was recrystallized from methanol to give 2.55 g (61.5%) of white crystals: mp 173–175°; ir, OH (3415, 3308), –C–O (1240, 1167, and 1036 cm^{-1}); nmr,[7] CH_3 (ring) and CH at τ 8.03, 7.88, 7.71 (total 10), α-CH_2 at 7.23 (2), CH_3O at 6.63 (3), –CH_2O– at 6.17 (4).

Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 65.72; H, 8.57.

Preparation of IV and V. A.—To a stirred solution of 0.62 g (0.0024 mol) of III in 20 ml of dry THF was added 1.2 g (0.0027 mol) of lead tetraacetate. The suspension was refluxed 15 min. Aqueous sodium hydroxide was added and the mixture was extracted with ether. On evaporation of the solvent from the dried ether solution there was obtained a red-yellow oily residue. This was dissolved in a small amount of acetonitrile and refrigerated. White plates crystallized in a yield of 0.15 g (28%), mp 159–160°. From the mother liquor, by recrystallization from THF–*n*-heptane a further yield of 0.13 g (23%) of white crystals, mp 159–160°, was obtained, and 0.07 g (12%) of yellow crystals melting at 79–79.5° were also obtained. The white crystalline material is IV and the yellow is V.

Anal. Calcd for $C_{13}H_{16}O_3$ (IV): C, 70.89; H, 7.32. Found: C, 71.02; H, 7.28.

Calcd for $C_{13}H_{18}O_4$ (V): C, 65.53; H, 7.61. Found: C, 65.46; H, 7.58.

The ir spectrum of IV showed C=O at 1683, 1644, and 1633 (C=C) and –C–O– at 1260, 1197, 1099, and 1040. That for V showed –OH at 3285; C=O (quinone) at 1630; and –CO– at 1303, 1260, and 1070 cm^{-1}. The nmr spectra[7] of IV showed CH_3 (ring) and CH_2 at 8.00 (3), 8.14 (6), and 7.77 (1); α-CH_2 at 7.24 (2); –CH_2–O at 6.06, 5.91, 5.72, and 5.58 (total 4).

B.—To 22.0 g (0.0866 mol) of III in 700 ml of THF was added 700 ml of water, then 44.0 g (0.995 mol) of lead tetraacetate. The suspension was stirred and refluxed for 30 min. After addition of sodium hydroxide, extraction with ether, and drying and evaporation of the ether, there was obtained a red-yellow residue. This was dissolved in a small amount of THF, and *n*-heptane was added. Compound V crystallized. The crude material was recrystallized from THF–*n*-heptane to yield 11.0 g (63.4%), mp 79.0–79.5°. From the mother liquor there was obtained 2.0 g (10.5%) of IV.

Preparation of VII. A.—A suspension of 1.0 g (0.0039 mol) of III in 30 ml of water and 30 ml of concentrated hydrochloric acid was refluxed, with stirring, for 9.5 hr. On cooling, the product crystallized. Recrystallization from acetonitrile gave 0.62 g (72%) of VII as white crystals: mp 171–172°; ir spectrum, OH [3300, 3150, (chromanol, 1610)] and –C–O– (1255, 1241, 1125 cm^{-1}); nmr,[7] CH_3 (ring) and CH at 8.29, 8.25, 8.17, (total 10), CH_2 at 7.92 (2), –CH_2O– at 6.69 (2), and 6.43 (2).

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.23; H, 8.16. Found: C, 70.06; H, 8.09.

B.—A solution of 0.50 g (0.0023 mol) of IV in 20 ml of THF was shaken in an atmosphere of hydrogen with a catalytic amount of 10% palladium charcoal at room temperature. Within 10 min 60 cc of hydrogen was absorbed (theory, 51 cc; probably the excess went to the solvent.) From the filtered solution there was obtained a pale yellow powder which on recrystallization from acetonitrile, yielded 0.40 g (80%) of white crytals, mp 171–172°. No depression was observed in mixture melting point with VII.

C.—A solution of 0.5 g (0.0021 mol) of V in 5 ml of glacial acetic acid and 15 ml of water was refluxed with 0.5 g of zinc powder for 0.5 hr. The mixture was neutralized with sodium hydroxide, extracted with ether, and the extract was dried and evaporated. The reddish residue was recrystallized from acetonitrile to give 0.28 g (60%) of VII, mp 171–172°.

Oxidative titration of VII with ceric ammonium nitrate in 90% aqueous acetic acid at 25° gave an equivalent weight of 114.5 (calcd, 111). The midpoint potential was about 0.657 V.

Ultraviolet Spectra.—The solvent, λ_{max} in mμ, and the molar extinction coefficient are given in that order: IV (CH_2Cl_2, 244, 1.09×10^4); V (CH_2Cl_2, 272, 1.65×10^4; CH_3OH, 269, 1.99×10^4); VI (CH_3OH, 289, 3.9×10^3); VII (CH_2Cl_2, 296, 2.29×10^3).

Registry No.—II, 16526-47-9; III, 16526-48-0; IV, 16526-49-1; V, 16526-50-4; VII, 16526-51-5; VIII, 16526-52-6.

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Reaction of Pseudoxazolones and Hydrazoic Acid

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The reaction of 4-arylidene-5-oxazolones with hydrazoic acid was reported by Awad, *et al.*[1,2] to produce tetrazolylacrylic acid derivatives in good yields. In examining the reactivity of 2-isopropylidene-4-methyl-3-oxazolin-5-one[3] (Ia, pseudooxazolone) with more than 2 mol of hydrazoic acid, we obtained white crystalline materials in 38% yield by their reaction condition as shown in Table I.

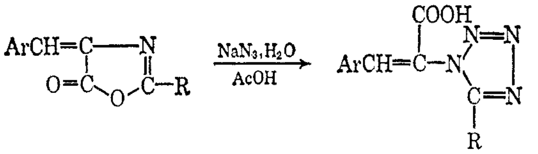

TABLE I

ELEMENTAL ANALYSES OF IV

R	Mp, °C	Crude yield, %	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
Me	210[a]	38	42.40	6.56	38.10	42.77	6.61	37.81
i-Pr	216[a]	71	48.10	7.60	33.00	48.59	7.55	32.18
i-Bu	216[a]	96	50.50	8.01	30.90	50.71	7.94	30.95

[a] Melted with decomposition.

That this product was a urea derivative was established by several spectral methods. The infrared spectrum showed strong absorptions at 3310, 2140,[4] and 1660 cm^{-1} arising from amide and urea N–H stretching, azide asymmetric stretching, and amide and urea carbonyl stretching vibrations, respectively. The nmr spectrum of the product displayed a 12-proton singlet at δ 1.44 due to four *gem*-methyl groups, a 6-proton doublet centered at 1.47; a 2-proton quartet centered at 5.65 (J = 6 cps); and a broad NH proton singlet at 3.66 in pyridine.

Mass spectra of IV offered a good indication of the presence of azide linkages and of the structure of IV. Each peak corresponded well to fragments formed from the molecular ion peak by cleavage at positions as shown in Chart I. In addition, elimination of methyl and isobutyl radicals gave rise to m/e 353 and 395 in IVa and IVc, respectively.

The first step in this transformation is postulated to be 1,4 addition of hydrazoic acid to I forming a satu-

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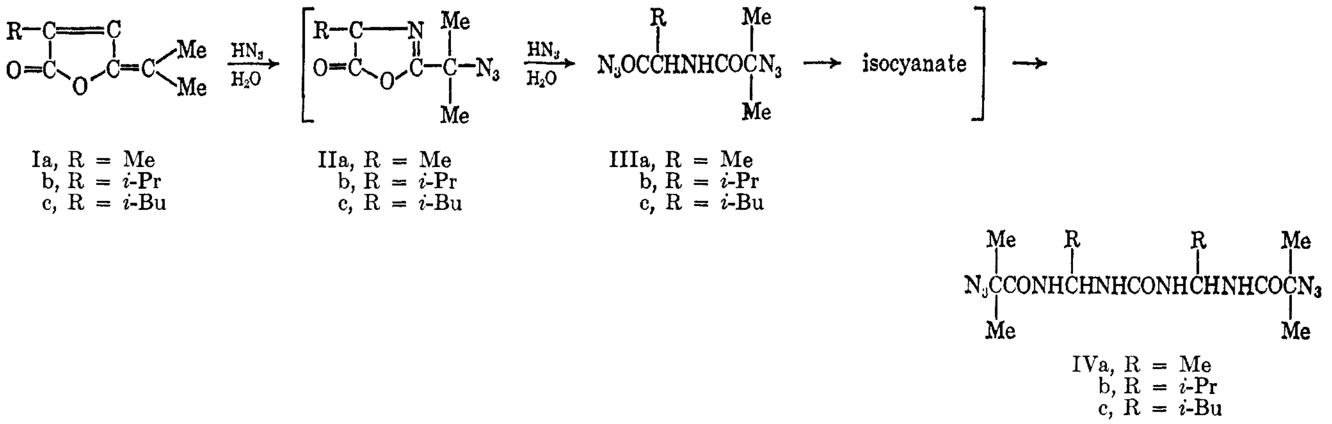


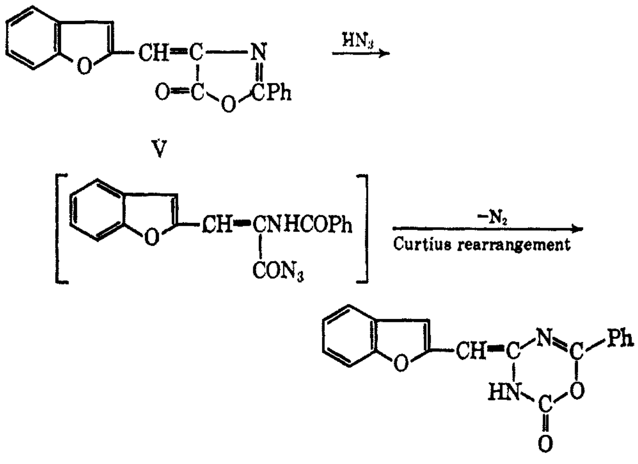
Ia, R = Me
b, R = *i*-Pr
c, R = *i*-Bu

IIa, R = Me
b, R = *i*-Pr
c, R = *i*-Bu

IIIa, R = Me
b, R = *i*-Pr
c, R = *i*-Bu

IVa, R = Me
b, R = *i*-Pr
c, R = *i*-Bu

rated 5-oxazolone (II) containing an alkyl azide group.[5,6] The acyclic intermediate (III) can then undergo Curtius rearrangement to the azido isocyanate which would immediately produce a symmetrical urea (IV) in the presence of water. For an example of the similar type of reaction, an oxadiazinone compound (VI) is prepared from hydrazoic acid and the 5-oxazolone (V) of 2-formylbenzofuran derivative *via* an isocyanate intermediate.[7]



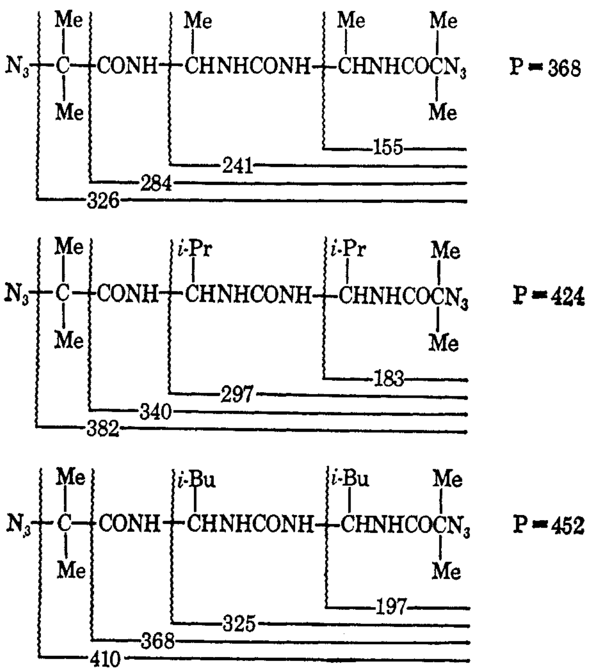
VI

Although we tried to make IVb react with two dipolarophiles, N-phenylmaleimide and N-morpholino-1-cyclohexene, to see whether triazoline derivatives could be obtained, IVb was recovered unchanged by the procedure reported in the literature[8,9] presumably owing to its steric hindrance. In fact, *t*-butyl azide does not satisfactorily form such derivatives as mentioned above.[10]

Experimental Section

A solution of sodium azide (10 g in 20 ml of water) was added to a solution of Ib (10 g in 20 ml of acetic acid) and the mixture was heated on a water bath for 1 hr. (In the case of Ia, a violent exothermic reaction occurred suddenly on heating). The resulting reaction slurry was then poured on crushed ice and the precipitate was collected, washed with water, and dried. The yield of the crude crystals of IVb was 71%. The crystals were recrystallized from a large amount of ethanol.

CHART I
FRAGMENT ION PEAKS OF IV



Major peaks in mass spectra were as follows: IVa, *m/e* 368, 353, 326, 284, 241, 225, 155, 113, 70, 56, 44, 42; IVb, 382, 340, 297, 253, 183, 169, 156, 125, 98, 72, 56, 43, 42; IVc, 410, 395, 368, 325, 267, 197, 86, 70, 69, 56, 44, 43, 42.

Nmr measurements. Nmr spectra were recorded on a Japan Electron Optics Lab. Co., Ltd. Model 4H-100, as an *ca.* 10% solution in CCl_4 with tetramethylsilane as an internal standard at 90°.

Registry No.—IVa, 16012-04-7; IVb, 16012-05-8; IVc, 16012-06-9; hydrazoic acid, 7782-79-8.

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