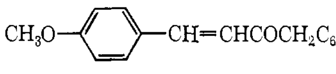
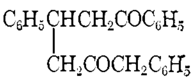
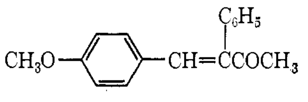
to form the α,β-unsaturated ketone V (mp 99–100°) and the conjugate addition product VI (mp 112–113°), respectively. Each of these products, which was obtained in about 50% yield, gave a satisfactory elementary analysis and a characteristic infrared spectrum.

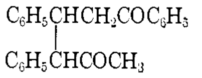

V


$$\underset{\displaystyle CH_2COCH_2C_6H_5}{C_6H_5CH}CH_2COC_6H_5$$
VI

The condensation of III'' with anisaldehyde was indicated to form initially the corresponding carbonyl addition product, but it was not isolated. The condensation of III'' with chalcone may have produced also some of the carbonyl addition product.

That the condensation products isolated were the terminal derivatives V and VI, not the possible methylene derivatives VII and VIII, respectively, was supported by their nmr spectra, neither of which showed peaks for an acetyl methyl group. The spectrum of V showed a methylene peak at 3.82 ppm and that of VI a corresponding methylene peak at 3.58 ppm. Also, the spectrum of V exhibited a vinyl proton at 6.80 ppm and that of VI two methylene absorptions (doublets) at 2.87 and 3.22 ppm, as well as a methinyl hydrogen at 3.91 ppm.

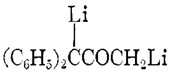

VII

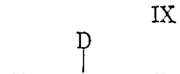

$$\underset{\displaystyle C_6H_5CHCOCH_3}{C_6H_5CH}CH_2COC_6H_5$$
VIII

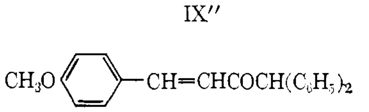
Similarly, diphenylacetone (IX), which fails to be converted by 2 equiv of potassium amide in liquid ammonia to a 1,3-dicarbanion satisfactory for terminal benzylation,[5] was converted by the present method to dilithio salt IX'', as evidenced by deuteration with deuterium oxide and by condensation with anisaldehyde to give IX-D_2 and X (mp 129–131°), respectively.

$(C_6H_5)_2CHCOCH_3$

IX


$$(C_6H_5)_2\overset{\displaystyle Li}{C}COCH_2Li$$
IX''

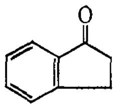

$$(C_6H_5)_2\overset{\displaystyle D}{C}COCH_2D$$
IX-D_2

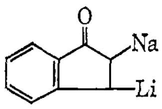

X

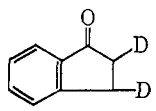
The structure of the deuterated ketone IX-D_2 was supported by its nmr spectrum, which showed 90–95% of one deuterium atom/molecule at the methyl group and about 80% of one deuterium atom/molecule at the methylene group. In a blank experiment, no deuterium was acquired from deuterium oxide in the presence of lithium deuterioxide.

The structure of the condensation product X was supported by its nmr spectrum and by agreement of its melting point with the reported value.[6]

Also, 1-indanone (XI) was converted by the present method to the 1,2-dialkali salt XI'', as evidenced by deuteration with deuterium oxide to form the 1,2-dideutero product XII.


XI


XI''


XII

The structure of XII was supported by its nmr spectrum, which showed 90% of one deuterium atom/molecule at the 3 position and 100% of one deuterium atom/molecule at the 2 position.

Work is in progress not only on other condensations of dianions III'', IX'', and XI'' but also on the preparations and reactions of other 1,3, 1,2, and other types of multiple anions. Moreover, nmr determinations on such anions are contemplated.

The present method, which involves the initial usage of an alkali amide to deactivate a ketone carbonyl group so that a more strongly basic organometallic compound may be employed for secondary ionization (and even for further ionization), represents a significant advance in the study of multiple anions that have not been available through usage of either of the two bases alone. Furthermore, the method may be applicable where initial deactivation of certain other functional groups is required for satisfactory subsequent ionizations.

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Received July 31, 1967

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[5] D. R. Bryant, Ph.D. Disseration, 1962, p 41.

[6] C. S. Marvel and M. I. Kohan, *J. Org. Chem.*, **16**, 741 (1951).

Synthesis of an 8,16-Methano-*cis*-[2.2]metacyclophane

Sir:

It is known from X-ray crystallographic data[1a] and from chemical studies[1b] that [2.2]metacyclophane,[2] first prepared by Pellegrin in 1899,[3] is represented by the three-dimensional projection I. This molecule, and apparently all [2.2]metacyclophanes reported to date,[4a–c] because of similarity in synthetic approach, possess *trans* or *anti* geometry. We wish to report the synthesis of a [2.2]metacyclophane possessing *cis* or *syn* geometry.

Condensation of 2 moles of 2,6-xylenol with *s*-trioxane in concentrated hydrochloric acid yields methylene-4,4'-bis(2,6-xylenol),[5] IIa, mp 175–177°, 72%, which is converted to methylene-4,4'-bis(2,6-dimethylanisole), IIb, mp 82–84°, 80%, by dimethyl sulfate–sodium hydroxide in a saturated sodium sulfate solution. Halomethylation of IIb by means of *s*-trioxane–hydrogen chloride followed by zinc chloride–lithium chloride in glacial acetic acid[6] produces the bis(chloro-

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[1] (a) W. Baker, J. F. W. McOmie, and J. M. Norman, *J. Chem. Soc.*, 1114 (1951); (b) C. J. Brown, *ibid.*, 3278 (1953).

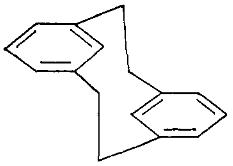
[2] The numbering and nomenclature of [2.2]metacyclophanes used here is that suggested by B. H. Smith, "Bridged Aromatic Compounds," Academic Press Inc., New York, N. Y., 1964, Chapter 1.

[3] M. Pellegrin, *Rec. Trav. Chim.*,**18**, 458 (1899).

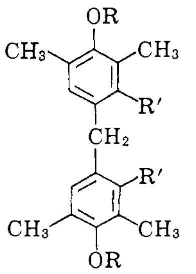
[4] (a) W. S. Lindsay, P. Stokes, L. G. Humber, and V. Boekelheide, *J. Am. Chem. Soc.*, **83**, 943 (1961); (b) A. Hanson, *Acta Cryst.*, **15**, 956 (1962); (c) W. Baker, K. M. Buggle, J. F. W. McOmie, and D. A. M. Waters, *J. Chem. Soc.*, 3594 (1958).

[5] G. Zigeuner, R. Pitter, and K. Voglar, *Monatsh.*, **86**, 517 (1955).

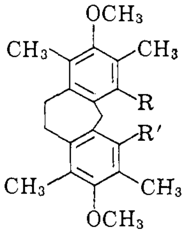
[6] (a) H. C. Brown and K. L. Nelson, *J. Am. Chem. Soc.*, **75**, 6292 (1953); (b) H. W. Earhart and W. G. DePierre, U. S. Patent 2,945,894 (1960); *Chem. Abstr.*, **54**, 24547 (1960).



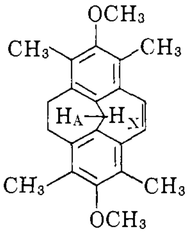
I



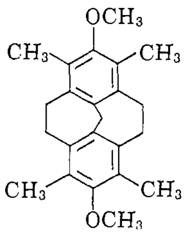
IIa, R = R' = H
b, R = CH3; R' = H
c, R = CH3; R' = CH2Cl



IIIa, R = R' = H
b, R = CH2Cl; R' = H
c, R = CH2Cl; R' = CHO
d, R = CH2P+ (Ph)3Cl−; R' = CHO



IV



V

methyl) compound IIc, mp 137–138°, 75%. The methyl groups in IIb serve to block the undesired introduction of chloromethyl groups *ortho* to the ether functions. Transformation of IIc into the 5H[*a,d*]-dibenzocycloheptene IIIa, mp 140–141°, 47%, was accomplished *via* a modified Wurtz procedure[4a,7] using sodium sand with tetraphenylethylene as catalyst. A second halomethylation carried out as above on IIIa yielded the monochloromethyl compound IIIb, mp 220–221°, 52%, as major product. Formylation of IIIb with dichloromethyl butyl ether[8] and stannic chloride occurred smoothly over a 24-hr period at room temperature with the formation in 76% yield of the chloromethyl aldehyde IIIc, mp 204–205° (1680 cm^{-1}, CHO).[9] The phosphonium salt IIId, mp 220–221° (1670 cm^{-1}, CHO), is obtained in 85% yield from the chloromethyl aldehyde by displacement with triphenylphosphine in refluxing toluene. Generation of the phosphorane[10] in anhydrous ethanol by addition of sodium ethoxide at reflux temperature forms the 8,16-methano-*cis*-[2.2]metacyclophane monoolefin IV, mp 184–185°, 85% ($\lambda_{\max}^{\text{cyclohexane}}$ 212 (ϵ 35,500), 256 (23,100), 286 (9300), and 298 mμ (8900)). The nmr spectrum[11] of IV shows resonances at τ 6.43 (singlet, two OCH_3), 6.75 (A_2B_2 multiplet, $-CH_2CH_2-$), 7.78 and 7.90 (equivalent singlets, four CH_3), *and importantly:* a two-proton singlet at 2.70 (–CH=CH–) and two widely separated doublets of an AX spin system at 5.95 and 7.70 (J_{AX} = 10 cps). These last resonances are assigned to the protons of the 8,16-methylene bridge; strong diamagnetic shielding of H_X (IV) by the adjacent bridge double bond[12] produces an upfield shift of 1.80 ppm.

The mass spectrum of IV shows the correct molecular weight, M^+ 334 (base peak), indicating intramolecular Wittig olefin formation from IIId. Other fragmentations seen at $M^+ - 14$ (19% of base peak), $M^+ - 15$ (25%), $M^+ - 30$ (30%), and $M^+ - 31$ (49%) are presumably due to loss of CH_2, CH_3, two CH_3, and two $CH_3 + H^+$, respectively.

That IV is the correct structure of the internal Wittig product is shown by its ready catalytic absorption of 1 mole of hydrogen to yield the saturated 5,13-dimethoxy-4,6,12,14-tetramethyl-8,16-methano-*cis*-[2.2]-metacyclophane,[2] V, mp 155° ($\lambda_{\max}^{\text{cyclohexane}}$ 220 (ϵ 36,700) and 264 mμ (8100), 90%, the nmr spectrum of which, in addition to resonances at τ 6.50 (singlet, two OCH_3), 6.88 (A_2B_2 multiplet, two $-CH_2CH_2-$), and 7.95 (singlet, four CH_3), shows a two-proton singlet at 6.36. This singlet corresponds to the now-equivalent protons of the methylene bridge and appears in proximity to the H_A resonance of IV, showing the similarity of environments. Mass spectral analysis[13] of V confirms the molecular weight, M^+ 336 (base peak), and shows important fragmentations at $M^+ - 15$ (76% of base peak) and $M^+ - 30$ (49% of base peak) which are tentatively assigned to successive losses of the methoxyl methyls. Loss of the 8,16-methylene group does not appear to be an important fragmentation pathway.

The *cis* geometry of V is required by the 8,16-bridging methano group. The chemistry of this new metacyclophane and its monoolefin IV will be reported at a later date.[14,15]

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(7) E. Müller and G. Röscheisen, *Chem. Ber.*, **90**, 543 (1957).

(8) H. Gross, A. Rieche, and E. Höft, *Chem. Ber.*, **94**, 544 (1961).

(9) Infrared spectra for all reported compounds were taken with KBr disks and are consistent with assigned structures.

(10) A. Maercker, *Org. Reactions*, **14**, 270 (1965).

(11) Nmr spectra were obtained in deuteriochloroform on a Varian A-60A using TMS as internal standard.

(12) R. C. Cookson, T. A. Crabbe, J. J. Frankel, and J. Hudec, *Tetrahedron Suppl.*, 7, 355 (1966), and references cited therein.

(13) Mass spectra were obtained by Dr. Paul Nicholson of these laboratories on a C.E.C. Model 21-103C instrument using a heated inlet operating at 180°; ionization potential 70 e.v.

(14) Satisfactory analyses were obtained for all new compounds.

(15) V. Boekelheide, B. A. Hess, and A. S. Bailey have recently reported the preparation of 8,16-oxido[2.2]metacyclophane, which must also possess *cis* or *syn* geometry (*cf. J. Am. Chem. Soc.*, **89**, 2746 (1967)). We wish to thank Professor Boekelheide for informing us of their results prior to publication.

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Quantitative Evidence Concerning the Relative Stabilities of Cycloalkynes and Arynes[1]

Sir:

Cyclooctyne is the cycloalkyne of smallest ring size to have been isolated; it is air sensitive and rearranges and polymerizes easily.[2] Considerable evidence has accumulated which suggests that cycloheptyne, cyclohexyne, and cyclopentyne can exist as short-lived reac-

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(1) This research was supported in part by National Science Foundation Grant No. GP-7423.

(2) (a) A. T. Blomquist and L. H. Liu, *J. Am. Chem. Soc.*, **75**, 2153 (1953); (b) G. Wittig and A. Krebs, *Ber.*, **94**, 3260 (1961).