Wieland reaction, on the other hand, proceeds successfully with toluene, benzene, chlorobenzene and ethylbenzoate.

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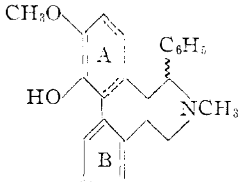
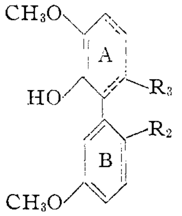
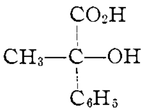
ASYMMETRIC INDUCTION AND ABSOLUTE CONFIGURATION IN THE BIPHENYL SERIES

Sir:

Methylmagnesium iodide converts the phenylglyoxylates of phenyldihydrothebaine (I) and its derivatives (IIa-c) (absolute configurations[1] as shown) to atrolactic esters. Saponification and isolation without optical fractionation give (−)-atrolactic acid (III) (absolute configuration[2] as shown) in optical yields of 70% from I and 91, 89, and 93%, respectively, from IIa-c. These are the highest optical yields known in the reactions of α-ketoesters with Grignard reagents.

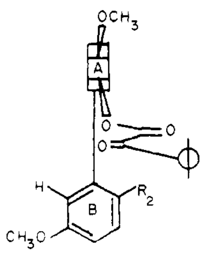

I

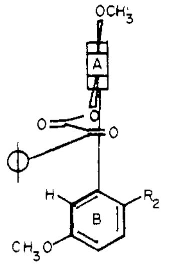



$$CH_3-\overset{\displaystyle CO_2H}{\underset{\displaystyle C_6H_5}{C}}-OH$$
III

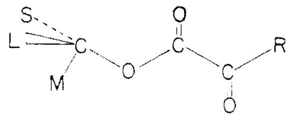
IIa, $R_2 = CH{=}CH_2$; $R_3 = CH_2CH(C_6H_5)N(CH_3)_2$
b, $R_2 = C_2H_5$; $R_3 = CH_2CH(C_6H_5)N(CH_3)_2$
c, $R_2 = CH{=}CH_2$; $R_3 = CH{=}CHC_6H_5$

The formation of III is most reasonably explained on the consideration that most of the product is derived from the two most stable ground state conformations IV and V, in which repulsive interactions are minimized by disposition of the two keto groups coplanar-transoid and the plane of the phenylglyoxylate chain as far away as possible from the ring A methoxyl and ring B, *i.e.*, perpendicular to ring A and at a dihedral angle of 60° with respect to ring B. Approach to the keto carbonyl group in IV and V by the attacking methyl must occur from the direction of ring A, since the underside of the keto group is shielded by ring B. If the rotational barrier between IV and V is high, the major proportion of the product is derived from V, which is more stable than IV because the phenylglyoxylate chain interferes with H instead of R. If the rotational barrier is low compared to the energy of activation for chemical reaction, the product proportions are controlled by the difference in free energy between the transition states derived from IV and V.[3] That from V is the more stable, since in it, the compression of the groups attached to the keto carbonyl as the latter begins to become tetrahedral is against H, whereas in that from IV, this compression is against the large group R. When the effective bulk of R increases (I → II), the stereoselectivity increases. A number of alternative interpretations ascribing special stability to other conformations because of chelate complexing, appear less probable. In particular, the conformation in which each carbonyl group is complexed with a ring methoxyl, and the plane of the phenylglyoxylate residue is perpendicular to ring A and parallel to ring B, would also lead to III. However, in order to explain on this basis the fact that the stereoselectivities with the phenylglyoxylates of IIa-c are 3.5 to 5.8 times greater than with that of I it is necessary to assume that the degree of complexing is less in the latter case. There is no obvious reason why this should be so and, at present, this alternative, while not rigorously excluded, appears unlikely.


IV


V

In elegant studies, McKenzie, Prelog, Turner and their respective co-workers have examined a large number of reactions of the general type $R_1COCO_2R_a + R_2MgX \rightarrow \rightarrow R_1R_2C(OH)CO_2H$. In eighteen such cases, complete resolution data are available on the product hydroxyacid and, using these, we have now calculated optical yields.[4] For a fixed asymmetric group (R_a), the optical yield is quite insensitive to the size of the incoming group (R_2), but becomes larger as the size of the group (R_1) *already attached* to the keto group increases. This phenomenon requires modification of the previously proposed[5] shielding effect theory of asymmetric induction in α-ketoesters. It is most readily encompassed by the hypothesis that the relative contribution to the total product made by conformation VI diminishes with increasing size of R_1 because of compression effects of the type discussed above.



VI

We are indebted to the National Science Foundation for financial support.

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[1] J. A. Berson, THIS JOURNAL, **78**, 4170 (1956).

[2] *Cf.* J. H. Brewster, *ibid.*, **78**, 4061 (1956).

[3] *Cf.* D. Y. Curtin, *Rec. Chem. Progress*, **15**, 111 (1954); D. Y. Curtin and M. C. Crew, THIS JOURNAL, **77**, 354 (1954).

[4] Complete literature references will be given in a forthcoming publication.

[5] V. Prelog, *Bull. soc. chim.*, 987 (1956), and references cited therein.

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RECEIVED FEBRUARY 9, 1957

CYANOCARBON CHEMISTRY—SYNTHESIS AND CHEMISTRY OF TETRACYANOETHYLENE

Sir:

Investigation of cyanocarbons, compounds containing only —C≡N groups attached to carbon,