Table III. Carbinyl Carbon ^{13}C Resonances in IV, V, and VI[a,b]

R =	Alcohol (ppm)	Carbonium ion (ppm)	Δδ, ppm
IV, H	60.6	86.8	−26.2
V, CH_3	65.5	117.6	−52.1
VI, C_6H_5	72.1	121.5	−49.4

[a] From ref 12. [b] Alcohol spectra are referenced to internal TMS, cation spectra (in concentrated sulfuric acid) to external TMS through the ^{19}F lock signal.

ion, smaller even than the comparable changes, Δδ, in the ferrocenylcarbinyl series (Table III). By way of comparison, Δδ for the carbinyl carbon atom when Me_2CHOH is converted to $Me_2CH^+[SbF_6]^-$ is 255.3 ppm.[6] Upon examination of Tables II and III, we note that the chemical shifts of the carbinyl carbon atoms in both series of carbonium ions follow the normal order observed when substituents on a fully substituted carbon atom are varied from R=H (most shielded) to CH_3 to Ph (least shielded), rather than for substituents on a electron-deficient trivalent carbon atom, where the CH_3-substituted carbon atom is less shielded than the analogous Ph-substituted carbon atom.[8] These results are a rather clear-cut indication that the carbinyl carbon atoms in I, II, and III are nearly fully bonded and only slightly electron deficient. The slight increase in shielding of the CH_3-carbon when II is formed from the alcohol and of the C-1 carbon of the phenyl group in III provides further confirmation of this.

The data in Table II suggest that the positive charge in I, II, and III has been delocalized to a large extent onto the cobalt atoms. The observed slight increase in shielding of the carbon atoms of the carbon monoxide ligands when the alcohols are converted to the carbonium ions speak in favor of this view. If the cobalt atoms are more electron deficient in the cations I, II, and III than in the corresponding alcohols, then the carbon monoxide ligands would be expected to be bonded more tightly in the cations. The consequent movement of the CO carbon atoms to a position closer to the cobalt atoms might be expected to result in increased shielding due to the diamagnetic anisotropic shielding effect of the cobalt atoms. Any change in chemical shift of the apical carbon atom of the CCo_3 cluster on going from the alcohol to the carbonium ion remains unknown since a signal due to this carbon atom was not observed in the ^{13}C nmr spectra of the alcohols and the carbonium ions. This is readily understandable; the line for this carbon atom would be broadened by the adjacent cobalt atoms (nuclear quadrupole broadening) and the three adjacent cobalt atoms would split this line into a 22-line pattern.[9]

On the basis of a comparison of the Δδ values in Tables II and III it is tempting to suggest that I, II, and III are somewhat more stabilized than IV, V, and VI. While this conclusion may not be valid, the $(OC)_9Co_3C$-substituted carbonium ions certainly appear to be at least as stabilized as the corresponding ferrocenylmethyl carbonium ions. While stabilization of π-complexed carbonium ions is a well-known phenomenon in transition metal–organic chemistry,[10] stabilization of carbonium ions in σ-bonded organo transition metal structures is much less well documented.[11] In IV, V, and VI the ^{13}C nmr spectra suggest that the positive charge is delocalized onto all carbon atoms of both ligands and, in some part, onto the iron atom.[12] A different mechanism of charge delocalization must be operative in I, II, and III. All the observations discussed above are compatible with our previous proposal[2] that I, II, and III are stabilized to a high degree by σ–π conjugation, *i.e.*, lateral overlap between the vacant *p* orbital of the carbinyl carbon atom and the filled σ-bonding orbital involving the C–Co bond of the cluster.

Although much of the positive charge in I, II, and III appears to reside at the cobalt atoms, many nucleophiles attack these cations at the carbinyl carbon atoms.[2] It is significant, however, that I, II, and III are rather weak electrophilic reagents. This is indicated by the fact that they will undergo electrophilic aromatic substitution reactions with only highly nucleophilic aromatic substrates such as *N*,*N*-dimethylaniline and pyrrole. It is noteworthy also that triphenylphosphine, which might be expected to form stable phosphonium salts on reaction with I, II, or III at the carbinyl carbon atom, reacts with the hexafluorophosphate salts of these cations to give immediate decomposition with violent gas evolution. Presumably the site of attack is at cobalt rather than at the carbinyl carbon atom.

Acknowledgment. The authors are grateful to the National Science Foundation (NSF Grant GP 31429X) for generous support of this work.

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(8) J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York, N. Y., 1972.

(9) (a) P. C. Lauterbur, *J. Chem. Phys.*, **42**, 799 (1965); (b) A. Lowenstein and M. Sporer, *Mol. Phys.*, **9**, 293 (1965).

(10) M. L. H. Green in "Organometallic Compounds," Vol. 2, 3rd ed, G. E. Coates, M. L. H. Green, and K. Wade, Ed., Methuen, London, 1968.

(11) Ref 10, Chapter 7, esp pp 209–217.

(12) G. H. Williams, D. D. Traficante, and D. Seyferth, *J. Organometal. Chem.*, **60**, C53 (1973).

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Received September 11, 1973

Synthesis of 1,4-Diketones by Reductive Coupling of α,α′-Dibromo Ketones

Sir:

1,4-Diketones are precursors of furans[1a] and pyrroles[1b] as well as thiophenes[1c] in the widely applicable Paal–Knorr synthesis[1d] and have also been used extensively as intermediates of natural products derived from cyclopentenones, especially jasmones, prostaglandins, and rethrolones.[2] During our work on allyl

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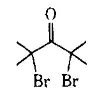
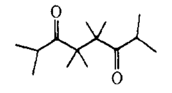
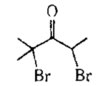
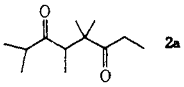
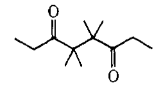
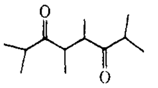
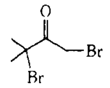
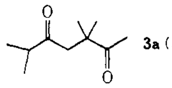
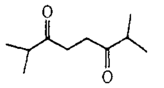
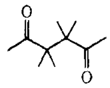
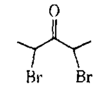
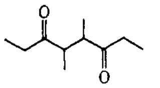
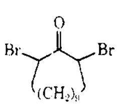
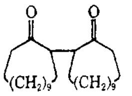
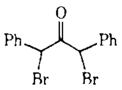
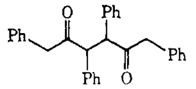
(1) (a) P. Bosshard and C. H. Eugster, *Advan. Heterocycl. Chem.*, **7**, 377 (1966); (b) E. Baltazzi and L. I. Krimen, *Chem. Rev.*, **63**, 511 (1963); (c) S. Gronovitz, *Advan. Heterocycl. Chem.*, **1**, 1 (1963); D. E. Wolf and K. Folkers, *Org. React.*, **6**, 410 (1951); (d) C. Paal, *Ber.*, **17**, 2756 (1884); L. Knorr, *ibid.*, **17**, 2863 (1884).

(2) For a recent review see R. A. Ellison, *Synthesis*, 397 (1973). See also T. Mukaiyama, K. Narasaka, and M. Furusato, *J. Amer. Chem. Soc.*, **94**, 8641 (1972); R. H. Schlessinger, *et al.*, *Tetrahedron Lett.*, 2595, 2599, 2603, 3267, 3271, 3275 (1973); A. Pelter, C. R. Harrison, and D. Kirkpatrick, *ibid.*, 4491 (1973); K. Utimoto, K. Uchida, and H. Nozaki, *ibid.*, 4527 (1973); Y. Sawa, I. Hashimoto, M. Ryang, and S. Tsutsumi, *J. Org. Chem.*, **33**, 2159 (1968).

Table I. 1,4-Diketones from Reductive Coupling of α,α^1-Dibromo Ketones with a Zinc-Copper Couple in N-Methylformamide

Reactant	Reaction time (hr) and temperature (°C)	Products[a]	% yield[b]
 **1**	2, −5°	 **1a** nmr (TMS, CCl_4) δ 1.0 (d, J = 7 Hz, 12 H), 1.2(s, 12 H), 3.02(sept, J = 7 Hz,2 H)	71
 **2**	2, −5°	 **2a** (56%) δ 0.85-1.2 (m, $6CH_3$) 2.3-3.3 (q u.sept,4 H)  **2b** (25%) δ 0.97 (t, J = 7 Hz, 6 H), 1.15 (s, 12 H) 2.54 (q, J = 7 Hz, 4 H)  **2c** (18%) δ 1.08 (d, J = 7 Hz, 18 H) 2.45-3.0 (m, 4 H)	65
 **3**	24, 25°	 **3a** (39%) δ 1.04 (d, J = 7 Hz, 6H), 1.12 (s, 6 H) 2.1 (s, 3H),2.64 (sept, J = 7 Hz, 1 H) 2.72 (s, 2 H)  **3b** (38%) δ 1.1 (d, J = 7 Hz, 12 H) 2.6 (s u.sept, J = 7 Hz, 6 H)  **3c**[c] (23%) δ 1.18 (s, 12 H) 2.08 (s, 6 H)	36
 **4**[d] *meso/dl* = 5:1	24,25°	 **4a**[e] (*meso/dl* = 1:1.2) δ 0.82-1.2 (m, 12 H), 2.22-2.96 (m, 6 H)	55
 **5** *meso*	24, 50°	 **5a**, mp 150-167°[f] δ 1.8-2.9(m, 36 H), 2.39-2.98(m, 6 H)	25
 **6** *meso/dl* = 1:1	12, 25°	 **6a**[g,h] δ 3.18 (s, 4 H), 4.68 (s, 2 H), 7.2 (brs, 20 H)	43

[a] All products described showed satisfactory spectroscopic and analytical data. By-products were the corresponding parent ketone, some trimer and *ca.* 10% 2,4-dimethyl-1-penten-3-one in the case of **1a**. Liquids were isolated and separated on a 20-ft carbowax 20M column at 200°, while solids were purified by crystallization and dry-column chromatography. [b] Yields refer to isolated pure materials. [c] Reference 4a, c. [d] The *meso/dl* ratio was determined by $NaBH_4$ reduction into the stereoisomeric dibromohydrins; *cf.* also E. W. Garbisch and J. Wohllebe, *J. Org. Chem.*, **33**, 2157 (1968); *Chem. Commun.*, 306 (1968). [e] Reference 4d, e. [f] Melting point varies according to *meso/dl* ratio of product. Other α,α'-dibromo cycloalkanones can be dimerized similarly, and the 1,4-diketone from 2,11-dibromocycloundecanone has been isolated and identified completely; J. G. Vinter, Ph.D. Thesis, University of London 1973. [g] R. C. Cookson and M. J. Nye, *J. Chem. Soc.*, 2009 (1965) have previously obtained **6a** by treatment of **6** with zinc in boiling acetonitrile. [h] Debromination of 1,3-dibromo-3-methyl-1-phenyl-2-butanone and 1,3-dibromo-1-phenyl-2-butanone in *N*-methylformamide (12 hr, 25°) gave isobullatenone (90%) and its monodemethylated analog (10%), respectively; the α-hydroxyketones were formed as by-products. See M. A. Barrow, A. C. Richards, R. H. Smithers, and H. M. R. Hoffmann, *Tetrahedron Lett.*, 3101 (1972).

cations which are generated from α,α'-dihalo ketones,[3] we have discovered a simple method for reductive coupling of these compounds. By using the polar and weakly protic solvent *N*-methylformamide in combination with a zinc–copper couple, the reaction can be carried out under mild conditions.

In a typical experiment a solution of 2,4-dibromo-2,4-dimethyl-3-pentanone (**1**) (5.44 g, 0.02 mol) in *N*-methylformamide (Fluka A.G.) (10 ml) is stirred into a suspension of zinc–copper couple (3.7 g, 0.06 mol) in *N*-methylformamide (25 ml) under nitrogen so that the temperature does not exceed −5°. After 2 hr the products are extracted continuously with isopentane, which is shaken with dilute HCl to remove traces of *N*-methylformamide, washed with water, dried, and evaporated to yield 2,4,4,5,5,7-hexamethyl-3,6-octanedione (**1a**) (71%). When aromatic dibromo ketones and *meso*-2,12-dibromocyclododecanone (**5**) are coupled, the reaction mixture is filtered to remove the metal and diluted with water; the resulting zinc salts are dissolved (dilute HCl) and the products are finally extracted with benzene and isolated in pure form by distillation, preparative glc, or recrystallization (*cf.* Table I).

Previously, a number of the 1,4-diketones shown in Table I has been obtained by free radical induced dimerization of α-alkylated ketones.[4,5] In fact, the coupling reaction described here seems similar to the Kharasch

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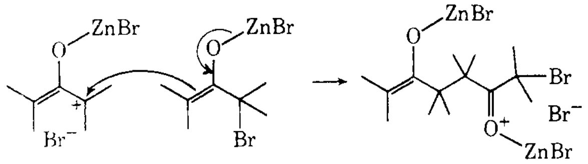
(3) (a) H. M. R. Hoffmann, K. E. Clemens, E. A. Schmidt, and R. H. Smithers, *J. Amer. Chem. Soc.*, **94**, 3201 (1972); (b) H. M. R. Hoffmann, K. E. Clemens, and R. H. Smithers, *ibid.*, **94**, 3940 (1972); (c) H. M. R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **12**, 819 (1973).

(4) (a) M. S. Kharasch, H. C. McBay, and W. H. Urry, *J. Amer. Chem. Soc.*, **70**, 1269 (1948); (b) C. G. Moore, *J. Chem. Soc.*, 236 (1951); (c) M. F. Ansell, W. J. Hickinbottom, and P. G. Holton, *ibid.*, 349 (1955); (d) D. Seebach, *Chem. Ber.*, **96**, 2712 (1963); (e) K. Schwetlick, J. Jentzsch, R. Karl, and D. Wolter, *J. Prakt. Chem.*, **25**, 95 (1964). For the copper promoted dimerization of ester enolates see M. W. Rathke and A. Lindert, *J. Amer. Chem. Soc.*, **93**, 4605 (1971).

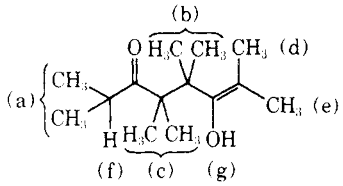
(5) The reaction of monobromo ketones with zinc copper couple has been studied by T. A. Spencer, R. W. Britton, and D. S. Watt, *J. Amer. Chem. Soc.*, **89**, 5727 (1967). Attempted coupling of the sodium enolate of cyclododecanone with 2-bromocyclododecanone gave Favorskii contraction and unidentified products: C. Chassin, unpublished.

procedure insofar as attempted cross-coupling (**1** with **3**, **1** with **4**) was not successful and afforded only those 1,4-diketones which had already been obtained by self-dimerization. However, whereas treatment of isopropyl methyl ketone with diacetylperoxide gave exclusively dimer **3c**[4a,c] as we have confirmed by analytical glc, our reaction produced all three possible isomers and the distribution of dimers could be influenced by the solvent and reducing agent.[6] Further, the dimerization described here is considered to be ionic rather than free radical and visualized to involve the combination of zinc oxyallyl[3c] and zinc enolate (Scheme I).

Scheme I



Thus, coupling of 2,4-dibromo-2,4-dimethyl-3-pentanone (**1**) in *N*-deuterio-*N*-methylformamide yielded the 2,7-dideuterio analog (52%) of 3,6-octanedione **1a**, implicating the solvent as the proton source. By recording consecutive nmr spectra immediately after removal of solvent pentane, it was possible to identify the trialkylated enol **7**[7] as the direct precursor of 3,6-octanedione **1a** in the postulated reaction sequence.



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After *ca.* 10 min at 25° the enol[8] had disappeared completely and **1a** was formed as the final product.

Acknowledgments. We thank the Science Research Council, the Dr. Carl Duisberg-Stiftung, and Schering A. G., Berlin, for support of this work.

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(6) By using NaI in acetonitrile, the most crowded diketone **3c** was formed exclusively in addition to some 3-bromo-3-methyl-2-butanone: R. Chidgey, unpublished.

(7) Pmr δ (TMS) (a) 0.95 (d, $J \sim 8$ Hz, 6 H), (b) 1.00 (s, 6 H), (c) 1.10 (s, 6 H), (d) 1.56 (s, 3 H), (e) 1.60 (s, 3 H), (f) 2.80 (sept, $J \sim 8$ Hz, 1 H) (g) 7.15 ppm (s, 1 H); the signals due to a and b were partly superposed.

(8) Other simple aliphatic trialkylated enols have recently been generated and identified chemically as well as spectroscopically; see H. M. R. Hoffmann and E. A. Schmidt, *J. Amer. Chem. Soc.*, **94**, 1373, 7832 (1972); H. M. R. Hoffmann and E. A. Schmidt, *Angew. Chem., Int. Ed. Engl.*, **12**, 239 (1973).

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Received October 16, 1973

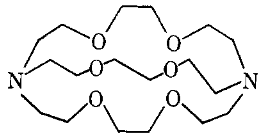
A Crystalline Salt of the Sodium Anion (Na^-)

Sir:

We wish to report the synthesis of a new crystalline compound which contains the sodium anion, Na^-. The mode of formation, stoichiometry, reactivity, crystal structure, and general appearance are consistent with this assignment. We believe that this compound, formed from sodium metal and the bicyclic polyoxadiamine, **1**, ("crypt"), represents the first example of a new class of compounds.

It has been presumed for some time that solutions of the alkali metals in amines and ethers contain species of stoichiometry M^-. This assignment is based upon the variation of the optical absorption band with metal, solvent, and temperature,[1,2] the oscillator strength,[3] the reactions following photolysis of the solutions,[4–7] and the kinetics of formation from M^+ and e^-_{solv}.[8,9]

We have recently shown[2,10–12] that cyclic polyethers which form "crown" [13] and "cryptate" [14] complexes with alkali cations greatly enhance the solubility of the alkali metals in amines and ethers. With **1** it is possible to control the composition of the solution by adjusting the ratio of complexing agent to total dissolved metal. By using an excess of sodium metal (which is insoluble in ethylamine in the absence of the complexing agent), solutions as concentrated as 0.4 *M* in total sodium in ethylamine can be prepared. Most of the dissolved material has the stoichiometry, $NaC^+ \cdot Na^-$, in which NaC^+ represents the cage complex formed by trapping a sodium cation inside of the "crypt." The complexation constant is large and the rate of release of Na^+ from the crypt is relatively slow.[15]



1

When a concentrated solution of $NaC^+ \cdot Na^-$ in ethylamine is cooled to Dry Ice temperatures, a gold-colored crystalline solid precipitates. Single crystals, grown by slow cooling, have the form of thin hexagonal plates. The crystals and also the powder have a shiny metallic appearance which changes reversibly in color from gold at −190° to bronze at +40°. Just below the decomposition temperature of 83° the color is dark brown. Crystals which have been repeatedly washed with *n*-hexane or diethyl ether are stable *in vacuo* for days at room temperature and below.

The stoichiometry and integrity of the compound $Na_2C_{18}H_{36}N_2O_6$ were checked in several ways.

(1) Elemental analysis (Spang Microanalytical Lab-

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(1) S. Matalon, S. Golden, and M. Ottolenghi, *J. Phys. Chem.*, **73**, 3098 (1969).

(2) M. T. Lok, F. J. Tehan, and J. L. Dye, *J. Phys. Chem.*, **76**, 2975 (1972).

(3) M. G. DeBacker and J. L. Dye, *J. Phys. Chem.*, **75**, 3092 (1971).

(4) J. G. Kloosterboer, L. J. Giling, R. P. H. Rettschnick, and J. D. W. Van Voorst, *Chem. Phys. Lett.*, **8**, 462 (1971).

(5) S. H. Glarum and J. H. Marshall, *J. Chem. Phys.*, **52**, 5555 (1970).

(6) A. Gaathon and M. Ottolenghi, *Isr. J. Chem.*, **8**, 165 (1970).

(7) D. Huppert and K. H. Bar-Eli, *J. Phys. Chem.*, **74**, 3285 (1970).

(8) J. L. Dye, M. G. DeBacker, J. A. Eyre, and L. M. Dorfman, *J. Phys. Chem.*, **76**, 839 (1972).

(9) J. W. Fletcher, W. A. Seddon, J. Jevcak, and F. C. Sopchyshyn, *Chem. Phys. Lett.*, **18**, 592 (1973).

(10) J. L. Dye, M. G. DeBacker, and V. A. Nicely, *J. Amer. Chem. Soc.*, **92**, 5226 (1970).

(11) J. L. Dye, M. T. Lok, F. J. Tehan, R. B. Coolen, N. Papadakis, J. M. Ceraso, and M. G. DeBacker, *Ber. Bunsenges. Phys. Chem.*, **75**, 659 (1971).

(12) J. L. Dye in "Electrons in Fluids," J. Jortner and L. R. Kestner, Ed., Springer-Verlag, West Berlin, 1973, p 77.

(13) C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967); **92**, 386 (1970).

(14) B. Dietrich, J. M. Lehn, and J. P. Sauvage, *Tetrahedron Lett.*, 2885, 2889 (1969).

(15) J. M. Ceraso and J. L. Dye, *J. Amer. Chem. Soc.*, **95**, 4432 (1973).