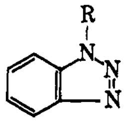
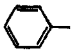
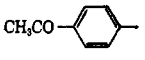
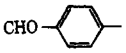
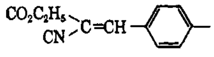
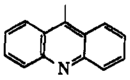
TABLE I

1-SUBSTITUTED BENZOTRIAZOLES



R	M.p. or b.p. (mm.), °C.	Yield, %	Calcd., % C	Calcd., % H	Calcd., % N	Found, % C	Found, % H	Found, % N
	89–90	52	73.8	4.6	21.6	74.0	4.5	21.5
	160–161	50	71.0	4.7	17.8	71.2	4.5	17.8
	156–157	50	70.0	4.0	18.8	69.7	4.0	18.6
	180–181	55	67.9	4.4	17.6	67.5	4.3	17.9
C_6H_{13}-	135–136 (0.2)	70	71.0	8.4	20.7	71.0	8.6	21.0
C_4H_9	127–128 (0.2)	68	68.5	7.4	24.0	68.3	7.5	23.8
	250 dec.	47	77.0	4.1	18.9	76.6	4.2	18.8

Experimental

General Procedure.—A solution of 7 g. (0.051 mole) of anthranilic acid in 60 ml. of acetone was added over a 2-hr. period to a refluxing mixture of 0.05 mole of the azide and 6 g. (0.058 mole) of butyl nitrite in 200 ml. of dichloromethane. The volatile components were stripped from the reaction mixture with an aspirator to leave a brown gum. In the examples with aliphatic azides, the residues were distilled. The residue obtained from the reaction with phenyl azide and with V were dissolved in benzene, chromatographed through Florisil, and, after evaporation of the benzene, the residues were recrystallized from petroleum ether (b.p. 35–60°) and ethanol, respectively. The brown gums obtained in the other examples listed on Table I were all recrystallized from benzene. Azides II, III, and IV were treated in the same manner as phenyl azide, but evaporation of the solution which had been passed through the chromatography column yielded only the starting azide.

Phenylacetyl Derivatives of Methylhydrazine[1]

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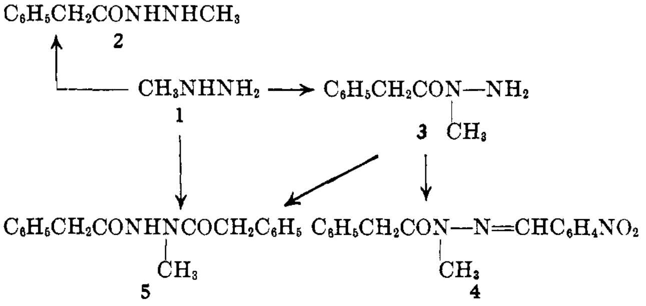
The only systematic studies of the acylation of alkylhydrazines have been reported by Hinman and Fulton,[2] who found that there action of methylhydrazine with esters gave mainly 1-acyl-2-methylhydrazines and with anhydrides, 1-acyl-1-methylhydrazines. Most of the products were characterized by paper chromatography. In connection with a projected pyridazone synthesis, we had occasion to examine the reactions of methylhydrazine (1) with various derivatives of phenylacetic acid, and have confirmed the earlier conclusions on the course of these acylations.

On refluxing 1 with ethyl phenylacetate, crystalline 2-methyl-1-phenylacetylhydrazine (2) was obtained in 76% yield; the n.m.r. spectrum[3] contained two one-proton peaks at 260 c.p.s. (broad, $-CONHNHCH_3$) and 434 c.p.s. ($-CONHNHCH_3$) which were exchangeable with D_2O. The reaction of 1 with phenylacetic anhydride gave an oil which was characterized as 1-methyl-1-phenylacetylhydrazine (3) by conversion to the *p*-nitrobenzalhydrazone (4). In each of these reactions a minor amount of the other isomer, 3 from the ester and 2 from the anhydride, was detected in the product mixture by thin-layer chromatography. The bis(phenylacetyl) derivative 5 was obtained from either 1 or 3 by treatment with phenylacetyl chloride; an intermediate monoacyl product could not be isolated.



Experimental[4]

1-Methyl-2-phenylacetylhydrazine (2).—A solution of 0.87 g. (18.8 mmoles) of methylhydrazine and 3.1 g. (18.8 mmoles) of ethyl phenylacetate in 1.6 ml. of ethanol was refluxed for 12 hr. On cooling, 1.59 g. (76%) of a fluffy crystalline precipitate, m.p. 113–116°, separated. Recrystallization from ethanol–ether gave white plates of 2: m.p. 126–127°; λ^{KBr} 3.02 and 6.13 μ; n.m.r., 149 (singlet, 3), 208 (s, 2), 260 (broad, 1), and 434 c.p.s. (multiplet, 6).

Anal. Calcd. for $C_9H_{12}N_2O$: C, 65.83; H, 7.37. Found: C, 65.76; H, 7.42.

The ethanolic mother liquor from 2 showed three spots on a t.l.c. plate, corresponding, in order of decreasing R_f value, to ethyl phenylacetate, 3 and 2.

1-Methyl-1-phenylacetylhydrazine (3).—To a solution of 887 mg. (19.3 mmoles) of methylhydrazine in 1.0 ml. of benzene was

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[1] Supported by Grant DA-CmL-18-108-61-G-24 from the Army Chemical Corps.

[2] R. L. Hinman and D. Fulton, *J. Am. Chem. Soc.*, **80**, 1895 (1958).

[3] N.m.r. spectra were obtained in $CDCl_3$ solutions (tetramethylsilane) with a Varian A-60 instrument.

[4] Melting points were observed on a Fisher-Johns block with a calibrated thermometer. Infrared spectra were obtained with a Perkin-Elmer Infracord. Thin layer chromatography was carried out on silica gel C in chloroform–methanol (25:2); the spots were visualized with iodine vapor.

added, with stirring, 2.45 g. (9.63 mmoles) of phenylacetic anhydride[5] in 5.0 ml. of benzene. The temperature rose slightly during the addition and the solution was then refluxed for 1 hr., cooled, and extracted with 5% aqueous KOH. The benzene layer was washed with water, dried, and evaporated, leaving 537 mg. (34%) of a viscous yellow oil which solidified upon chilling: $\lambda_{\max}^{\mathrm{KBr}}$ 2.94 and 6.08 μ. A t.l.c. plate showed two spots, the larger one due to **3** having the higher R_f value, and the smaller having the same R_f as **2**.

1-Methyl-1-phenylacetyl-*p*-nitrobenzalhydrazone (4).—To a solution of 78 mg. (0.48 mmole) of 1-methyl-1-phenylacetylhydrazine in 0.3 ml. of ethanol was added a solution of 76 mg. (0.50 mmole) of *p*-nitrobenzaldehyde in 0.5 ml. of ethanol. The solution was refluxed for 10 min. on a steam bath. Upon cooling a precipitate separated which was filtered and washed with ethanol, yielding 96 mg. (68%) of **4**, m.p. 171–172°. Recrystallization from acetone–ethanol gave pale yellow needles: m.p. 172–173°; $\lambda_{\max}^{\mathrm{KBr}}$ 5.94, 6.33, and 6.63 μ.

Anal. Calcd. for $C_{16}H_{15}N_3O_3$ (297.30): C, 64.63; H, 5.09; N, 14.14. Found: C, 64.61; H, 5.09; N, 14.17.

1-Methyl-1,2-diphenylacetylhydrazine (5).—To a stirred solution of 866 mg. (18.8 mmoles) of methylhydrazine in 1.6 ml. of water at 10° was added 2.90 g. (18.8 mmoles) of phenylacetyl chloride followed by a solution of 1.29 g. of K_2CO_3 in 1.5 ml. of water. After 1 hr. the mixture was extracted three times with ethyl acetate and the ethyl acetate solution was dried and evaporated to a pale yellow oil, which crystallized after standing for 3 days; 1.35 g. (49%), of white crystals, m.p. 75–83°, was obtained. Recrystallization from ethanol–ether gave white crystals: m.p. 85–86°; $\lambda_{\max}^{\mathrm{KBr}}$ 3.02 and 5.94 μ; n.m.r., 182 (s, 3) 208 (s, 2), 212 (s, 2), 437 (multiplet, 10), and 467 c.p.s. (1, exchangeable with D_2O in presence of acid).

Anal. Calcd. for $C_{17}H_{18}N_2O_2$: C, 72.32; H, 6.43. Found: C, 72.46; H, 6.60.

Treatment of crude **3** with phenylacetyl chloride under similar conditions gave **5** in 79% yield.

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[5] I. M. Heilbron, D. H. Hey, and B. Lythgoe, *J. Chem. Soc.*, 297 (1936).

The Structure of Alloocimene Dioxide[1]

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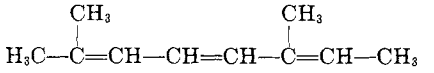
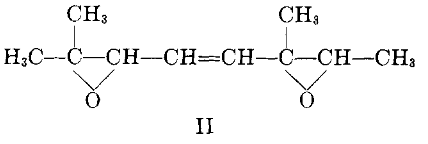
Received April 18, 1963

In 1950, Desalbres[2] described a product, $C_{10}H_{16}O_2$, obtained from the spontaneous depolymerization of the insoluble gummy product resulting from autoxidation of alloocimene (I). This work was repeated in 1953 by Dranishnikov,[3] who further showed that the monomeric product reacted as a diepoxide, giving a crystalline tetrol, $C_{10}H_{16}(OH)_4$, and a dihydroxy dimethyl ether, $C_{10}H_{16}(OH)_2(OCH_3)_2$ (V), by reaction with water and methanol, respectively, in the presence of catalytic amounts of acid.

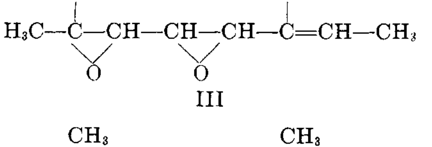


$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH=CH-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_3$

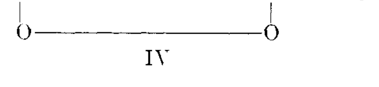
I



II



III



IV

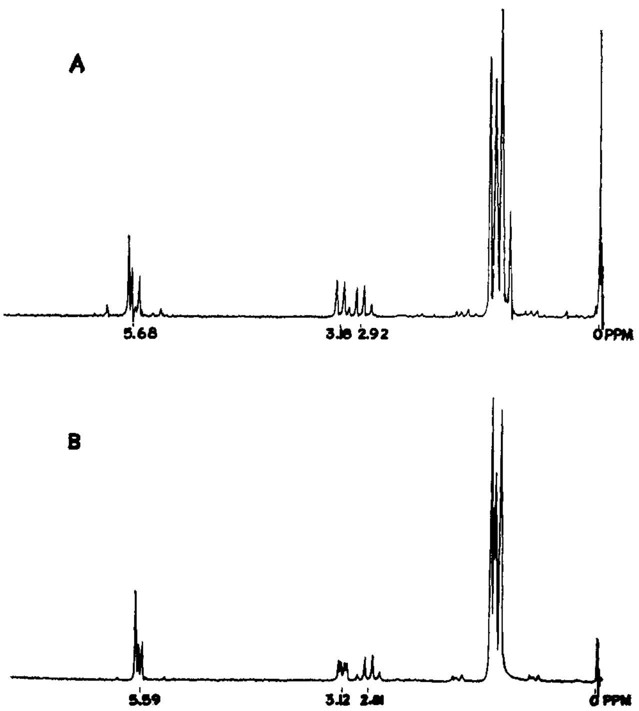
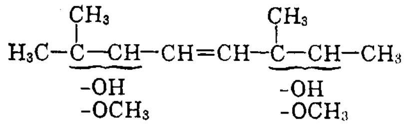


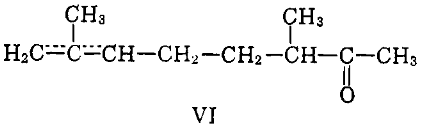
Fig. 1.—N.m.r. spectra at 60 Mc./sec. relative to tetramethylsilane: A, IIa; B, IIb.

Later, each of these authors proposed a different structure for the monomeric dioxide, with Desalbres[4] favoring the 2,3,6,7-diepoxide II based on conversion to a known mixture of C_{10} methyl ketones (VI), while Dranishnikov[5] felt that the 2,3,4,5-diepoxide structure (III) was necessary to explain the results of his oxidation experiments. Previous work in our laboratory[6] suggested that the monomer as normally prepared might contain significant amounts of the cyclic peroxide IV.



$H_3C-\underset{\substack{-OH\\-OCH_3}}{\underbrace{\overset{\overset{\displaystyle CH_3}{|}}{C}-CH}}-CH=CH-\underset{\substack{-OH\\-OCH_3}}{\underbrace{\overset{\overset{\displaystyle CH_3}{|}}{C}-CH}}-CH_3$

V



$H_2C=\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_2-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-\underset{\underset{\displaystyle O}{\|}}{C}-CH_3$

VI

In view of these conflicting results, we have repeated the work of Desalbres, *et al.*, and in addition have obtained further evidence in support of structure II,

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[1] Presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

[2] L. Desalbres, *Bull. soc. chim. France*, 1245 (1950).

[3] G. L. Dranishnikov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 470 (1953).

[4] Yves-Rene Naves, L. Desalbres, and P. Ardizio, *Bull. soc. chim. France*, 1768 (1956).

[5] G. L. Dranishnikov, *Izv. Vysshikh Uchebn. Zavendenii, Lesn. Zh.*, **3**, 127 (1960).

[6] J. H. Stump, Jr., and O. G. Wilson, U. S. Patent 3,038,906 (June 12, 1962).