

466. *Synthetical Studies on Terpenoids. Part II.\* The Structure of "Tagetone."*

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Isolation of the fraction described as "tagetone" from the essential oil of *Tagetes glandulifera* Schrank gave a mixture of two components, interconverted by iodine, which are believed to be the *cis*- and *trans*-isomers (IV) and (V). A stereospecific synthesis of ketone (V) gave a product inseparable by gas-liquid chromatography from one of these compounds, and spectroscopic results leave no doubt that it was in fact identical with the natural product.

JONES and SMITH<sup>1</sup> gave the name "tagetone" to the unsaturated ketone they found in the highest-boiling fraction of the oil derived from the flowers and the leaves of *Tagetes glandulifera* Schrank. "Tagetone," representing 50—60% of the essential oil,<sup>2</sup> was described as a pale yellow oil, b. p. ca. 205—210°/760 mm. and 62°/3—4 mm.,  $d^{15.5}$  0.8803,  $n_D^{20}$  1.4895, which was difficult to obtain pure owing to its tendency to resinify. The only derivative described was an oily oxime. Whilst the carbon skeleton of tagetone was proved to be that of 2,6-dimethyloctan-4-one (I), the position of the double bonds was less certain. Oxidative evidence suggested a mixture of ketones (II) and (III), with (II) predominating. Its ultraviolet absorption spectrum, on the other hand, resembled that of crotylideneacetone<sup>3</sup> and thus favoured structure (III). It was suggested<sup>4</sup> that tagetone was best described as a tautomeric mixture of ketones (II), (III), and the enol of ketone (II). With the better understanding of structure-light absorption relations more importance could be attached to the spectroscopic data, and recently the dienone structure (III) appeared the more likely. This left open the possibility of *cis-trans*-isomerism (IV—V). It seemed that a comparison by gas chromatography of the two stereoisomeric 2,6-dimethylocta-5,7-dien-4-ones with the oil of *Tagetes glandulifera* might settle the matter, and a stereospecific synthesis of the *trans*-form (V), starting from *trans*-3-methylpent-2-en-4-yn-1-ol (X), was therefore attempted along with preliminary work on the corresponding *cis*-compounds.

Oroshnik<sup>5</sup> prepared *cis*- and *trans*-3-methylpent-2-en-4-yn-1-ol (VI) and (X) by fractional distillation of the rearrangement product of 3-methylpent-1-en-4-yn-3-ol, and assigned the configurations on the basis of the reactivity of the corresponding dienol acetates with maleic anhydride. This assignment was supported by the close agreement between the *cis* : *trans* intensity-ratio of the ultraviolet absorption maxima of alcohols (VI) and (X)

\* Part I, *J.*, 1958, 1994.

<sup>1</sup> Jones and Smith, *J.*, 1925, 127, 2530.

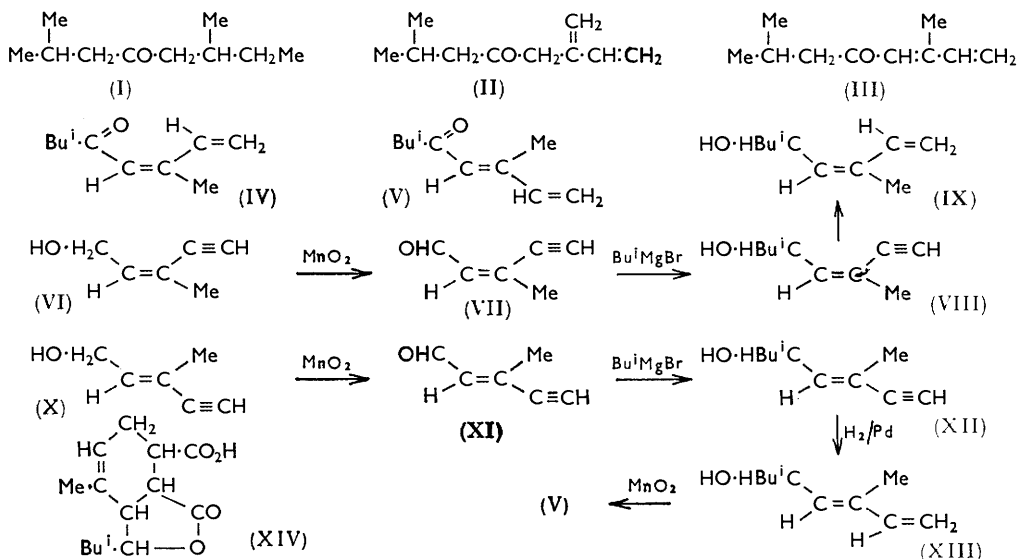
<sup>2</sup> Jones, *Proc. Roy. Soc., Queensland*, 1934, 45, 45.

<sup>3</sup> Jones and Lahey, *University Queensland Papers, Dept. Chem.*, 1942, 1, No. 22; *Chem. Abs.*, 1943, 37, 3342.

<sup>4</sup> Simonsen and Owen, "The Terpenes," 2nd edn., Cambridge, 1947, Vol. I, p. 104; Naves, *Helv. Chim. Acta*, 1948, 31, 29.

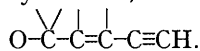
<sup>5</sup> Oroshnik, *J. Amer. Chem. Soc.*, 1956, 78, 2651.

and similar ratios obtained for a number of related *cis-trans*-isomers of known configuration.<sup>6</sup> Additional proof of the correctness of Oroshnik's assignments has now been obtained by nuclear magnetic resonance. Jackman and Wiley<sup>7</sup> found for a number of *cis-trans*-pairs of  $\alpha\beta$ -unsaturated  $\beta$ -methyl esters that the protons of the methyl group are deshielded by 0.25 p.p.m. by the *cis*-alkoxycarbonyl group. The two aldehydes (VII) and (XI) were



obtained by oxidising the stereoisomeric alcohols (VI) and (X), respectively, with manganese dioxide and each was shown by infrared measurements to be free from the other. Again, the methyl group *cis* to the aldehyde residue in the *trans*-aldehyde (XI) was found to be deshielded (0.18 p.p.m.) by the  $-\text{CHO}$  residue.

The aldehydes (VII)/(XI) have been obtained before<sup>8,9</sup> by methods involving acidic conditions. In such circumstances the pure stereoisomers are rapidly equilibrated, the equilibrium mixture consisting very largely (<98%) of the *cis*-form (VII), according to infrared measurements. This stability relation is presumably the result of a more adverse steric interaction between the  $\text{CH}_3$  and the  $\text{CHO}$  group in aldehyde (XI) than that between  $\text{HC}\equiv\text{C}$  and  $\text{CHO}$  in (VII). This may also be responsible for the markedly greater rate of decomposition of the *trans*-compound (XI) on storage. As expected, the *trans*-isomer (XI) showed ultraviolet absorption of higher intensity and of longer wavelength than that of the *cis*-compound (VII), and formed a 2,4-dinitrophenylhydrazone of higher melting point. The *trans*-aldehyde, but not the *cis*-isomer, could be subjected to gas-liquid chromatography on dinonyl phthalate; presumably the *cis*-aldehyde underwent ready cyclisation, as has been observed in these laboratories with many *cis*-compounds



3-Methylpent-2-en-4-ynal has also been prepared, by Isler *et al.*,<sup>10</sup> by a method which would possibly not have equilibrated the stereoisomers, and might therefore have corresponded in configuration to the alcohol used.

Condensation of the *trans*-aldehyde (XI) with isobutylmagnesium bromide gave the secondary alcohol (XII). Addition of the Grignard reagent to the aldehyde rather than

<sup>6</sup> Bell, Jones, and Whiting, *J.*, 1957, 2597.

<sup>7</sup> Jackman and Wiley, *J.*, 1960, 2886.

<sup>8</sup> Jones and Weedon, *J.*, 1946, 937.

<sup>9</sup> Heilbron, Jones, and Julia, *J.*, 1949, 1430.

<sup>10</sup> Isler, Chopard-dit-Jean, Montavon, Rügge, and Zeller, *Helv. Chim. Acta*, 1957, 40, 1256.

*vice versa* proved to be essential for obtaining a fair yield (55%) in this reaction. In the next step a 10% overhydrogenation in the selective hydrogenation of the triple bond provided a reaction mixture from which the dienol (XIII) was isolated by fractional distillation. When analysed by gas chromatography, the alcohol (XIII) appeared to be homogeneous; it separated well from the *cis*-isomer (IX) (see below). The dienol (XIII) reacted readily with maleic anhydride to give the crystalline lactonic acid<sup>11</sup> (XIV). The oxidation of the alcohol (XIII) with manganese dioxide in methylene chloride stopped when *ca.* 40% of the alcohol remained unchanged, and increased amounts of manganese dioxide did not effect further oxidation. Fractional distillation and analysis of the fractions obtained showed that, besides the unchanged alcohol (XIII) and the desired ketone (V), two by-products were formed. One of these appeared in the cold trap and gave a 2,4-dinitrophenylhydrazone which did not depress the melting point of isovaleraldehyde dinitrophenylhydrazone; the other was isolated as its semicarbazone, identified spectroscopically as that of 3-methylpenta-2,4-dienal.<sup>9</sup> The ketone (V) and alcohol (XIII) formed the high-boiling fraction and were separated by chromatography on alumina. The ketone (V) so obtained proved to be homogeneous when examined by gas chromatography on dinonyl phthalate, polypropylene sebacate, and polypropylene adipate as the stationary phases, and had the expected ultraviolet and infrared spectra. The refractive index,  $n_D^{20}$  1.4880, agreed well with that reported for "tagetone." The 2,4-dinitrophenylhydrazone, however, was a red oil which failed to crystallise.

In the *cis*-series, the aldehyde (VII), when treated with isobutylmagnesium bromide, gave the secondary alcohol (VIII), which on hydrogenation gave the corresponding dienol (IX), approximately 80% pure. This product was not purified, nor was the complex reaction mixture obtained from it by oxidation with manganese dioxide investigated further, but its preparation confirmed the stereospecificity of the reaction leading to the *trans*-alcohol (XIII). This alcohol (IX) failed to react with maleic anhydride.

A sample of the oil of *Tagetes glandulifera* was obtained from Australia. The natural oil was analysed by gas chromatography on polypropylene adipate, and the retention times of the peaks of its main constituents were compared with the retention time of the peak obtained by ketone (V). This showed clearly that the synthetic ketone was not identical with any of the *major* constituents of the natural oil under examination. Its retention time coincided, however, with that of a peak representing one of the minor constituents (A) of the oil. This was also true when the chromatographic separation was effected with dinonyl phthalate. This constituent could be largely separated from a major constituent (B) by gas chromatography on polypropylene adipate as stationary phase (dinonyl phthalate gave a less satisfactory separation). Gas chromatography of an oil sample to which some of the ketone (V) was added showed a relative increase of the peak corresponding to A. Thus an indication was obtained that the *trans*-ketone (V) was identical with material A, and hence not a major constituent of the natural oil, in spite of the fact that its physical constants agreed well with those reported for "tagetone." It seemed desirable at this stage to repeat Smith and Jones's<sup>1</sup> fractionation of the oil and to check by gas chromatography the homogeneity of "tagetone." A spinning-band column was used for the fractionation, and the separation of the components was followed by ultraviolet and infrared spectra, refractive index, and gas chromatography. The last revealed that the unsaturated ketone fraction thus obtained was composed of B (83%), A (12%), and *ca.* 5% of components appearing in earlier fractions. As the losses during fractionation were appreciable and the 5% contamination did not interfere with the investigation of compounds A and B, this fraction, containing A and B in a 1:7 ratio, was used without further purification. Indeed, in view of the similar retention times of A and B, it was thought probable that A and B could not be separated even by repeated fractional distillation; and the 1:7 mixture of A and B therefore probably represents

<sup>11</sup> Heilbron, Jones, McCombie, and Weedon, *J.*, 1945, 84.

Smith and Jones's "tagetone." There was hardly any difference in the ultraviolet absorption spectra of the synthetic ketone and this "tagetone" fraction, and it seemed that *cis-trans*-isomerism was the only plausible explanation for the difference between materials A and B. If that was so, the *cis*-isomer (B) evidently predominated in Nature, and isomerisation with iodine or any of the reagents used for this purpose might cause an increase of the *trans*-isomer (A). The "tagetone" fraction was treated with iodine in light petroleum, and, as expected, the composition of the reaction mixture was changed quantitatively: it now contained A and B in a 2·2 : 1 ratio. Ultraviolet absorption and nuclear magnetic resonance spectral data confirmed this interpretation. As expected for a *cis-trans* conversion during the iodine treatment, the mixture thus obtained exhibited stronger light absorption than "tagetone" itself, and indeed, although a mixture, it gave somewhat larger  $\epsilon$ -values than the synthetic *trans*-ketone (V). This small discrepancy is probably due to instrumental errors or partial decomposition or polymerisation of the synthetic sample before its examination. Indeed the synthetic ketone had deteriorated considerably during storage for *ca.* 12 months at  $-5^\circ$  while the work on the natural ketone was completed, and it was then found to contain a small proportion of the *cis*-isomer (B), according to gas-liquid chromatography, as well as several unidentified contaminants of comparable volatility.

The nuclear magnetic resonance spectra of the two natural tagetone fractions, before and after equilibration, were consistent with the view that they were 1 : 7 and 2·2 : 1 mixtures of isomers (IV) and (V). In particular, the methyl group *cis* to  $-\text{COBu}^1$  in ketone (V) was deshielded by 0·29 p.p.m. as expected. The infrared spectra of the 1 : 7 and 2·2 : 1 mixtures were exceedingly similar (and the very slight differences in relative intensity may have been affected by the small proportion of non-tagetone materials). The spectra of both fractions, but especially of the 2·2 : 1 *trans-cis*-mixture, were very similar indeed to that of the synthetic *trans*-isomer; had an appreciable quantity of ketone (II) been present, for example, this could not have been true.

We suggest that the two ketones (IV) and (V) be called "*cis*-tagetone" and "*trans*-tagetone," and we believe that the work described above approximates to a total synthesis of the latter, despite difficulties of identification due to its instability.

*Tagetes glandulifera* Schrank is a native of South America, and also grows in Australia and East Africa: according to the Index Kewensis this name is synonymous with *Tagetes minuta* L. Dr. G. E. Howard, of the Tropical Products Institute (London, W.C.1.), has compared the oil of "*T. minuta*" from Kenya with that of *T. glandulifera* from Australia, using gas chromatography on polypropylene sebacate. Although the peaks present in the latter were also observed in the *T. minuta* oil, including A and B, these two materials were not major components, and two new peaks of about twice the retention time of A and B and similar in degree of separation and relative size were present. The taxonomic situation may therefore be more complex than had been thought.

#### EXPERIMENTAL

M. p.s were determined on a Kofler block. Infrared spectra were recorded on a Perkin-Elmer model 21 spectrophotometer. Ultraviolet absorption spectra were measured in a Unicam S.P. 500 (synthetic material) and a Cary 14M-50 (natural-oil fractions) spectrophotometer. The nuclear magnetic resonance spectra of the synthetic *cis*- and *trans*-aldehyde (determined and interpreted by Dr. L. M. Jackman) were obtained for *ca.* 10% carbon tetrachloride solutions at 56·4 Mc./sec., the spectra of "tagetone" by Dr. E. O. Bishop at 29·92 Mc./sec. The manganese dioxide used was a commercial sample supplied by J. Woolley and Sons Ltd. The alumina used was Spence's "Grade H" deactivated with 5% of its volume of 10% acetic acid. In the gas-chromatographic analyses of the natural ketone Embacel was the support, and dinonyl phthalate (20%; 200 mm.; at 108·5°) and polypropylene adipate (20%; 400 cm.) were the stationary phases, with hydrogen as the carrier gas. A flame ionisation detector-recorder combination with linear response was used. The percentage compositions (*ca.*  $\pm 1\%$

accuracy) were obtained by cutting out and weighing the various peaks. Unless otherwise stated, all the synthetic intermediates gave single peaks on gas chromatography with a dinonyl phthalate column at temperatures in the range 95—120°.

*trans*-3-Methylpent-2-en-4-yn-1-al (XI).—*trans*-3-Methylpent-2-en-4-yn-1-ol (X) (8.0 g.) and manganese dioxide (80 g.) in methylene chloride (300 c.c.) were shaken together at room temperature in darkness for 3 hr. (or until the increase in absorption intensity at *ca.* 2600 Å and the decrease of intensity at *ca.* 2200 Å stopped). The manganese dioxide was filtered off and thoroughly washed with hot methylene chloride. A trace of quinol was added and the solvent was removed under partial reflux. The residue was distilled, giving the *aldehyde* (XI) (5.1 g., 66%), b. p. 58—59°/10 mm., as a deep yellow lachrimatory liquid (Found: C, 76.2; H, 6.3. C<sub>8</sub>H<sub>8</sub>O requires C, 76.6; H, 6.4%), which solidified at -40° and polymerised rapidly at room temperature, becoming red; even at -40° decomposition was complete after one week. It had  $n_D^{19}$  1.5190,  $\lambda_{\max}$ . (in EtOH) 2620 ( $\epsilon$  20,200), (in hexane) 2575 Å ( $\epsilon$  18,800),  $\nu_{\max}$ . (in CS<sub>2</sub>) 3247s, 1678vs, 1183s, 1105s, 862m, and 813w cm<sup>-1</sup>,  $\tau$  7.69 ( $\beta$ -C-Me). The 2,4-dinitrophenylhydrazone formed deep violet-red needles (from ethanol), m. p. 165—166° (on a block preheated to 130°) (Found: C, 53.0; H, 4.0; N, 19.9. C<sub>12</sub>H<sub>10</sub>N<sub>4</sub>O<sub>4</sub> requires C, 52.6; H, 3.7; N, 20.4%),  $\lambda_{\max}$ . (in EtOH) 3850 ( $\epsilon$  32,800), 2950 ( $\epsilon$  9500), and 2625 Å ( $\epsilon$  13,600).

*cis*-3-Methylpent-2-en-4-yn-1-al (VII).—*cis*-3-Methylpent-2-en-4-yn-1-ol (VI) (8.0 g.), treated as above, gave the *aldehyde* (VII) (6.4 g., 80%), b. p. 58—60°/10 mm., as a pale-yellow lachrimatory liquid which solidified at -10° (Found: C, 76.35; H, 6.4. C<sub>8</sub>H<sub>8</sub>O requires C, 76.6; H, 6.4%), and had  $n_D^{20}$  1.5005,  $\lambda_{\max}$ . (in EtOH) 2600 ( $\epsilon$  12,500), (in hexane) 2525 Å ( $\epsilon$  14,300),  $\nu_{\max}$ . (in CS<sub>2</sub>) 3268s, 1695vs, 1681vs, 1167s, 844m, and 797w cm<sup>-1</sup>,  $\tau$  7.87 ( $\beta$ -C-Me). The 2,4-dinitrophenylhydrazone formed orange-red needles (from ethanol), m. p. 139.5—140.5° (Found: C, 52.3; H, 3.9%),  $\lambda_{\max}$ . (in EtOH) 3850 ( $\epsilon$  33,500) and 2600 Å ( $\epsilon$  15,500).

*Isomerisation of trans*-3-Methylpent-2-en-4-ynal.—The conditions used simulated the preparation of the *aldehyde* from 1-chloro-3-methylpent-1-en-4-yn-3-ol.<sup>8,9</sup> The *trans*-*aldehyde* (1.0 g.) in dioxan (1 c.c.) was added to 10% sulphuric acid (80 c.c.) and hydrochloric acid (0.32 g., *d* 1.16) and stirred under nitrogen in the dark for 4 days at 20°. Isolation of the neutral fraction with ether and distillation gave a liquid (680 mg.), b. p. 60—65° (bath temp.)/10 mm.,  $n_D^{20}$  1.5000, which showed an infrared spectrum virtually identical with that of *cis*-3-methylpent-2-en-4-ynal, except for weak absorption at 862 cm<sup>-1</sup> where the *trans*-compound has a strong band. Its intensity suggested the presence of about 1.5% of the *trans*-compound.

*trans*-2,6-Dimethyloct-5-en-7-yn-4-ol (XII).—Isobutylmagnesium bromide [from magnesium (4.6 g.) and redistilled isobutyl bromide (29 g.)] in tetrahydrofuran (250 c.c.) was added dropwise during 60 min. to a stirred solution of the *aldehyde* (XI) (15 g.) in tetrahydrofuran (50 c.c.); the temperature of the reaction mixture was kept during the addition at 0—5°. After the addition, stirring was continued for another 30 min. and the mixture was allowed to warm to room temperature. Working up in the usual way and removal of the solvent left a residue which was rapidly distilled with a trace of quinol. Redistillation gave the *alcohol* (XII) (13.8 g., 57%), b. p. 50—51°/0.15 mm. (Found: C, 78.7; H, 10.5. C<sub>10</sub>H<sub>18</sub>O requires C, 78.9; H, 10.6%),  $n_D^{25}$  1.4784,  $\lambda_{\max}$ . (in EtOH) 2230 Å ( $\epsilon$  14,900).

*cis*-2,6-Dimethyloct-5-en-7-yn-4-ol (VIII).—The method of synthesis was analogous to that employed for the *trans*-isomer (XII). The *alcohol* (VIII) boiled at 42—44°/0.1 mm. (Found: C, 78.6; H, 10.6%),  $n_D^{25}$  1.4720,  $\lambda_{\max}$ . (in EtOH) 2230 Å ( $\epsilon$  12,600).

*trans*-2,6-Dimethyloct-5,7-dien-4-ol (XIII).—The acetylenic *alcohol* (XII) (12.0 g.) in ethyl acetate (100 c.c.) was hydrogenated with Lindlar's catalyst<sup>12</sup> (1.5 g.) in the presence of quinoline (0.5 g.); 2100 c.c. of hydrogen (20°/759 mm., ~1.1 mol.) were taken up in 30 min. The residue obtained by removal of the catalyst and solvent was fractionated through the spinning-band column (see below). Sixteen cuts were taken and combined into 3 fractions on the basis of their refractive indices and retention times: (i) b. p. 30—40°/0.5 mm.,  $n_D^{25}$  1.4770—1.4816 (330 mg.); (ii) b. p. 40—48°/0.5 mm., 1.4816—1.4868 (1.7 g.); and (iii) b. p. 48—49°/0.5 mm., 1.4868—1.4880 (7.61 g., 63%). When redistilled, fraction (iii) gave the *alcohol* (XIII), b. p. 49—50°/0.5 mm. (Found: C, 78.2; H, 11.5. C<sub>10</sub>H<sub>18</sub>O requires C, 77.9; H, 11.8%),  $n_D^{25}$  1.4874,  $\lambda_{\max}$ . (in EtOH) 2290 Å ( $\epsilon$  31,000). The *alcohol* (XIII) readily formed an adduct with maleic anhydride when refluxed in a benzene solution for 15 min. Recrystallised from water, the lactonic acid, 1,3,3a,4,5,7a-hexahydro-1-isobutyl-7-methyl-3-oxoisobenzofuran-4-carboxylic acid (XIV), melted at 182—183° (Found: C, 66.5; H, 7.9. C<sub>14</sub>H<sub>20</sub>O<sub>4</sub> requires C, 66.6; H, 8.0%).

<sup>12</sup> Lindlar, *Helv. Chim. Acta*, 1952, **35**, 446.

*cis*-2,6-Dimethylocta-5,7-dien-4-ol (IX).—The method of synthesis was analogous to that employed for the *trans*-isomer. The alcohol (IX) had b. p. 43°/0.1 mm. (Found: C, 78.2; H, 11.9%),  $n_D^{18}$  1.4715,  $\lambda_{\max}$  (in EtOH) 2300 Å ( $\epsilon$  21,900). It showed two peaks, of relative areas 80:20, on gas-liquid chromatography on dinonyl phthalate, the major peak being separable from that of alcohol (XIII).

*trans*-2,6-Dimethylocta-5,7-dien-4-one (V).—The alcohol (XIII) (7.2 g.), manganese dioxide (130 g.), and methylene chloride (300 c.c.) were stirred for 10 hr. in the dark at 20°. Filtration, thorough washing of the manganese dioxide, removal of the solvent, and simple distillation of the residue resulted in a product (6.1 g.), which, distilled through the spinning-band column, gave: (i) a low-boiling liquid (ca. 200 mg.) of pungent smell which was collected in the cold traps, had  $\nu_{\max}$  1725, 2717  $\text{cm}^{-1}$ , and gave a 2,4-dinitrophenylhydrazone, m. p. 124°, undepressed on admixture with the corresponding isovaleraldehyde derivative, m. p. 123°; (ii) crude 3-methylpenta-2,4-dienal (440 mg.), b. p. 32–36°/4 mm. (Found: C, 72.2; H, 8.4.  $\text{C}_6\text{H}_8\text{O}$  requires C, 74.95; H, 8.4%),  $n_D^{25}$  1.5240–1.5258,  $\lambda_{\max}$  (in EtOH) 2675 Å ( $\epsilon$  28,000),  $\nu_{\max}$  1724  $\text{cm}^{-1}$  [semicarbazone, m. p. 166–167°  $\lambda_{\max}$  (in EtOH) 2075 ( $\epsilon$  4600), and 2950 Å ( $\epsilon$  34,100); Heilbron *et al.*, give  $\lambda_{\max}$  m. p. 166–167°,  $\lambda_{\max}$  2950 Å ( $\epsilon$  32,000)] (iii) a fraction (610 mg.), b. p. 36–70°/4 mm.,  $n_D^{25}$  1.5250–4780,  $R_T$  8.4, 25.2, 54.4 min. (dinonyl phthalate) [this fraction was a mixture of the carbonyl compound from (ii), the ketone (V), and unchanged alcohol (XIII)]; and (iv) a fraction (3.42 g.) with b. p. 70–75°/4 mm.,  $n_D^{25}$  1.4780–1.4864,  $R_T$  25.2, 54.4 min. (dinonyl phthalate). This mixture (iv) of ketone (V) and the unchanged alcohol (XIII) was chromatographed on deactivated alumina (100 g.) and eluted with light petroleum (b. p. 40–60°), followed by light petroleum–benzene (9:1). Evaporation of the light petroleum eluate gave this ketone fraction (1.22 g.), and evaporation of the light petroleum–benzene eluate gave the unchanged alcohol (1.86 g.) and a trace of the ketone. Distillation of the former fraction (bath-temp. 44–45°/0.1 mm.) gave the ketone (V) (1.02 g., 14%) (Found: C, 79.25; H, 10.6.  $\text{C}_{10}\text{H}_{16}\text{O}$  requires C, 78.9; H, 10.6%),  $n_D^{21}$  1.4880,  $\lambda_{\max}$  (in EtOH) 2675 Å ( $\epsilon$  18,300),  $\nu_{\max}$  (in  $\text{CS}_2$ ) 2985s, 1845w, 1733w, 1689vs, 1361m, 986s, and 917vs  $\text{cm}^{-1}$ ,  $\nu_{\max}$  (in  $\text{CCl}_4$ ) 1689 and 1626  $\text{cm}^{-1}$ .

The 2,4-dinitrophenylhydrazone was a red oil.

*Fractional Distillation of Tagetes glandulifera Oil.*—A sample of the oil was distilled at 3.5 mm., manostatically maintained, through a Nester and Faust semimicro spinning-band column (length 18", bore 6 mm.). Early fractions, b. p. 41–45°, were poor in carbonyl compounds, but those of b. p. 54–63°,  $n_D^{20}$  1.485–1.487, showed intense absorption at 2650 Å ( $E_{1\text{cm}}^{1\%}$ , ca. 1100), in alcohol,  $\nu_{\max}$  (liquid film) 3070w, 2930s, 2860s, 1868w, 1680s, 1620s, 1580vs, 1462m, 1378m, 1364m, 1333w, 1286m, 1240m, 1172m, 1146m, 1080m, 1050s, 1003m, 988w, 958w, 923s, 888m, 823w, 731w, 720 inf. and gave dominant peaks in the gas-liquid chromatogram on polypropylene adipate at 32.5 and 35.5 min., at 108.5°, 60 c.c./min., relative magnitude 1:7. Treatment with iodine solution in light petroleum (0.3%) at 20° for 3 hr. in daylight and recovery gave a product with  $E_{1\text{cm}}^{1\%}$  1300, equivalent to  $\epsilon = 20,200$  if the ketone had been pure, and an almost unchanged infrared spectrum. The same two peaks dominated the gas chromatogram, but in the ratio 2.2:1.

We thank Professor F. N. Lahey of the University of Queensland, Brisbane, Australia, who arranged for the extraction of the oil from the leaves and flowers of *Tagetes glandulifera* to be carried out in his Laboratory. We thank also Dr. G. E. Howard from the Tropical Products Institute, London, W.C.1., for information about the *Tagetes* family, and for the comparison of the oils from *Tagetes glandulifera* and *Tagetes minuta*. We are particularly grateful to Professor E. R. H. Jones, F.R.S., for suggesting this investigation and for helpful discussions.