pared in a standard fashion.[11] Methyl 2-iodo-3-methylbenzoate[12] and 2-fluoroiodobenzene were subjected to the Ullmann reaction[7] to give, after saponification, 2-methyl-2′-fluoro-6-carboxybiphenyl (amber oil, 76%), which, without purification, was heated with polyphosphoric acid to afford 4-fluoro-5-methylfluorenone (**3**) (mp 149–150°, 34%). A Wolff–Kishner reduction of this ketone gave 4-fluoro-5-methylfluorene (**2**) (mp 37°, 27%). **2** was also conveniently characterized as the 2,4,7-trinitrofluorenone 1:1 complex (mp 184°) and could be regenerated in a pure state by passing the complex through alumina.

The proton nmr spectrum of **1** (60 MHz, $CDCl_3$) shows a sharp singlet at 2.12 ppm[13] and a multiplet centered at 6.48 ppm in the anticipated ratio of 1:2. These absorptions are assigned to the methyl group[14] and the aromatic protons, respectively. In stark contrast to **1**, the proton nmr spectrum of **2** (60 MHz, $CDCl_3$) exhibits a *doublet* at 2.73 ($|J|$ = 8.3 Hz),[15] a broad singlet at 3.85, and a multiplet centered at 7.18 ppm in the anticipated ratio of 3:2:6. These absorptions are assigned to the methyl, methylene, and aromatic protons, respectively. Clearly, the methyl group in **2** must be coupled to the fluorine atom, six bonds away. This is the largest $^{6}J_{\mathrm{HF}}$ yet observed, from the few examples known.[16]

Because of the lack of observable splitting in **1** and because of the gross similarity between **1** and **2** *except* for the CH_3–F internuclear distance,[17] ~2.84 Å in **1** and ~1.44 Å in **2**, we feel that the evidence is overwhelmingly in favor of a dominant through-space (direct) contribution to the coupling mechanism in **2**.[18] As might be expected, the sum of the van der Waals radii of hydrogen and fluorine (~2.55 Å) lies between the measured internuclear H–F distance for **1** and **2**.

The long-range splitting is also observed for derivatives of **2**: 4-fluoro-5-methylfluorenone (**3**), $|^{6}J_{\mathrm{CH_3,F}}|$ = 7.3 Hz; 4-fluoro-5-methylfluoren-9-ol (**4**), $|^{6}J_{\mathrm{CH_3,F}}|$ = 7.8 Hz; 4-fluoro-5-methyl-9-chlorofluorene (**5**), $|^{6}J_{\mathrm{CH_3,F}}|$ = 8.1 Hz; and 4-fluoro-5-methyl-9-acetoxyfluorene (**6**), $|^{6}J_{\mathrm{CH_3,F}}|$ = 7.8 Hz.[19] These values are roughly in accord with increased coupling as the internuclear distance decreases. The shorter C–C bonds to the bridging atom in ketone **3** (sp^2) result in an increased separation of methyl and fluorine (measured distance ~1.60 Å). Likewise, the electronegative substituents in **4**, **5**, and **6** should enrich the per cent s character in the bridging bonds relative to **2**, increasing the CH_3–F distance and leading to smaller values of $|J_{\mathrm{CH_3,F}}|$, as observed. Due to the substantial electronic difference between **2** and **3**, it might also be argued that if a significant "through-bond" contribution was present then a larger difference in the methyl–fluorine couplings between **2** and **3** than 1 Hz would be observed.

This system and related ones would appear to be ideal for the study of other long-range couplings and nuclear Overhauser effects. Our work in this area continues.[20]

Acknowledgment. It is a pleasure to acknowledge financial support of this work by the Petroleum Research Fund, administered by the American Chemical Society, the Research Corporation, the National Heart Institute (Fellowship to J. R. D.), and in part by the National Science Foundation. We also wish to thank Dr. Elizabeth K. Weisburger (National Cancer Institute) and Professor T. Lloyd Fletcher (University of Washington) for helpful correspondence and samples, Dr. Paul Demarco (Eli Lilly) for obtaining the 100-MHz nmr spectrum, Professor David G. I. Kingston (SUNY at Albany) for obtaining the mass spectra, and Professor David M. Lemal (Dartmouth) and a referee for valuable comments.

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[11] H-L. Pan and T. L. Fletcher, *J. Med. Chem.*, **8**, 491 (1965).

[12] F. Mayer, *Ber.*, **44**, 2303 (1911).

[13] Chemical shifts are reported in parts per million downfield from internal tetramethylsilane.

[14] The chemical shift for the methyl group in 1-methylbiphenylene is reported to be 2.16 ppm: J. F. W. McOmie, private communication.

[15] The proximity of the fluorine in **2** is reflected in the unusually low-field absorption of the methyl protons.

[16] The previously observed largest $^{6}J_{\mathrm{HF}}$ appears to be 3.8 Hz.[2h]

[17] The proton–fluorine closest approach distance as measured with Dreiding models.

[18] A through-bond contribution is expected to be small in any event: $|^{6}J_{\mathrm{CH_3,F}}|$ in *p*-fluorotoluene is 0.9 Hz; R. E. Richards and T. Schaefer, *Trans. Faraday Soc.*, **54**, 1447 (1958).

[19] The observed splitting is field independent: $|^{6}J_{\mathrm{CH_3,F}}|$ = 7.3 Hz at 100 MHz ($CDCl_3$) for **3**.

[20] All new isolated compounds gave satisfactory combustion analyses and/or mass spectra, and all new compounds exhibited nmr and infrared spectra in accord with their assigned structures.

[21] (a) Address correspondence to this author. (b) Recipient of a National Heart Institute Undergraduate Research Fellowship, 1969–1970, administered by the Dartmouth Medical School.

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Silver(I) Ion Catalyzed Rearrangements of Strained σ Bonds. II. Application to the Synthesis of Semibullvalene[1]

Sir:

Recent developments have given evidence that molecules endowed with highly strained σ bonds can interact sufficiently strongly with certain metallic reagents to experience skeletal rearrangements not directly available to them under ordinary conditions because of orbital symmetry restrictions. Of the various agents known to effect such valence isomerizations, silver(I) ion is rapidly emerging as a unique catalyst, in the sense that interaction of its atomic orbitals with a given set of σ bonds apparently leads to concerted bond rearrangements.[1–3] In contrast, rhodium-on-carbon and coordination complexes of rhodium seem to promote isomerizations by way of nonconcerted carbon–carbon bond insertion mechanisms.[4] We wish now to describe an extension of our earlier work on silver(I) ion catalyzed rearrangements of 1,1′-bishomocubyl systems[1] to the synthesis of semi-

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[1] Part I: L. A. Paquette and J. C. Stowell, *J. Amer. Chem. Soc.*, **92**, 2584 (1970).

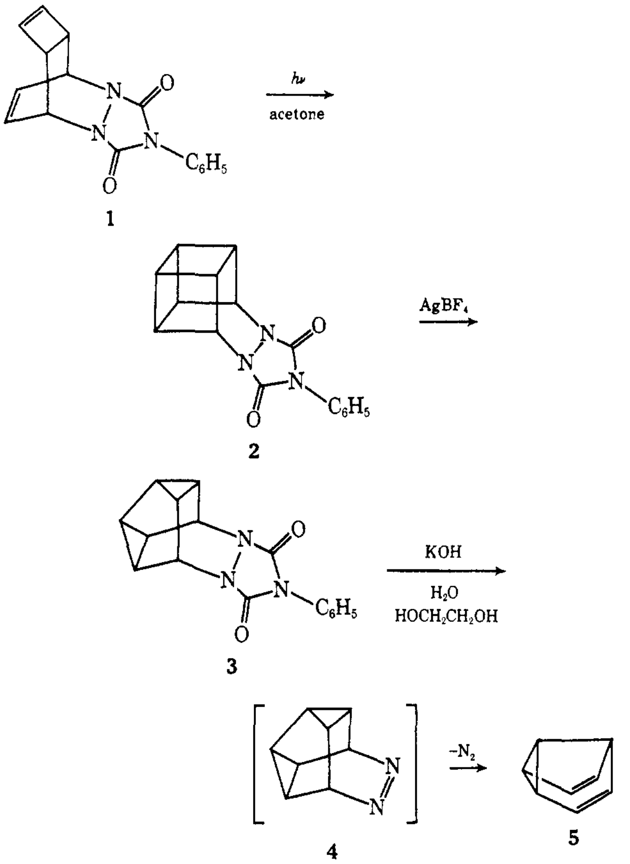
[2] (a) L. A. Paquette and G. R. Allen, Jr., unpublished observations; (b) W. G. Dauben, M. G. Buzzolini, C. H. Schallhorn, D. L. Whalen, and K. J. Palmer, *Tetrahedron Lett.*, 787 (1970); (c) footnote 24a of ref 4a.

[3] For theoretical discussions of this point, see (a) F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, **89**, 2484 (1967); (b) R. Pettit, H. Sugahara, J. Wristers, and W. Merk, *Discuss. Faraday Soc.*, **47**, 71 (1969); (c) F. D. Mango, *Advan. Catal.*, **19**, 291 (1969).

[4] (a) L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, **92**, 3515 (1970); (b) T. J. Katz and S. Cerefice, *ibid.*, **91**, 2405, 6519 (1969); (c) H. Hogeveen and H. C. Volger, *ibid.*, **89**, 2486 (1967); (d) H. Hogeveen and H. C. Volger, *Chem. Commun.*, 1133 (1967); (e) H. C. Volger and H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, **86**, 830 (1967).

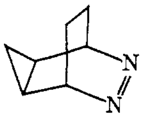
bullvalene (**5**). The relative simplicity of the overall sequence now makes this interesting, though heretofore somewhat elusive,[5] hydrocarbon readily available in gram quantities.

Acetone-sensitized photocyclization of the readily available *N*-phenylurazole diene **1**[6] resulted in smooth conversion to 4-phenyl-2,4,6-triazahexacyclo[5.4.2.$0^{2,6}$.$0^{8,11}$.$0^{9,13}$.$0^{10,12}$]tridecane-3,5-dione (**2**),[7] mp 193–194°, in 85% yield. The characterization of **2** is based on its nmr spectrum in $CDCl_3$ which consists of a multiplet (5 H) centered at δ 7.45, a septet (2 H) at 5.08, and quintets at 3.78 (4 H) and 3.20 (2 H). Exposure of dilute chloroform solutions of **2** to silver fluoroborate at room temperature resulted in a very slow $_{\sigma}2_a + {}_{\sigma}2_a$ transposition.[1] However, after refluxing for 5–7 days with intermittent introduction of small additional quantities of $AgBF_4$, followed by removal of the silver salts by filtration through silica gel, and recrystallization from ethanol, **3** was consistently isolated in 80% yield.[8] The gross structure of **3**, mp 183–184°, was established on the basis of its elemental analysis [calcd for $C_{16}H_{13}N_3O_2$: C, 68.80; H, 4.69; N, 15.05. Found: C, 68.75; H, 4.69; N, 15.06] and nmr spectrum in $CDCl_3$: δ 7.48 (m, 5 H), 5.12 (m, 2 H), and 2.05 (m, 6 H).



To continue the route to hydrocarbon **5**, **3** was treated with excess potassium hydroxide in aqueous ethylene glycol at ~100°, during which time the vessel was constantly purged with dry, oxygen-free[9] nitrogen. In this way, the ethylene glycol could be partially removed by distillation without concomitant oxidation and loss of the liberated hydrazo compound. Careful extraction of the resultant solution with methylene chloride and mild air oxidation afforded semibullvalene, bp 60–62° (50 mm), as the sole volatile product in 65–70% yield. The structure of **5** was established by comparison of its infrared and nmr spectra with published data.[5a]

The instability of presumed azo intermediate **4** with respect to semibullvalene and nitrogen is not unexpected. This highly symmetrical molecule is clearly more strained than **6** which is known to be 10^{17} times more reactive than **7** in its decomposition with loss of nitrogen.[10] In addition, **4** is so constructed that the nitrogen molecule must depart in a direction anti to the fragmenting σ bond of one of the cyclopropane rings, a stereoelectronic condition which is particularly favorable for the operation of the concerted retrograde homo Diels–Alder mechanism.[11] In fact, the alignment of the σ electrons taking part in the $_{\sigma}2_s + {}_{\sigma}2_s + {}_{\sigma}2_s$ bond reorganization approximates very closely what may be considered the "ideal geometry."[12]



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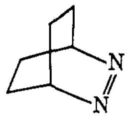
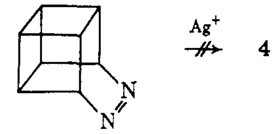


7

Attempts to rearrange 7,8-diazapentacyclo[4.2.2.$0^{2,5}$.$0^{3,9}$.$0^{4,10}$]dec-7-ene (**8**)[7,13] directly to **4** with silver ion have not been successful. Rather, **8** rapidly affords dark purple solutions when exposed to $AgBF_4$. The possibility of isolating **4** under alternative mild conditions continues under investigation.



The utilization of substituted cyclooctatetraenes[14] at the outset of the synthetic sequence outlined herein should permit ready access to a wide spectrum of semibullvalene derivatives.[15] Exploration of this in-

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[5] Semibullvalene has previously been prepared from: (a) barrelene, H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *J. Amer. Chem. Soc.*, **91**, 3316 (1969); (b) tricyclo[3.3.0.$0^{2,6}$]octa-3,7-diene, J. Meinwald and D. Schmidt, *ibid.*, **91**, 5877 (1969) and H. E. Zimmerman, J. D. Robbins, and J. Schantl, *ibid.*, **91**, 5878 (1969); and (c) cyclooctatetraene, H. E. Zimmerman and H. Iwamura, *ibid.*, **92**, 2015 (1970).

[6] D. G. Farnum and J. P. Snyder, *Tetrahedron Lett.*, 3861 (1965).

[7] J. P. Snyder, Ph.D. Thesis, Cornell University, Ithaca, N. Y., 1965; *Dissert. Abstr.*, **26**, 5728 (1966). We thank Professor Farnum for making available to us the details of the synthesis of **2** in advance of publication.

[8] In the absence of silver(I) ion, **2** is completely stable in refluxing chloroform.

[9] A zinc amalgam–sodium metavanadate–4 *N* sulfuric acid scrubber was employed.

[10] E. L. Allred and J. C. Hinshaw, *Chem. Commun.*, 1021 (1969). See also, M. Martin and W. R. Roth, *Chem. Ber.*, **102**, 811 (1969).

[11] J. A. Berson and S. Olin, *J. Amer. Chem. Soc.*, **91**, 777 (1969).

[12] A further manifestation of this structural feature is revealed in the high solvolytic reactivity of the closely related 9-pentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonane *p*-nitrobenzoate molecule [R. M. Coates and J. L. Kirkpatrick, *ibid.*, **90**, 4162 (1968)].

[13] We wish to thank Professor Farnum for a gift of this material during the early phases of this work.

[14] The author wishes to acknowledge the generosity of Badische Anilin und Soda Fabrik in providing him with a supply of cyclooctatetraene required for this investigation.

[15] Full experimental details of this semibullvalene synthesis may be obtained in advance of our full paper on this subject by writing directly to the author.

triguing possibility is in progress and will be reported separately.

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A New β-Keto Ester Synthesis. The Triethyloxonium Ion Catalyzed Homologation of Ketones with Diazoacetic Esters

Sir:

We have discovered a novel technique for the one-carbon homologation of ketones, which should have broad synthetic utility in view of its experimental simplicity and generally high yields. The new reaction involves the insertion of a carbalkoxymethylene group from an alkyl diazoacetate into a carbonyl–alkyl or –aryl bond under the catalytic influence of triethyloxonium fluoroborate.[1]

Cyclohexanone does not react with ethyl diazoacetate in methylene chloride solution in the absence of Lewis acid catalysts. Furthermore, we have found that there is no discernible reaction between these individual components and triethyloxonium fluoroborate in this solvent (at 0°). However, when these three substances are combined in methylene chloride at 0–25°, rapid evolution of nitrogen is noted, and after its cessation a high yield of 2-carbethoxycycloheptanone may be obtained by quenching with aqueous bicarbonate solution followed by simple extraction. Generally, the only identifiable by-product (0–5%) is the glycidic ester derived from the ketone and the diazoacetate.

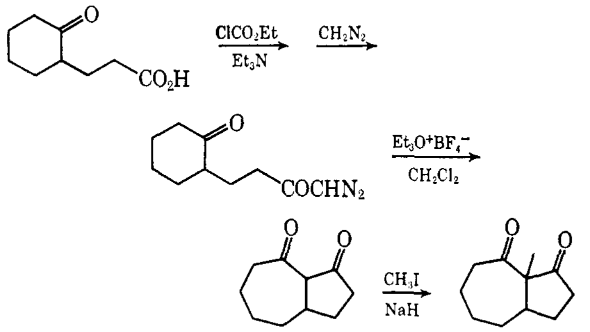
A model experimental procedure for the reaction is appended to this report. With respect to the scope of this technique the following points are pertinent. (1) Yields are uniformly high (Table I). (2) Since the rate-determining step has been shown to involve alkylation of the ketone, selectivity may be anticipated depending upon the environment of the carbonyl group. (3) Since the triethyloxonium fluoroborate is a true catalyst (and does not otherwise enter into the reaction), massive amounts may be used to force unfavorable cases. (4) Further control may be exercised by manipulation of temperature; the reaction has been observed to proceed at as low as −20° and in refluxing methylene chloride (40°). (5) The homologation stops after the introduction of one carbethoxy group; no biscarbethoxy ketone is formed. (6) The carbethoxy group may be removed by hydrolysis and decarboxylation; in view of the high yields, it is feasible to build large size rings by sequential expansion from more readily accessible medium ring ketones. (7) The β-keto ester product is highly suitable for further functionalization (*e.g.*, alkylation) prior to removal of the carbethoxy group. (8) Examination of migratory aptitudes in the homologation step is at a preliminary stage; however, there does not appear to be great discrimination between possible products in unsymmetrical ketones. (9) The technique appears to be extendible to other diazo compounds; we have prepared 2-cyanocycloheptanone in 58% yield from cyclohexanone and diazoacetonitrile.

Table I. Ketone Homologations with Ethyl Diazoacetate and Triethyloxonium Fluoroborate[a]

Cyclohexanone → 2-carbethoxycycloheptanone	90%[b]
Cycloheptanone → 2-carbethoxycyclooctanone	81%
Cyclooctanone → 2-carbethoxycyclononanone	73%[c]
Acetone → ethyl 2-methylacetylacetate	78%
3-Pentanone → ethyl 2-ethylpropionylacetate	86%
Acetophenone → ethyl 2-phenylacetylacetate	74%
+ ethyl 2-methylbenzoylacetate	6%

[a] Standard procedure similar to that found optimal for cyclohexanone. [b] Typical yield of distilled material may contain 0–5% of glycidic ester and diethyl diglycolate; however, it has independently been established that there was an 8% loss of product upon distillation—yields of this and the other equally unstable keto esters may be adjusted upwards accordingly. [c] Contaminated with unknown by-products.

Whereas analogous expansion does not seem to occur in satisfactory fashion with simple diazo ketones (diazoacetone in place of ethyl diazoacetate), we have found that the intramolecular counterpart constitutes an especially promising synthetic route to polycyclic diketones. Conversion of (2-oxocyclohexane)propionic acid to the corresponding diazo ketone,[2] followed by treatment with triethyloxonium fluoroborate, gave apparently complete conversion to the novel diketone[3] shown (eq 1). The product was characterized by methylation (to give a diketone[3] clearly containing five- and seven-membered ring carbonyls, λ_{max} 5.72 and 5.91 μ, respectively) and by basic cleavage to (3-oxocycloheptane)propionic acid.[4] Clearly this method, which combines annelation with ring expansion and produces an intermediate highly suitable for further manipulation, has great potential in organic synthesis for the construction of elaborate polycyclic ring systems.



(1)

2-Carbethoxycycloheptanone. A solution of 4.9 g (0.05 mol) of cyclohexanone in 150 ml of methylene

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[1] In fact, our procedure is a variant of that reported by W. T. Tai and E. W. Warnhoff (*Can. J. Chem.*, **42**, 1333 (1964)), in which the same reaction is catalyzed by boron trifluoride etherate. The new technique is superior from the point of view of yield (Warnhoff's procedure, which we have found unsuccessful in some cases, was reported as giving 38% conversion of cyclohexanone to 2-carbethoxycycloheptanone *vs.* our >90% yield with complete conversion) and other experimental factors as subsequently discussed.

[2] It appears to be necessary to use the mixed anhydride method: D. S. Tarbell and J. A. Price, *J. Org. Chem.*, **22**, 245 (1957); T. L. Burkoth, *Tetrahedron Lett.*, 5049 (1969); D. Hodson, G. Holt, and D. K. Wall, *J. Chem. Soc. C*, 971 (1970).

[3] Carbon and hydrogen analyses within 0.3% of theoretical values have been obtained.

[4] This represents an otherwise not readily accessible type of keto acid. It was characterized by Wolff–Kishner reduction to cycloheptanepropionic acid, to which comparison was made with authentic material (amide, mp and mmp 81.5–82.5°). Similarly, it was shown that (3-oxocyclopentane)valeric acid was absent (<0.5%) in the hydrolysate of the diketone.