Electroreduction of α,α'-Dibromoketones. 2,4-Dibromo-2,4-dimethyl-3-pentanone

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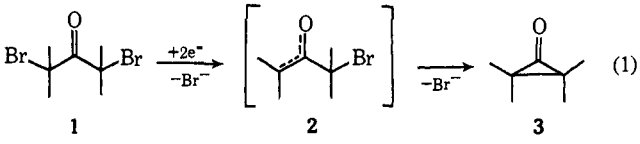
Abstract: Electroreduction of 2,4-dibromo-2,4-dimethyl-3-pentanone proceeds smoothly in polar aprotic solvents with the consumption of 2 Faradays/mol to produce a reactive intermediate, which is stable for a short time at $-32°$, and which reacts with a variety of added nucleophilic reagents. Possible structures for the intermediate are discussed, and the results are interpreted in terms of a zwitterion or an enol allylic bromide intermediate.

Of the various methods available for the closure of 3-carbon rings, the electroreduction of 1,3-dihalides offers an attractive possibility, due to the potential mildness of reaction conditions, and the electrochemical characteristic that many reaction variables remain in the control of the experimenter.[2a] The possibility of electroreductive ring closure was advanced by Zavada[2b] to account for the single polarographic wave observed during the reduction of 1,3-dibromopropane and 1,6-dibromocyclodecane. The suggestion with respect to the former case has received experimental verification by Rifi,[3] who reported the high-yield preparation of several strained cyclic and bicyclic hydrocarbons. The procedure has more recently been extended to the synthesis of cyclopropanol and phenylcyclopropane by Gerdil.[4]

The possibility of adapting 1,3-electroreductive ring closure to the synthesis of cyclopropanones represented an especially challenging objective. Two-electron reduction of α,α'-dihaloketones could lead to an anion which should undergo the electrochemical equivalent of Favorskii ring closure[5] (eq 1). The



(1)

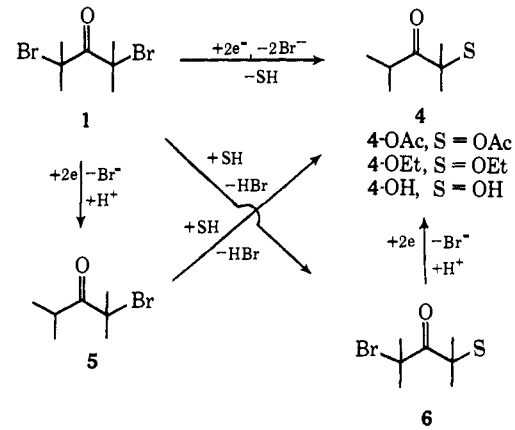
1 2 3

preparation of cyclopropanones[6] and their very high reactivity toward nucleophiles has been demonstrated recently for cyclopropanone,[7] for the 1,1-dimethyl,[8] and for the tetramethyl[9] derivatives. The electroreduction of 2,4-dibromo-2,4-dimethyl-3-pentanone (**1**) was carried out to examine this possible synthesis, and the unexpected result is the topic of this paper.

Results and Discussion

Compound **1** displayed a single polarographic reduction wave, $E_{1/2} = -0.26$ V[10] (CH_3CN, 0.1 *M* $LiClO_4$, dropping Hg cathode), typical of α-bromoketones.[11] Preparative electroreduction of **1** was carried out in a jacketed, divided cell (see Experimental Section), at a stirred mercury cathode, using controlled-potential electrolysis (cpe) or controlled-current electrolysis (cce). All reactions were continuously deoxygenated by a stream of argon, and were carried out using carefully dried dimethylformamide (DMF) or acetonitrile as solvent, with or without added nucleophiles, at several different temperatures, using a variety of supporting electrolytes (see Table I). Cpe of **1** in DMF in the presence of acetic acid–sodium acetate (Table I, entry 1), consumed 2.0 Faradays/mol of **1**, and the catholyte yielded, as the major product, 2-acetoxy-2,4-dimethyl-3-pentanone (**4**-OAc) (Scheme I). The possibility

Scheme I



that simple electroreduction of **1** to **5** had occurred, followed by solvolysis of **5** to **4**-OAc, could be readily excluded by a control experiment in which **5** was shown to be solvolytically unreactive toward acetic acid–sodium acetate under the conditions of the reduction (Table II, entry 1). Moreover, acetolysis of **1** to **6**-OAc, followed by simple electroreduction to **4**-OAc, could be shown not to occur by the reduction of **1** in DMF, which consumed 2.0 Faradays/mol at $-32°$ in the

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(2) (a) A. J. Fry, M. Mitnick, and R. G. Reed, *J. Org. Chem.*, **35**, 1232 (1970); (b) J. Zavada, J. Krupicka, and J. Sicher, *Collect. Czech. Chem. Commun.*, **28**, 1644 (1963).

(3) M. F. Rifi, *J. Amer. Chem. Soc.*, **89**, 4442 (1967); *Tetrahedron Lett.*, 1043 (1969).

(4) R. Gerdil, *Helv. Chim. Acta*, **53**, 2100 (1970).

(5) (a) A. S. Kende, *Org. React.*, **11**, 261 (1960); (b) C. Rappe, *Acta Chem. Scand.*, **20**, 862 (1966).

(6) For a recent review, see N. J. Turro, *Accounts Chem. Res.*, **2**, 25 (1969).

(7) (a) J. M. Pochan, J. E. Baldwin, and W. H. Flygare, *J. Amer. Chem. Soc.*, **90**, 1072 (1968); (b) N. J. Turro and W. B. Hammond, *ibid.*, **88**, 3672 (1966).

(8) W. B. Hammond and N. J. Turro, *ibid.*, **88**, 2880 (1966).

(9) (a) N. J. Turro, P. A. Leermakers, H. R. Wilson, D. C. Neckers, G. W. Byers, and G. F. Vesley, *ibid.*, **87**, 2613 (1965); (b) N. J. Turro, W. B. Hammond, and P. A. Leermakers, *ibid.*, **87**, 2774 (1965); (c) N. J. Turro and W. B. Hammond, *ibid.*, **87**, 3258 (1965); (d) N. J. Turro and W. B. Hammond, *Tetrahedron*, **24**, 6017, 6029 (1968).

(10) All potentials reported in this paper are measured *vs.* a saturated calomel electrode (sce) unless otherwise stated.

(11) P. J. Elving and R. E. Van Atta, *Anal. Chem.*, **27**, 1908 (1955).

Table I. Electroreduction of 2,4-Dibromo-2,4-dimethyl-3-pentanone (**1**)

Entry	Solvent	Electrolyte (concn, *M*)	Potential, $-V$,[a] V	Temp, °C	Trapping agent (vol %)	Product ratios 8	4-OH	4	9	10	Others
1	DMF	NaOAc (0.2)	1.3	14	AcOH (5)		1	5.8			
2	DMF	*n*-Bu_4NBF_4 (0.2)	42[b]	−32	AcOH–NaOAc (30)[c]	0.5	1	17			13
3	CH_3CN	*n*-Bu_4NBF_4 (0.2)	1.0	14	EtOH (1)	0.1	1	7.0			1.0
4	DMF	LiCl (1.0)	0.7	40	H_2O (7.4)	0.1	1				0.05
5	DMF	LiCl (1.0)	1.6	−8	H_2O (5)		1[d]				
6	DMF	$LiClO_4$ (0.2)	27[b]	40	None	40	1				23
7	CH_3CN	$LiClO_4$ (0.4)	0.9	0	None	1.6	1				58
8	CH_3CN	*n*-Bu_4NBF_4 (0.2)	0.9	14	Furan (14)	0.5	1		1	2	0.1
9	DMF	*n*-Bu_4NBF_4 (0.2)	16[b]	−17	None[e]	1					
10	DMF	*n*-Bu_4NBF_4 (0.2)	22[b]	−20	None[f]	1					
11	HMPA	LiCl (0.2)	32[b]	48	None[g]	1					
12	HMPA	LiCl (0.2)	31[b]	43	None[h]	1					

[a] Cpe; all potentials were measured *vs.* sce unless otherwise designated. [b] Cce; applied potential. [c] AcOH–NaOAc was added to the reaction mixture following electrolysis. [d] Only product. [e] This run was carried out under vacuum (3 mm). The cold trap (−190°) contained only DMF. The undistilled residue gave only **8**. [f] The cell contents were distilled at 0° (0.015 mm) into a cold trap (−190°). The results were the same when the cold trap contained AcOH–NaOAc. [g] This experiment was carried out under vacuum (0.5 mm). The cold trap (−190°) contained **8** as the sole product. [h] This run was performed under vacuum (0.7 mm). AcOH–NaOAc was placed in the cold trap (−190°), but **8** was the only product.

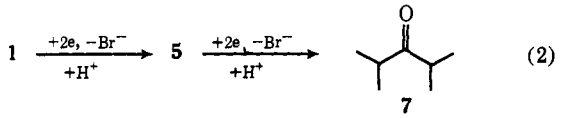
Table II. Experiments with 2-Bromo-2,4-dimethyl-3-pentanone (**5**)

Entry	Solvent	Electrolyte (concn, *M*)	Potential, $-V$,[a] V	Temp, °C	Trapping agent (vol %)	Product ratios 7	4-OH	5
1	DMF	NaOAc (0.2)	*b*	14	AcOH (5)			1[b]
2	CH_3CN	*n*-Bu_4NBF_4 (0.2)	*b*	25	EtOH (1)			1[b]
3	DMF	LiCl (1.0)	1.0	25	H_2O (7.4)	2	1	
4	DMF	LiCl (0.5)	2.1	−5	H_2O (5)	7	1	

[a] Cpe; all potentials were measured *vs.* sce unless otherwise specified. [b] Control run; no current was passed. Recovered starting material **5** was the only product obtained.

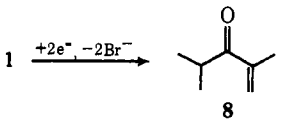
absence of added nucleophile, *followed* by the addition of acetic acid–sodium acetate (Table I, entry 2), a reaction which also yielded **4**-OAc as the major product. This latter experiment provided unequivocal evidence for the presence of an electrochemically produced, reactive species, which was stable at least for a short time at −32°.

When cpe of **1** was carried out using acetonitrile to which ethanol had been added (Table I, entry 3), the catholyte yielded keto ether **4**-OEt as the major product (*ca.* 70%). Monobromide **5** gave no **4**-OEt in a control experiment (Table II, entry 2). Hence, **4**-OEt cannot have arisen from simple reduction followed by solvolysis (**1** → **5** → **4**-OEt). Further evidence that monobromide **5** was not present in significant concentration during the electroreduction of **1** is provided by the observation that 2,4-dimethyl-3-pentanone (**7**) was either absent, or present in trace amounts, from the reduction of **1**, whereas reduction of **5** under similar conditions always yielded **7** as the principal or exclusive product, even when nucleophilic species such as ethanol or water were present during the reduction (eq 2).



(2)

The cpe of **1** in DMF to which water had been added provided a somewhat more complex, but nevertheless useful, third example of nucleophilic addition to the reactive intermediate. The cpe of **1** in DMF–H_2O at 40° gave **4**-OH and 2,4-dimethylpent-1-en-3-one (**8**) (eq 3) in the ratio of 6.1:1, but *no* 2,4-dimethyl-3-pentanone (**7**) (Table I, entry 4), whereas the same reaction at −8° gave **4**-OH and **8** in the ratio of 20:1 (Table I, entry 5), also without the formation of **7**. Cpe of monobromide **5** under the same conditions, but at 25°, produced **4**-OH and 2,4-dimethyl-3-pentanone (**7**) in the ratio of 0.5:1, but *no* 2,4-dimethylpent-1-en-3-one (**8**) (Table II, entry 3). Similarly, **5**, reduced at −5°, gave **4**-OH and **7** in the ratio 0.14:1. Keto alcohol **4**-OH was clearly a solvolysis product in the reaction of monobromide **5**, and its formation could be greatly suppressed by lowering the temperature. However, lower temperature in the reduction of **1** did not similarly suppress the formation of **4**-OH and produce **7**. Indeed, the absence of **7** in the dibromide reductions and the absence of **8** in the monobromide reductions lends credence to the postulate that monobromide **5** is not an important intermediate in the reduction of dibromide **1**.

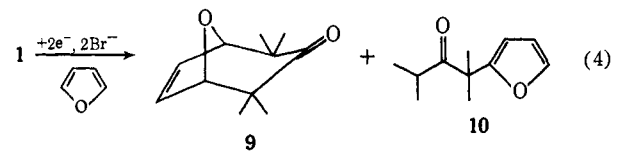


(3)

In the absence of a deliberately added proton source, the electroreduction of **1** in DMF or acetonitrile led to a complex mixture of products, mostly high boiling, which invariably contained **8** and **4**-OH (Table I, entries 6 and 7). Adventitious water was always present in sufficient amount to account for the formation of **4**-OH. The exact composition of product mixtures was difficult to reproduce within a series of experiments, indicating a strong sensitivity of the reaction course to environmental factors.

When dibromide **1** was reduced in acetonitrile in the

presence of furan, the principal products, besides some **8** and **4**, were adducts **9** and **10** (eq 4) (Table I, entry 8).

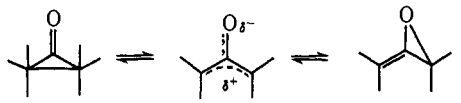


9 10 (4)

Cycloadduct **9** had been previously reported by Cookson[12a] and Richey[12b] as the product of tetramethylcyclopropanone (**3**) and furan, and the rate of this reaction was examined in detail by Turro.[13] However, the open-chain adduct **10** had not been previously described as a product of **3** with furan.[14]

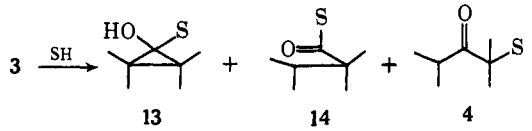
Several experiments directed toward isolation or external trapping of the reactive intermediate were without success. The cce of **1** was conducted in DMF at −17° in a cell fitted with a cold trap (−190°) while the cell was evacuated (3 mm), until 2.0 Faradays/mol of **1** had passed (Table I, entry 9). The cold trap contained only DMF, and the undistilled residue, after standing at room temperature overnight, gave an excellent yield of enone **8**. When a similar cce of **1** was carried out in DMF at −20°, and the contents of the cell were transferred to a high-vacuum line and partly distilled at 0° (0.015 mm), the only volatile product found was enone **8**, in DMF solution (Table I, entry 10), even when the volatile product was distilled into a cold trap (−190°) containing acetic acid–sodium acetate. Hence, no volatile reactive species had escaped the cell. This conclusion was reinforced by two further reductions, using hexamethylphosphoramide (HMPA) as solvent, run at 48 and 43°, respectively (Table I, entries 11 and 12). Cce of **1** *in vacuo* (0.5 mm) in these cases gave only enone **8** in the cold trap, even when the cold trap contained acetic acid–sodium acetate.

While the experiments described here provide clear evidence for a two-electron reduction process which produces a reactive intermediate, data regarding the nature of the intermediate are ambiguous. Isomeric structures **3**, **11**, and **12** (eq 5) could all reasonably arise from



3 11 12 (5)

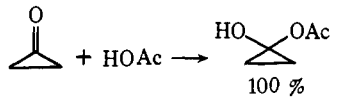
anion **2**, but none of these intermediates alone can adequately explain the array of products observed. It was noted earlier by Turro[6,9a] and Crandall[15] that the possible equilibrium between the cyclopropanone (**3**), the oxyallyl zwitterion[16] (**11**), and the allene oxide (**12**) introduced uncertainty into assigning structures to such intermediates from product analysis only. Whereas nucleophilic attack on cyclopropanones leads to both ring-closed and ring-opened products,[6] formation of products of structures **13** and **14** predominates in the reactions of **3**[9a,c,17,18] (eq 6). It has been shown that



13 14 4 (6)

3 gives a cycloadduct with furan,[9,13] and undergoes thermal ring opening to give enone **8**.[9a]

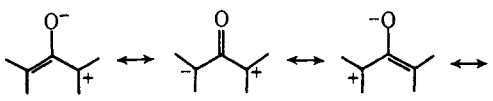
Interception of a cycloadduct from the Favorskii reaction by furan has been reported in yet another case.[19] Yet the absence of products of type **13** and **14** renders unlikely the proposal that a cyclopropanone is intermediate in the present reaction, particularly in view of the report[6] that "little ring opening" occurs when cyclopropanone is treated with acetic acid (eq 7).



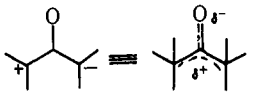
(7)

Crandall[15] proposed allene oxide **12** as the unisolated intermediate in the peracid oxidation of tetramethylallene, a proposal which has received some support in related allenic systems.[20,21] The major product of the reaction carried out in acetic acid was acetoxy ketone **4**-OAc. Allene oxide **12** has also been proposed as the reactive intermediate in the chemical reduction of **1**,[22] a procedure which leads to products of structure **4** when nucleophiles are added to the reaction mixture. Hoffmann was able to distill a DMF solution of **12** at −10° (0.002 mm), and to record its spectral characteristics. Our efforts to isolate **12** from the electroreduction of **1** by a procedure similar to that of Hoffmann's (Table I, entry 10) were unsuccessful. Moreover, enone **8**, a recurring product in the electroreduction of **1**, is conspicuously absent from the products of reactions in which **12** is postulated to be the reactive intermediate. Hence **12**

(16) Contributions to **11** from structures such as i, ii, and iii sub-



i ii iii



iv 11

substantially reduce charge localization (*viz.* **11**), and render plausible the notion that the zwitterion could be an intermediate in polar solution.[9a]

(12) (a) R. C. Cookson, M. J. Nye, and G. Subrahmanyan, *Proc. Chem. Soc.*, 144 (1964); (b) H. G. Richey, Jr., J. M. Richey, and D. C. Clagett, *J. Amer. Chem. Soc.*, **86**, 3906 (1964).

(13) S. S. Edelson and N. J. Turro, *ibid.*, **92**, 2770 (1970).

(14) A third major product, of undetermined structure, could be isolated from the furan reaction. It contained no furanyl residue (nmr) and displayed a molecular formula $C_{14}H_{26}O_2$, from the parent peak of the mass spectrum. The nmr spectrum was not consistent with the simple reductive coupling product of **5** as the structure of this compound, and the molecular formula precludes that it is a simple dimer of $C_7H_{12}O$.

(15) (a) J. K. Crandall and W. H. Machleder, *Tetrahedron Lett.*, 6037 (1966); (b) J. K. Crandall and W. H. Machleder, *J. Amer. Chem. Soc.*, **90**, 7292 (1968).

(17) (a) N. J. Turro, W. B. Hammond, P. A. Leermakers, and H. T. Thomas, *Chem. Ind. (London)*, 990 (1965); (b) N. J. Turro and W. B. Hammond, *J. Amer. Chem. Soc.*, **88**, 3672 (1966).

(18) C. Rappe, L. Knutsson, N. J. Turro, and R. B. Gagosian, *ibid.*, **92**, 2032 (1970).

(19) A. W. Fort, *ibid.*, **84**, 4979 (1962).

(20) (a) J. K. Crandall, W. H. Machleder, and M. J. Thomas, *ibid.*, **90**, 7346 (1968); (b) J. K. Crandall and W. H. Machleder, *ibid.*, **90**, 7347 (1968).

(21) R. L. Camp and F. D. Greene, *ibid.*, **90**, 7349 (1968).

(22) H. M. R. Hoffmann and R. H. Smithers, *Angew. Chem.*, **82**, 43 (1970).

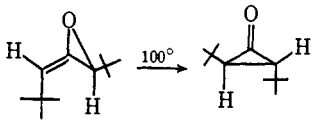
Table III. Electroreduction of 1,3-Dibromoacetone (**20**)

Entry	Solvent	Electrolyte (concn, *M*)	Potential, $-V$, V	Temp, °C	Trapping agent (concn, *M*)	Product ratios **21**	**22**
1	DMF	PhCOONa (0.1)	1.0[a]	14	PhCOOH (0.1)	4.3	1
2	DMF	$LiClO_4$ (0.2)	11[b]	14	None[c]		

[a] Cpe; the potential was measured *vs.* sce. [b] Cce; applied potential. [c] This experiment was performed using vacuum (1 mm). AcOH–NaOAc was placed in the cold trap (−190°), but no addition product of acetic acid was obtained.

is not a reasonable candidate for intermediacy in the present reaction.

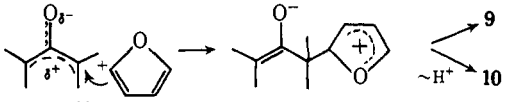
Stable compounds of both the cyclopropanone and allene oxide skeleton have been reported. A highly substituted allene oxide (**15**) has been isolated as the primary product from peracid oxidation of 1,3-di-*tert*-butylallene and was shown[21] to undergo thermal isomerization to *trans*-2,3-di-*tert*-butylcyclopropanone (**16**)[23a] (eq 8).



15 **16** (8)

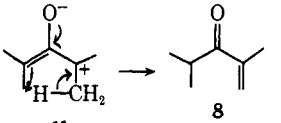
It is reasonable to speculate that the zwitterionic oxyallyl intermediate, **11**, could play a major product-determining role. Greene and coworkers[23b] have postulated an oxyallyl zwitterion as the most attractive intermediate for the racemization of **16**.

Reactions of **11** with nucleophiles should lead to products of structure **4** rather than **13** or **14**. A reasonable polar mechanism for the formation of furan adducts **9** and **10** can be advanced (eq 9). Bipolar intermediate



11 **17** (9)

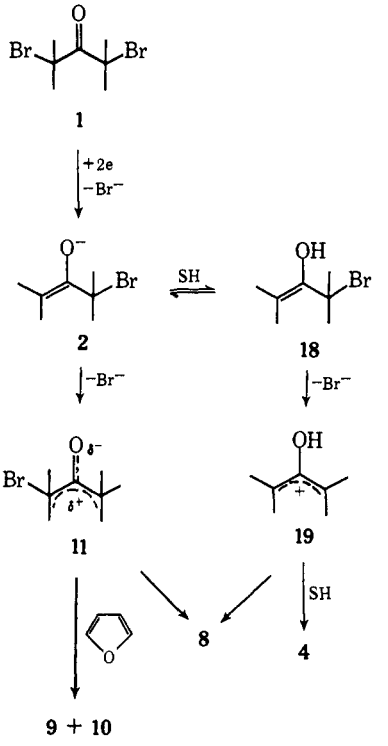
17, formed by electrophilic attack of **11** on furan, could be a common precursor to **9** (by ring closure) and **10** (by proton transfer). The formation of enone **8** may be viewed as a base-catalyzed elimination reaction (*e.g.*, eq 10).



11 **8** (10)

Perhaps the most instructive mechanistic analogy can be drawn from recent work of Bordwell and Carlson,[24] in which they examined the effect of structural change in the α position of halo ketones on the mechanism of the Favorskii rearrangement. Their results were convincingly rationalized by assuming that products arose from *both* the enolate bromide and its conjugate acid, the enol allylic bromide, which were in equilibrium in protic medium. Applied to the present system, such an interpretation would take the form of Scheme II. In aprotic medium enolate bromide **2** would lose bromide

Scheme II



ion to produce zwitterion **11**, as previously postulated. This dipolar ion would be precursor to both the furan adducts and enone **8**. In protic medium, enol allylic bromide **18** would surely predominate in equilibrium, and might proceed, *via* hydroxyalkyl cation **19** to the products of elimination (**8**) or substitution (**4**).[25]

In the examples of Bordwell and Carlson, low base concentration favored the formation of products of structure **4**, while high base concentration favored the normal Favorskii product, thus suggesting the role of equilibrium **2** ⇌ **18** in product determination. It should be noted, however, that elimination products analogous to **8** were not reported by Bordwell and Carlson, although it appears that such would have been detected by the methods used, had they been present.

Intermediates **11** or **19**, highly solvated in DMF which contains dissociated salts, would not be expected to distil readily from the reaction mixture, thus rationalizing the failure to isolate the reactive intermediate by high-vacuum techniques. Efforts to conduct the reaction in DMF at low temperatures (−35 to −10°) and to examine the cell contents directly by nmr were inconclusive, revealing starting material and enone **8** as the only identifiable peaks upfield of the DMF resonance signal.

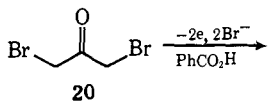
Experiments conducted using 1,3-dibromoacetone (**20**) as the substrate revealed that SN2 displacement played a complicating role in reaction of this system (Table III). Cpe of **20** at 14° in DMF to which ben-

(23) (a) J. F. Pazos and F. D. Greene, *J. Amer. Chem. Soc.*, **89**, 1030 (1967); (b) C. B. Sclove, J. F. Pazos, R. L. Camp, and F. D. Greene, *ibid.*, **92**, 7488 (1970).

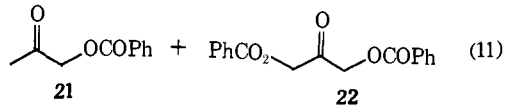
(24) (a) F. G. Bordwell and M. W. Carlson, *ibid.*, **92**, 3370 (1970); (b) F. G. Bordwell and M. W. Carlson, *ibid.*, **92**, 3377 (1970).

(25) The authors thank a referee for drawing their attention to this mechanistic possibility.

zoic acid–sodium benzoate had been added gave a 4:1 mixture of monobenzoate (**21**) and dibenzoate (**22**) (Table III, entry 1) (eq 11). The latter could only



20



(11)

21 **22**

have been formed by displacement of benzoate ion on **20**. An experiment designed to remove the reactive intermediate from reduction of **20** by vacuum distillation (Table III, entry 2) was unrewarding. Thus, the electroreduction of 2,4-dibromo-2,4-dimethyl-3-pentanone is shown to produce a reactive chemical species which can be intercepted by a variety of nucleophilic reagents but which so far has eluded direct observation and characterization.

Experimental Section

General. Boiling points are uncorrected. Ir spectra were determined with a Perkin-Elmer Model 257 grating spectrophotometer using carbon tetrachloride solutions. Nmr spectra were recorded on a Varian A-60 spectrophotometer using carbon tetrachloride solutions with TMS as internal standard, or with a Varian T-60 spectrophotometer using the same solvent but with external TMS as standard. Mass spectra were obtained with an LKB 9000 mass spectrometer coupled to a gas chromatograph. Microanalyses were performed by the Microanalytical Laboratories of the Chemical Center, University of Lund. Analytical glpc was performed using a Perkin-Elmer Model 880 instrument equipped with a 2 m × 0.3 cm column of 5% neopentyl glycol succinate on Chromosorb P (80–100 mesh). Preparative glpc was performed using a Varian-Aerograph A-90-P instrument equipped with a 10 ft × $^3/_8$ in. column of 25% Carbowax 20M on Chromosorb W (45–60 mesh).

Chemicals. 2,4-Dibromo-2,4-dimethyl-3-pentanone (**1**) was prepared by the procedure of Claesson and Thalén:[26] bp 92–93° (12 mm); n^{20}D 1.5065 (lit.[26] bp 84.5–86.5° (10 mm), n^{20}D 1.5062). It displayed a single nmr (T-60) peak at δ 2.13 (CH_3). 2-Bromo-2,4-dimethyl-3-pentanone (**5**) was obtained by the method of House and Frank:[27] bp 52–53° (12 mm); n^{20}D 1.4538 (lit.[27] bp 50–51° (10 mm); n^{20}D 1.4526), and an nmr spectrum identical with that reported.[27] 1,3-Dibromoacetone (**20**) was prepared according to the procedure of Rappe,[28] bp 82–83° (12 mm), twice distilled (lit.[28] bp 79.5–80.5° (9 mm)), and displayed an nmr spectrum identical with that previously reported.[28] Acetonitrile (Eastman White Label, <0.01% water) was used without further purification. In certain cases, when acetonitrile from other sources was employed, the solvent was purified by stirring with calcium hydride overnight, followed by filtration and distillation from phosphorous pentoxide (bp 81–82°). Dimethylformamide (DMF) was stirred with calcium hydride for 2 days, separated by filtration, and distilled from phthalic anhydride,[29] bp 64° (30 mm). Hexamethylphosphoramide (HMPA) was distilled from phthalic anhydride using a Vigreux column, and then redistilled, bp 59–66° (0.5 mm).[29] Lithium chloride (Mallinkrodt Anhydrous Analytical Reagent) was dried in an oven overnight at 110° just prior to use. Lithium perchlorate (Fluka Pure Grade, <0.5% water) was used without further purification. Sodium acetate (Merck Anhydrous) was dried in an oven overnight at 110° just prior to use. Tetra-*n*-butylammonium fluoroborate was prepared by the method of Nyberg.[30]

Electrolysis Experiments. The electrolysis cell used in this work was a water-jacketed, 300-ml vessel (75 mm i.d., 70-mm height) equipped with a magnetic stirring bar. The mercury cathode was a *ca.* 5-mm pool of mercury placed at the bottom of the electrolysis cell. Electrical connection was made *via* a small piece of platinum sealed in glass and immersed in the mercury. A carbon anode (45 × 24 × 5 mm) was placed in a porous ceramic bucket (4.5 cm o.d.) that was supported in the cell by a glass tripod. A small hole was drilled through the carbon anode near the top, and electrical connection was made *via* a small platinum wire sealed in glass. A cell cover with five standard tapered joints was used, and a ground-glass flange provided a gas-tight seal between the cover and cell. Two joints were used for the electrode connections and one provided a connection for an argon inlet tube, which was immersed to the mercury surface. During controlled-potential electrolyses, achieved by means of a potentiostat,[31] the remaining two joints were fitted with an agar bridge to a saturated calomel electrode (sce) and a calcium chloride drying tube. When electrolyses were performed under vacuum, the cell was fitted with a cold trap in place of the drying tube. The trap was cooled with liquid nitrogen and was designed so that the contents could be pumped directly into a high-vacuum line after electrolysis was completed. Constant current was provided by a variable-voltage power supply.[32] All components of the cell were dried in an oven overnight at 110° prior to use. The mercury was washed with water, dilute nitric acid (two times), water (four times), acetone (four times), and ether (two times), and partly dried by pouring through a pin hole in a filter paper. It was pumped overnight at 1 mm before use to dry it. The ceramic bucket was cleaned between runs by placing it in a Soxhlet extractor with refluxing acetone for 2 days. This procedure was most important, for the acetone usually extracted *ca.* 5 g of material, mostly solvent of the previous run, from the bucket. The bucket was then dried in an oven overnight at 110°. The mono- and dibromides (2–10 mmol) were reduced in the electrolysis cell using 100 ml of solvent containing a supporting electrolyte and, in some cases, added nucleophiles (see Table I). To determine the products, the electrolysis solution was worked up in a different manner depending upon the solvent and the supporting electrolyte. The following procedures are representative.

Acetonitrile Solutions. The catholyte of an acetonitrile–*n*-Bu_4NBF_4 electrolysis was evaporated at aspirator pressure. Ether was added and the solution was shaken vigorously, causing the *n*-Bu_4NBF_4 to precipitate. The solution was filtered and then concentrated for analysis by glpc.

DMF Solutions. DMF solutions (100-ml volume) were diluted with water (160 ml) and extracted with ether (three 70-ml portions). The combined ethereal extract was washed with water (four 50-ml portions) and dried over anhydrous magnesium sulfate. The ether was removed by distillation through a Vigreux column (two 20-cm portions) at atmospheric pressure to avoid loss of volatile compounds. HMPA runs were worked up in a similar manner. When acetic acid was used in an experiment, the ethereal extract was washed several times with a saturated sodium bicarbonate solution until the aqueous wash was pH > 7.

Control Experiments. Control experiments were carried out in exactly the same manner as the electroreduction reactions with the exception that no current was passed through the cell. When the control was terminated, mercury was removed and the solution was worked up as described previously. The results are summarized in Table III.

2,4-Dimethylpent-1-en-3-one (8). Enone **8** was collected by preparative glpc at 195° column temperature (see Table I). The ir [1680 (conjugated C=O), 1630 (conjugated C=C), 860, and 920 cm^{-1} (C=CH_2)] and nmr [5.83 (1, m, =CH_a), 5.63 (1, m =CH_b), 3.18 (1, h, −COCH<, J = 7 Hz), 1.80 (3, m, =CCH_3), 1.05 (6, d, −$CH(CH_3)_2$, J = 7 Hz)] were in agreement with values previously reported.[27]

2-Ethoxy-2,4-dimethyl-3-pentanone (4-OEt). Keto ether **4**-OEt was collected from preparative glpc using a column temperature of 108° (see Table I): ir 1715 (C=O) and 1170 cm^{-1} (COC); nmr δ 3.34 (2, q, CH_2CH_3, J = 7 Hz), 3.3 (1, m, −COCH<, J = 7 Hz), 1.22 (6, s, $-CO(CH_3)_2O$), 1.15 (3, t, $-CH_2CHCH_3$, J = 7 Hz), 1.02 (6, d, −$CH(CH_3)_2$, J = 7 Hz); mass spectrum *m/e* 159 (M + 1)$^+$,[33] 87 [$(CH_3)_2C$=OCH_2CH_3]$^+$, 59 [$(CH_3)_2C$=OH]$^+$, 43 [$(CH_3)_2CH$]$^+$.

Anal. Calcd for $C_9H_{18}O_2$: C, 68.31; H, 11.46. Found: C, 67.9; H, 11.4.

2-Hydroxy-2,4-dimethyl-3-pentanone (4-OH). Hydroxy ketone **4**-OH was collected by preparative glpc using a column temperature

(26) G. Claesson and A. Thalén, *Acta Chem. Scand.*, **17**, 1172 (1963).
(27) H. O. House and G. A. Frank, *J. Org. Chem.*, **30**, 2948 (1965).
(28) C. Rappe, *Ark. Kemi*, **21**, 503 (1964).
(29) C. K. Mann in "Electroanalytical Chemistry," Vol. 3, A. J. Bard, Ed., Marcel Dekker, New York, N. Y., 1969, pp 78–92.
(30) K. Nyberg, *Acta Chem. Scand.*, **24**, 1609 (1970).
(31) Amel Model 555, Milan, Italy.
(32) Radiak, Stocksund, Sweden.
(33) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," Wiley, New York, N. Y., 1967, p 17.

of 195° (see Table I). The ir [3500 (OH), 1710 cm^{-1} (C=O)] and nmr [δ 3.43 (1, b, OH), 3.00 (1, m, $-COCH<$, J = 7 Hz), 1.27 (6, s, $-C(OH)(CH_3)_2$), 1.04 (6, d, $-CH(CH_3)_2$, J = 7 Hz] were in agreement with the values previously published.[27]

2-Acetoxy-2,4-dimethyl-3-pentanone (4-OAc). Keto ester **4-OAc** was collected by preparative glpc using a column temperature of 195° (see Table I): ir 1744 and 1723 (C=O), 1252 cm^{-1}; nmr δ 2.90 (1, h, $-COCH<$, J = 7 Hz), 2.01 (3, s, $-O_2CCH_3$), 1.43 (6, s, $-C(OCOCH_3)(CH_3)_2$), 1.03 (6, d, $-COCH(CH_3)_2$, J = 7 Hz); mass spectrum m/e 172 $[M]^+$, 129 $[(CH_3)_2CHCOC(CH_3)_2O]^+$ and/or $[CH_3CO_2C(CH_3)_2C{\equiv}O]^+$, 101 $[CH_3CO_2C(CH_3)_2]^+$, 71 $[(CH_3)_2CHC{\equiv}O]^+$, 59 $[CH_3CO_2]^+$, 43 $[(CH_3)_2CH]^+$, and/or $[CH_3C{\equiv}O]^+$. The ir and nmr values were in agreement with values previously reported in the literature.[15b]

Anal. Calcd for $C_9H_{16}O_3$: C, 62.76; H, 9.37. Found: C, 62.7; H, 9.30.

1-(2-Furanyl)-2,4-dimethyl-3-pentanone (10). Adduct **10** was collected using preparative glpc, column temperature 190°. From the ir [1715 (C=O), 1145 cm^{-1} (COC)], nmr [δ 7.23 (1, m, α-H of furan), 6.17, 5.90 (2, m, β-H of furan), 3.17–2.27 (4, m, $-CH_2CH<$, HCCO–, $-COCH$), 1.05, 1.02, 0.90 (9, three overlapping doublets, CH_3–, J = 7 Hz)], and mass spectra {m/e 180 $[M]^+$, 137 $[C_4H_3OCH_2CH(CH_3)C{\equiv}O]^+$, 109 $[C_4H_3OCH_2CH(CH_3)]^+$, 81 $[C_4H_3OCH_2]^+$, 71 $[(CH_3)_2CHC{\equiv}O]^+$, 43 $[(CH_3)_2CH]^+$}, structure **10** is assigned to this compound.

2,2,4,4-Tetramethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (9). Cycloadduct **9** was collected by preparative glpc using a column temperature of 190° (see Table I): ir 1710 (C=O), 1380, 1065, 920 cm^{-1}; nmr 6.27 (2, s, =CH), 4.27 (2, s, >CH), 1.30 (6, s, CH_3), 0.88 (6, s, CH_3). The ir and nmr are in agreement with those previously reported,[12a] with the exception that ir bands at 805 and 735 cm^{-1} were not observed.

2,4-Dimethyl-3-pentanone (7). Saturated ketone **7** was isolated (for example, 43%, Table II, entry 4) by distillation of the reaction mixture at atmospheric pressure (bath temperature, 125–160°): ir 1710 cm^{-1} (C=O); nmr δ 2.63 (2, h, $(CH_3)_2CH$–, J = 7 Hz), 0.93 (12, d, CH_3, J = 7 Hz). The ir, nmr, and glpc were identical with those of an authentic sample.

1,3-Dibenzoyloxy-2-propanone (22). Keto diester **22** was obtained by crystallization of the crude reaction mixture (see Table III, entry 1), using ether–pentane: mp 119° (lit.[34] mp 118–119°); ir 1735 cm^{-1} (C=O); nmr δ 8.2 (4, b, *o*-CH), 7.6 (6, b, *m*-, *p*-CH), 5.11 (4, s, CH_2). The filtrate from crystallization of **22** was concentrated and distilled in vacuum, to give **4-OCOPh**: ir 1735 cm^{-1} (C=O) (lit.[35] 1725 cm^{-1}); nmr δ 8.0 (2, b, *o*-CH), 7.5 (3, b, *m*-,*p*-CH), 4.77 (2, s, CH_2), 2.19 (3, s, CH_3). The ratio of mono- to dibenzoate could be calculated directly from an nmr of the crude reaction mixture (see Table III).

Acknowledgments. Partial support for this research by the Swedish Natural Science Research Council is gratefully acknowledged. One of us (J. C.) is indebted to the Petroleum Research Fund of the American Chemical Society and to the Committee for the International Exchange of Persons (Fulbright-Hayes).

(34) H. L. White, *J. Amer. Chem. Soc.*, 74, 3451 (1952); K. Heyns and W. Stein, *Justus Liebigs Ann. Chem.*, 558, 194 (1947).

(35) E. Schaetzle, H. Urheim, M. Theurkauf, and M. Rottenberg, *Helv. Chim. Acta*, 46, 2418 (1963).

Preparation and Chemistry of Some Cyclic Phosphoranes[1]

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Abstract: The reactions of the phosphines **1**–**8** with diethyl peroxide have been studied. The products from **1** and **2** have the properties of pentasubstituted phosphorus compounds **9** and **10**. The products from **4** and **5** consist of equilibrium mixtures of pentasubstituted phosphorus compounds and alkoxyphosphonium alkoxides. The product from **7** undergoes reverse cycloaddition to isoprene and diethyl phenylphosphonite. The product from **8** rearranges to that from **7**. The relative rates of reaction of the phosphines with diethyl peroxide in cyclopentane are **1**, 3.8, **6**, 2.0, **4**, 1.3, and **3**, 1.0; in methylene chloride the relative rates are **1**, 3.1, **6**, 1.7, **4**, 1.6, and **3**, 1.0. The relative rates of reaction of the phosphines with ethyl iodide in acetonitrile are **4**, 1.5, **3**, 1.0, **6**, 0.9, and **1**, 0.33. The rate orders for these two reactions are the reverse of each other. The rate order for the diethyl peroxide reaction supports the concept of this being a biphilic displacement process in which the phosphorus atom is bonding to both oxygens in the transition state of the rate-controlling step.

In earlier work it was shown that a wide variety of trisubstituted phosphorus compounds react with diethyl peroxide to give the appropriate pentasubstituted phosphorus compound.[4,5] In particular, a series of cyclic and acyclic phosphites was shown to give phosphoranes, as were acyclic phosphines. In the present study a variety of cyclic phosphines have been allowed to react with diethyl peroxide. The aims of this investigation were to continue to test the peroxide route as a method of preparing phosphoranes, to learn more about the mechanism of the reaction, and to investigate the chemistry of the products of these reactions. The reactions of diethyl peroxide with trisubstituted phosphorus compounds usually yield the pentasubstituted material which is contaminated with varying amounts of tetrasubstituted material, *e.g.*, phosphate, phosphine oxide, etc. In general it has not been possible to purify the pentasubstituted materials to the point where good analytical data can be obtained. Similarly, attempts to observe a parent molecular ion by mass spectrometry have been fruitless, with the compounds being reported here. The structural assignments have been made on the basis of ^1H and ^{31}P nmr spectroscopy, method of

(1) This research has been supported by the National Science Foundation under GP 4997X and GP 12829. This investigation was supported by Public Health Service Research Grant No. CA-10737 from the National Cancer Institute.

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(4) D. B. Denney and D. H. Jones, *J. Amer. Chem. Soc.*, 91, 5821 (1969).

(5) D. B. Denney and D. Z. Denney, B. C. Chang, and K. L. Marsi, *ibid.*, 91, 5243 (1969).