71750-30-6; *N,N*-dimethyl-*N'*-*tert*-butylsulfamide, 71750-31-7; *tert*-butylamine, 75-64-9; *N,N*-dimethylsulfamoyl chloride, 13360-57-1; *N*-*tert*-butoxy-*p*-nitrobenzenesulfonamide, 71750-32-8; *N,N*-dimethyl-*N*-*tert*-butoxysulfamide, 71750-33-9; *O*-*tert*-butylhydroxylamine hydrochloride, 39684-28-1; *p*-toluenesulfonyl chloride, 98-59-9; *N*-*tert*-butoxymethanesulfonamide, 71750-34-0; *N*-*tert*-butoxyhydroxylamine, 71750-35-1; 2,6-dimethyl-4-*tert*-butylbenzenesulfonyl chloride, 70823-04-0.

Electrochemical Generation of the Azo Linkage. Synthesis of Bicyclic Azo Compounds, Precursors of 1,3-Diyls

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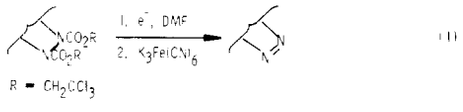
In conjunction with our efforts to utilize cyclopenta-1,3-diyls (e.g., **1**; see Scheme I) as useful intermediates for the synthesis of linearly fused tricyclopentanoids (e.g., hirsutene, hirsutic acid, the coriolins, capnellane), bicyclo[5.3.0]decanes (e.g., damsin, the mexicanins, helenalin, etc.), and modified prostaglandins,[1] we required a route to bicyclic azo compounds (e.g., **2**) subject to the following conditions: (1) reactions leading to **2** must be conducted at or below room temperature to avoid or at least minimize thermal decomposition of the product; (2) the reagents, reaction conditions, and byproducts must be compatible with the survival of the C_7–C_8 π system for a variety of different substituents A and B; (3) the sequence should bypass the formation of hydrazo compounds since they are often unstable. Furthermore, the conditions used to effect their conversion to azo compounds are often incompatible with the survival of the product; (4) the sequence must (obviously) be efficient.

Table I displays several routes for the conversion of dicarbamates to azo compounds along with comments regarding specific disadvantages of these methods especially in relation to the synthesis of compounds such as **2** for a variety of substituents A and B.

In this paper we describe a new electrochemical method for the synthesis of azo compounds which fulfills the conditions described above. The method, illustrated in eq 1, utilizes a controlled-potential reductive cleavage of a



(1)

bis(2,2,2-trichloroethyl) dicarbamate followed by oxidation using aqueous potassium ferricyanide at 0 °C. Undoubtedly, the ferricyanide oxidation could be replaced by an electrochemical oxidation, but, considering the convenience and efficiency of the present procedure, we see no compelling reason to do so.

Scheme I

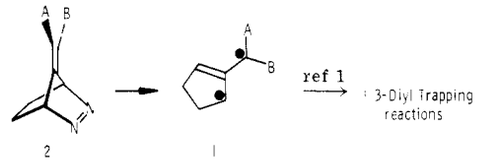
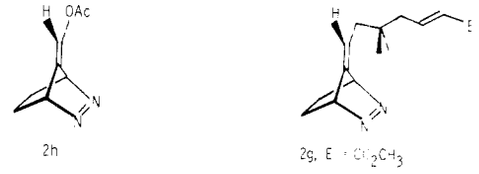


Table II summarizes our results. The reduction potentials were determined by using cyclic voltammetry and are reported vs. a silver–silver chloride reference electrode in DMF with 0.1 N lithium perchlorate as the supporting electrolyte. The choice of a silver–silver chloride rather than a calomel (SCE) reference electrode was suggested by the well-established problems of using an aqueous calomel electrode in a nonaqueous solvent.[8] While there are several ways to obviate these problems,[9] we decided to opt for the silver–silver chloride electrode since it is known to be compatible with a number of organic solvents.[10] (For comparison, one might wish to note that E = −0.045 V vs. SCE for Ag/AgCl(s), KCl(s).)[11]

Two entries deserve special comment. Entry **3h** illustrates the synthesis of a bicyclic azo compound which we have been unable to synthesize by using any other method. An obvious limitation upon any method which might be used to synthesize **2h** is the acid and base sensitivity of



the enol acetate group along with the propensity of C_7 to become sp^3 rather than sp^2 hybridized. Thus, the result is significant even though the yield for the formation of **2h** is only a modest 40–50%. Entry **3g** illustrates that use of the method in an instance where there is more than one readily reduced functional group. In this case, reductive cleavage of the trichloroethyl group occurs in preference to the reduction of the α,β-unsaturated ester unit.[12] This result was anticipated on the basis of the results of cyclic voltammetry studies. Presumably, if required, even greater selectivity could be achieved through the use of a tribromo- rather than a (trichloroethoxy)carbonyl group.[13]

Experimental Section

^{1}H NMR spectra were obtained by using a Varian T-60 spectrometer. The spectral data are reported in δ relative to $(CH_3)_4Si$ as an internal standard with $CDCl_3$ as the solvent. The dicarbamates were prepared by using a Diels–Alder reaction of the appropriate fulvene and bis(2,2,2-trichloroethyl) azodicarboxylate followed by selective monohydrogenation at atmospheric pressure by using 10% Pd/C as the catalyst or, in the case of **3a**, by

(1) Tricyclopentanoids, see: (a) Little, R. D.; Bukhari, A.; Venegas, M. G. *Tetrahedron Lett.* **1979**, 305–8. (b) Venegas, M. G.; Little, R. D. *Ibid.* **1979**, 309–12. (c) Little, R. D.; Muller, G. W. *J. Am. Chem. Soc.* **1979**, in press. Bicyclo[5.3.0]decanes and modified prostaglandins, unpublished results of L. Dang and L. Brown, respectively.

(2) For examples, see inter alia: (a) Gassman, P. G.; Mansfield, K. H. *Org. Synth.* **1969**, *49*, 1. (b) Berson, J. A.; Bushby, R. J.; McBride, J. M.; Tremelling, M. J. *J. Am. Chem. Soc.* **1971**, *93*, 1544. (c) Zimmerman, H. E.; Boettcher, R. J.; Buehler, N. E.; Keck, G. E.; Steinmetz, M. G. *Ibid.* **1976**, *98*, 7680.

(3) Wildi, E. A.; Carpenter, B. K. *Tetrahedron Lett.* **1978**, 2469.

(4) Little, R. D.; Venegas, M. G. *J. Org. Chem.* **1978**, *43*, 2921–3.

(5) Heyman, M. A.; Snyder, J. P. *Tetrahedron Lett.* **1973**, 2859.

(6) Masamune, S.; Nakamura, N.; Spadara, J. *J. Am. Chem. Soc.* **1975**, *97*, 918.

(7) For example, see: Semmelhack, M. F.; Foos, J. S.; Katz, S. *J. Am. Chem. Soc.* **1973**, *95*, 7325.

(8) Lund, H.; Iversen, P. *Org. Electrochem.* **1973**, 204–8.

(9) For example, see ref 8 and: Coetzee, J. F.; Padmanabhan, J. R. *J. Phys. Chem.* **1962**, *66*, 1708.

(10) See ref 8 and: Synnott, J. C.; Butler, J. N. *Anal. Chem.* **1969**, *41*, 1890.

(11) See p 207 of ref 8.

(12) Baizer has extensively studied the electrochemistry of α,β-unsaturated esters and nitriles. For example, see: (a) Wagenknecht, J. H.; Baizer, M. M. *J. Org. Chem.* **1966**, *31*, 3885. (b) Anderson, J. D.; Baizer, M. M.; Petrovich, J. P. *Ibid.* **1966**, *31*, 3890. (c) Petrovich, J. P.; Anderson, J. D.; Baizer, M. M. *Ibid.* **1966**, *31*, 3897.

(13) The preparation of bis(2,2,2-trichloroethyl) azodicarboxylate is described in: Little, R. D.; Venegas, M. G. *Org. Synth.*, in press.

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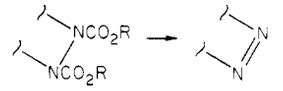
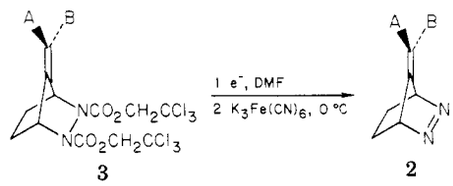
Table I. Comparison of Methods for the Synthesis of Bicyclic Azo Compounds from Dicarbamates



entry	ref	R	method	comments
1	2	C_2H_5	^-OH, ROH, Δ	utilizes elevated temperatures and ^-OH; generates a hydrazo compound
2a	2	CH_3	^-OH, ROH, Δ	same as above
2b	3	CH_3	12 equiv of KO-*t*-Bu and 2 equiv of H_2O	utilizes a large excess of a strong base; generates ^-OH; scale up is inconvenient due to the large excess of reagents required; generates a hydrazo compound
2c	4	CH_3	(a) CH_3SLi, HMPA; (b) $K_3Fe(CN)_6$, H_2O	in some cases, RS^- attacks at C_8, leading to cleavage of the C_1-N_2 bond (S_N2'); the byproduct (Me_2S) stinks; HMPA was used
3	5	CH_2Ph	H_2, catalyst	in some cases, hydrogenolysis and hydrogenation of the C_7-C_8 π bond occur at comparable rates
4	6	C_2H_4Ts	DBN or DBU	this is a very mild, efficient procedure; however, preparation of $TsCH_2CH_2O_2CN{=}NCO_2CH_2CH_2Ts$, used in the preparation of the dicarbamates, utilizes phosgene and chloroethanol
5a	7	CH_2CCl_3	Zn or Zn(Cu)	the byproduct is a Lewis acid ($ZnCl_2$), and in several cases, the C_7-C_8 π bond is attacked and destroyed despite attempts to scavenge the $ZnCl_2$
5b		CH_2CCl_3	(a) e^-, DMF, $LiClO_4$; (b) $K_3Fe(CN)_6$	see text

Table II. Electrochemical Generation of Bicyclic Azo Compounds



3 2

entry	A	B	potential,[d] V	yield, %
3a	H	CH_3	−1.80	92[a]
3b	CH_3	CH_3	−1.70	95[a]
3c	$(CH_2)_5$		−1.75	91[a]
3d	*p*-$CH_3OC_6H_4$	H	−1.75	97[b]
3e	Ph	Ph	−1.75	99[b]
3f	$C_7{=}C(AB)$ replaced by CHC_2H_5		−1.75	97[a]
3g	(*E*)-$CH_2C(CH_3)_2CH_2CH{=}CHCO_2CH_3$	H	−1.75	50[a]
3h	H	$OCOCH_3$	−1.70	40–50[b,c]

[a] Isolated yield. [b] NMR yield. [c] The product is acid, base, and heat sensitive. [d] The potential is referenced to a silver–silver chloride reference electrode.[11]

hydrogenation with diimide. With the exception of compounds **2a,g,h**, each of the products are known compounds.[4]

Voltammetry. A standard H-cell fitted with a nitrogen-inlet tube and a fine-grade glass frit was filled with DMF containing 0.1 N lithium perchlorate. In one half of the cell, a glass J-tube containing mercury served as the cathode while a platinum wire served as the anode. In the other half of the cell was placed a silver–silver chloride reference electrode. The appropriate dicarbamate was dissolved in enough DMF to achieve a 1.0 mM concentration, and the resulting solution was degassed prior to but not during the voltammogram. For each compound examined, a voltammogram characteristic of an irreversible reduction was obtained over the range 0 to −1.95 V. The potential used for the preparative runs was determined from the voltammogram by noting the voltage at the current maximum and then using a slightly (ca. 0.1 V) more negative potential.

General Procedure for Preparative-Scale Runs. Mercury (ca. 30 mL) was added to the main compartment of the preparative-scale apparatus through a three-way T-stopcock (Teflon) located at the base of the cell. To the same compartment was added 150 mL of 0.19 N lithium perchlorate dissolved in DMF. To the other compartment, separated from the first by a 3-cm diameter fine-grade glass frit, were added 20 mL of 0.19 N lithium perchlorate dissolved in DMF and a platinum wire which was situated as close to the glass frit as possible. An electrolyte-filled, inverted U-tube fitted with fine-grade glass frits at each end was used to make electrical contact between the main cell compartment and a silver–silver chloride reference electrode. The dicarbamate (0.1 mmol), dissolved in 5 mL of DMF, was then added, and the resulting solution was degassed for 15 min. The potential was adjusted to −1.70 to −1.80 V, and the solution was stirred by using an overhead stirrer until the current dropped from 185 mA to ca. 5–10 mA (1–2 h). The mercury pool was drained through one bore of the three-way stopcock located at the base of the main compartment, and the reaction mixture was drained through the other bore into a round-bottom flask cooled in an ice bath. (The base of the cell was constructed to slant ca. 5° with respect to the horizontal to facilitate the transfers.) Following the dropwise addition of 3.0 equiv of aqueous ferricyanide, the resulting solution (cooled in an ice bath) was allowed to stir another 5–10 min and was then washed with pH 6 brine, extracted with eight 50-mL portions of either pentane or 1:1 pentane/ether, and rewashed with four 100-mL portions of pH 6 brine. The organic layers were combined, dried ($MgSO_4$), and concentrated in vacuo to afford the azo compounds listed in Table II.

^{1}H NMR Data for 2a,g,h. The ^{1}H NMR data for **2b–f** have been reported previously.[4] Due to their thermal instability, compounds **2a,g,h** were fully characterized as the corresponding dicarbamates rather than as the azo compounds. The ^{1}H NMR data for azo compounds **2a,g,h** show the following: for **2a** δ 5.43 (br s, 1 H, bridgehead), 5.13 (br s, 1 H, bridgehead), 5.16 (q, 1 H, J = 7 Hz, vinyl), 1.67 (d, 3 H, J = 7 Hz, CH_3), 1.13 (m, 4 H, ethano bridge); for **2g** δ 7.01 (dt, 1 H, J = 16, 8 Hz, β-vinyl), 5.87 (dt, 1 H, J = 16, 1 Hz, α-vinyl), 5.40 (br s, 1 H, bridgehead), 5.20

(t, 1 H, J = 8 Hz, C_7=CHR), 5.17 (br s, 1 H, bridgehead), 3.78 (s, 3 H, CO_2CH_3), 2.13 (2 H, γ to ester), 1.90 (d, 2 H, J = 8 Hz, $HC_8CH_2C(CH_3)_2$), 1.2 (m, 4 H, ethano bridge), 0.92 (s, 6 H, $(CH_3)_2C$); for **2h** δ 6.8 (s, 1 H, vinyl), 5.53 (m, 1 H, bridgehead), 5.2 (m, 1 H, bridgehead), 2.13 (s, 3 H, CH_3), 1.7 (br m, 4 H, ethano bridge).

Acknowledgment. We are very grateful to Professor Arthur Hubbard and Dr. Ross Lane of UCSB for sharing with us their expertise in electrochemistry. We also acknowledge the encouragement of Professor Hubbard and Dr. M. Baizer during the early stages of our work. Professor H. Offen (UCSB) gratiously allowed us to use his X-Y recorder for our cyclic voltammetry studies.

This investigation was supported by Grant No. CA21144-02 awarded by the National Cancer Institute, DHEW; we are most grateful for their support.

Registry No. 2a, 71807-24-4; **2b**, 31689-32-4; **2c**, 66322-88-1; **2d**, 70713-02-9; **2e**, 66322-90-5; **2f**, 71807-25-5; **2g**, 71807-26-6; **2h**, 71807-27-7; **3a**, 71807-16-4; **3b**, 71807-17-5; **3c**, 71807-18-6; **3d**, 71807-19-7; **3e**, 71807-20-0; **3f**, 71807-21-1; **3g**, 71807-22-2; **3h**, 71807-23-3.

Decomposition of 5-Aryl-5-(*tert*-butylperoxy)-3,4-diphenyl-2(5*H*)-furanones

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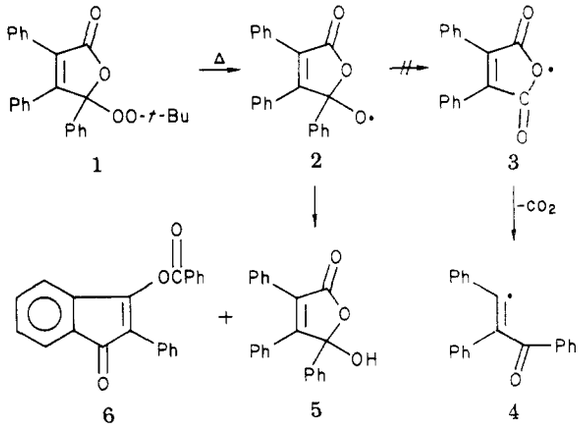
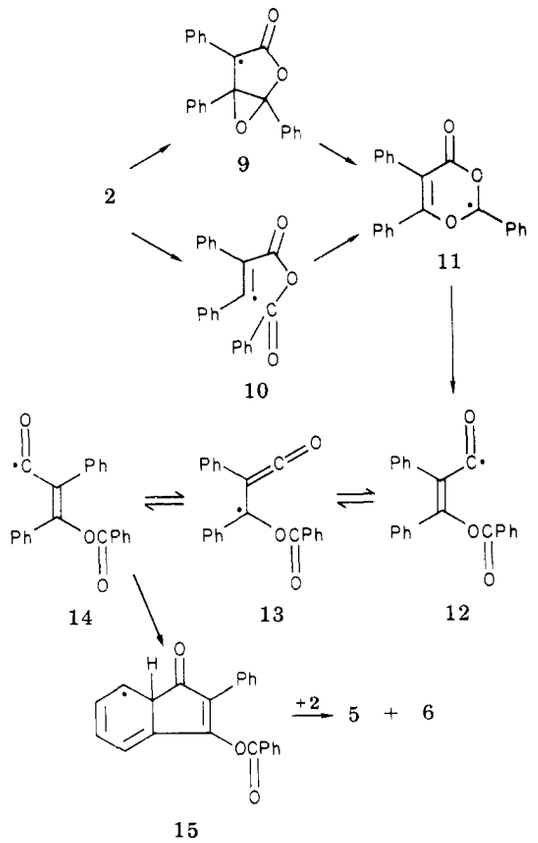
In light of recent interest in γ-lactone systems, namely, Padwa's investigation of migratory aptitude in the photochemical rearrangement of 2(5*H*)-furanone[1] and Tidwell's work on cyclization by radical displacement on ester groups and conversion of acetals to lactones,[2] we wish to report the radical rearrangement of the lactone, 5-(*tert*-butylperoxy)-3,4,5-triphenyl-2(5*H*)-furanone (**1**). In the course of seeking a route to β-aroylvinyl radicals,[3] we presumed that the decomposition of **1** under nitrogen in bromobenzene would lead to the oxy-2(5*H*)-furanone radical **2**. This intermediate might then be expected to open to the carboxy radical **3** and, upon decarboxylation, generate the β-benzoylvinyl radical **4** (see Scheme I). However, when compound **1** was heated, neither β-benzoylvinyl radical nor any product of decarboxylation was detected. Instead, the reaction gave 48% of the reduced 5-hydroxy-3,4,5-triphenyl-2(5*H*)-furanone (**5**) and 42% of rearranged oxidized product, 3-(benzoyloxy)-2-phenyl-1-indenone (**6**).

Scheme I



Scheme II



Results and Discussion

Compound **1** was prepared from the known 5-chloro-3,4,5-triphenyl-2(5*H*)-furanone (**7**), utilizing *tert*-butyl hydroperoxide in pyridine–benzene, a modification of Bartlett and Hiatt's procedure.[4] The stable perester, mp 102.5–104.5 °C, had spectra and an elemental analysis in agreement with its structure. Synthesis of the precursors to **7** was straightforward (see Experimental Section).

The initial reaction conditions for the thermal decomposition of compound **1** involved a 0.01 M solution of **1** in bromobenzene which was degassed and heated in a sealed tube at 110–120 °C for 24 h. The reaction afforded **5** and **6** in approximately equal amounts. Compound **6** was identified by degradation in base to 2-phenyl-1*H*-indene-1,3(3*H*)-dione (**8**) and benzoic acid. Compounds **5**, **6**, and **8** were unequivocally identified by comparison with authentic samples.

A plausible mechanism for the decomposition of **1** is depicted in Scheme II.[5] The oxygen–oxygen bond of peroxide **1** is initially homolyzed to give oxyfuranone radical **2** which could either epoxidize to form radical **9** or ring open to yield vinyl radical **10**. Rearrangement of either **9** or **10** would lead to the six-membered heterocyclic radical **11** which is stabilized by the adjacent phenyl group and oxygen atoms. A fragmentation of radical **11** between the carbonyl–oxygen bond of the ester would lead to

(1) A. Padwa, T. Brookhart, D. Dehm, and G. Wubbels, *J. Am. Chem. Soc.*, **100**, 8247 (1978).
(2) C. Rynard, C. Thankachan, and T. Tidwell, *J. Am. Chem. Soc.*, **101**, 1196 (1979).
(3) James Weinberg, Ph.D. Thesis, University of Connecticut, 1978.
(4) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958).
(5) Of course, subtle variations of some of the steps are also possible.

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