pentanedibutanol (**15**): $n^{20}{}_{D}$ 1.4798; ir (film) 1060 (OH) and 3400 cm^{-1} (OH). The *p*-nitrobenzoate derivative of **15** was prepared, and an analytical sample (mp 83.5–84.5°) was obtained after several recrystallizations from 95% ethanol.

Anal. Calcd for $C_{27}H_{32}O_2N_8$: C, 63.27; H, 6.29; N, 5.47. Found: C, 63.41; H, 6.10; N, 5.31.

Registry No.—**7b**, R = Et, 26269-16-9; **8a**, 26269-17-0; **8a**, *p*-nitrobenzoate, 26269-18-1; **8b**, 26269-19-2; **8b** 2,4-DNP, 26269-20-5; **9b**, 26269-21-6; **12**, 26269-22-7; **13a**, 26269-23-8; **13b**, 26269-24-9; **13c**, 26269-25-0; **15**, 26269-26-1; **15** *p*-nitrobenzoate, 26269-27-2.

Acknowledgment.—We are indebted to the Petroleum Research Fund administered by the American Chemical Society for support of a portion of this work.

The Pyrolysis of Some Cyclobutanone Benzenesulfonylhydrazones

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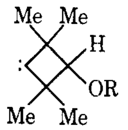
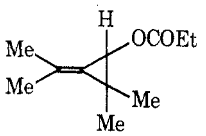
Received May 29, 1970

Some related 4-substituted 2,2,3,3-tetramethylcyclobutanone benzenesulfonylhydrazones have been pyrolyzed in a modified Bamford–Stevens reaction. Products were isolated and identified which suggested that the main reaction proceeds *via* the diazo compounds to the corresponding carbenes which undergo methyl insertion to form 2-substituted 1,3,3-trimethylbicyclo[2.1.0]pentanes. Some transformation products of these bicyclopentanes are described. In particular, the 2-propionyloxy derivative underwent homoallylic rearrangement to give 4-propionyloxy-1,3,3-trimethylcyclopentene. Unpredictable products also obtained from these pyrolyses included a novel nitrogen heterocycle.

The carbene **1** has been the reported intermediate[2–5] in attempts, finally successful,[5] to obtain the cyclopropane **2**,[5–8] once thought to be the cockroach sex attractant.[7] We prepared **1a** and examined some of its numerous transformation products in the hope of finding the bicyclobutane **3**.[6]



1a, R = COEt
b, R = H
c, R = tetrahydropyranyl[4]



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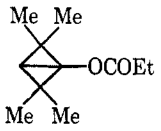

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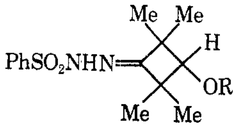

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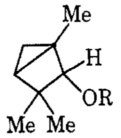

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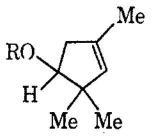

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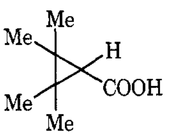
Starting from the hydrazone **4a** we thus obtained the known bicyclic ester **5a**[5a] and the unsaturated ester **6a**, already reported,[3a,5a] and in addition we also isolated isobutyronitrile, the acid **7**,[9] and a trimer[10] presumed to be **8** of the Schiff's base **9**.

A plausible route to **7** is from **2** *via* the isomeric methylenecyclopropane **10** (more stable than a cyclopropene[11]) which can then hydrolyze and oxidize (air) to the acid.



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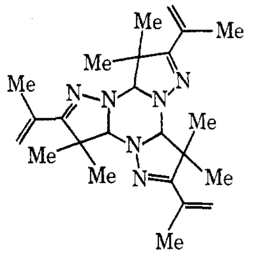

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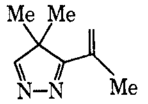

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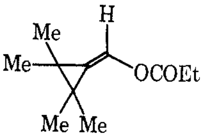

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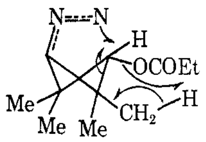

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The production of **9** must involve transannular attack of the "hot" diazo group with loss of propionic acid accompanied by ring opening. A radical reaction in the gas phase is contemplated and a tentative mechanism **11** proposed.

When we generated the carbene **1b** from **4b**, it gave mainly the stable bicyclopentane alcohol **5b**. The latter on propionylation underwent homoallylic rearrangement to ester **6b**.

We found further indication for the intermediacy of a bicyclopentane when we pyrolyzed the dry salt of **12**, obtained using sodium methoxide. The carbene generated gave the known ester **14**[12] as major product, presumably *via* the ketone **13** and derived ketene which picked up residual methanol. This reaction is homol-

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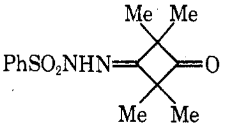
ogous to that of cyclobutenones which react similarly.[13] The azine **15** was a by-product of our reaction.



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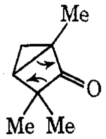

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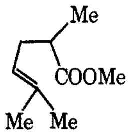

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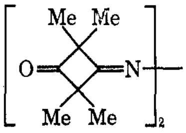

15

Experimental Section[14]

2,2,4,4-Tetramethylcyclobutane-1,3-diol Mono- and Dipropionates.—To the diol, 14.4 g (0.1 mol), was added 13 ml (0.15 mol) of propionyl chloride in 40 ml of pyridine. After 2 hr, water was added and an ether extract was taken, dried ($MgSO_4$), and fractionated giving 17 g (77%) of esters. Chromatography on 25 parts alumina (Peter Spence grade H) gave the diester, 5 g, bp 132° (15 mm), $n^{20}D$ 1.4525, on elution with 5 l. of petroleum ether, followed by 7 g of monoester, bp 126° (22 mm), $n^{20}D$ 1.4555, on elution with 2.5 l. of 1:1 ether–petroleum ether.

Anal. Calcd for $C_{14}H_{24}O_4$: C, 56.5; H, 9.45. Found: C, 66.0; H, 9.4. Calcd for $C_{11}H_{20}O_3$: C, 65.95; H, 10.05. Found: C, 65.65; H, 10.05.

1-Propionyloxy-2,2,4,4-tetramethylcyclobutan-3-one.—The distilled mono/dipropionate ester mixture, 67 g, in 700 ml of acetone was cooled in ice. Chromic oxide, 6 *N* in sulfuric acid,[15] 75 ml, was added with shaking. Water was then added and the mixture was extracted with methylene chloride. The organic layer was washed until neutral, dried ($MgSO_4$), and distilled, and efficient fractionation gave 28 g of keto ester[2,3b] (40%). In our hands this was a solid, mp 30°, bp 95° (12 mm), $n^{20}D$ 1.4442 (supercooled). The benzenesulfonylhydrazone **4a** had mp 87° (crystallized from cyclohexane).

Anal. Calcd for $C_{17}H_{24}N_2SO_4$: C, 57.95; H, 6.9; N, 7.95; S, 9.1. Found: C, 58.2; H, 6.9; N, 8.15; S, 9.2.

Pyrolysis of the Sodium Salt of 4a Giving the Trimer 8 of 3,3-Dimethyl-2-isopropylideneisopyrazole (9) and Other Products.—This reaction[16-18] involved the solvent when done in acetamide.

In glycerol, the unique product **8** was collected in the condenser: mp 161°, crystallized from ethanol (12%); uv max (ethanol) 212 mμ (log ε 3.16), 295 (3.54); nmr ($CDCl_3$) δ 1.2–1.4 (6 s, 18), 1.9–2.0 (3 m, 9, *J* = 5 Hz), 4.15 (s, 1), 4.2 (s, 1), 5.08 (s, 1), 5.1–5.4 (m, 6); mass spectrum (70 eV) *m/e* (rel intensity) 408 (16), 272 (100), 137 (49). Metastable peaks were found for the transitions 408 (trimer **8** of **9**) → 272 (dimer) and 272 → 137 (**9** + H).

Anal. Calcd for $C_{24}H_{36}N_6$: C, 70.55; H, 8.88; N, 20.6. Found: C, 70.2; H, 9.02; N, 20.3.

To prepare the solvent-free sodium salt, 75 g of hydrazone **4a** was added to 1 equiv of sodium in absolute methanol and the solvent removed without heating, leaving a thick oil which was spread evenly over the inside of the 1-l. flask by rotating it. Vacuum was applied when the oil foamed and set. After 12 hr *in vacuo* over phosphorus pentoxide, the salt was further dried at 100°. The flask was then set up for distillation using a water condenser, acetone–solid CO_2 cooled receiver, and a trap cooled by liquid nitrogen. The flask was heated in an oil bath until steady decomposition began. By this method,[19] a modification of the Bamford–Stevens reaction,[20] we obtained 24.3 g (62%) of distillate which was pink in color and evolved nitrogen, indicating the presence of the diazo compound. After distillation and vpc, the following compounds were obtained from 10 g of material, having the given retention times on the analytical column.

Methanol had a retention time of 1.8 min, small amounts, identified by ir.

Isobutyronitrile had a retention time of 3.5 min, 0.26 g, identified spectroscopically.

2,2,3,3-Tetramethylcyclopropanecarboxylic acid (7) had a retention time of 15 min, 0.22 g: mp 121° (lit.[8] 121°] from cyclohexane; nmr (C_6H_6) δ 0.92 (s, 6), 1.25 (s, 7), 12.2 (s, 1); nmr ($CDCl_3$) 1.75 (s, with shoulder, 7), 1.8 (s, 6); mass spectrum (70 eV) *m/e* (rel intensity) 142 (2), 127 (100).

2-Propionyloxy-1,3,3-trimethylbicyclo[2.1.0]pentane (5a) had a retention time of 24.5 min. This compound was unstable on our preparative vpc columns and difficult to separate. A small sample of pure material (few mg) was obtained following two preparative runs, using a GPO column[14] and identified by comparison of its ir spectrum with one kindly supplied by Drs. Maier and Strasser[5b] who obtained a pyridine solution of **5a** by precipitating accompanying **2** with osmium tetroxide. After subtraction of bands due to pyridine, the spectra are in good agreement. They also found when attempting to extract final traces of pyridine that **5a** is acid labile.

4-Propionyloxy-1,3,3-trimethylcyclopentene (6a) had a retention time of 33.5 min, 0.28 g: uv max not significant; ir (CCl_4) 1745 (ester CO), 1650 cm^{-1} (C=C); nmr (CCl_4) 0.95 (s, 3), 1.05 (s, 3), 1.1 (t, 3), 1.65 (d, 3, *J* = 1.5 Hz, C=CMe), 7.7 (q, 2), 1.95–2.9 (octet, 2, *J* = 16 Hz, ring CH_2), 4.95 (q, 1, *J* = 5 and 7 Hz with ring CH_2, $-CH_2CHOCOCH_2CH_3$); mass spectrum (70 eV) *m/e* (rel intensity)182 (s), 108 (84), 57 (100, $EtCO^+$).

Spin decoupling confirmed the nmr assignments. Following loss of propionic acid, the mass spectrum, apart from the base peak, was essentially that of 1,1,3-trimethylcyclopenta-2,4-diene.[21]

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.5; H, 9.95. Found: C, 72.2; H, 10.2.

Hydrolysis of Ester 6a to 4-Hydroxy-1,3,3-trimethylcyclopentene (6b).—The ester, 20 mg, was hydrolyzed to the alcohol which gave one peak only on vpc on the GEO column: retention time, 37.5 min; nmr (CCl_4) 0.95 (s, 3), 1.0 (s, 3), 1.7 (d, 3).

Oxidation of 6b—Oxidation[15,22] was slow, possibly due to steric hindrance. There were three peaks on vpc. The crude material had uv max (ethanol) 225 mμ, ir (CCl_4) 3630 (OH), 1752 (CO), 1733 cm^{-1} (CO). These results indicate that some isomerization *to the conjugated enone may* have taken place and that the starting alcohol was not allylic which is in agreement with the proposed structure.

3-Keto-2,2,4,4-tetramethylcyclobutan-1-ol Benzenesulfonylhydrazone (4b).—The ketone **12** (see below), 46 g in 500 ml of ethanol, was treated with 6 g of sodium borohydride in water. After 8 hr, water and excess dilute sulfuric acid were added. Extraction with methylene chloride gave, after evaporation of the dried ($MgSO_4$) extract, 40.6 g (88%) of alcohol **4b**: mp 146° (crystallized from toluene); ir (CH_2Cl_2), 3570 (OH), 3330 cm^{-1} (NH).

Anal. Calcd for $C_{14}H_{20}N_2SO_3$: C, 57.05; H, 6.7; N, 9.7; S, 11.1 Found: C, 56.75; H, 6.8; N, 9.45; S, 10.8.

This compound was characterized as its dipropionate, mp 96–97° crystallized from aqueous methanol: ir (CS_2) 1740 (ester CO), 1725 cm^{-1} (amide CO).

Anal. Calcd for $C_{20}H_{28}N_2O_5S$: C, 58.8; H, 6.9; N, 6.9; S, 7.8. Found: C, 58.5; H, 6.9; N, 6.9; S, 8.0.

Partial hydrolysis of the dipropionate gave the *N*-monopropionate: ir (CH_2Cl_2) 3570 (OH), 1725 cm^{-1} (amide CO), also obtained by partial propionylation of **4b**.

Pyrolysis of Sodium 3-Keto-1,1,3,3-tetramethylcyclobutan-1-ol Benzenesulfonylhydrazone (4b) Giving 2-Hydroxy-1,3,3-tri-

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[13] J. E. Baldwin and M. C. McDaniel, *J. Amer. Chem. Soc.*, **90**, 6118 (1968).

[14] Analytical vpc was done on GEO 100 at 80°. Preparative vpc was done on the F & M 700 using GEO 100 and then silicone at 75° programmed upward. Further vpc was done on GPO 20. (GEO 100 and GPO 20 are low polymeric condensates of glycerol and ethylene oxide or propylene oxide, respectively.) Nmr spectra are at 60 MHz; mass spectra were run on the AEI MS 9. No attempt was made to optimize yields.

[15] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

[16] J. W. Powell and M. C. Whiting, *Tetrahedron*, **7**, 305 (1959); **12**, 163 (1961).

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methylbicyclo[2.1.0]pentane (5b).—The above hydrazone, 12.8 g, as the salt, gave by the method described, 4.2 g (76%) of a liquid, almost pure by vpc, retention time 28 min. After fractionation, a middle cut, bp 67–68° (15 mm), was purified by preparative vpc: uv no absorption; ir no C=C; nmr[23] δ (CCl_4) 0.4 (m, 1), 0.7 (s, 3, Me), 1.0 (m, 1), 1.2 (s, 3, Me), 1.4 (s, 3, Me), 1.75 (m, 1), 3.4 (broad 1, -CHOH), 3.6 (broad, 1, OH); mass spectrum (70 eV) *m/e* (rel intensity) 126 (15), 125 (15), 111 (94), 43 (100). These spectra are consistent with structure **5b**.

Anal. Calcd for $C_8H_{14}O$: C, 76.15; H, 11.2. Found: C, 76.0; H, 11.0.

Propionylation of the Bicyclic Alcohol 5b Giving 6a.—Treatment of the alcohol **5b** with propionic anhydride in pyridine gave a product with the same retention time and ir spectrum as ester **6a**. This experiment was repeated and the result confirmed.

1,1,3,3-Tetramethylcyclobutan-2,4-dione Monobenzenesulfonylhydrazone (12).—The dione, 14 g (0.1 mol), and 8.6 g (0.05 mol) of benzenesulfonylhydrazine were dissolved in 150 ml of methanol and the solution left to stand 5 days. Filtration gave a small residue of bissulfonylhydrazone, mp 275° (recrystallized from dioxane–water), ir (Nujol) 1670 cm^{-1} (C=N).

Anal. Calcd for $C_{20}H_{24}N_4O_4S_2$: C, 53.6; H, 5.4; N, 12.5; S, 14.3. Found: C, 53.75; H, 5.6; N, 12.4; S, 14.1.

Evaporation of the filtrate to dryness, followed by extraction of the residue with hot petroleum ether to recover unused dione left **12**: 9 g (61%); mp 141° (crystallized from aqueous methanol); ir (CH_2Cl_2) 1800 (CO), 1680 (C=N) cm^{-1}.

Anal. Calcd for $C_{14}H_{18}N_2SO_3$: C, 56.9; H, 5.7; N, 9.8; S, 11.3. Found: C, 57.1; H, 6.1; N, 9.5; S, 10.9.

Pyrolysis of the Salt of 12 Giving Bis-1,1,3,3-tetramethylcyclobutan-4-one Azine (15) and Methyl 2,5-Dimethyl-4-hexenoate (14).—**12** (34.5 g) was converted to its sodium salt and pyrolyzed as described above, giving 8 g (43%) of distillate plus a solid which collected in the condenser. The latter had mp 187°; uv max 227 mμ (log ε 4.0), 288 (2.26); ir (CCl_4) 1820 (C=O), 1800 (C=O), 1690 cm^{-1} (C=N); nmr ($CDCl_3$) δ 1.45, 1.35 (1:1); mass spectrum (70 eV) *m/e* (rel intensity) 276 (21), 248 (35), 139 (12), 69 (100). These spectra support the proposed structure **15**.

Anal. Calcd for $C_{16}H_{24}N_2O_2$: C, 69.5; H, 8.8; N, 10.15. Found: C, 69.2; H, 8.6; N, 10.2.

The distillate had one major component on vpc with retention time 26.5 min. Fractionation gave 3 g of pure material: bp 72° (12 mm); $n^{23}D$ 1.442; ir (CS_2) 2850 (OMe), 1740 (ester CO), 1160 (CO), 3020, 1670, 820 cm^{-1} (Me_2C=CH–); nmr (CCl_4) δ 1.1 (d, 3, *J* = 6.5 Hz), 1.6 (d, 3, *J* = 1 Hz) and 1.7 (d, 3, *J* = 1 Hz, Me_2C=CH–), 2.3 (m, 2 + 1), 3.6 (s, 3, OMe), 5.1 (t, 1, Me_2C=CH–); mass spectrum (70 eV) *m/e* (rel intensity) 156 (32), 125 (11), 88 (83), 69 (100). The process $M^+ \rightarrow m/e$ 88 ($MeCH_2COOMe$) + 66 was interpreted as a McLafferty rearrangement, in line with the proposed structure **14**.

Anal. Calcd for $C_9H_{16}O_2$: C, 69.2; H, 10.2. Found: C, 69.5; H, 10.25.

Registry No.—**4a,** 26308-71-4; 1-propionyloxy-2,2,-4,4-tetramethylcyclobutan-3-one, 1133-07-9; **4b,** 26308-73-6; **4b** dipropionate, 26308-74-7; **5b,** 26308-75-8; **6a,** 26308-76-9; **6b,** 26308-77-0; **7,** 15641-58-4; **8,** 26308-64-5; **12,** 26308-65-6; **14,** 26308-66-7; **15,** 26308-67-8; 2,2,4,4-tetramethylcyclobutane-1,3-diol monopropionate, 26308-68-9; 2,2,4,4-tetramethylcyclobutane-1,3-diol dipropionate, 26308-69-0; 1,1,3,3-tetramethylcyclobutane-2,4-dione bisbenzenesulfonylhydrazone, 26308-70-3.

Acknowledgment.—We thank the British Petroleum Company for financial support and Mr. C. J. Ball for help with the vpc.

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Synthetic Studies Related to the Bird-Cage System. III. Derivatives of Pentacyclo[$5.4.0.0^{2,6}.0^{3,10}.0^{5,9}$]undecane, Tetracyclo[$4.4.0.0^{3,9}.0^{4,8}$]decane, and Pentacyclo[$4.4.0.0^{2,5}.0^{3,9}.0^{4,8}$]decane[1]

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Synthetic sequences leading to derivatives of the "one-winged" (pentacycloundecane) and "wingless" (tetracyclodecane) congeners of the bird-cage hydrocarbon and to representatives of the 1,3′-bishomocubane (pentacyclodecane) system are described. The chlorinated methanonaphthalenes **2**, **8**, and **11**, prepared by stereoselective Diels–Alder condensation of appropriate precursors, were photochemically cyclized to the one-winged bird-cage structures **3**, **9**, and **12**. Orthodox manipulation of the functional groups and dehalogenation with lithium led to the ketal **4**, the ketone **5**, the hydrocarbon **6**, and the amine **15**. The tetrachloro ketone **16** was subjected to a Favorskii-type contraction to enter the 1,3′-bishomocubane series **17**, **18**, **21**, and **22**. Base-catalyzed opening of **18** yielded the wingless bird-cage imine **19**, which was hydrolyzed to the ketone **20**. These are the first reported representatives of the wingless bird-cage system. Nmr and mass spectral characteristics of the compounds are discussed.

Previous reports from these laboratories have described the synthesis of a variety of derivatives of the bird-cage hydrocarbon.[1,3,4] Our continued interest in the possible biological activity of cage compounds led us to investigate the preparation of some representatives of the related "one-winged" (pentacyclo[$5.4.0.0^{2,6}.0^{3,10}.0^{5,9}$]undecane) and "wingless" (tetracyclo[$4.4.0.0^{3,9}.0^{4,8}$]decane) bird-cage systems (*e.g.*, **6** and **20**, respectively) which lack one or both of the one-carbon bridges of the complete bird cage. In this paper we report the synthesis of the one-winged bird-cage hydrocarbon and some of its functionalized derivatives, and the extrusion of the single bridge with formation of a new cage bond to give representatives of the 1,3′-bishomocubane[5] (pentacyclo[$4.4.0.0^{2,5}.0^{3,9}.0^{4,8}$]decane) system (*e.g.*, **22**).

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[1] Part II: R. J. Stedman and L. S. Miller, *J. Org. Chem.*, **32**, 3544 (1967).

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[3] R. J. Stedman, A. C. Swift, and J. R. E. Hoover, *Tetrahedron Lett.*, 2525 (1965).

[4] R. J. Stedman and L. S. Miller, *J. Org. Chem.*, **32**, 35 (1967).

[5] See W. L. Dilling, C. E. Reineke, and R. A. Plepys, *ibid.*, **34**, 2605 (1969), for an explanation of the bishomocubane nomenclature.