCHEME II



Experimental Section

2-Isopropylquinoline (2) from 3-Ethoxy-2,2-dimethylcyclobutanone (1).—A mixture of 142 g. (1.0 mole) of **1**, 140 g. (1.5 moles) of aniline, 2 g. of *p*-toluenesulfonic acid, and 600 ml. of toluene was refluxed for 6 hr. The reaction solution was washed with sodium bicarbonate solution and water and was dried over anhydrous magnesium sulfate. Distillation through a 12-in. packed column gave 42.5 g. of unchanged aniline and 33.0 g. (27%) of formanilide, b.p. 121–133° (1.2 mm.), n^{20}D 1.5864. It also gave 89 g. (52%) of **2**: b.p. 122–128° (8 mm.); n^{20}D 1.5834; n.m.r. spectrum (neat),[6] doublet at 1.37 and septet at 3.18 (isopropyl group), doublet at 6.98 (3-proton), multiplet at 7.37 (5-, 6-, and 7-protons), doublet at 7.76 (4-proton), and doublet at 8.31 p.p.m. (8-proton).

The picrate of **2** melted at 156–158.5° (lit.[7] m.p. 155–157°). The infrared spectrum of the formanilide was identical with that of a known sample.

Anal. Calcd. (for **2**) for $C_{12}H_{13}N$: C, 84.2; H, 7.6; N, 8.2. Found: C, 84.0; H, 7.5; N, 7.8.

N-(3-Ethoxy-2,2-dimethylcyclobutylidene)aniline (3).—A mixture of 71 g. (0.5 mole) of **1** and 56 g. (0.6 mole) of aniline in 400 ml. of toluene and 2 g. of aniline hydrochloride was refluxed at 48° at a reduced pressure of 68 mm. with the use of a Dean–Stark water collector. After 3 hr. separation of water virtually stopped, when 5.1 ml. (57%) had been collected. Analysis by g.l.p.c. showed that considerable amounts of unchanged starting materials remained. Distillation through an 8-in. packed column gave 66 g. (61%) of **3**: b.p. 94° (0.1 mm.); n^{20}D 1.5237; infrared absorptions (smear),[8] 5.9 and 8.95 μ; n.m.r. spectrum (neat), singlet at 1.28 (*gem*-dimethyl group), triplet at 1.11 and quartet at 3.31 (ethoxy group), doublet at 2.84 (methylene group), triplet at 3.59 (methylidyne proton), and multiple peaks at 7.05 p.p.m. (aromatic protons).

Anal. Calcd. for $C_{13}H_{19}NO$: C, 77.4; H, 8.8; N, 6.5. Found: C, 77.2; H, 8.7; N, 6.5.

2-Isopropylquinoline from 3.—**3** (1.0 g., 0.0046 mole) was added slowly with stirring under a nitrogen atmosphere to 10° ml. of 96% sulfuric acid at 10°. The resulting solution was left at 25° for 4 hr., drowned on ice, and made basic with sodium hydroxide solution. **2** (0.6 g., 76%) separated as an oil. The infrared spectrum of this material was identical with that of 2-isopropylquinoline.

N-(3-Ethoxy-1-isopropylallylidene)aniline (4).—**3** (9.8 g.) was maintained at 150° for 30 min. under a nitrogen atmosphere. Distillation through a 6-in. Vigreux column gave 8.0 g. (82%) of **4**: b.p. 87–91° (0.07 mm.); n^{20}D 1.5450; infrared absorptions (smear), 6.17, 6.25, and 8.35 μ; n.m.r. spectrum (CCl_4), doublet at 1.22 and septet at 2.82 (isopropyl group), triplet at 1.10 and quartet at 3.54 (ethoxy group), doublet at 5.31 (J = 13.3 c.p.s., $-CH{=}\overset{|}{C}-O-$), and multiple peaks at 7.0 p.p.m. (other olefinic proton and aromatic peaks).

Anal. Calcd. for $C_{14}H_{19}NO$: C, 77.4; H, 8.8; N, 6.5. Found: C, 77.4; H, 8.7; N, 6.5.

N-(1-Isopropyl-3-piperidinoallylidene)aniline (5).—A solution of 5.0 g. (0.023 mole) of **3** and 2.5 ml. (0.025 mole) of piperidine

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[6] N.m.r. spectra were recorded on a Varian A-60 instrument at 60 Mc. with tetramethylsilane as an internal standard.

[7] *Chem. Tech.* (Berlin), **7**, 518 (1955).

[8] Infrared spectra were determined on a Baird AB-2 instrument.

in 10 ml. of anhydrous toluene was refluxed under a nitrogen atmosphere for 7 hr. Solvent removal *in vacuo* left a crystalline residue of **5**, which, after one washing and one recrystallization from a small volume of hexane, weighed 2.6 g. (44%), m.p. 63.5–66.5°. A sample for analysis was recrystallized from hexane: m.p. 65–66°; infrared absorptions (KBr), 6.20 and 6.30 μ; n.m.r. spectrum (CCl_4), doublet at 1.18 and septet at 2.85 (isopropyl group), broad peak at 1.44 (three methylene groups of piperidine ring), broad peak at 2.85 ($-CH_2\overset{|}{N}CH_2-$), doublet at 4.77 (J = 14.4 c.p.s., $-CH{=}\overset{|}{C}{-}N<$), and multiple peaks at 6.95 p.p.m. (other olefinic proton and aromatic protons).

Anal. Calcd. for $C_{17}H_{24}N_2$: C, 79.6; H, 9.4; N, 10.9. Found: C, 79.6; H, 9.4; N, 11.0.

2-Isopropylquinoline from 4.—A solution of 1 g. of **4** in 10 ml. of *o*-dichlorobenzene and a few milligrams of *p*-toluenesulfonic acid was refluxed for 21 hr. under an atmosphere of nitrogen. Distillation gave 0.55 g. (70%) of **2**, b.p. 70–73° (0.07 mm.). The infrared spectrum of this material was identical with that of authentic 2-isopropylquinoline.

Reaction of Piperidine with 4.—A solution of 0.65 g. (0.003 mole) of **4** and 0.33 ml. (0.0033 mole) of piperidine in 3 ml. of toluene was refluxed 5 hr. under a nitrogen atmosphere. The volatile material was removed *in vacuo*. The residue (0.62 g.) had an infrared spectrum identical with that of **5** which was prepared by the action of piperidine on **3**. The residue was treated with hexane to give crystals, m.p. 61.5–65°, m.m.p. with authentic **5** 62–65°.

N,N′-(3-Isopropyl-1-propen-1-yl-3-ylidene)dianiline (7).—When 6.5 g. (0.03 mole) of **4** was added to a solution of 2.8 g. (0.03 mole) of aniline in 15 ml. of hexane, the solution became warm spontaneously. After 15 hr. the solvent was removed *in vacuo*, leaving a crystalline residue, which, after washing with hexane, gave 5.6 g. (70%) of **7**: m.p. 65–67°; infrared absorptions (KBr), 6.15, 6.28, 6.45, 6.73, 7.75, 9.70, 13.25, 13.50, and 14.4 μ; n.m.r. spectrum (CCl_4), doublet at 1.04 and septet at 2.83 (isopropyl group), doublet at 4.98 (J = 8.4 c.p.s., $-CH{=}\overset{|}{C}{-}N<$), and multiple peaks at 7.1 p.p.m. (other olefinic proton, -NH-, and aromatic protons).

Anal. Calcd. for $C_{18}H_{20}N_2$: C, 81.8; H, 7.6; N, 10.6. Found: C, 81.7; H, 7.7; N, 10.8.

Reactions of 1 with *p*-Phenylenediamine.—A mixture of 112 g. (0.8 mole) of **1**, 38 g. (0.35 mole) of *p*-phenylenediamine, 1.6 g. of *p*-phenylenediamine hydrochloride, and 640 ml. of toluene was refluxed at 50° at a reduced pressure of 70 mm. with the use of a Dean–Stark water collector. After 7 hr. 10.6 ml. (84%) of water had separated. The resulting solution was concentrated to a final pot temperature of 75° at 0.1 mm. The 115 g. of crude **8** that remained was added during 20 min. to 1250 ml. of stirred 96% sulfuric acid at 15–20°. The resulting black solution was left at 25° for 4 hr., and then drowned on 5 kg. of ice and made basic with sodium hydroxide. The mixture of products that separated was taken up in ethyl ether and dried over solid potassium hydroxide. Rapid distillation gave 60 g. of a fraction boiling at 140–175° (0.1 mm.). Refractionation through a 6-in. packed column gave 13 g. (19%) of **9**, b.p. 135–143° (0.07 mm.). **9** readily formed a hydrate, m.p. 116° dec. An additional distillation fraction boiled at 143–160° (0.07 mm.). Treatment of this fraction with hexane gave 2 g. (2%) of **10** as an insoluble solid. Recrystallization from methanol gave pure **10**, m.p. 166–168°. The hexane-soluble portion of the above fraction was redistilled through a 6-in. packed column to give 38 g. (42%) of **11**, b.p. 158° (0.07 mm.), m.p. 34–39°.

9 had infrared absorptions (KBr) at 2.95, 3.05, 3.14, 6.12, 6.20, 6.65, 7.25, 7.31, 8.87, 9.60, 11.59, 11.65, and 12.08 μ; n.m.r. spectrum ($C_2H_2Cl_4$), doublet at 1.37 and septet at 3.32 (isopropyl group), singlet at 4.74 (amino group), close doublet at 6.98 (J = 2.3 c.p.s., 5-proton), pair of doublets at 7.97 and 8.06 (4- and 8-protons), doublet at 7.27 (J = 8.8 c.p.s., 3-proton), and a pair of doublets at 8.18 p.p.m. (J = 9.1 and 2.3 c.p.s., 7-proton).

Anal. Calcd. for $C_{12}H_{14}N_2\cdot 0.5H_2O$: C, 73.8; H, 7.7; N, 14.4. Found: C, 73.9; H, 7.7; N, 14.1.

10 had infrared absorptions (KBr) at 6.22, 11.23, and 12.18 μ; n.m.r. spectrum (CCl_4), doublet at 1.40 and septet at 3.21 (isopropyl group), doublet at 7.16 (3- and 8-protons), doublet at 8.12 (4- and 9-protons), and singlet at 8.43 p.p.m. (5- and 10-protons).

Anal. Calcd. for $C_{18}H_{20}N_2$: C, 81.8; H, 7.6; N, 10.6. Found: C, 81.9; H, 7.6; N, 10.8.

11 had infrared absorptions (KBr) at 6.26, 11.8, and 12.15 μ; n.m.r. spectrum (CCl_4), doublet at 1.38 and septet at 3.21 (isopropyl group), doublet at 7.18 (2- and 9-protons), singlet at 8.08 (5- and 6-protons), and doublet at 8.40 p.p.m. (1- and 10-protons).

Anal. Calcd. for $C_{18}H_{20}N_2$: C, 81.8; H, 7.6; N, 10.6. Found: C, 81.4; H, 7.3; N, 10.5.

The Reaction of Organoboranes with N-Chlorodialkylamines. A New Synthesis of Primary Alkyl Chlorides from Olefins by Hydroboration

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N-Chlorodialkylamines have recently been shown to react with olefins to form tertiary amines by free-radical[1] as well as ion-radical[2–4] mechanisms. Amination has also been reported by Kavacic[5,6] for toluene with trichloramine and a Lewis acid catalyst and by Brown[7] from the reaction of organoboranes with chloramine or hydroxylamine-O-sulfonic acid.

We wish to report that the only basic products from the reaction of N-chlorodialkylamines with trioctyl- and tricyclohexylboranes were the parent secondary amines. The data in Table I show that the neutral products obtained with N-chlorodiethylamine and N-chloropiperidine were cyclohexyl chloride from tricyclohexylborane and a mixture of 93% 1-chloro- and 7% 2-chlorooctane from the mixture of organoboranes prepared from 1-octene; these products were identified and analyzed by vapor phase chromatography and infrared spectroscopy. N-Chloro-*n*-butylamine and tri-*n*-octylborane gave only tars and no isolable products.

This "anti-Markovnikov" addition of the elements of HCl is a new method for preparing primary alkyl chlorides from terminal olefin bonds and should be applicable to the preparation of primary chlorides from olefins with central double bonds which Brown[8] has isomerized through their organoboranes. The 93 and 7% yields of 1-chloro- and2-chloroct ane, respectively, are similar to the 93–94% to 6–7% ratio of 1- to 2-alkanols.

Experimental Section

Reactions were carried out under dry nitrogen and in a typical run 11.0 ml. (70 mmoles) of 1-octene, dried and distilled over sodium and under dry nitrogen, was injected with a hypodermic

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