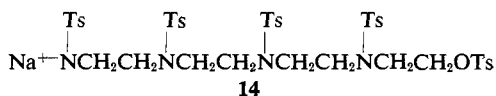


cations of **2** with tetramethylammonium cations still affords greater than 50% of **1a**; this rules out a template effect as a dominant factor.



Further observations pertaining to the mechanism of this reaction will be reported. We are investigating the preparation and chemistry of these new and highly interesting macroheterocyclic systems.

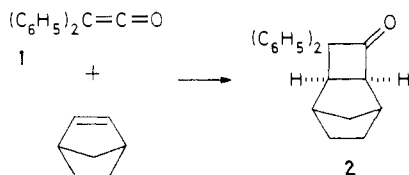
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Jack E. Richman,* Thomas J. Atkins
Contribution No. 2110, Central Research Department
E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898
Received January 5, 1974

2:1 Adducts of Diphenylketene and Norbornene

Sir:

The $2 + 2 \rightarrow 4$ cycloadditions of ketenes and alkenes are concerted reactions¹ which are interpreted to be $[\pi 2_a + \pi 2_s]$ processes.² The reactions take place faster as the ketenophilic double bond becomes more electron-rich.³ Concurrent formation of 1:1 and 2:1 adducts from dimethylketene and *N*-isobutyryldialkylamines indicates a second mechanistic pathway.⁴



Refluxing of diphenylketene (**1**) with norbornene in benzene for 14 days produces the cyclobutanone **2** in 84% yield.⁵ However, on heating **1** in excess norbornene under N_2 to 70° for 20 days, one obtains 10–16% of a 2:1 adduct, $\text{C}_{35}\text{H}_{30}\text{O}_2$, mp $193.5\text{--}194.5^\circ$,⁶ along with 45–68% **2**. Our proposal of structure **3** for the 2:1 adduct rests on the following evidence. Two carbonyl frequencies at 1770 and 1650 cm^{-1} are consistent with a cyclobutanone ring and an unsaturated six-membered ring ketone ($\text{C}=\text{C}$ 1614 cm^{-1}). Besides 15 aromatic hydrogens, the nmr shows two cis coupled vinyl protons as AB spectrum at τ 3.80 and 4.33 ($J = 10.5\text{ Hz}$); in addition, the B part is split into doublets by $J \approx 2\text{ Hz}$.

On catalytic hydrogenation the dihydro derivative **4** (mp $239\text{--}240^\circ$) is obtained. The vinylic hydrogens are lost and the uv_{max} (dioxane) of **3** at $295\text{ m}\mu$ ($\log \epsilon$ 4.28) is shifted to $255\text{ m}\mu$ (4.00) in **4**.

Short heating to 200° converts **3** to the isomeric 2:1

(1) R. Huisgen, L. A. Feiler, and G. Binsch, *Chem. Ber.*, **102**, 3460 (1969).

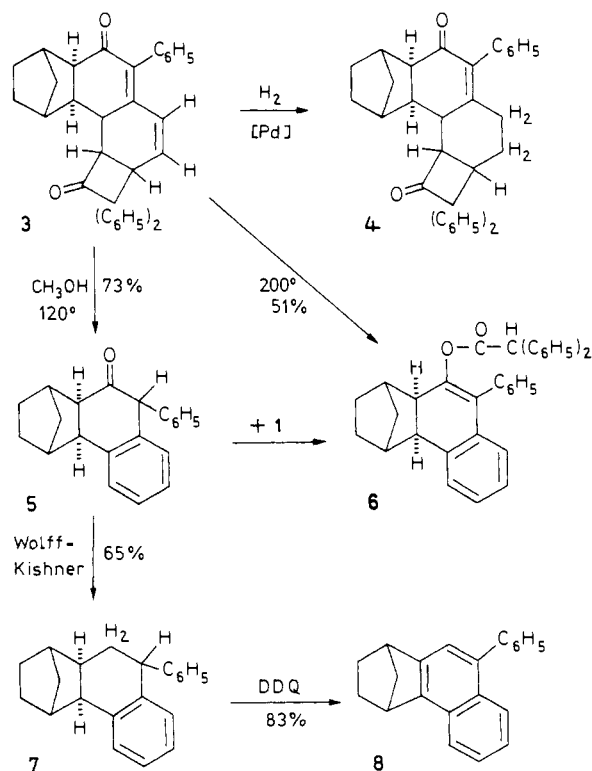
(2) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(3) R. Huisgen, L. A. Feiler, and P. Otto, *Chem. Ber.*, **102**, 3444 (1969).

(4) R. Huisgen and P. Otto, *J. Amer. Chem. Soc.*, **91**, 5922 (1969).

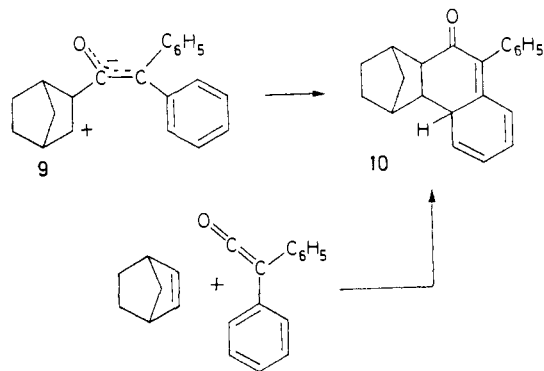
(5) R. Huisgen and L. A. Feiler, *Chem. Ber.*, **102**, 3391 (1969).

(6) All new compounds gave satisfactory CH analyses. Molecular weight determinations by vapor pressure osmometer or mass spectrometer.



adduct **6**, mp $154\text{--}156^\circ$, 51% yield. The single $\text{C}=\text{O}$ frequency at 1743 cm^{-1} and the $\text{C}=\text{C}$ at 1668 cm^{-1} are consistent with an enol ester group. The nmr reveals 19 aromatic hydrogens and a benzhydryl proton singlet at τ 5.15. The lack of coupling between the endo protons of the norbornane system (AB at τ 6.69 and 7.17 with $J = 10.8\text{ Hz}$) with the bridgehead hydrogens is evidence for the exo ring fusion. The orange color observed during the thermal "rearrangement," $3 \rightarrow 6$, suggests cleavage of the cyclobutanone ring of **3** with regeneration of **1** which in turn attacks the residual part of the molecule at another functional group. Indeed, methanolysis of **3** at 120° (22 hr) yields 91% of methyl diphenylacetate (**1** + CH_3OH) and 73% of **5**, mp $110\text{--}112^\circ$. The $\text{C}=\text{O}$ frequency at 1711 cm^{-1} is in accord with a β -tetralone derivative (α -tetralone 160 cm^{-1}). The enol ester **6** is prepared from **5** + **1**, even at 100° , with triethylamine as a catalyst.

The Wolff-Kishner procedure in diethylene glycol at 200° converts the ring ketone **5** into the tetraline derivative **7**, a colorless oil. Finally, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone dehydrogenates **7** to the tri-substituted naphthalene **8**. Its uv spectrum with maxima at 301.5 and $234.4\text{ m}\mu$ ($\log \epsilon$ 3.92 and 4.69) is strikingly similar to that of 1,2-dimethyl-4-phenyl-naphthalene.



Two observations are pertinent to the mechanistic elucidation of the 2:1 adduct **3** formation: (1) the cyclobutanone **2** is not converted to **3** by heating with **1** at 75° (18 days in cyclohexane); (2) the reaction of norbornene with **1** in acetonitrile (70°, 20 days) furnishes not **3** but the second, more stable 2:1 adduct **6** in 16% yield along with **2**.

Two pathways for the initial step of **3** formation are conceivable, assuming that an unknown catalyst is not responsible for the conversion $2 + 1 \rightarrow 3$: (a) some zwitterion, **9**, is formed from the reactants in a process which competes with the concerted formation of **2** and **9** cyclizes to **10** which is the σ -complex formed in an electrophilic aromatic alkylation; (b) as a 1,3-diene, **1** combines with norbornene in a Diels-Alder reaction, and the strain relief of norbornene would favor the formation of the six-membered ring, **10**, rather than the annellation of the four-membered ring in **2**.

Conversion of the σ -complex **10** to the benzene derivative **5** includes a suprafacial 1,3-hydrogen shift which is forbidden by orbital symmetry to be concerted.² The interception of the cyclohexadiene derivative **10** with a second molecule of **1** to form **3** appears to be faster than the intermolecular prototropic shift $10 \rightarrow 5$. In acetonitrile, however, the reaction of **10** does proceed via **5** to the second 2:1 adduct **6**.

We have obtained from **1** and *cis*- β -methylstyrene a 2:1 adduct of a structure corresponding to that of **3**. In contrast to the behavior of the mentioned ketenophiles, the 2:1 adducts of **1** and α -methylstyrene⁷ or 1,1-diphenylethylene⁷⁻⁹ are of the enol ester type, like **6**.

(7) R. Huisgen and P. Koppitz, manuscript in preparation.

(8) J. E. Baldwin, M. F. Breckinridge, and D. S. Johnson, *Tetrahedron Lett.*, 1635 (1972); J. E. Baldwin and D. S. Johnson, *J. Org. Chem.*, 38, 2147 (1973).

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Leander A. Feiler, Rolf Huisgen,* Peter Koppitz
 Institut für Organische Chemie der Universität
 8 Munich 2, Germany
 Received October 30, 1973

Optically Active Tris(dithiocarbamato)cobalt(III) Complexes

Sir:

There is considerable current interest in geometrical and optical (inversion) isomerism of tris-chelated transition metal complexes. Essentially two limiting mechanisms have been found in such systems. Isomerism and inversion occur *via* a trigonal bipyramidal transition state for unsymmetrical β -diketonato cobalt(III) complexes¹ while a trigonal prismatic transition state is favored for the corresponding tropolonato complexes.²

The results of recent studies on tris(*N,N*-disubstituted dithiocarbamato)metal(III, IV) complexes, $M^{III}(\text{dtc})_3$ and $M^{IV}(\text{dtc})_3\text{BF}_4$, where $M = \text{Fe(III), Fe(IV), Ru(III), Co(III), and Rh(III)}$, indicate a trigonal prismatic transition state which is achieved by a twisting motion of the trigonal antiprismatic reactant around the C_3

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(2) (a) S. S. Eaton, J. R. Hutchison, R. H. Holm, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 94, 6411 (1972); (b) S. S. Eaton and R. H. Holm, *ibid.*, 93, 4913 (1971).

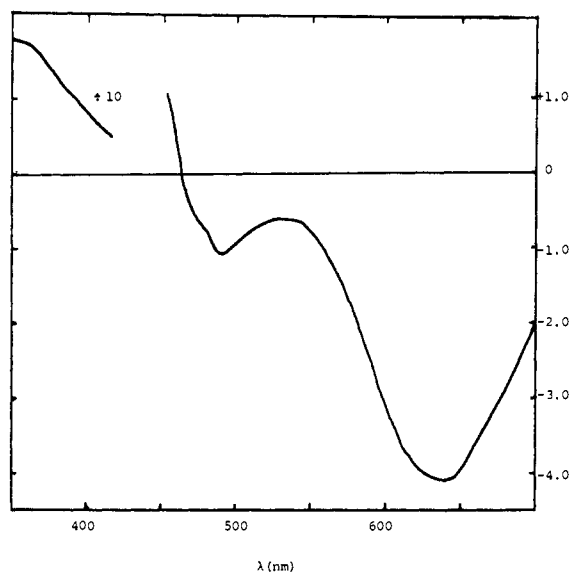


Figure 1. CD spectrum of $(+)_{546}\text{Co}(\text{Ph}_2\text{dtc})_3$.

axis. The rates of metal centered inversion ($\Delta \rightleftharpoons \Lambda$) have been shown to be strongly metal dependent.³

To date all inversion studies on the dithiocarbamate complexes have involved pmr line-shape analysis on racemic species containing diastereotopic groups which are used as a probe for the inversion reaction.³

The partial resolution of tris(*N-p*-hydroxyphenyl-*N*-methylthiocarbamato)cobalt(III) by preferential absorption of enantiomers on a starch substrate has been described. The compound was reported to racemize in 4 days at room temperature, but no thermodynamic parameters were detailed.⁴ We wish to report a general method for the preparation of optically active $\text{Co}^{III}(\text{dtc})_3$ complexes by a facile ligand exchange reaction between optically active $\text{K}[\text{CoEDTA}]$ or $\text{K}[\text{CoPDTA}]$ ⁵ and the sodium salt of the appropriate dithiocarbamate. Some preliminary details of metal-centered inversion obtained from *direct* polarimetric measurements on the optically active species are also discussed.

In a typical preparation, $\text{Na}[\text{Ph}_2\text{dtc}]$ (0.5 g) in acetone (10 ml) was added to an aqueous solution (10 ml) containing $(+)_{546}\text{-K}[\text{CoEDTA}]$ ⁶ (0.1 g; $[\alpha]_{546} + 980$). The solution was stirred rapidly and, after 10 min, the insoluble green, optically active $(+)_{546}\text{-Co}(\text{Ph}_2\text{dtc})_3$ ($[\alpha]_{546} + 1480^\circ$) was collected by filtration and washed thoroughly with water. The CD spectrum of the compound in toluene solution is shown in Figure 1.

The following $\text{Co}(\text{R,R-dtc})_3$ compounds have also been obtained in optically active form using this method: $\text{R} = \text{Me, Et, } i\text{-Pr, } n\text{-Bu, } i\text{-Bu, Bz, cych, pyr, pip}$. Full details of the preparations and optical activity studies including assignment of absolute configurations will be reported later.^{7,8}

(3) (a) L. H. Pignolet, D. J. Duffy, and L. Que, Jr., *J. Amer. Chem. Soc.*, 95, 295 (1973); (b) M. C. Palazzotto, D. J. Duffy, B. L. Edgar, L. Que, Jr., and L. H. Pignolet, *ibid.*, 95, 4537 (1973).

(4) H. Krebs and R. Rasche, *Naturwissenschaften*, 41, 63 (1954).

(5) Abbreviations used in this paper are: EDTA, ethylenediaminetetraacetic acid; PDTA, 1,2-propanediaminetetraacetic acid; R,R-dtc, *N,N*-disubstituted dithiocarbamate where $\text{R} = \text{Me, methyl; Et, ethyl; } i\text{-Pr, isopropyl; } n\text{-Bu, } n\text{-butyl; } i\text{-Bu, isobutyl; Ph, phenyl; Bz, benzyl; cych, cyclohexyl; R,R} = \text{pyr, pyrrolidyl; R,R} = \text{pip, piperidyl}$.

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(7) L. R. Gahan, J. G. Hughes, and M. J. O'Connor, investigations in progress. The reaction of optically active $\text{K}[\text{CoPDTA}]$ with excess