shows CF_3 (116.2, q, J (C–F) = 285.5 Hz) and $C{=}O$ (161.4, q, J (C–F) = 44 Hz). The Si–CH_3 resonances in the ^1H NMR spectrum at 0.44, 0.42, and 0.52 ppm for the $E,Z/Z,E$, and E,E, and the Z,Z isomer, respectively, were also used for analytical purposes.

Experimental Section

Proton NMR spectra were determined on JEOL JNM-MH-100 and JEOL JNM-PS-100 instruments (100 MHz) and at the National NMR Center, Canberra, Australia (270 MHz); ^{13}C NMR spectra were determined on a JEOL JNM-FX-100 instrument (25 MHz **and** at the National NMR Center (68 MHz); ^2H NMR spectra were obtained at 15.29 MHz on the JEOLJNM-FX-100. All spectra were run in CDCl solutions with Me_4Si or $CHCl_3$ as internal standard. Gas chromatographs were obtained by using a Varian Aerograph 200 GC instrument with a SGE GSB/SE30/S SGOT glass capillary column (minimum effective plate number of 20 000). Mass spectra were recorded at 70 eV on an MS902S spectrometer.

1-Allyl-1,2,5-trimethyl-1-silacyclopentane. The Grignard reagent, prepared magnesium (0.96 g, 40 mM) and allyl bromide (4.8 g, 40 mM) in dry ether (50 mL), was reacted with 1-chloro-1,2,5-trimethyl-1-silacyclopentane (1.6 g, 10 mM) of isomeric composition $E,E:E,Z/Z,E:Z,Z$ = 31:47:23, followed by hexane (50 mL). Most of the ether was removed by distillation and the reaction mixture was refluxed on a hot water bath for ~24 h. The filtered reaction mixture was reduced in volume, hydrolyzed with water, extracted into ether, and distilled to yield a crude product (1.3 g) (ca. 30% yield with allowance for the hexane present), bp ~115 °C (80 mm), which contains some residual hexane. The mass spectrum of the crude product showed the following peaks: m/e (relative intensity) 168 (11), 127 (51), 126 (24), 99 (100), 85 (56), 59 (53), 57 (40), 56 (53), 43 (36). NMR spectroscopy and GC analysis showed the product to be composed of two isomers of the title compound $E,E:E,Z/Z,E$ = 47:53 with the ~40% hexane. The retention times for the $E,Z/Z,E$ and E,E isomers on analytical GC were 15.2 and 15.8 min respectively at 80 °C. Careful distillation under reduced pressure gave product free of hexane, bp ~100 °C (60 mm), with the isomers in the ratio $E,E:E,Z/Z,E$ = 31:69 perhaps containing a small amount of the Z,Z isomer.

Reactions of 1-Allyl-1,2,5-trimethyl-1-silacyclopentane. With Hydrogen Chloride. The allyl derivative (ca. 0.05 g) in dry ether solution, (ca. 5 mL) was treated with excess HCl dissolved in dry ether (ca. 5 mL) for ca. 5 min at room temperature after which the ether and excess HCl were removed by cold rotary evaporation and the product examined by gas chromatography as described in ref 2.

With Mercuric Chloride. The allyl derivative (ca. 0.1 g) in dry ether solution (ca. 10 mL) was treated with 1 equiv of $HgCl_2$ (ca. 0.15 g) and the suspension was refluxed for ca. 12 h. Hexane was added, most of the ether removed by evaporation, and then filtration followed by evaporation yielded the product which was examined by gas chromatography and by NMR spectroscopy. Metallic mercury, and probably also Hg_2Cl_2, were produced during the reaction and were removed during workup. No allyl mercurials were detected after workup but these may well not survive.

With Bromine. The allyl derivative (ca. 0.1 g) in carbon tetrachloride solution (ca. 20 mL) was treated with a solution of bromine in carbon tetrachloride until the bromide color persisted. A complex reaction product was obtained from which by careful distillation material containing 1-(2,3-dibromopropyl)-1,2,5-trimethyl-1-silacyclopentane, identified by ^1H and ^{13}C NMR spectroscopy, was obtained. The product also contains bromosilanes which seem to be formed by decomposition of the dibromopropyl derivative during attempts at purification.

With Trifluoroacetic Acid. The allyl derivative (0.16 g, 1 mM) in $CDCl_3$ (2 mL) was treated with trifluoroacetic acid (ca. 0.3 g, 3 mM) and after 3 h, the ^{13}C NMR spectrum was recorded. Further, acid was added and after several hours ^1H, ^2H, and ^{13}C NMR spectra were employed to analyze the reaction product.

1-(Trifluoroacetoxy)-1,2,5-trimethyl-1-silacyclopentane. Method A. 1-Chloro-1,2,5-trimethyl-1-silacyclopentane (0.18 g, 1.1 mM) of isomeric composition $E,Z/Z,E:E,E:Z,Z$ = 46:47:7 in CDL_3 (3.46 g) was shaken with silver trifluoroacetate (0.36 g, 1.7 mM) for 12 h. After filtration the solution was examined by ^1H and ^{13}C NMR spectroscopy and found to contain the trifluoroacetates with composition $E,Z/Z,E:E,E:Z,Z$ = 47:35:18.

Method B. 1,2,5-Trimethyl-1-silacyclopentane (0.15 g, 1.2 mM) of isomeric composition $E,Z/Z,E:E,E$ = 41:59 in $CDCl_3$ (3.28 g) was shaken with mercuric trifluoroacetate (0.58 g, 1.5 mM) for 12 h. The solution was decanted and filtered before examination by ^1H and ^{13}C NMR spectroscopy. The product contained unreacted hydride with $E,Z/Z,E:E,E$ = 48:52 and trifluoroacetates with $E,Z/Z,E:E,E:Z,Z$ = 37:46.5:16.5.

Acknowledgment. Support of our work by the Australian Research Grants Commission is gratefully acknowledged. We thank V. Alberts and H. H. Feldman for experimental assistance, L. Lambert for assistance with ^{13}C NMR spectroscopy, and Professor M. D. Sutherland for providing gas chromatographic analytical facilities. Mass spectra were recorded by G. A. Macfarlane and Dr. R. F. Evans.

Registry No. Allyl bromide, 106-95-6; (*E,E*)-1-chloro-1,2,5-trimethyl-1-silacyclopentane, 71518-76-8; (*E,Z*)-1-chloro-1,2,5-trimethyl-1-silacyclopentane, 71564-07-3; (*Z,Z*)-1-chloro-1,2,5-trimethyl-1-silacyclopentane, 71564-08-4; (*E,E*)-1-allyl-1,2,5-trimethyl-1-silacyclopentane, 88916-34-1; (*E,Z*)-1-allyl-1,2,5-trimethyl-1-silacyclopentane, 88979-74-2; (*Z,Z*)-1-allyl-1,2,5,-trimethyl-1-silacyclopentane, 88979-75-3; (*E,E*)-1-(trifluoroacetoxy)-1,2,5-trimethyl-1-silacyclopentane, 88979-76-4; (*E,Z*)-1-(trifluoroacetoxy)-1,2,5-trimethyl-1-silacyclopentane, 88916-36-3; (*Z,Z*)-1-(trifluoroacetoxy)-1,2,5-trimethyl-1-silacyclopentane, 88979-77-5; 1-(2,3-dibromopropyl)-1,2,5-trimethyl-1-silacyclopentane, 88916-35-2; hydrogen chloride, 7647-01-0; mercuric chloride, 7487-94-7; bromine, 7726-95-6; trifluoroacetic acid, 76-05-1.

Heterocyclic Studies. 48. Multiple Rearrangments of a 9-Methyl-1,9-diazabicyclo[4.2.1]nonadienone[1]

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The pyrazolopyran **5** is obtained by thermal rearrangement of the diazabicyclooctadienone **3**; a concerted [3.3] sigmatropic process is suggested. Treatment of **3** with sodium methoxide in methanol leads to the tetrahydropyridazine **14** and the tetrahydroindazolone **16** via the acyclic carbanion **13**. Photoisomerization of **3** gives the caged ketone **18**.

The diaz. dienones **1** and **3**, available by 1,3-dipolar cycloaddition of dimethyl acetylenedicarboxylate to diazepinium azomethine imines[3] contain an unusual array of functional groups and present the possibility of rather

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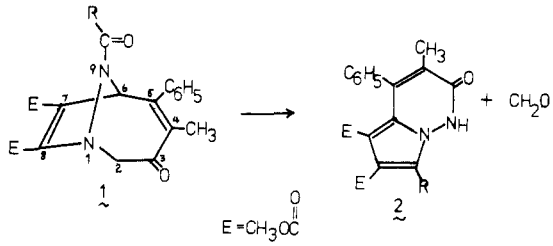
complex chemistry. The reactions of the 9-acyl compound **1** were reported some time ago.[4] Under conditions of acid or base catalysis or simple thermal activation as a melt, a single reaction occurs, leading in high yield to the pyrrolopyridazinone **2** and formaldehyde.



In contrast to the acyl compounds, the 9-methyl bicyclic ketone **3** gives rise to two rearrangement products on thermolysis and two other products on mild treatment with base. The ring system is stable to acid; hydrolysis to the monocarboxylic acid is the only reaction observed. In a previous note we described briefly the thermal products, one of which was found to be the tetrahydroindazolone **4**[5] (Scheme I). We now report the structures of three other rearrangement products, as well as a photoisomer of **3**.

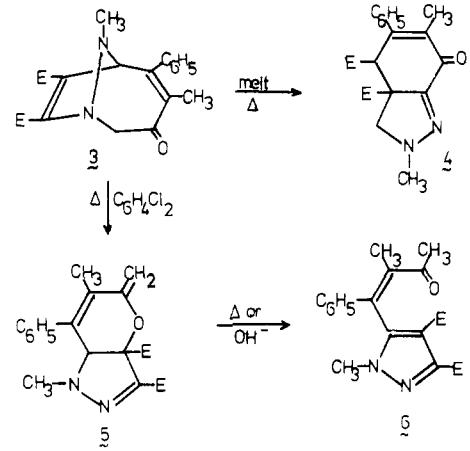
Thermal Rearrangements. Thermolysis of **3** in a melt at 170 °C give **4** and a second compound (**5**), also isomeric with **3**, in variable amounts, with **4** usually predominating; total yields were 20–30%.[5] When the thermal reaction was carried out in dichlorobenzene, however, NMR showed initial formation of only **5**, followed by slower generation of a third compound, **6**; **4** was not detected in these mixtures. At 195 °C after 1 h, **5** was isolated by direct crystallization in 60% yield. The NMR spectra contained peaks from which the presence of a $=CH_2$ group could be inferred [^{1}H, 4.72 (d, 1, J = 1.5 Hz), 4.93 (d, 1, J = 1.5); ^{13}C, δ 95.4 (t)], but there was insufficient information to derive a complete structure. The pyrazolopyran structure **5** was revealed by crystallography. A stereoview of the molecule is shown in Figure 1.

The product of further thermal rearrangement of **3** or **5**, noted in the NMR experiments, was also readily obtained from **5** by mild treatment with base. This compound is an oil whose ^{1}H NMR contained a fifth methyl signal for CH_3CO, and no others except for those for CH_3 and C_6H_5 groups. From this spectrum and its origin for **5**, we assign the (*Z*)-pyrazolylbutenone structure **6**. Impurity peaks in the ^{13}C NMR spectra of **6** suggest the presence of a small amount of *E* isomer.

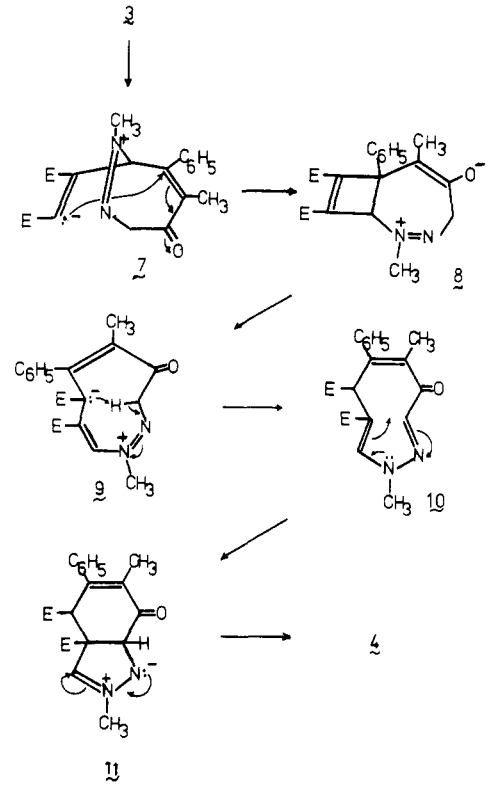
Considering possible pathways to these thermolysis products, the structure of indazolone **4** requires at some stage rebonding of the acetylene unit from N-1 of **3** to C-5. This could occur by elimination of the ester enolate to give the dipolar intermediate **7** followed by readdition. Subsequent steps via **8**–**11** as indicated in Scheme II are well precedented in the chemistry of acetylenedicarboxylate adducts[6] and 6π-heterocyclizations.[7]

In the formation of **5**, elimination of the ketone enolate

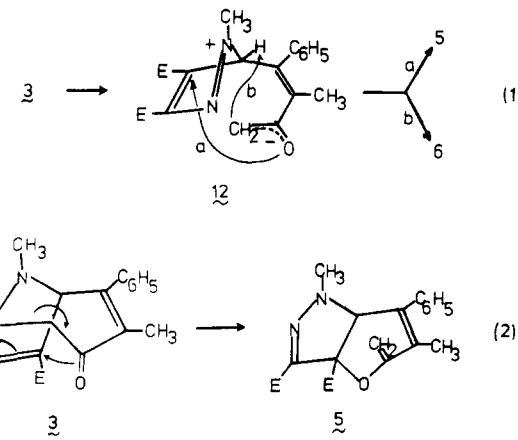
Scheme I



Scheme II



Scheme III



to a second dipolar intermediate **12** (eq 1, Scheme III), which undergoes O-addition (path a) at C-7, might be envisioned. However this mechanism requires formation

(1) Part 47: Moore, J. A.; Yokelson, H. B.; Freeman, W. F.; Blount, J. F. *J. Org. Chem.* **1978**, *44*, 2683.
(2) Illinois State University.
(3) Rothenberger, O. S.; Taylor, R. T.; Dalrymple, D. L.; Moore, J. A. *J. Org. Chem.* **1972**, *37*, 2640.
(4) Moore, J. A.; Gearhart, R. C.; Rothenberger, O. S.; Thorstenson, P. C.; Wood, R. H. *J. Org. Chem.* **1972**, *37*, 3774.
(5) Gearhart, R. C.; Wood, R. H.; Thorstenson, P. C.; Moore, J. A. *J. Org. Chem.* **1974**, *39*, 1007.
(6) Acheson, R. M.; Elmore, N. F. *Adv. Heterocycl. Chem.* **1978**, *23*, 263.
(7) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *12*, 947.

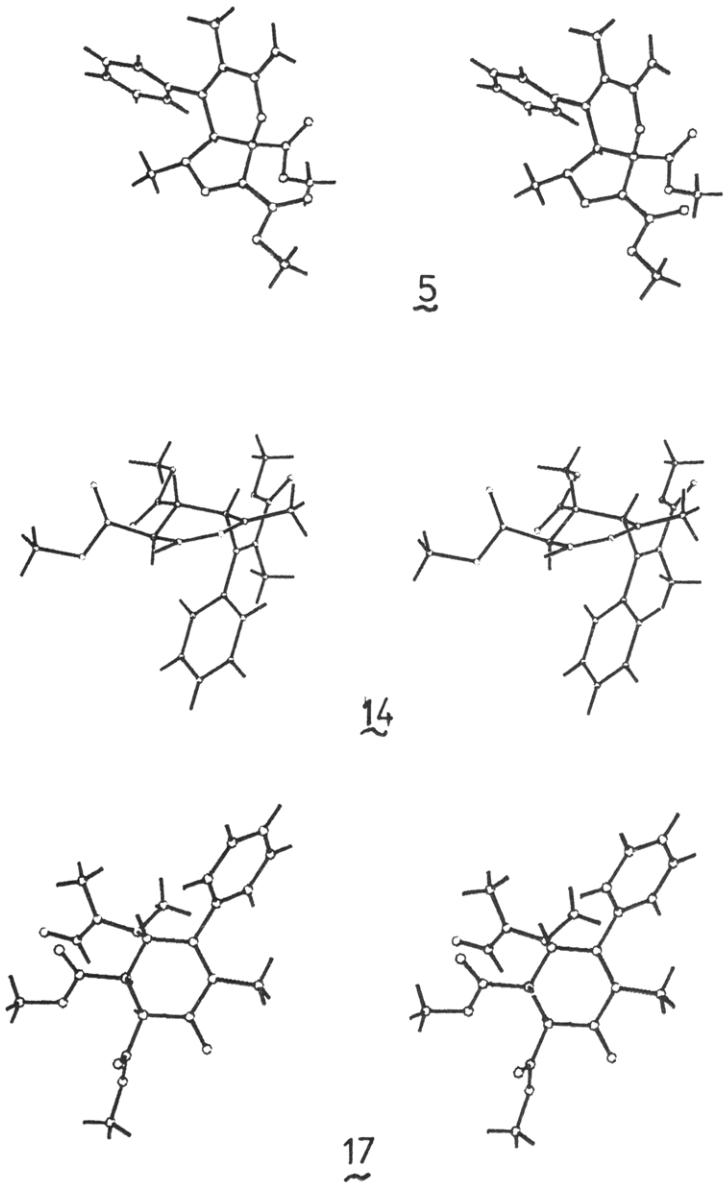
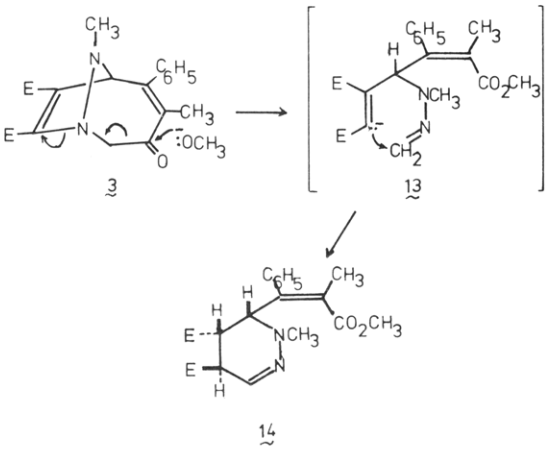


Figure 1. Stereoviews of **5**, **14**, and **17**.

of two zwitterions in the melt and only one in dichlorobenzene; moreover, it seems probable that removal of the C–6 proton (path b, eq 1) would lead directly to the pyrazole **6** rather than the pyran **5**. We therefore suggest as an alternative that **5** is formed from **3** by a concerted [3.3] sigmatropic rearrangement (eq 2). In this view, a reaction involving an ionic intermediate predominates in the presumably more polar medium of the melt, and a concerted process occurs in the less polar dichlorobenzene. It should be noted that the reaction in eq 2 involves conversion of a carbonyl group to an enol ether, the reverse of the usual oxa-Cope reaction,[8] and has not been previously observed to our knowledge.

Reactions in Base. Treatment of the *N*-methyl ketone **3** with sodium methoxide in methanol leads to a mixture from which two compounds **14** and **16** were isolated by TLC in yields of about 20–25%. Reaction with *tert*-butoxide in *t*-BuOH did not give either of these substances. The less polar methoxide product **16** was isomeric with **3**; the more polar compound **14** was a methanol adduct of **3**. The tetrahydropyridazine diester structure of **14** was established by crystallography. This compound appears to

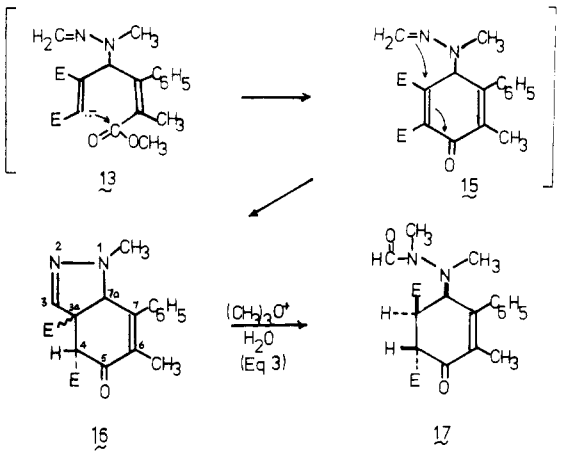
Scheme IV



arise from attack of methoxide at the C–3 carbonyl group of **3** followed by fragmentation to give the carbanion **13** (Scheme IV). Cyclization of this intermediate and subsequent proton shifts then lead to **14**, with the methoxycarbonyl groups diequatorial. A stereoview is shown in Figure 1.

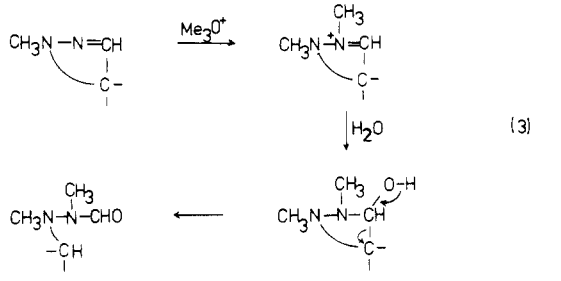
(8) Rhoads, S. J.; Raulins, N. R. *Org. React.* (*N.Y.*) **1975**, *22*, 1.

Scheme V



The isomeric methoxide product **16** crystallized in a triclinic space group containing eight molecules in the unit cell, and a crystallographic solution to the structure has not been found. The spectra of the compound showed the presence of a ketone and two ester carbonyls and a —CH=N group. For further characterization the compound was methylated with Me_3OBF_4. The molecular formula of the product isolated after aqueous workup indicated incorporation of the elements of CH_2 and H_2O. Crystallography of this compound established the cyclohexenone structure **17** (Scheme V), in which the methoxycarbonyl groups are equatorial and the dimethylformylhydrazine chain is axial. A stereoview of the molecule is shown in Figure 1.

Formation of an *N*-methyl-*N*-formylhydrazine group in the methylation reaction suggests the sequence of steps in eq 3, in which a ring is opened at a C–C bond. A sat-

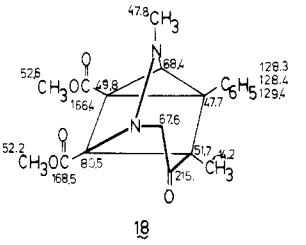


(3)

isfactory structure for the second methoxide product A could be derived from consideration of eq 3 and the recognition that this product must contain a C–C bond that is not present in either the precursor **3** or the methyl derivative **17**. We assume that the process involves the same carbanion intermediate **13** that give rise to **14**. Alternative attack at the methoxycarbonyl group in a Dieckmann reaction leads to the cyclohexadienone **15**. The methylenehydrazine group is well situated for a further Mannich cyclization to give the tetrahydroindazole **16**, which is the structure assigned to the less polar methoxide product. Methylation by the steps in eq 3 then reopens the five-membered ring to the formylhydrazine **17**.

The NMR spectra of **16** are consistent with the assigned structure: the stereochemistry is uncertain. In the ^1H NMR, H-3 and H-7a are both coupled to H-4 with ^4J = 2.4 and 3.3 Hz, respectively.

Photolysis of 3. A final item in the chemistry of **3** is the smooth reaction that occurs on irradiation to give a crystalline photoisomer in 60% yield. The ^1H NMR spectrum showed no signals below δ 3.8 except for the phenyl protons; the ^{13}C spectrum (see **18**) showed only C_{sp^3}, phenyl, and carbonyl signals. From these spectra and



numerous analogies in the [2 + 2] photocycloaddition of α,β-unsaturated ketones,[9] the structure of this product can be assigned as the tetracyclic caged ketone **18**. This compound was extremely labile and decomposed extensively at room temperature in a few days or rapidly on treatment with acid or base.

In summary, the diverse rearrangement products **4**, **5**, **14**, and **16** appear to arise by three different primary events from the ketone **3**. None of these reactions was predictable ab initio, and it should be pointed out that for none of these products could the ring system by identified without the power of X-ray crystallography.

Experimental Section

NMR spectra were obtained at 60 MHz on a Varian A-60 spectrometer; ^1H spectra at 250 MHz and ^{13}C spectra were obtained on a Bruker WM-250 spectrometer. Melting points were determined on Fisher-Johns block.

Thermolysis of 3. A solution of 250 mg of **3**[3] in 1 mL of *o*-dichlorobenzene was heated in a 195 °C bath. After 1 h the NMR spectrum showed nearly complete conversion to **5** plus a small amount of **6**. The solution was cooled and the resulting crystals were washed with ether to give 136 mg of colorless **5**: mp 167–170 °C (65%); ^{13}C NMR δ 15.3 (q), 40.3 (q), 52.1 (q); 52.3 (q), 72.2 (d), 83.7 (s), 95.4 (t), 124.5 (s), 128.12, 128.68, 128.87, 136.0, 138.60, 152.75, 169.59, 181.0; IR, ^1H NMR, Anal.–see ref 5.

On further heating at 190–200 °C, the NMR spectrum of a similar solution showed progressive increase in the peaks due to **6**; after 5 h **6** was the major component.

4-[1-Methyl-3,4-bis(methoxycarbonyl)-5-pyrazolyl]-3-methyl-4-phenyl-3-buten-2-one (6). A suspension of 100 mg of **5** in 5 mL of methanol was treated with 0.1 mL of 10% NaOMe in MeOH and refluxed 25 min. The resulting solution was acidified, diluted with water, acidified, and extracted with CH_2Cl_2. The dried CH_2Cl_2 solution was evaporated to give 75 mg of **6** as a pale orange oil. A sample was distilled in vacuo (short path) at 140–170 °C for spectra: IR 1760–1740 (br, s), 1700 cm^{-1}; ^1H NMR δ 2.10 (s), 2.12 (s), 3.70 (s), 3.78 (s), 3.91 (s), 7.3–7.5 (br s); ^{13}C NMR δ 17.4 (q, C-2, CH_3), 28.5 (q, CH_3CO), 37.8 (N-1 CH_3), 52.0, 52.5 (q, OCH_3), 114 (C-4), 128.3–129.2 (phenyl), 129.6 (ipso), 136.4 (s, C-7), 142.2 (s, C-6), 144.0 (s, C-3), 145.8 (s, C-5), 162.0, 162.8 (s, ester CO), 203.7 (C-8 CO); mass spectrum, *m/e* (relative intensity) 356 (M^+) (1.3), 325 (6.1), 313 (100). Calcd for M^+ of $C_{19}H_{20}N_2O_5$ *m/e* 356.137, found 356.140.

Reaction of 3 in Base. To a deoxygenated solution of 1.00 g of **3** in 20 mL of methanol was added 0.1 mL of 5% NaOMe–MeOH. After 2 h under a nitrogen atmosphere at 25 °C the yellow solution was treated with charcoal, filtered, and evaporated. The residue was dissolved in CH_2Cl_2 and water, and the dried CH_2Cl_2 was evaporated to an oil; the NMR spectrum showed peaks due to **14** and **16** in equal amounts, with no peaks for **3**. The oil was chromatographed on a 1-mm silica gel plate, eluting twice with ether–pentane (1:1). The slower moving pale yellow band furnished 250 mg of **16** as a crystalline solid. The slower moving pale yellow band furnished 250 mg of **16** as a crystalline solid. Recrystallization from ether–pentane gave pale yellow crystals, mp 138–139 °C; λ_{max}^{MeOH} (ϵ 13 400), 286 (8300); IR ν^{KBr} 1740, 1660 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.85 (s, 3), 2.62 (s, 3), 3.71–3.74 (m, 1), 3.74 (s, 3), 3.87 (s, 3), 4.67 (d, 1, J = 3.3 Hz), 6.94 (d, 1, J = 24 Hz), 7.3–7.5 (m, 5); ^{13}C NMR δ 13.1 (q, C-6 CH_3), 42.0 (d, C-4), 44.6 (q, N-1 CH_3), 52.6, 52.7 (OCH_3), 54.8 (s, C-3a), 59.7 (d, C-7a)

(9) Chapman, O. L.; Lenz, G. *Organic Photochemistry* **1966**, *1*, 283. Baldwin, S. W. *Ibid.* **1981**, *5*, 123.

Table I. Crystal and Intensity Data Collection Summary

	14	17	5
mol. formula	$C_{20}H_{24}N_2O_6$	$C_{20}H_{24}N_2O_6$	$C_{19}H_{20}N_2O_5$
form. wt	388.42	388.42	356.38
mol. wt	388.42	388.42	356.38
a, Å	10.198 (3)	19.855 (8)	29.82
b, Å	13.634 (3)	7.563 (2)	10.085 (2)
c, Å	15.132 (5)	26.820 (8)	12.377 (7)
β, deg	104.97 (2)	104.91 (3)	106.34
V, Å^3	2932.6 (9)	3941 (2)	3571 (3)
crystal systems	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$C2/c$
ρ(calcd), g cm^{-3}	1.268	1.306	1.33
Z	4	8	8
crystal dimensions, mm	0.38 × 0.30 × 0.10	0.22 × 0.41 × 0.42	0.25 × 0.30 × 0.35
radiation	graphite-monochromated Mo K$\bar{\alpha}$		
abs. coeff, μ(Mo Kα), cm^{-1}	1.24	0.91	0.91
temp, °C	26.0	26.0	26.0
scan speed, deg min^{-1}	variable 4.0-20.0	variable 4.0-20.0	3.00 fixed
scan type	θ-2θ	θ-2θ	θ-2θ
scan range	2.0 + $\Delta(\alpha_1 - \alpha_2)$	1.4 + $\Delta(\alpha_1 - \alpha_2)$	2.0 + $\Delta(\alpha_1 - \alpha_2)$
stds monitored	3/144	3/144	3/144
2θ limits, deg	$3 < 2\theta < 40$	$3 < 2\theta < 45$	$3 < 2\theta < 40$
reflections collected	$h,+k,+l$	$+h,k,l$	$+h,k,l$
No. reflections collected	4214	5905	1920
unique reflections	1915	5161	1812
unique reflections used	1639	3635	1260
$(F_{obsd})^2 > n\sigma(F_{obsd})^2$	$n = 2.0$	$n = 2.0$	$n = 2.0$
weighting factor, g[a]	0.00003	0.001412	0.00063
$R(F)$[b]	0.0747	0.0802	0.0640
$R(F_w)$[c]	0.0572	0.0777	0.0599
GOF	1.566	1.240	1.209
highest peak on final difference map	0.33	0.34	0.32

[a] Weight = $1/[\sigma^2(F) + |g|(F^2)]$. [b] $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$. [c] $[R_w = [\Sigma w^{1/2}(|F_o| - |F_c|)|\Sigma w^{1/2}(F_o)$.

125.5 (d, C-3), 128.3–129.2 (phenyl), 132.7 (s, ipso), 139.4 (s, C-6), 147.4 (s, C-7), 168.7, 169.3 (ester CO), 190.4 (C-5). Anal. Calcd for $C_{19}H_{20}N_2O_5$ (356.4): C, 64.03, H, 5.66; N, 7.86. Found: C, 64.16; H, 5.58; N, 7.68.

The faster moving region of the plate above the band for **16** was eluted to give 200 mg of crystalline **14**. Recrystallization from ether gave colorless crystals: mp 136–138 °C; IR ν^{KBr} 1740, 1725 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 1.62 (s, 3), 2.79–2.84 (dd, 1, J = 1.7, 12.5 Hz, H-4), 3.28–3.36 (m, 1, H-5), 3.30 (s, 3), 3.63 (s, 3), 3.70 (s, 3), 3.83 (s, 3), 5.07 (d, 1, J = 6.5 Hz, H-6), 5.88 (d, 1, J = 1.7 Hz, H-3), 7.02–7.05 (m, 2), 7.28–7.32 (m, 3); ^{13}C NMR δ 18.1 (C-8 CH_3), 38.3 (d, C-5), 40.8 (d, C-4), 43.1 (q, NCH_3), 51.9, 52.1, 52.4 (q, OCH_3), 57.6 (d, C-6), 125.0 (d, C-3), 128.0–129.5 (phenyl), 132.5 (s, ipso), 137.7 (s, C-8), 140.3 (s, C-7), 170.1, 171.0, 171.4 (ester CO). Anal. Calcd. for $C_{20}H_{24}N_2O_6$ (388.4): C, 61.84; H, 6.23; N, 7.21. Found: C, 62.07; H, 6.16; N, 7.39.

Methylation of 16. To a solution of 150 mg of **16** in 5 mL of acetone was added 300 mg of trimethyloxonium fluoborate. After 15 min, triethylamine was added and the solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2, and the solution was extracted thrice with water, then dried, and evaporated. The residue crystallized from ether to give 50 mg (31%) of **17**: mp 148–149 °C; IR 1770, 1750, 1680 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) (60 MHz) 1.87 (s, 3), 2.45 (s, 3), 2.54 (s, 3), 3.75 (s, 3), 3.78 (m, 1, partially hidden), 3.84 (s, 3), 4.27 (d, 1, J = 12.5 Hz), 4.64 (d, 1, J = 2.9 Hz), 7.46 (s, 5), 8.13 (s, 1). Anal. Calcd for $C_{20}H_{24}N_2O_6$: C, 61.84; H, 6.24; N, 7.21. Found: C, 61.70; H, 6.43; N, 7.06.

Photolysis of 3. A solution of 200 mg of **3** in 150 mL of spectrograde methanol was irradiated through quartz with a medium pressure mercury lamp for 1 h. Evaporation of the solution gave an oil, which crystallized from ether. Recrystallization gave 120 mg of long white needles of **18**: mp 114–115 °C; IR ν_{KBr} 1750, 1720 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 1.23 (s, 3), 2.72 (s, 3), 3.47 (dd, 1, J = 16, 1.3 Hz), 3.75 (d, 1, J = 1.3), 3.80 (s, 3), 3.82 (est 1), 3.86 (s, 3) 7.34 (m, 5); ^{13}C–see structure. Anal. Calcd for $C_{19}H_{20}N_2O_5$: C, 64.03; H, 5.66; N, 7.86. Found: C, 63.93; H, 5.58; N, 7.85.

Crystallography. Crystals of **5**, **14**, and **17** were obtained by slow crystallization from ether solutions and were attached with epoxy cement to glass fibers. Data for each were collected on a Nicolet R3 diffractometer using graphite monochromated Mo Kα radiation. A summary of pertinent crystallographic parameters is presented in Table I.

The structures were solved and refined by using the Nicolet SHELXTL (Version 3.0) programs. No correction for decay was required for any crystals. The direct methods technique (SOLV) yielded the positions of the majority of the non-hydrogen atoms. The remaining non-hydrogen atoms were located by difference-Fourier techniques. All non-hydrogen atoms were refined anisotropically by using blocked-cascade, least-squares refinement methods. The hydrogen atom coordinates were calculated in idealized positions on the basis of d(C–H) = 0.96 Å and thermal parameters equal to 1.2 times the isotropic equivalent value for the atom to which the hydrogen atom is attached.

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Registry No. **3**, 35324-31-3; **5**, 89066-12-6; **6**, 89066-13-7; **14**, 89088-12-0; **16**, 89066-14-8; **17**, 89066-15-9; **18**, 89066-16-0.

Supplementary Material Available: ORTEP drawings with atomic numbering schemes and tables of atomic coordinates, thermal parameters, bond lengths, and bond angles for **5**, **14**, and **17** (16 pages). Ordering information is given on any current masthead page.