# *Tropones. V.* Addition Reaction of Tropone and Maleic Anhydride***

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Troponoid compounds were at first considered to be resistant to the Diels-Alder type addition reactions because of their high aromaticity[1,2] but later, Sebe and others[3] found that hinokitiol underwent an addition reaction with maleic anhydride. Since then, the Diels-Alder reactions of tropolone, its methyl ether[4], 4-methyltropone[4], and 2-phenyltropone[5] have been reported. There still remained many points to be examined regarding the configuration of these adducts.

The present series of works was at first undertaken in order to examine the unsaturation characteristics of tropone and during the course of this work, some observations were gained regarding the configuration of the addition compound, which are described herein.

It has been pointed out[6] that the unsaturation characteristics of a tropone is greater than that of a tropolone and, as anticipated, the heating of tropone with two molar equivalents of maleic anhydride in xylene for a few hours easily effected reaction, affording the adduct I, m. p. 181.5~182.5°C, in a good yield of around 95%.

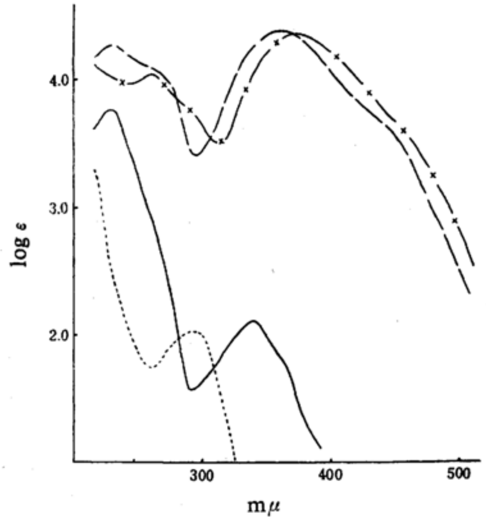

Fig. 1. —— I ----- II
-×- 2.4 DNP of V
— — 2.4 DNP of VI

Catalytic reduction of the adduct I in ethyl acetate or acetone with palladium-carbon as a catalyst, results in absorption of 2 molar equivalents of hydrogen to form a tetrahydro compound II. This shows the presence of two ethylenic linkages in I. The ultraviolet absorption spectra of I and II are shown in Fig. 1 and the spectrum of (I) exhibits a typical absorption of $\alpha\beta$-unsaturated ketone[7].

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* Part IV. T. Mukai, This Bulletin, **33**, 238 (1960).

** A part of this work was presented as a paper at the 6th Annual Meeting of the Chemical Society of Japan, Kyoto, April 5, 1953. Cf T. Nozoe, T. Mukai, K. Takase and T. Nagase, *Proc. Japan Acad.*, **28**, 477 (1952).

[1] R. D. Brown, *J. Chem. Soc.*, **1951**, 2670.

[2] J. W. Cook, A. R. Gibb, R. A. Raphael and A. R. Somerville, ibid., **1951**, 503.

[3] E. Sebe and C. Ôsako: Paper read before the 4th Annual Meeting of the Chemical Society of Japan in April, 1951. cf. *Proc. Japan Acad.*, **28**, 282.

[4] T. Nozoe, S. Seto and T. Ikemi, *Proc. Japan Acad.*, **27**, 10 (1951).

[5] T. Nozoe, T. Mukai, J. Minegishi and T. Fujisawa, *Sci. Repts. Tohoku Univ.*, Ser. I, **37**, 388 (1953).

[6] T. Mukai, This Bulletin, **31**, 846 (1958).

[7] R. B. Woodward, *J. Am. Chem. Soc.*, **63**, 1123 (1941); **64**, 72, 76 (1942).

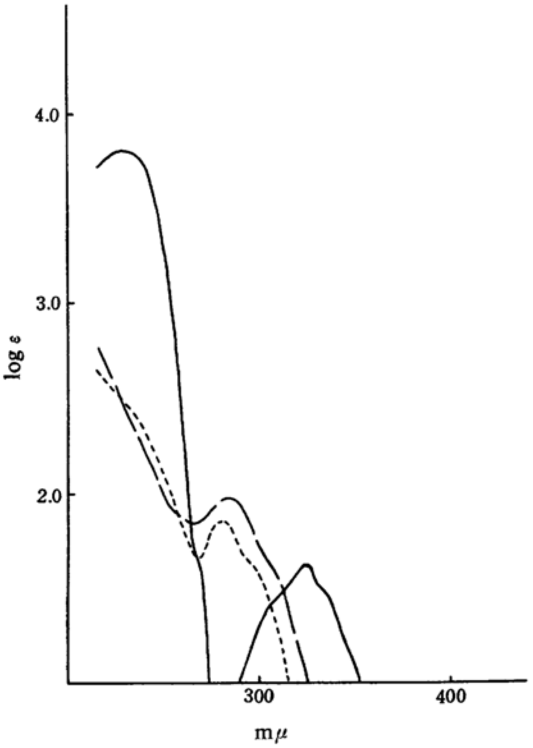


Fig. 2. —— VIII ------ X —— XI

The infrared spectra of I and II are shown in Table I. The absorption of a carbonyl in the acid anhydride of a five-membered ring is common to I and II, but while the absorption of an $\alpha\beta$-unsaturated ketone appears at 1665 $\text{cm}^{-1}$ in the spectrum of I, absorption of a saturated ketone is present at 1700 $\text{cm}^{-1}$ in that of II.

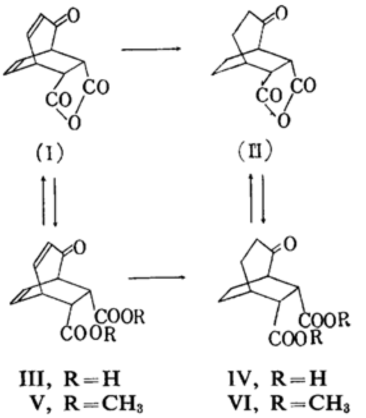
The presence of an $\alpha\beta$-unsaturated ketone in I not only offers an important clue to the structure of I but also proves the addition occurring at C-2 and C-5 positions in the tropone ring.

Treatment of the adduct I with hot water or sodium bicarbonate solution results in facile hydrolysis and a dibasic acid III is formed. The acid III is known to be dibasic from its analytical values and titration, as well as from its infrared spectrum (Table I) which shows the presence of two carbonyls.

TABLE I.

| | $\nu_{OH}$ $\text{cm}^{-1}$ | $\nu_{C=O}$ $\text{cm}^{-1}$ | $\nu_{C=C}$ $\text{cm}^{-1}$ |
|---|---|---|---|
| I | | 1840, 1780 | 1665, 1625 |
| II | | 1840, 1775, 1700 | |
| III | 3250, 2960 | 1740, 1710 | 1650, 1625 |
| V | | 1730 | 1670, 1633 |
| VIII | 3320 | 1770, 1730 | 1675 |
| XI | | 1780, 1726, 1706 | |

Determination of the melting point of III indicates decomposition at 167.5°C but solidification of the melt and reexamination of the melting point shows it melting at 182.5°C, the same as that of I. This is considered to be due to the facile dehydration of III to form the anhydride.



Actually, drying of III at 100°C under a reduced pressure results in the formation of I and such a fact naturally indicates that the two carboxyls are in *cis* configuration.

The tetrahydro compound II is also easily hydrolyzed and forms a dibasic acid (IV) which undergoes facile dehydration as in the case of III. Catalytic reduction of the unsaturated dibasic acid III in acetone, with palladium-carbon as a catalyst, results in absorption of two molar equivalents of hydrogen to form IV. Methylation of these two dibasic acids (III and IV) with diazomethane affords respective dimethyl esters (V and VI). It has been found, however, that reaction of III and excess of diazomethane also affords a compound (VII) of $C_{14}H_{16}O_5N_2$, besides V. In general, it is known that a reaction of $\alpha\beta$-unsaturated ketone and diazomethane results in formation of a pyrazole ring[8] and VII is considered to be this kind of product.

Both the methyl esters (V and VI) easily form crystalline 2,4-dinitrophenylhydrazones whose ultraviolet absorption spectra are indicated in Fig, 1. The absorption of the 2,4-dinitrophenylhydrazone of V shows a shift of 13 mμ to the longer wavelength region than that of VI and this fact indicates the presence of $\alpha\beta$-unsaturated ketone in V.[9] Catalytic reduction of V in ethyl acetate over palladium-carbon gives an oily product whose derivation to 2,4-dinitrophenylhydrazone proved that the oily product is VI.

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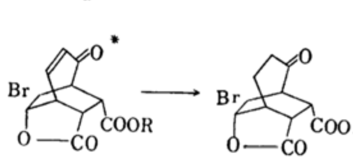
[8] H. Gilman, "Org. Chem.", Vol. IV, John Wiley & Sons., Inc., London, (1953), p. 780.

[9] E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, **1945**, 498.

Bromination of the adduct I in aqueous solution by the method of Alder-Stein[10] results in addition to the double bond and a bromo-lactone VIII is obtained in a good yield. Titration of VIII shows it to be a monobasic acid and the presence of a carboxyl (3320 and 1730 cm$^{-1}$) and a $\gamma$-lactone (1770 cm$^{-1}$) is also indicated from the infrared spectral values listed in Table I. In addition, there is an absorption of $\alpha\beta$-unsaturated carbonyl at 1675 cm$^{-1}$ in the spectrum of VIII. This fact is also certain from the ultraviolet spectrum of V shown in Fig. 2. These facts indicate that the addition of BrOH occurs at the non-conjugated double bond of the two ethylenic linkages present in I. It is therefore concluded that VIII has the configuration shown in Fig. 2 and that the structure of I to VI is in *endo-cis* form.

The unsaturated bromo-lactone VIII forms a monomethyl ester IX on methylation with diazomethane and IX easily forms a 2,4-dinitrophenylhydrazone. The ultraviolet spectrum of 2,4-dinitrophenylhydrazone of IX exhibits absorption maximum at 371 m$\mu$ and this corresponds to that of 2,4-dinitrophenylhydrazone of an $\alpha\beta$-unsaturated ketone.



VIII, R=H    X, R=H
IX, R=CH$_3$    XI, R=CH$_3$

Catalytic reduction of VIII over palladium-carbon in ethyl acetate results in absorption of one mole equivalent of hydrogen and saturated bromo-lactone (X) is produced. The structure of X was confirmed by the derivation of a monomethyl ester (XI) by reaction with diazomethane since it failed to undergo crystallization.

## Experimental

**Diels-Alder Reaction of Tropone and Maleic Anhydride; Formation of Tropone-Maleic Anhydride Adduct (I).**—A mixture of 8.36 g. (0.079 mol.) of tropone and 15.70 g. (0.16 mol.) of maleic anhydride in 60 cc. of dry xylene was refluxed in an oil bath for 2 hr. by which pale yellow crystals began to be deposited on the wall of the vessel. After refluxing for 4.5 hr, the mixture was allowed to stand overnight in a cool place and 16.6 g. (95%) of pale yellow crystals, m. p. 175~179°C, that precipitated out were collected by filtration. Several recrystallizations from acetone afforded I as colorless prismatic crystals, m. p. 181.5~182.5°C.

Found: C, 64.77; H, 4.14%. Cald. for $C_{11}H_8O_4$: C, 64.70; H, 3.95%.

I is easily soluble in acetone, ethyl acetate, ethanol, methanol and chloroform, and sparingly soluble in ether, petroleum ether, carbon tetrachloride and benzene.

**Catalytic Reduction of I; Formation of the Tetrahydro Compound (II) of the Adduct.** — A solution of 500 mg. of I dissolved in 20 cc. of ethyl acetate, to which 20 mg. of 5% palladium-carbon had been added, was submitted to catalytic reduction at ordinary pressure. After absorption of 2.05 mole equivalent (109 cc.) of hydrogen, the product (500 mg.) was obtained as colorless crystals of m. p. 168~181°C and several recrystallizations from acetone-ether mixture afforded II as colorless leaflets, m. p. 191~192°C.

Found: C, 63.67; H, 5.39%. Calcd. for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81%.

The use of acetone in place of ethyl acetate as a solvent in this reduction also results in absorption of two mole equivalent of hydrogen and the same product is obtained.

**Hydrolysis of I; Formation of the Dicarboxylic Acid (III) of the Adduct.**—*a) Hydrolysis with Water:* A solution of 1 g. of I dissolved in 30 cc. of hot water was allowed to stand overnight and 530 mg. of a colorless prismatic crystals, m. p. 162.5°C (decomp.), was obtained. Concentration of its filtrate on a water bath afforded a second crop of colorless crystals, m. p. 160°C (decomp.). The two kinds of crystals were combined and washed with acetone, affording (III) as colorless crystals, m. p. 167.5°C.

Found: C, 59.34; H, 4.35%. Calcd. for $C_{11}H_{10}O_5$: C, 59.46; H, 4.54%.

*b) Hydrolysis with Sodium Bicarbonate Solution:* To a solution of 420 mg. (0.005 mol.) of sodium bicarbonate dissolved in 4 cc. of water, 500 mg. of I was added and warmed on a water bath to dissolve all the crystals. The reaction mixture was concentrated acidified with hydrochloric acid while cooling with water and 400 mg. of colorless microneedles, m. p. 164~165°C (decomp.). The crystals were collected and washed several times with hot acetone, giving III as colorless microneedles, m. p. 167.5°C.

Ultraviolet spectrum: $\lambda_{\max}^{\mathrm{MeOH}}$ m$\mu$ (log $\varepsilon$): 228 (3.87), 337 (2.49).

The acid III obtained by both the foregoing methods (a) and (b) showed no depression of the melting point on admixture with I. The melted III, upon solidification, melted at 181.5~182.5°C, same as I.

**Dehydration of III; Formation of I.** — The Acid III obtained from the both methods (a) and (b) as above was each kept in a vacuum (10 mmHg) desiccator over phosphorus pentoxide

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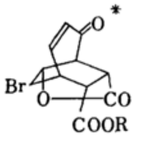
[10] K. Alder und G. Stein, *Anal. Chem.*, **514**, 4 (1934).



In this case there are two possible structures to VIII. Detailed reports on the structure of VIII will be made elsewhere.

[11] All m. p. are uncorrected. The microanalyses were carried out by Miss Ayako Iwanaga of this laboratory to whom the authors are indebted.

at 100°C for 2 days. Determination of the melting point of resultant product showed formation of 45 mg. of a product of m. p. 181.5∼182.5°C from 50 mg. of III. No depression of the melting point was observed on admixture with I.

Found: C, 64.59; H, 4.00%. Calcd. for $C_{11}H_8O_4$: C, 64.70; H, 3.95%.

**Hydrolysis of II; Formation of Dicarboxylic Acid (IV) of the Tetrahydro Derivative of the Adduct.**—A solution of 150 mg. of II dissolved in 3 cc. of hot water was allowed to cool and colorless crystals that separated out were collected to 100 mg. of IV as colorless microneedles, m. p. 173°C (decomp.).

Found: C, 58.33; H, 5.80%. Calcd. for $C_{11}H_{14}O_5$: C, 58.40; H, 6.24%.

The filtrate was concentrated at room temperature under a reduced pressure and a second crop of crystals was obtained as 80 mg. of colorless crystals, m. p. 169∼170°C (decomp.).

Ultraviolet spectrum: $\lambda_{\max}^{\mathrm{MeOH}}$ m$\mu$ (log $\varepsilon$): 285 (1.84).

Admixture of IV and II showed no depression of the melting point. Determination of the melting point after solidification of melted II showed m. p. 191∼192°C.

**Dehydration of IV; Formation of the Tetrahydro Compound (II) of the Adduct.**—Thirty milligrams of IV was kept over phosphorus pentoxide in a vacuum (10 mmHg) desiccator at 100°C for two days and 28 mg. of the resultant product melted at 171∼172°C, alone and in admixture with II.

Found: C, 58.43; H, 6.30%. Calcd. for $C_{11}H_{12}O_4$: C, 58.40; H, 6.24%.

**Catalytic Reduction of III; Formation of IV.**—A solution of 500 mg. of III dissolved in 70 cc. of acetone, added with 20 mg. of 5% palladium-carbon, was submitted to catalytic reduction at ordinary pressure and 2.08 mole equivalents of hydrogen (105 cc.) was absorbed. The catalyst was removed by filtration and the filtrate was concentrated, affording 460 mg. of colorless crystals, m. p. 154∼155.5°C. The crystals were washed several times with warm acetone and (IV) was obtained as colorless crystals of m. p. 173°C (decomp.).

Found: C, 58.30; H, 5.93%. Calcd. for $C_{11}H_{14}O_5$: C, 58.40; H, 6.24%.

The compound (IV) obtained by this means easily lost one mole of water to form II, as was the case with IV obtained by the hydrolysis of II.

**Raction of (III) and Diazomethane.**—*a) Formation of the Dimethyl ester (V) of III*: To a suspension of 220 mg. (ca. 0.001 mol.) of finely pulverized III in 10 cc. of ethyl acetate, 3.6 cc. (0.002 mol.) of ether solution of diazomethane was added dropwise at room temperature by which a vigorous reaction set in and III dissolved almost completely. The solution was evaporated on a water bath, the concentrated solution was cooled in ice, and 20 mg. of colorless crystals VII, m. p. 212°C, separated out.

Concentration of the mother liquor left 200 mg. of yellow oil which solidified gradually upon standing. Recrystallization from a small volume of methanol afforded V as yellow microneedles, m. p. 83∼88°C.

Found: C, 62.42; H, 5.52%. Calcd. for $C_{13}H_{14}O_5$: C, 62.39; H, 5.64%.

Ultraviolet spectrum: $\lambda_{\max}^{\mathrm{MeOH}}$ m$\mu$ (log $\varepsilon$): 227 (3.90), 337(2.40).

*b) Formation of VII*: To a suspension of 300 mg. (0.0014 mol.) of III in 20 cc. of ethyl acetate, 9 cc. (0.0042 mol.) of ether solution of diazomethane was added in drops at room temperature by which III dissolved to form a uniform yellow solution. On standing, colorless crystals separated out which were collected and recrystallized from water to 340 mg. of colorless needles (VII), m. p. 212°C (decomp.).

Found: C, 57.19; H, 5.13%. Calcd. for $C_{13}H_{14}O_5 \cdot CH_2N_2$: C, 57.53; H, 5.52%.

Ultraviolet spectrum: $\lambda_{\max}^{\mathrm{MeOH}}$ m$\mu$ (log $\varepsilon$): 235 (3.36), 307(3.68).

*c) 2,4-Dinitrophenylhydrazone of V*: A solution (conc. sulfuric acid, 1.3 cc., methanol, 6.5 cc.) of 250 mg. (0.0013 mol.) of 2,4-dinitrophenylhydrazine was added to a solution of 250 mg. (0.001 mol.) of V dissolved in 2.5 cc. of methanol by which a fine orange powder precipitated out immediately. The mixture was stirred and allowed to stand overnight at room temperature. The solid was collected and recrystallized several times from acetone-methanol mixture to 230 mg. of VII as lustrous orange powder, m. p. 221.5∼222°C.

Found: C, 52.80; H, 3.96; N, 13.07%. Calcd. for $C_{19}H_{18}O_8N_4$: C, 53.02; H, 4.22; N, 13.02.

**Formation of the Dimethyl Ester (VI) of IV.**—(a) The calculated amount (0.004 mol.) of the ether solution of diazomethane was added dropwise at room temperature into a solution of 450 mg. (0.002 mol.) of IV dissolved in 20 cc. of ethyl acetate by which a vigorous effervescence set in. After standing at room temperature for a few hours, the solvent was distilled off and left 480 mg. of pale yellow oil. This oily residue was dissolved in acetone and purified by passage through alumina layer, from which 420 mg. of pale yellow oil (VI) was obtained.

Ultraviolet spectrum: $\lambda_{\max}^{\mathrm{MeOH}}$ m$\mu$ (log $\varepsilon$): 284(1.19).

b) Catalytic reduction of 50 mg. of V dissolved in 10 cc. of ethyl acetate, with 5% palladium-carbon as a catalyst, resulted in absorption of 2 mol. equivalents (5 cc., calcd. 4.5 cc.) and 50 mg. of pale yellow oil (VI) was obtained.

Ultraviolet spectrum: $\lambda_{\max}^{\mathrm{MeOH}}$ m$\mu$ (log $\varepsilon$): 284(1.20).

*c) Formation of 2,4-Dinitrophenylhydrazone of VI*: The hydrazone was prepared as in the case of V and recrystallized from methanol to fine orange needles, m. p. 89°C (decomp.).

Found: C, 52.50; H, 4.90; N, 12.87%. Calcd. for $C_{19}H_{22}O_8N_4$: C, 52.53; H, 5.10; N, 12.90%.

**Formation of Bromolactone-monocarboxylic Acid (VIII).**—To a solution of 500 mg. (0.0025 mol.) of I dissolved in 30 cc. of water, 500 mg. (0.0031 mol.) of bromine was dropped in under ice-cooling and stirring. After some time, pale yellow crystals began to precipitate out. The mixture was stirred under ice-cooling for a further 4 hr., the excess of bromine was removed by addition of sodium bisulfite, and the mixture was filtered, affording 570 mg. of fine colorless crystals, m. p. 185°C (decomp.). After drying over phosphorus pentoxide in a vacuum desiccator, the crystals were recrystallized from acetone to 500 mg. of colorless plates (VIII), m. p. 219°C (decomp.). VIII dissolved in cold, saturated solution of sodium bicarbonate with effervescence and colors green to the Beilstein test.

Found: C, 43.81; H, 2.99%. Calcd. for $C_{11}H_9O_5Br$: C, 43.87; H, 3.01%.

**Formation of the Methyl Ester (IX) of the Bromo-lactone VIII.**—To a solution of 300 mg. (0.001 mol.) of VIII dissolved in 10 cc. of ethyl acetate, 1.9 cc. (0.001 mol.) of the ether solution of diazomethane was added in drops and the mixture was allowed to stand for a few days from which 150 mg. of colorless scaly crystals of m. p. 213∼215°C separated out. These crystals were collected by filtration, the filtrate was concentrated, and a second crop of crystals were obtained as 150 mg. of pale yellow crystals, m. p. 178∼195°C. The two crops of crystals were combined and recrystallized from acetone-methanol mixture to IX as colorless scales, m. p. 216∼217°C.

Found: C, 45.69; H, 3.25%. Calcd. for $C_{12}H_{11}O_5Br$: C, 45.73; H, 3.52%.

Ultraviolet spectrum: $\lambda_{\max}^{\mathrm{MeOH}}$ m$\mu$ (log $\varepsilon$): 232 (3.82), 320(2.37).

*2,4-Dinitrophenylhydrazone of IX:* A mixture of 200 mg. of IX dissolved in 20 cc. of methanol and methanolic solution (3.5 cc. of methanol and 0.9 cc. of conc. sulfuric acid) of 150 mg. of 2,4-dinitrophenylhydrazine was refluxed on a water bath for 3.5 hr. Concentration of this solution until only a part of the solvent remained left 220 mg. of dark brown crystals which were collected and recrystallized repeatedly from methanol to dark brown, fine needles, m. p. 146∼147°C (decomp.).

Found: C, 43.50; H, 3.00; N, 11.02%. Calcd. for $C_{18}H_{15}O_8N_4Br$; C, 43.65; H, 3.05; N, 11.31%.

Ultraviolet spectrum: $\lambda_{\max}^{\mathrm{MeOH}}$ m$\mu$ (log $\varepsilon$): 255 (4.13), 371(4.43).

**Catalytic Reduction of VIII; Formation of Dihydro-bromo-lactone (X) and Methyl Ester (XI). of X,**—A solution of 240 mg. of VIII dissolved in 20 cc. of ethyl acetate, to which 20 mg. of palladium-carbon was added, was submitted to reduction at ordinary pressure and 0.95 mole equivalent (24.5 cc.) of hydrogen was absorbed. The product obtained therefrom was 220 mg. of yellowish brown oil (X) which failed to crystallize.

A calculated amount of ether solution of diazomethane was added to a solution of 120 mg. of above oil dissolved in 1 cc. of ethyl acetate and the mixture was allowed to stand overnight, from which 100 mg. of colorless crystals precipitated out. This was recrystallized from methanol-acetone mixture to colorless fine powder (XI), m. p. 167.5°C.

Found: C, 45.46; H, 4.02%. Calcd. for $C_{12}H_{13}O_5Br$: C, 45.44; H, 4.13%.

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