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THE CAMPHOKETENE DIMERS

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TREATMENT of an ethereal solution of d-camphor-3-carbonyl chloride (I) with quinoline or triethylamine yields two isomeric products, $C_{22}H_{28}O_4$, which were considered by Staudinger and Schotz[1] to be stereoisomers of the 1,3-cyclobutanedione derivative II, arising by dimerization of "camphoketene" (III). Pyrolysis of these camphoketene dimers or of I gives a third isomer which has been assigned structure IV.[1] We now propose that the camphoketene dimers be assigned structure IV and the pyrolysis product structure V. These proposals serve to rationalize all the previously reported data, including results explicable only with difficulty on the basis of the earlier formulations, and are uniquely in accord with the new data now to be presented.

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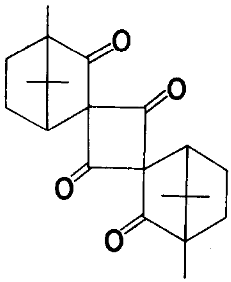
[1] H. Staudinger and S. Schotz, Ber. 53, 1105 (1920).



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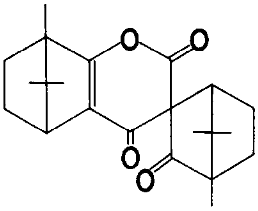

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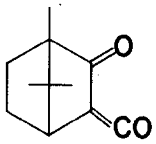

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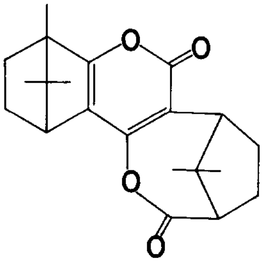
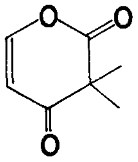


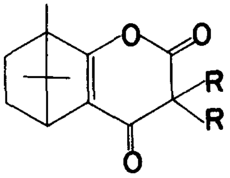
V

We find that, as previously reported, the two camphoketene dimers have similar m.p.'s (147.5-149.5°, 150-151.5°) and widely divergent optical rotations [66.3°, 132° (c = 5 in ethyl acetate)], but that, contrary to the original report, neither compound gives an immediate $FeCl_3$ test. The assignment of the formula $C_{22}H_{28}O_4$ to both compounds has been confirmed (Found: (i) C, 74.24; H, 7.97; M.W., 363 (ii) C, 74.01; H, 7.99; M.W., 388. $C_{22}H_{28}O_4$ requires C, 74.13; H, 7.92; M.W., 356). Their infrared spectra are very similar, showing bands at *ca.* 5.55, 5.70, 5.96 and 6.18 μ; their ultraviolet spectra show maxima at 297 mμ (ε 5700) and 293 mμ (ε 5300). The close similarity of their spectra corroborates their formulation as stereoisomers. The infrared spectra are incompatible with II but can be interpreted in terms of IV, with assignment of the bands at 5.96 and 6.18 μ to the αβ-unsaturated ketone system, and those at 5.55 and 5.70 μ to the enol lactone and saturated ketone groups, respectively. The ultraviolet spectra also are incompatible with II but are in accord with IV, as shown by comparison with the spectra of the model compounds VI-VIII, whose structures have been independently established.[2]



VI

λ_{max}^{EtOH} 250 mμ (ε 7400)



VII R = C_6H_5 λ_{max}^{EtOH} 293 mμ (ε 6700)

VIII R = CH_3 λ_{max}^{EtOH} 282 mμ (ε 7050)

Hydrolysis[1] of either stereoisomer with hydrochloric acid in acetic acid at room temperature gave an acid, m.p. 258-258.5° dec. (Found: C, 70.43; H, 8.04. $C_{22}H_{30}O_5$ requires C, 70.56; H, 8.08), which is now formulated as IX. Its infrared spectrum (λ_{max}^{KBr} 3-4, 5.92, 6.05, 6.17 and 6.45 μ) is compatible with this structure and its ultraviolet spectrum [λ_{max}^{EtOH} 316 mμ (ε 10,000), shifted to 302 mμ (ε 10,000) on addition of NaOH] closely resembles that of the model compound X [2] [λ_{max}^{EtOH} 311 mμ (ε 10,300), shifted to 299 mμ (ε 10,700) on addition of NaOH]. Hydrolysis of IX with hot aqueous potassium hydroxide gave an acid, m.p. 188-189.5°

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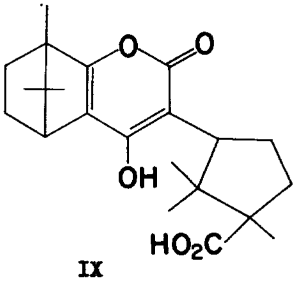
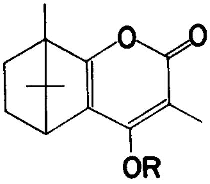
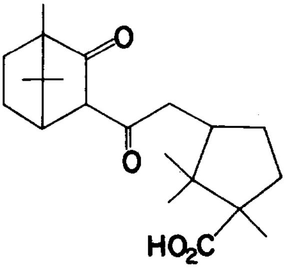
[2] P. Yates and E. A. Chandross, to be published.

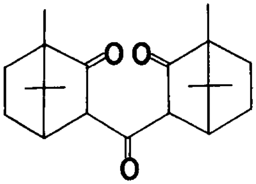

IX

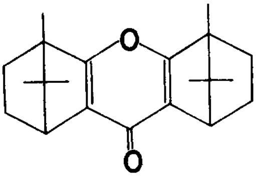

X R = H

XIV R = $COCH_3$

(Found: C, 72.12; H, 9.09. $C_{21}H_{32}O_4$ requires C, 72.38; H, 9.26) which is formulated as XI. Its infrared spectrum $[\lambda_{max}^{CH_2Cl_2}$ 3-4, 5.75, 5.90 (br) and 6.18 $\mu]$ and ultraviolet spectrum $[\lambda_{max}^{EtOH}$ 280 mμ (ϵ 6500), shifted to 313 mμ (ϵ 21,000) on addition of NaOH$]$ resemble those of d-3-isobutyrylcamphor[2] $[\lambda_{max}^{CH_2Cl_2}$ 5.71, 5.86, 5.95 and 6.18 μ; λ_{max}^{EtOH} 279 mμ (ϵ 4970), shifted to 311 mμ (ϵ 22,000) on addition of NaOH$]$. It reacted with phenylhydrazine to give an N-phenylpyrazole derivative, m.p. 216-217° [Found: C, 77.15; H, 8.61; N, 6.72. $C_{27}H_{36}N_2O_2$ requires C, 77.10; H, 8.63; N, 6.66]. Oxidation with alkaline $KMnO_4$ gave a mixture of d-camphoric and d-homocamphoric acids.

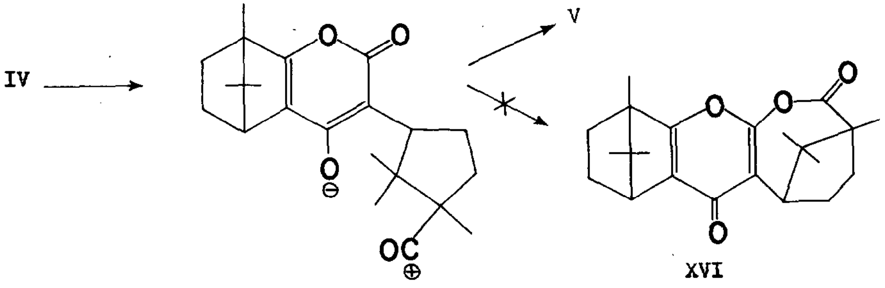

XI


XII


XIII

Alkaline hydrolysis of the stereoisomeric dimers with aqueous pyridine gave the triketone XII, obtained by Staudinger and Schotz by hydrolysis with aqueous NaOH.[1] This product, m.p. 183-185° (Found: C, 75.90; H, 9.15. $C_{21}H_{30}O_3$ requires C, 76.32; H, 9.15) showed bands in its infrared spectrum (CH_2Cl_2) at 5.72, 5.90 (br) and 6.16 µ, and λ_{max}^{EtOH} 280 mµ (ε 2430), shifted to 318 mµ (ε 22,000) on addition of NaOH (cf. the spectra of d-3-isobutyrylcamphor, above). The rates of alkaline hydrolysis of the dimers differed slightly and a tentative assignment of stereochemistry can be made on this basis. Treatment of XII with hot sulfuric acid led to a dehydration product, m.p. 167-168° (Found: C, 80.78; H, 9.03. $C_{21}H_{28}O_2$ requires C, 80.73; H, 9.03), rationally formulable as the γ-pyrone derivative XIII. Its infrared and ultraviolet spectra [$\lambda_{max}^{CH_2Cl_2}$ 6.14, 6.27 µ; λ_{max}^{EtOH} 260 mµ (ε 18,300)] are in accord with this formulation.

When I was heated at 160-170° it was converted to a product, m.p. 197-198°, whose formulation as an isomer of the camphoketene dimers was confirmed (Found: C, 73.98; H, 8.13; M.W. 353. $C_{22}H_{28}O_4$ requires C, 74.13; H, 7.92; M.W. 356). The same product was also obtained by heating either camphoketene dimer at 180°. Its infrared spectrum (CH_2Cl_2) shows bands at 5.68, 5.91, 6.13 and 6.39 µ and its ultraviolet spectrum (EtOH) a maximum at 326 mµ (ε 9300). The excellent correspondence of these spectra with those of the model compound XIV [2] [$\lambda_{max}^{CH_2Cl_2}$ 5.64, 5.86, 6.15 and 6.38 µ; λ_{max}^{EtOH} 324 mµ (ε 10,500)] strongly supports the newly proposed structure, V. Treatment of the pyrolysis product with concentrated hydrochloric acid in the cold led to a mixture of the acids IX and XI; the latter product only was obtained when the reaction was carried out on the steam bath. When IX was heated in vacuo the pyrolysis product was regenerated. These hydrolysis products serve to confirm V as the structure of the pyrolysis product. Thermal fission of one bond of IV would give the stabilized zwitterion XV, which could recyclize to give either V or the γ-pyrone XVI; the latter is rejected as the structure of the pyrolysis product on the basis of the spectral data.[2]



XV

XVI

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